

Research article

Indirect sulfonation of telechelic poly(styrene-ethylene-butylene-styrene) via chloromethylation for preparation of sulfonated membranes as proton exchange membranes

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Abstract. The indirect sulfonation, via chloromethylation, of poly(styrene-(ethylene-butylene)-styrene) (polySEBS), under mild conditions, is here reported as an alternative route for the conventional use of chlorosulfonic acid. This indirect sulfonation reaction is an effective route to insert sulfonic groups in the aromatic rings of SEBS to impart a proton exchange capability. The chloromethylated polySEBS was chemically modified by the isothiuronium group, afterward hydrolyzed and oxidized to generate sulfonic acid groups selectively into the aromatic portion (polystyrene) of the polySEBS, to a great extent. The chloromethylated and sulfonated polymeric membranes were characterized by NMR, FT-IR, water uptake, TGA, ion exchange capacity (IEC), and ion conductivity. The obtained results show that as the oxidation time increased in performic acid, the water uptake achieved up to 79.6% due to the conversion of isothiuronium to the sulfonic acid groups into the polymer structure. Furthermore, the sample after 7 hours of oxidation reaction (sSEBS-7H) showed 59% of sulfonation, determined by RMN, and had an IEC value of 1.46 meq/g and also an ion conductivity value of 18.7 mS/cm at *RT*, which are 46 and 75% higher than those of Nafion 115, a commercial polymer conventionally used for proton exchange membranes (PEM). Thus, the as-prepared sSEBS-7H membrane, via chloromethylation, can be used for PEM since it exhibits good ionic conductivity and structural stability.

Keywords: polymer membranes, indirect sulfonation, chloromethylation, proton exchange membrane, polySEBS

1. Introduction

The depletion of energy resources derived from fossil fuels, and the problem of climate change associated with these, have prompted the search for different alternatives for energy production. Consequently, electrochemical systems related to hydrogen, such as proton exchange polymeric membrane (PEM) fuel cells, have caused great attention due to their zero-emission of pollutants into the environment

during operation. However, there are high costs of these electrochemical systems related to platinum-based-catalyst and commercial polymeric membranes based on perfluorosulfonated polymers such as Nafion [1, 2].

The main function of a PEM-type membrane is to act as a proton conductor, which is related to the presence of sulfonic acid groups into polymers due to their excellent dissociation in the presence of water

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molecules, which in turn promote the transport of protons within the membrane. The study on the chemical modification of aromatic polymers such as polyether ketones, polyimides, polybenzimidazoles, polyphenylenes, polysulfones, and other copolymers, have been considered as the main alternative to obtaining proton exchange membranes with similar performance than Nafion but at low cost as well as with good chemical and thermal stability [3–8]. Studies regarding the insertion of sulfonic groups on aromatic moieties, like polystyrene, have provided insights into how parameters such as reaction time, temperature, and particle size of polystyrene play an important role in sulfonation degree, ion exchange capacity, and morphology [9].

Therefore, some investigations are focusing on sulfonation of copolymers with polystyrene, such as the poly(styrene-*b*-butadiene-*b*-styrene) (polySBS), poly(styrene-*b*-isoprene-*b*-styrene) (polySIS) and their corresponding hydrogenated versions, the poly(styrene-*b*-ethylene-*co*-butylene-*b*-styrene) (polySEBS) and poly(styrene-*b*-ethylene-*alt*-propylene-styrene) (polySEPS) [10–14]. The polySEBS, poly(styrene-*b*-ethylene-butylene-*b*-styrene) triblock copolymer, is an interesting commercially available material for industrial and technological use due to its properties as ion-conducting and electroactive copolymer when it is selectively functionalized on the aromatic rings of the polystyrene blocks, especially with sulfonic groups. The elastomeric central segment of such copolymer has the advantage of high thermal resistance since it does not contain labile double liaisons, and its chemical constitution, as well as the aromatic groups in a telechelic position, impart an elastomeric thermoplastic characteristic not usual to find in a single polymer. Also, this polymer is expected to provide a significant cost reduction compared to Nafion as proton exchange membranes [15, 16]. Commonly, direct sulfonation is the used method to introduce sulfonic groups in the aromatic groups to produce hydrophilic polymer membranes appropriate for fuel cell applications, where strong acids such as sulfuric or chlorosulfonic acid are used, which in turn have the disadvantage of lack of the precise control over the degree of sulfonation, site-specificity, and the possibility of side reactions, or even degradation of the polymer by backbone scission that represent important drawbacks for the mechanical and chemical stability of the membranes [17–19].

However, an option to overcome such drawbacks is the use of alternative chemical modification. So far, it has not been proposed the direct chloromethylation of polySEBS as a possible sulfonation route since the main approach that has been conferred on chloromethylation is to obtain anionic membranes by the reaction between the chloromethyl group and tertiary amines [20, 21]. The two-steps chemical modification strategy (chloromethylation followed by sulfonation) has been used in other polymers such as polyethersulfone [22, 23], and polysulfone in search to graft firstly a functional group into the benzene ring; the method can be used to derivative different functionalized polymers [24] because the polymers that have been chloromethylated can be modified by nucleophilic substitution for the formation of new substituents [25, 26]. Also, radiation-induced grafting with vinyl-based monomers is another method to produce chloromethyl groups in polymers, which can be converting into sulfonic acid with a methylene spacer via the formation of thiouronium salt with thiourea, base-catalyzed hydrolysis for the formation of thiol, and a final step of oxidation of thiol groups [27–29].

The aim and novelty of this work is the synthesis of sulfonated poly(styrene-ethylene-butylene-styrene), which was carried out using the chloromethylation route by the addition of 1,2-dimethoxymethane, zinc chloride, silicon tetrachloride, and chloroform as a solvent in the reaction. The prepared membranes were characterized by determining the ionic conductivity, ion exchange capacity, and water absorption as key parameters to evaluate its potential use in PEM. This sulfonated poly(SEBS) has the advantage that is high-temperature resistant, it keeps its flexibility after immersion in water and gets dried, and exhibits better conductivity performance than conventional material used for PEM as Nafion.

