Degree of Sulfonation (DS) - Determination by Different Analytical Techniques in Ionomers Derived from Polystyrene

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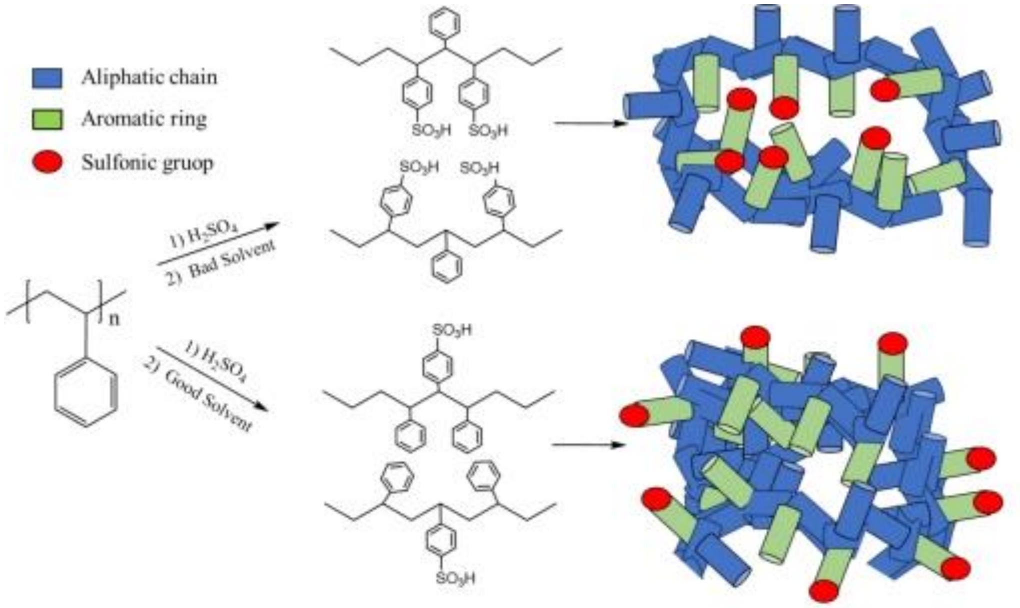
ABSTRACT

Polymers with ion charges anchored to their structure, known as ionomers, are slightly modified materials with notable applications for electrochemical processes. However, the characterization and quantification of those sulfonic groups grafted to the polymer is uncommon, which can lead to inaccurate data regarding their performance. A styrene-co-butyl acrylate copolymer (80:20) was synthesized and further sulfonated with concentrated sulfuric acid. Analytical techniques such as proton nuclear magnetic resonance (^{1}H NMR) and thermogravimetric analysis (TGA) were employed to characterize ionomers and used to calculate the degree of sulfonation (DS). Membranes were prepared by casting from the sulfonated copolymer, using two different solvent systems; then, the ion exchange capacity (IEC) was evaluated to be able to calculate DS values. For the ionomer, a DS of 35.2% was obtained by ^{1}H NMR and 38.4% by TGA, while from membranes IEC results the DS ranged from 4.9% to 28%, depending on the solvent system used for membrane preparation. The DS evaluation in the ionomer is similar for both analytical techniques used, since measuring the presence of sulfonic groups; however, the most popular IEC technique to measure DS value must be taken with care, since the method is more related to the structural condition, where

the ionic groups are available to exchange, highly affected by the membrane preparation method.

GRAPHICAL ABSTRACT



KEYWORDS

Degree of sulfonation (DS), Ionomer, Ion exchange capacity (IEC), analytical techniques.

1. INTRODUCTION

The growth in energy demand has led to a steady increase in production levels necessary to meet society's needs, driven by factors such as population growth, rapid urbanization, and industrial progress [1]. These factors have resulted in unprecedented energy consumption, posing a significant challenge: maintaining this demand could become unsustainable in the current context [1]. In the 21st century, one of the main challenges is to reduce greenhouse gas emissions by promoting the development and implementation of clean energy sources. Various international agreements have set ambitious goals for the current decade, aiming to drastically reduce emissions and limit the rise in global temperature, a consequence of excessive reliance on fossil fuels [2]. Additionally, the accelerated depletion of natural resources and the associated cost increases have spurred the search for innovative solutions and the modernization of inefficient energy processes to foster sustainable growth [3].