2. Experimental

2.1. Materials

The poly(styrene-*b*-ethylene-butylene-*b*-styrene) copolymer (polySEBS) with a reported molecular weight of 118 000 g/mol, and with 30% by weight of styrene, was provided by Dynasol (Altamira, Tamps. Mexico). 1,2-Dimethoxymethane (DMOM) (>99%) and silicon tetrachloride (SiCl₄) (>99%), both from Sigma-Aldrich (St. Louis, MO, USA), were used as precursors for chloromethylation of poly(SEBS).

Anhydrous zinc chloride (>99% ZnCl_2) was purchased from Lachema (Brno, Czech Republic); it was used as Lewis acid to catalyze the chloromethylation reaction. Chloroform (>99%) and toluene (>99%), both from the Lach-Ner company (Neratovice, Czech Republic), were used as solvents in the chloromethylation reaction and the preparation of membranes, respectively.

Ethanol (technical grade), thiourea (>98%, Lachema, Brno, Czech Republic), sodium hydroxide (>99%, PENTA, Prague, Czech Republic), hydrogen peroxide (30%, Lach-Ner, Neratovice, Czech Republic), and formic acid (>95%, Sigma-Aldrich, St. Louis, MO, USA) were used for the sulfonation reaction of the chloromethylated membranes. All reagents were used as they were received without further purification.

2.2. Synthesis of chloromethylated SEBS

PolySEBS (12.5 g) in chloroform solution was stirred with the methylating agent DMOM (0.27 mol) and the catalyst ZnCl_2 (0.032 mol) for 1 h approximately. The chlorinating agent SiCl_4 (0.032 mol) was added to the mixture to promote chloromethylation. The reaction solution was kept stirred for 30 hours at room temperature, with a gradual change from colorless to brown color. After the indicated reaction time, the solution was diluted with additional chloroform and subsequently precipitated in ethanol. The precipitate was filtered and diluted in toluene 5% (w/w).

2.3. Membrane preparation

The 5% (w/w) solution of the chloromethylated polymer in toluene was poured onto a Teflon plate to obtain the membrane by the solvent evaporation method, inside a flow box at room temperature to maintain constant evaporation of the solvent, and the membrane was obtained after 24 hours. Once the membranes were obtained, different reactions were subsequently carried out, described below.

S-alkylation

The chloromethylated membranes were cut to a size of 10×10 cm and were immersed in a 10% (w/w) thiourea solution for 48 hours at 60 °C to carry out a heterogeneous reaction in the alkyl halide group for the formation of isothiuronium. The membranes were washed with distilled water until the excess of thiourea solution was removed and dried at room temperature.

Hydrolysis

Subsequently, the membranes were immersed in a 10% (w/w) solution of NaOH in ethanol for 48 hours at 60 °C to carry out the hydrolysis of the isothiuronium groups, and thus the formation of thiol groups into the aromatic groups of the membrane. Similarly, the membranes were washed several times with distilled water and were dried at room temperature.

Oxidation

Finally, the membranes were immersed in a formic acid solution, which was prepared 1 h previously (A mixture of 88% formic acid and 30% hydrogen peroxide solutions in the ratio of 7:3, respectively). The oxidation reaction of the thiol groups in the presence of the formic acid was carried out at different times (1, 3, 5, and 7 hours) to observe the conversion toward sulfonic acid groups in the polymeric matrix of the membrane. The membranes were washed with distilled water several times after the indicated reaction time.

2.4. Membranes pre-treatment

Prior to characterization, the membranes were treated according to a methodology for better reproducibility in the results; the steps are shown below [21, 30]:

- 1) Immersion of the membrane in deionized water for 24 hours.
- 2) Immersion of the membrane in a 1.0 N HCl solution for 24 hours. Then, washing with deionized water for 10 minutes.
- 3) Immersion of the membrane in 1.0 N NaOH for 24 hours. Then, it was washed with deionized water for 10 minutes.
- 4) Immersion of the membrane in HCl 1.0 N for 24 hours. Then, it was washed with deionized water for 10 minutes.
- 5) Immersion of the membrane in deionized water for 24 hours.

2.5. Characterization

2.5.1. FTIR spectroscopy

FTIR spectroscopy was used to identify the functional groups present in the different samples. This analysis was performed at room temperature on the Nicolet 6700 IR spectrometer ThermoScientific (Waltham, MA, USA), using the Attenuated Total Reflectance (ATR) technique in the range 400–4000 cm^{-1} , 64 scans with a resolution of 4 cm^{-1} .

2.5.2. Elemental analysis

Elemental analysis measurements were carried out to determine the C, N, S, and H of the samples using a 2400 Series II Instrument Elemental Analysis of CHNS/O (Perkin Elmer, Waltham, MA, USA). 10 mg of sample were burned under an oxygen atmosphere in a combustion tube. The determination of elements is for the gaseous combustion products which pass through the combustion catalysts and absorption agents.

2.5.3. Thermogravimetric analysis

Thermogravimetric analysis was used to observe the thermal stability of the membranes subjected to a programmed increase in temperature, measuring the loss of weight of the sample as a function of temperature. For this test, 10 ± 0.5 mg of each sample to be evaluated were weighed. The calorimeter model Q500 TA Instrument (New Castle, DE, USA) was used, in the range of 25 to 600 °C and with a heating rate of 10 °C/min, in an atmosphere of N₂ and with a flow of 20 ml/min thereof.

2.5.4. Water uptake

The water uptake property is a significant characteristic, which indirectly confirms the incorporation of the hydrophilic groups within the membrane. For this, a certain amount of membrane was dried at 35 °C under vacuum for 24 hours, and then its dry mass was recorded. Subsequently, the membrane was immersed in deionized water for 24 hours at *RT*, and after that, the excess water was removed to determine its wet weight. The water absorption capacity was calculated by measuring the weight of the wet (W_{wet}) and dry (W_{dry}) samples, which correspond to the weight after immersion and to the dried sample (initial sample, before immersion), respectively, as indicated in Equation (1):

$$W [\%] = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \cdot 100 \quad (1)$$

2.5.5. Atomic force microscopy

Topography and phase images of the membranes were analyzed using atomic force microscopy (NaiοAFM, Nanosurf, Liestal, Switzerland) under tapping mode. The AFM images were obtained with a maximum scan range of $48.7 \times 48.7 \mu\text{m}^2$. The resonance frequency was adjusted around 150 kHz.

2.5.6. Scanning electronic microscopy

Morphology of samples' surfaces was obtained by SEM, which has been carried out using an FEI Quanta 250 scanning electron microscope (ThermoFisher Scientific, Waltham, MA, USA). The chloromethylated membrane (CM-SEBS) and the sulfonated SEBS after 7 hours of oxidation membrane (sSEBS-7H) samples were freeze-fractured in liquid nitrogen to investigate the cross-section of them. Images were recorded, and EDX mapping was performed to identify the element distribution across the membranes.

2.5.7. Ion exchange capacity

Ion exchange capacity (*IEC*) is a fundamental characteristic of ion-exchange membranes. The *IEC* of the membrane was determined by the back titration method [31]. For this, 0.25 grams of the membrane was weighed with a previous vacuum drying at a temperature of 35 °C for 24 hours; the membrane was immersed in 25 ml of a 0.1 N sodium hydroxide solution for 24 hours with constant stirring. Then, 7 ml aliquots were drawn and titrated with a 0.1 N HCl solution in an automatic titrator. The *IEC* was determined using Equation (2):

$$IEC = \left(\frac{C_{\text{NaOH}} - C_{\text{HCl}} \cdot V_{\text{HCl}}}{V_{\text{sample}}} \right) \left(\frac{V_{\text{NaOH}}}{m} \right) \quad (2)$$

were C_{NaOH} – NaOH concentration 0.1 N, C_{HCl} – HCl concentration 0.1 N, V_{HCl} – volume of HCl 0.1 N used on the titration, V_{sample} – sampling volume (7 ml), V_{NaOH} – volume of 0.1 N NaOH used to immerse the membrane (25 ml), m = dry membrane weight.

2.5.8. Ion conductivity

The resistance, R [Ω] of the membranes was measured by impedance spectroscopy in a four-electrode configuration using a potentiostat/galvanostat Autolab PGSTAT302N (Metrohm, Herisau, Switzerland) and by applying platinum working and Ag/AgCl reference electrodes, respectively. The equilibrated membrane sample was placed at 25 °C between two 25 ml chambers filled with 0.5 M KCl. The frequency range and current applied were $8 \cdot 10^5 - 1$ Hz and 1 mA, respectively. Considering the surface area, A [cm^2], thickness, L [cm] and resistance, R (obtained from Nyquist plot) of the membranes, their area resistance ($R_A = R \cdot A$ [$\Omega \cdot \text{cm}^2$], the specific resistance ($R_S = R_A/L$ [Ω/cm], and the ionic conductivity ($\sigma = 1/R_S$ [mS/cm]) were computed [32].

2.5.9. Nuclear magnetic resonance

Solid-state NMR (ssNMR) spectra were recorded at 11.7 T using an AVANCE III HD spectrometer (Bruker, Billerica, MA, USA). The 4 mm cross-polarization magic-angle spinning (CP/MAS) probe was used for ^1H and ^{13}C ssNMR experiments at Larmor frequencies of $\nu(^1\text{H}) = 500\ 181\ \text{MHz}$ and $\nu(^{13}\text{C}) = 125\ 783\ \text{MHz}$, respectively. ^{13}C and ^1H NMR chemical shifts were calibrated using α -glycine (^{13}C : 176.03 ppm; carbonyl signal) and adamantane (^1H : 1.85 ppm), respectively, as external standards. All ssNMR spectra were acquired at the speed of the sample spinning of 11 kHz. The ^1H MAS NMR spectra were recorded with a 2 s recycle delay. The ^{13}C MAS and CP/MAS NMR experiments were recorded with 15, and 2 s recycle delays, respectively. A cross-polarization (CP) contact time of 1.5 ms was used in both ^{13}C CP/MAS NMR experiments. High-power ^1H decoupling (SPINAL64) was used for the removal of heteronuclear coupling.

Samples were packed into ZrO_2 rotors and subsequently kept at room temperature. All NMR experiments were conducted under active cooling in order to compensate for frictional heating caused by the rotation of the samples. All experiments were done at 298 K temperature. Bruker TopSpin 3.2 pl5 software package was used for the processing of the spectra.

2.5.10. Mechanical evaluation

The mechanical properties of the membranes were measured using the Universal testing machine model 3369 (Instron, Norwood, MA, USA) at room temperature. At least five specimens per sample were tested. The size of the specimens was 30 mm \times 10 mm (test area), and they were tested in tensile mode with a strain rate of 10 mm/min.

3. Results and discussion

3.1. Polymeric synthesis and its structural analysis

The chloromethylation of polySEBS was carried out as shown in Figure 1, where the chloromethyl group was introduced into the styrene blocks of the polymer by an aromatic electrophilic substitution.

PolySEBS chloromethylation was achieved for obtaining membranes, as described in the methodology section, which was chemically modified at different stages. Firstly, thiourea in ethanol was used to displace chlorine by sulfur through the formation of

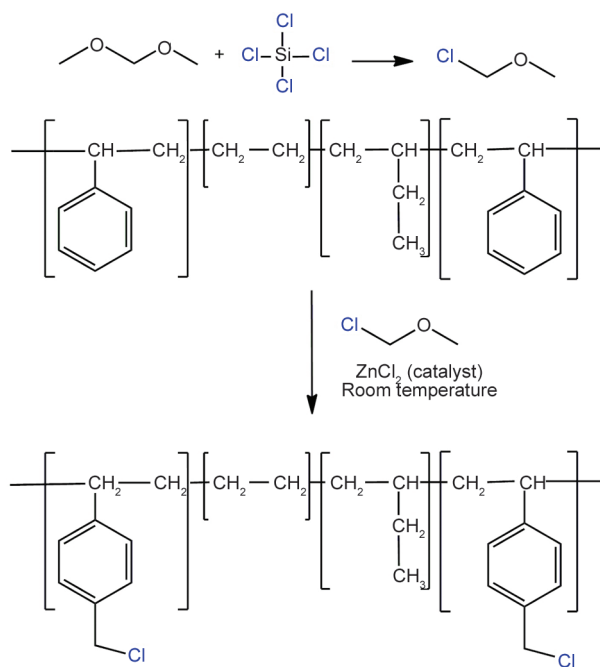


Figure 1. PolySEBS chloromethylation.