In this context, ionomers emerge as a promising solution to address current energy uncertainties. In recent decades, these materials in their membrane form, have demonstrated significant potential in ionic transport due to their unique properties, making them ideal for applications in renewable energy technologies and contributing significantly to environmental benefits.

Among the first polymeric materials to be converted into ionomers is polystyrene, primarily due to its low cost and availability [4]. However, this material presented certain significant drawbacks. One of them was that a high modification could reach a DS close to 100%, turning it into overfull swelling material in polar solvents, such as water [5]. This posed a considerable challenge for specific electrolytic applications, such as in chlor-alkali cells, where the medium is predominantly an aqueous solution [6]. Additionally, the absence of structural crosslinking limited its mechanical properties, restricting its applicability in environments requiring greater mechanical strength [4].

One of the ionomers transformed into a membrane that revolutionized the market was the perfluorosulfonic acid derivatives, commercially known as Nafion®, developed in the 1970s [7]. These membranes stand out for their excellent ability to transport cationic species, thanks to their sulfonic (SO_3H) termination, as well as their remarkable chemical and thermal stability [8]. However, they present certain limitations, such as poor mechanical stability, decreased conductivity at high temperatures, a complex synthesis process and a high cost exceeding \$1,000 USD/m^2 [9].

This has sparked a controversy in terms of sustainability, leading to intensified efforts to develop easily accessible ionomers with outstanding mechanical properties and exceptional performance in the transport of ionic species.

In recent years, research has resumed for the development of ionomers based on polystyrene, such as styrene-co-acrylic acid copolymers [8], styrene-co-butyl acrylate copolymers [9] and terpolymers like acrylonitrile-butadiene-styrene (ABS) [10]. These combinations aim to overcome the initial shortcomings of the PS homopolymer and, additionally, to address the limitations of Nafion®, by improving key properties such as mechanical strength, ionic conductivity at high temperatures, maintaining relatively accessible costs.

For these materials, the ionic site is responsible for ionic transport. However, in many cases, the calculation of the DS is at the same time reported in different ways, making it difficult to obtain a general and precise reproducibility. For example, Hongying Hou et al. [11] analyzed the thermal stability of a sulfonated poly (ether ether ketone) (SPEEK), using TGA technique, revealed a significant weight loss at 270 ºC attributed to the decomposition of sulfonic groups. Based on this weight loss, they determined the DS. For instance, P. Baulding et al. [12] determined the DS in sodium polystyrene sulfonate synthetized and a commercial resin for ^{1}H NMR. Additionally, Baigl y col [13] monitored the evolution of the DS in sulfonated polystyrene with different DS levels using ^{1}H NMR. Furthermore, Abdul G. Al Lafi et al [14] determined the DS of SPEEK using information obtained from different techniques like as, IEC, TGA, and ^{1}H NMR, achieving a correlation among the methods employed.

Since the determination of DS through different analytical techniques, each requiring specific interpretation depending on the material, this manuscript presents a comparative study of three widely used methodologies: TGA, ^{1}H NMR, and IEC. The material selected for this study was a sulfonated styrene-co-butyl acrylate (sSt-co-BuA) ionomer, whose composition and physicochemical properties were considered for each analytic method [12,14] .

2. MATERIALS AND METHODOLOGY

2.1. Materials

The styrene monomer (St), butyl acrylate monomer (BuA), benzoyl peroxide (BPO) initiator, and a sodium polystyrene sulfonate resin (SPSNA) to use as a model, were purchased from Sigma-Aldrich, along with sulfuric acid (H_2SO_4, 96–99%), sodium chloride (NaCl, 99%), and sodium hydroxide (NaOH, 97%). Dichloromethane (DCM, 99%), hydrochloric acid (HCl, 37%), tetrahydrofuran (THF, 99%), chloroform (CH_3Cl, 99%), 2- butanone or methyl ethyl ketone (MEK, 99%), acetone (99.5%), and toluene (99.5%) were obtained from J.T. Baker. The monomers were pre-purified using a resin inhibitors remover purchased from Sigma-Aldrich [15].