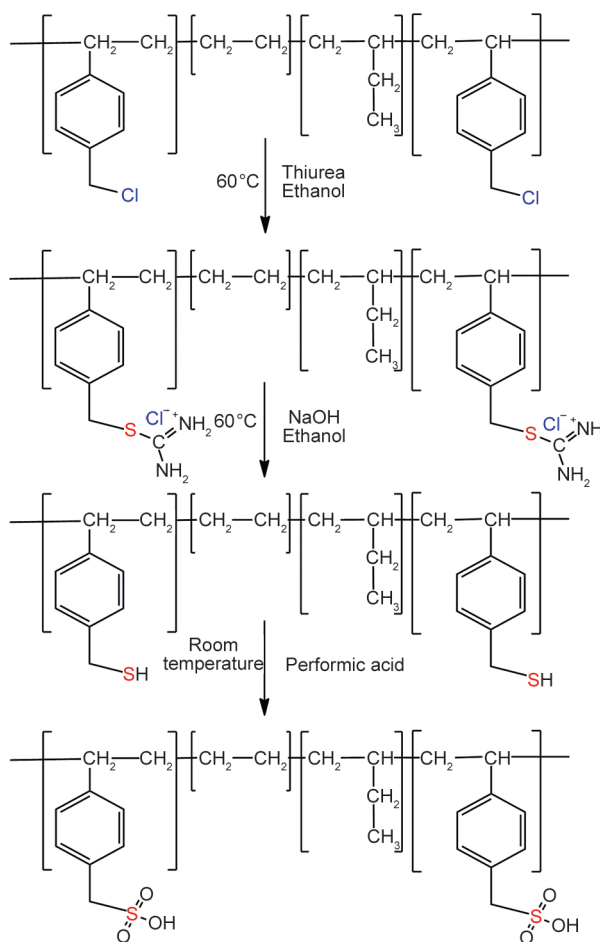


Figure 2. Membrane sulfonation steps.

thiuronium salts, and then the hydrolysis and oxidation of the membranes were carried out to form the sulfonic acid groups, shows that Figure 2. Sulfonic

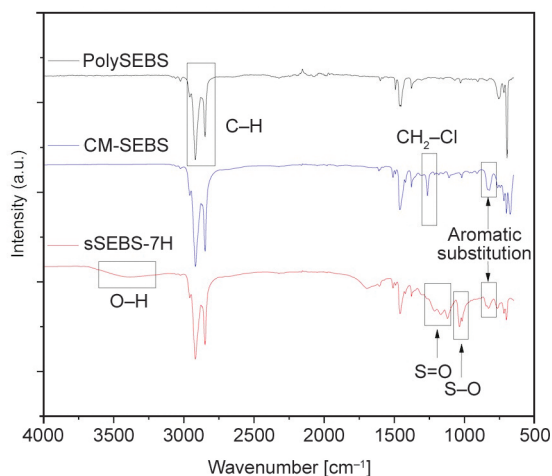


Figure 3. FT-IR spectra for different prepared membranes.

acid groups on the membranes were bound to the aromatic ring with the methylene as a spacer [27]. The incorporation of the functional groups into the polymer chains was confirmed by FT-IR, whose spectra are shown in Figure 3. In this figure, the spectra for the polySEBS, chloromethylated SEBS (CM-SEBS), and sulfonated SEBS after 7 h of oxidation (sSEBS-7H) samples are observed, which exhibit various bands that correspond to the different functional groups present in the different samples. In the case of polySEBS, the bands at 2915 and 2848 cm^{-1} correspond to the asymmetric and symmetric stretching of the C–H bond of the methylene group, respectively. While the other bands at 1455, 1372, and 698 cm^{-1} correspond to the asymmetric stretching of the C–H bond of CH_3 of the elastomeric portion (butylene-ethylene), to the deformation of the C–H bond of CH_2 , and the aromatic groups of styrene, respectively [33–35].

Once SEBS was (chloro)methylated, changes in its spectrum were observed, especially with the appearance of a new band at 1263 cm^{-1} , due to the presence of the $\text{CH}_2\text{--Cl}$ chloromethylated groups [20]. Furthermore, the wide band located between 800 and 850 cm^{-1} is due to the substitution of chloromethyl that takes place in the aromatic rings of the styrene blocks, which shift the original position (698 cm^{-1}) [36]. The bands at 2915 and 2848 cm^{-1} are maintained, which is indicative of the selectivity of the chloromethylation reaction towards the electron-rich π system of the styrene aromatic ring.

In relation to the sulfonated sample after 7 hours of oxidation (sSEBS-7H), its spectrum shows clear changes, due to the presence of the bands at 1032 and 1006 cm^{-1} , they are related to the stretching of the

S–O bond due to the formation of the groups sulfonic acid, and in turn, it is possible to identify between 1100 and 1247 cm^{-1} the bands associated with the symmetrical and asymmetric vibration of the double ligature S=O of said group. Furthermore, the wide band observed between 3200 and 3600 cm^{-1} corresponds to the vibration of the O–H bond associated with the absorption of water molecules [16, 36]. The substitution of chloromethylated groups allowed a high content of sulfonic groups during the last stage of the oxidation reaction.

3.2. Elemental analysis

The polySEBS material was analyzed after the chloromethylation reaction and in its sulfonated form to know the elemental content of chlorine and sulfur, respectively. Table 1 summarizes the carbon, hydrogen, chloride, and sulfur content for each of the samples. These values indicate that chloromethylation was carried out successfully, as well as the substitution of chlorine by sulfur for the formation of sulfonic groups.

It is important to point out that the 3.2% chlorine in the chloromethylated polymer demonstrates a greater substitution of the chloromethyl groups compared to another study of chloromethylation of the polySEBS where a percentage of the elemental chlorine content of 1.75% was achieved [17]. Furthermore, the sulfur content confirms that the chlorine substitution was complete.

3.3. Thermogravimetric analysis

Figure 4 shows the thermograms for the analyzed membranes. The pristine polySEBS thermogram shows that the initial degradation temperature of the polymer chain is 377 $^{\circ}\text{C}$, which is similar in all samples. The first weight loss (7.56%) of CM-SEBS occurred between 150 and 377 $^{\circ}\text{C}$ related to the decomposition of the chloromethylated groups present in the polymer matrix.

In the case of sSEBS-7H, an initial weight loss of 6.3% is observed in the range of 30–150 $^{\circ}\text{C}$, which is associated with the evaporation of water, mainly,

Table 1. Elemental analysis results.

Sample	C [%]	H [%]	Cl [%]	S [%]
polySEBS	87.4	12.3	–	–
CM-SEBS	83.2	11.4	3.2	–
sSEBS-7H	74.4	10.8	–	3.9

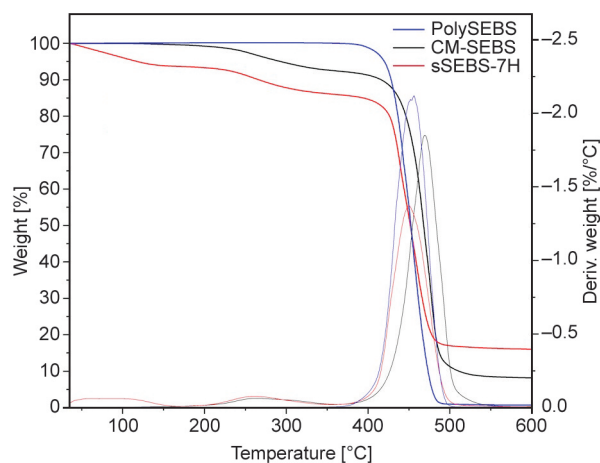


Figure 4. Thermogravimetric analysis of prepared membranes.

and eventually organic solvents [37]. The second weight loss occurs between 150 and 377 °C, corresponding to a weight loss of 7.94%, which is associated with the loss of the sulfonic groups from the polymer [38]. The percentage of loss for the sulfonated sample is according to the percentage of loss for the chlorinated sample, which corroborates that the oxidation reaction is effective to completely replace chlorine with sulfur to generate the sulfonic groups. Also, the residual values are according to the sample type, being the lowest value for the poly-SEBS, then the CM-SEBS, and the highest value for the sulfonated sample because the carbon content was reduced. Finally, the decomposition temperature of the functionalized pristine polymers occurred around 400 °C. It should be noted that the sulfonated membrane is thermally stable up to 150 °C, sufficient for application in fuel cells, which usually operate between 20 and 80 °C [39].

3.4. Water uptake

The water content within an ion exchange membrane is a crucial parameter during the operation of a fuel cell because the dimensional stability of the membrane is affected by water; if there is an excess of it, the membrane suffers an important dimension change [40]. According to Table 2, the water uptake of the membranes increased as the oxidation time in performic acid was increased.

The sSEBS-7H membrane had the highest average water uptake (79.7%), and the other sulfonated samples showed a gradual increase in such parameters as the reaction time elapsed. Although the sulfonic groups in the membrane favor the increase of water uptake due to the easy ionic interaction with the water

Table 2. Water uptake of sulfonated membranes.

Sample	Water uptake [%]
sSEBS-1H	61.5±1.9
sSEBS-2H	63.3±2.1
sSEBS-3H	68.8±3.1
sSEBS-7H	79.7±2.7

molecules, high water uptake by the membrane can promote a reduction of mechanical properties or even the fracture of the membranes [41]. The formation of ionic sites is important since they help the absorption of water molecules, which favors their mobility through the membranes according to the Grotthuss mechanism, which results in a better proton conductivity through the membrane of ion exchange [42]. Thus, there must be an adequate balance between water uptake and the mechanical integrity of the membrane to be functional for PEM.

3.5. Atomic force microscopy

Atomic force microscopy was used to investigate the topology of the membranes. Figure 5 shows the unmodified (pristine polySEBS) and sulfonated polymer membrane (sSEBS-7H), which were prepared by solvent evaporation as described in the methodology.

The image of the pristine SEBS membrane does not have a specific topology or homogeneous texture without obvious changes in the membrane's surface. In the case of the image of the sSEBS-7H membrane, the surface has revealed roughness due to the phase interaction of hydrophilic ($-\text{SO}_3\text{H}$, polar group) and hydrophobic (polymer backbone, nonpolar structure) domains dependent on the chemical structure [43–45]. There are relevant investigations that associate this topological change as a result of interaction between sulfonated styrene block and ethylene-butylene block in the polymer backbone, which suggest alternating hard and soft regions [10, 46]. In addition, researchers have demonstrated that darker regions correspond to clusters or domains of hydrophilic sulfonic groups associated with water molecules [6]. As it is observed in Figure 5b, such clusters are well distributed across the sample, which implies that the sulfonic groups are effectively present in most of both aromatic portions (polystyrene) of the polymeric chains. It is important to mention that in this type of triblock copolymers (ABA-type), the polystyrene portions are able to generate microdomains (clusters) by attraction forces between them. Thus, the sulfonic groups attached to polystyrene are associated, and

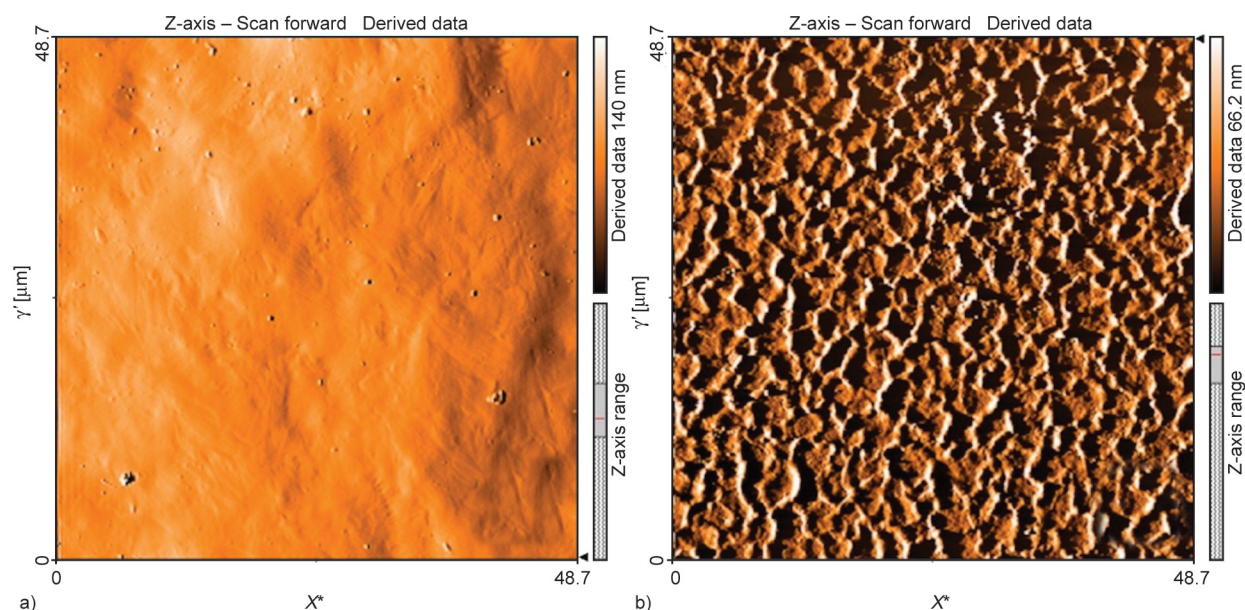


Figure 5. Atomic force microscopy images of a) Pristine SEBS and b) modified polymer sSEBS-7H.

they manifest such association giving contrast (darker) regions in the AFM images.

3.6. Scanning electronic microscopy

The SEM images for the CM-SEBS sample are presented in Figure 6. As it can be observed in Figure 6a, the image confirms a well-compacted dense and uniform membrane without the existence of big pores. Figure 6b shows the EDX element mapping giving chlorine presence all along the membrane, which confirms that chloromethylation of polySEBS was successful.

Regarding the used treatment for the chemical modification of the chloromethylated membrane, it did not affect the uniformity and continuity of such

membrane, according to Figure 7a. The SEM-EDX mapping image (Figure 7b) illustrates that sulfur is distributed uniformly in the polymer matrix, which implies the effective preparation of the sulfonated membrane after 7 hours of oxidation in performic acid treatment.

This result revealed that the chlorine was replaced perfectly by sulfur during the sulfonic acid functionalization of polySEBS.

3.7. Ion conductivity, specific resistance, and ion exchange capacity

Ionic conductivity (σ) is a fundamental parameter in ion-exchange membranes that is reflected in the efficiency of fuel cells. This parameter is affected by

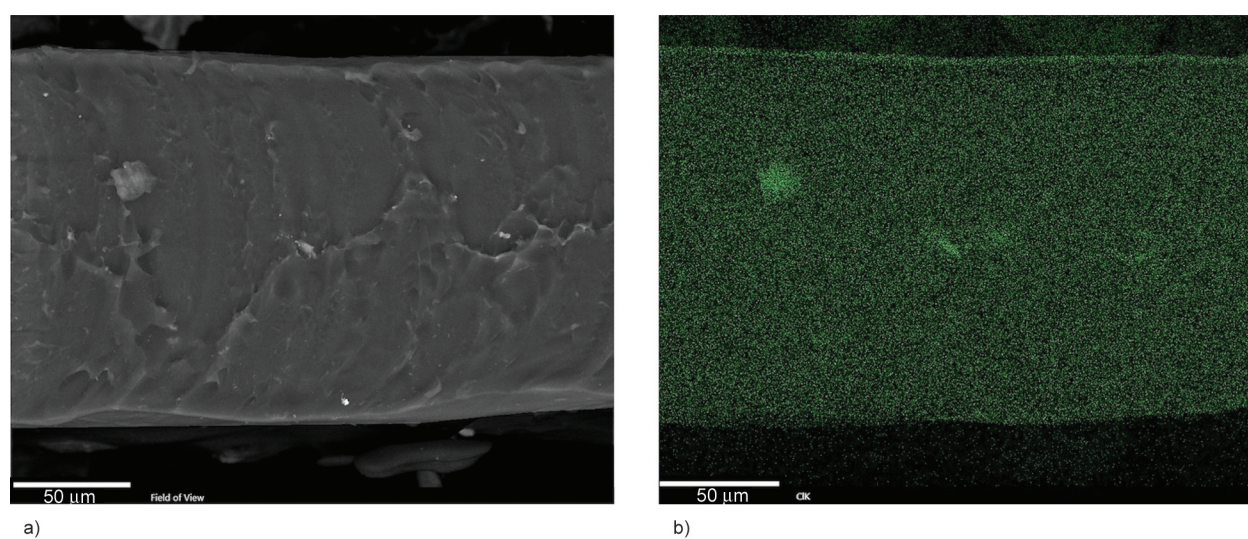


Figure 6. SEM images of the CM-SEBS membrane of a) cross-section area, and b) EDX mapping.

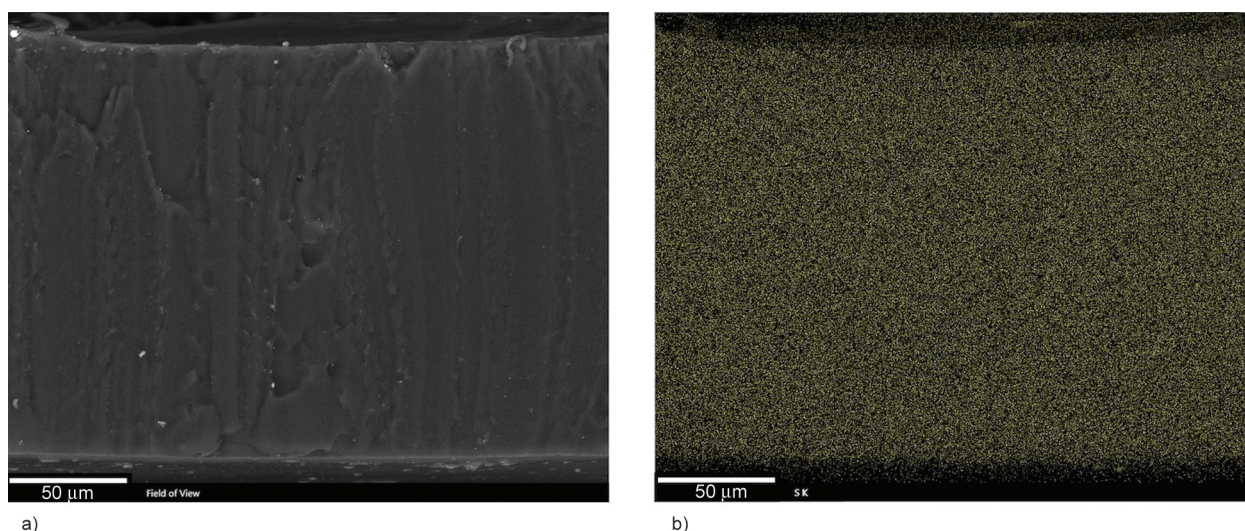


Figure 7. SEM images of the sSEBS-7H membrane of a) cross-section area, and b) EDX mapping.

the temperature, the content of ionic groups, and the membrane thickness, and therefore its evaluation was made at 25 °C.

Figure 8 shows representative Nyquist plots for sulfonated samples, sSEBS-1H and sSEBS-7H, which indicates lower resistance as the sulfonation reaction proceeded. Thus, the sample at 7 h (sSEBS-7H) has better ionic conductivity than sample sSEBS-1H, with just 1 hour of sulfonation reaction.

The values obtained for the ionic conductivity, specific resistance, ion exchange capacity, and thickness

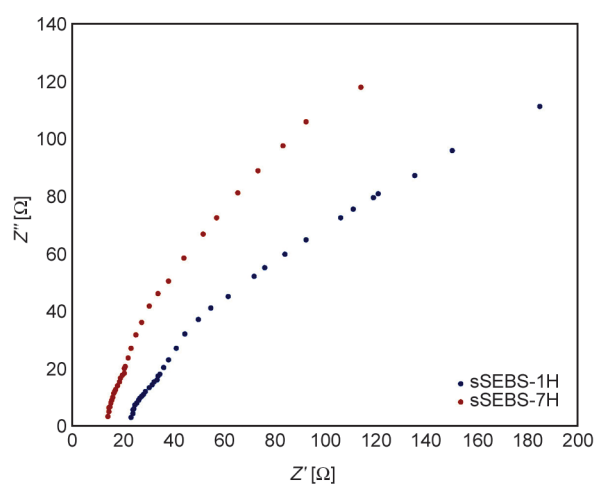


Figure 8. Nyquist plot for sulfonated samples.

of the sulfonated membranes at different times of immersion in formic acid (PFA), as well as of Nafion 115, which is a material widely used in ion-exchange membranes [32], are presented in Table 3.

As can be seen from Table 3, the increase in ionic conductivity of the hydrated membranes depends on the content of sulfonic acid groups formed at the different oxidation times (1, 3, 5, and 7 h) in performic acid. Likewise, the variation of the specific resistance is inversely proportional to the content of sulfonic groups, which is consistent with the ionic conductivity values. The specific resistance difference percentage between the samples with the shortest and longest reaction times was 66.5%, while the difference in ionic conductivity between them was 49.2%, which is indicative that ion transport is also affected by the effect of diffusion (membrane thickness), although the transport efficiency for these membranes was relatively high (75%), as a consequence of the insertion of sulfonic groups.

In previous works, it has been reported that the ionic conductivity of Nafion 115 was 6.19 mS/cm at the same measurement conditions to which the results of this work were obtained [32]. In comparison, the values of conductivity and specific resistance of

Table 3. Results of specific resistance and ionic conductivity for sulfonated membranes.

Sample	Specific resistance [Ω·cm]	Ion conductivity [mS/cm]	Ionic wxchange capacity [meq/g]	Membrane thickness [μm]
sSEBS-1H	83.5	11.97	1.39	216
sSEBS-3H	68.8	14.53	1.43	211
sSEBS-5H	58.8	17.00	1.46	204
sSEBS-7H	55.5	18.01	1.47	213
Nafion 115	161.6 [32]	6.19	0.91	127

Nafion represent 34 and 191 % of the best values obtained in the study, despite having a lower membrane thickness. Likewise, the value of the ion exchange capacity for the membrane with the highest sulfonation sSEBS-7H was 60% greater than the value of the commercial polymer Nafion 115 ($IEC = 0.91$ meq/g). The results of both ionic conductivity and IEC are indicative that the alternative sulfonation pathway is promising in the fabrication of fuel cell membranes.

3.8. Nuclear magnetic resonance

The ^1H and ^{13}C ssNMR spectroscopy was used for the investigation of neat and sSEBS-7H membranes (Figure 9 and Figure 10). Firstly, the ^{13}C CP/MAS NMR spectra (Figure 9, left-hand column) of neat and sSEBS-7H membranes were analyzed. The peak at 11 ppm was assigned to methyl groups ($-\text{CH}_3$), and peaks between 25–50 ppm were assigned to aliphatic (methylene $-\text{CH}_2-$ and/or methine $>\text{CH}-$) groups, respectively. Moreover, the signals at 126 and 145 ppm corresponding to the aromatic carbons ($=\text{CHAr}-$ and $=\text{CAr}<$) were detected. As evident from Figure 9b left-hand column, a new peak at 57 ppm appeared, confirming the existence/presence of $-\text{CH}_2-$ group(s) on the aromatic ring(s). This indicates a successful sulfo-methylation reaction in the para position of the benzene ring(s). The presence of sulfonic acid was confirmed using ^1H MAS NMR spectroscopy (Figure 9, right-hand column), where a new peak at 8.3 ppm was detected and attributed to $-\text{SO}_3\text{H}$ group(s) [47].

Secondly, the content of the sulfonation was calculated by Equation (3) using peak intensities of

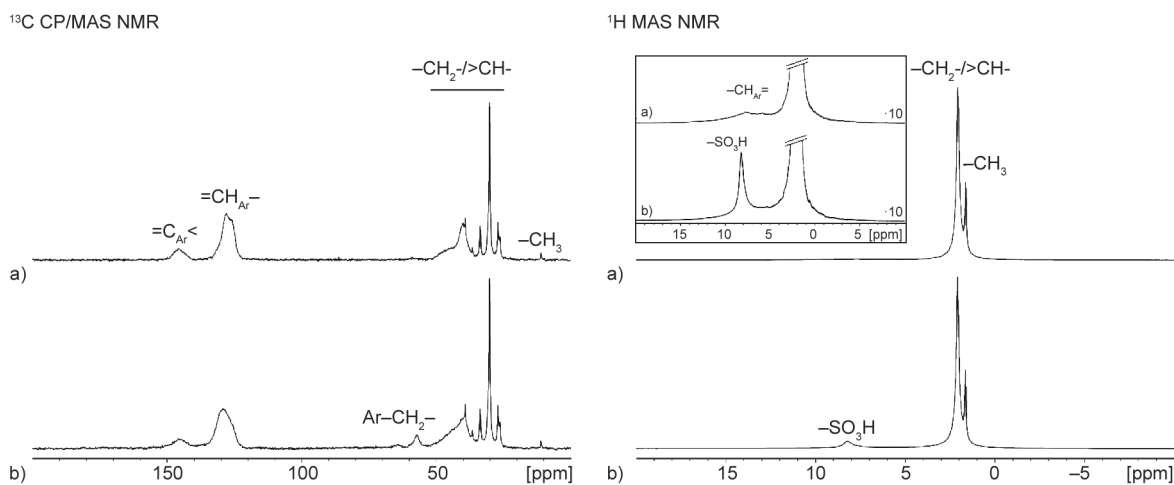


Figure 9. Experimental ^{13}C CP/MAS NMR spectra (left-hand column) and ^1H MAS NMR spectra (right-hand column) with magnified inset (dashed box) of neat (a) and sSEBS-7H (b) membranes, respectively.

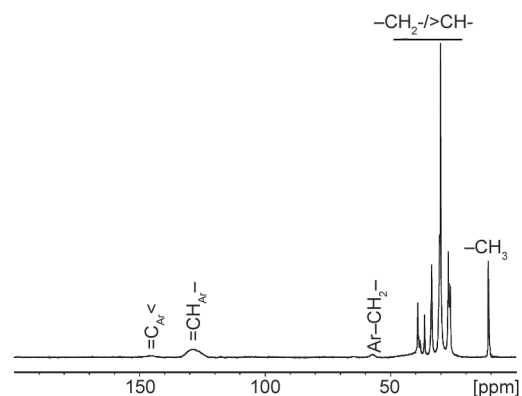


Figure 10. Experimental ^{13}C MAS NMR spectrum of the sSEBS-7H membrane, used for calculation of % degree of sulfonation reaction.

corresponding signals in ^{13}C MAS NMR spectrum of the sSEBS-7H membrane, see Figure 10.

% degree of sulfonation

$$= \frac{I(\text{Ar}-\text{CH}_2-)}{I(=\text{CAr}<)+I(=\text{CHAr}-)} \cdot 100 \quad (3)$$

The extent of the sulfonation reaction of the sSEBS-7H membrane was calculated to 59%. Finally, from the comparison of ^{13}C MAS NMR and ^{13}C CP/MAS NMR spectra, it can be defined that the prepared sSEBS-7H membrane is a two-phase system containing rigid polystyrene and flexible polyethylene-polybutylene domains.

3.9. Mechanical evaluation

The mechanical evaluation was essential to know the tensile properties of the sulfonated membranes in

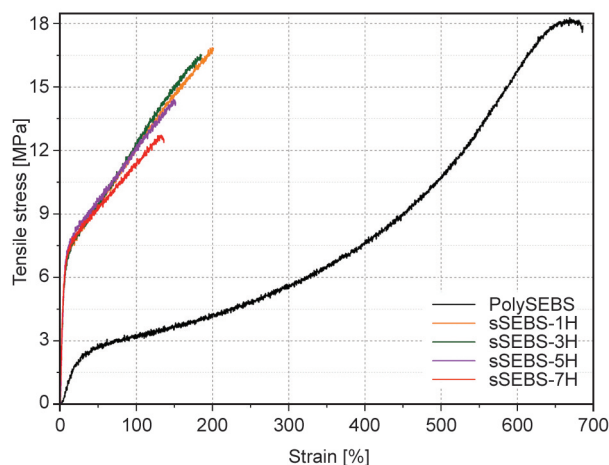


Figure 11. Representative stress-strain behavior of pristine polySEBS membrane and sulfonated membranes with different oxidation times.

comparison with the pristine polymer membrane. The typical tensile curves are shown in Figure 11. The Young's modulus, tensile strength, and elongation at break for the different evaluated samples are summarized in Table 4.

The sulfonic acid group into the polymer matrix enhances the ion conductivities of the cation membranes but also increases the rigidity (see Young's modulus in Table 4) due to the sulfonic groups ($-\text{SO}_3\text{H}$), which are voluminous, reducing the chain mobility [48]. It can be inferred that the space between the aromatic ring and sulfonic acid group, promoted by the methyl, could benefit the chain mobility of the sulfonated membranes, but it is not the case. As shown in Table 4, Young's modulus has not a clear trend as a function of the functionalization time of polySEBS. On the other hand, there is a certain trend to reduce the elongation at break, tensile strength, and toughness as functionalization time increases, especially for the sSEBS-7H membrane, which is related to its chemical structure, due to the sulfonic acid group's formation. The introduction of sulfonic acid groups can be caused some loss of elastomeric character of the membranes, reducing the chain mobility [48, 39].

Table 4. Mechanical characteristics of pristine polySEBS membrane and sulfonated membranes.

Sample	Young's modulus, E [MPa]	Tensile strength, σ_b	Elongation at break, ϵ_b [%]	Energy at break, toughness [mJ·mm ⁻³]
polySEBS	5.4±0.2	17.6±1.4	685.8±10.5	54.4±1.4
sSEBS-1H	144.8±3.4	16.8±0.5	201.1±8.7	23.9±1.0
sSEBS-3H	139.2±8.3	16.5±0.5	185.5±11.8	21.6±1.4
sSEBS-5H	161.0±4.9	14.3±0.3	151.3±8.9	16.2±1.2
sSEBS-7H	147.7±8.7	12.4±0.4	136.1±7.2	13.4±0.9

4. Conclusions

Indirect sulfonation of polySEBS by chloromethylation route is an alternative method to the direct sulfonation by using strong acids, allowing to obtain efficient, structurally stable, and resistant membranes. Sulfonic acid groups were generated during oxidation of thiol groups in the membranes, where water uptake, ion exchange capacity, and ion conductivity increased with the conversion time of the reaction. Surface roughness was identified for high sulfonated membrane by AFM; the topology was generated for hydrophilic ($-\text{SO}_3\text{H}$) and hydrophobic parts (polymer backbone) on the membrane. The prepared membrane sSEBS-7H showed an IEC value of 1.46 meq/g and high ionic conductivity (18.7 mS/cm at 25 °C) in comparison with reported values for commercial membranes, such as Nafion 115. According to TGA, acid groups of sulfonated membranes prepared by indirect sulfonation were thermally stable up to 150 °C, offering great potential for its use in fuel cells.

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