2.2. Synthesis

The preparation of the styrene-co-butyl acrylate copolymer followed a methodology from a previous work [9,16]. The copolymerization reaction was carried out using bulk free-radical chain copolymerization for the styrene (St) and butyl acrylate (BuA) comonomers [16]. The reaction scheme is shown in Figure 1.

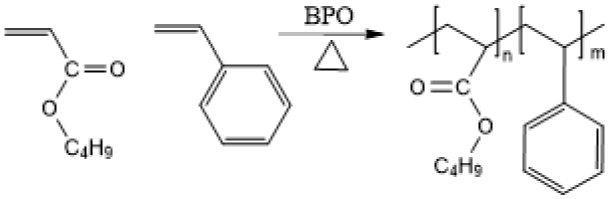


Figure 1. St-co-BuA (83:17) reaction scheme

2.3. Sulfonated polymer

Preparations of sulfonated St-co-BuA also followed a methodology published in literature [9] . Direct sulfonation stands out among techniques for modifying polymeric materials, particularly polystyrene derivatives. This process involves an electrophilic substitution, as the oxygen atoms bonded to the sulfur atom, being more electronegative, attract electronic charge toward themselves. This creates an electron density deficiency in the sulfur atom, making it an electrophilic center. This center can react with electron-rich aromatic rings (Figure 2); the process is facilitated by the delocalization of π-electrons in the aromatic system [17].

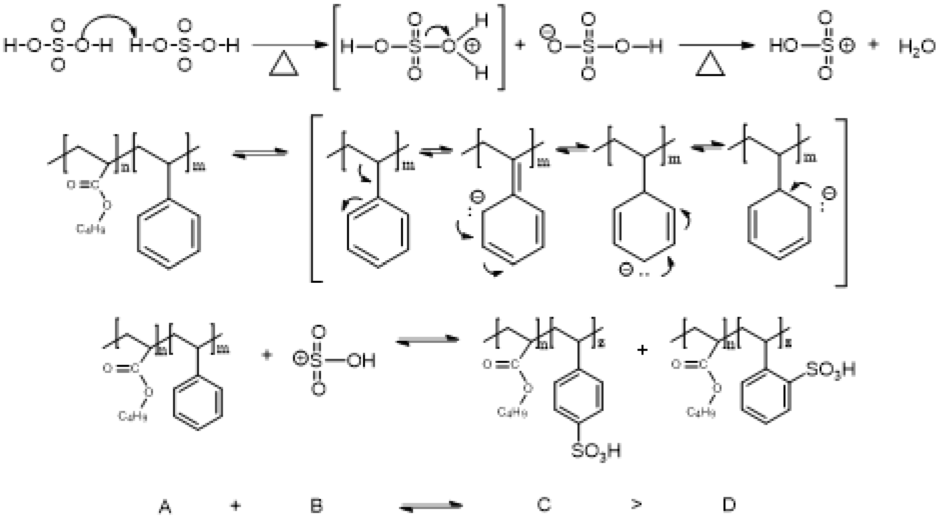


Figure 2. Schematic representation of an electrophilic substitution in a polystyrene chain [18].

2.4. Membranes preparation

Two cation exchange membranes were prepared from the obtained ionomer: MEK as the solvent and another with a THF/toluene mixture as a solvent/non-solvent blend. The solution concentration was 100 mg/ml, prepared under constant magnetic stirring. Once complete solubility was achieved, the solutions were deposited onto a smooth surface and spread using a motorized blade, controlling the blade height relative to the base to ensure better thickness control. The blade speed during the spreading process was set at 10 mm/s^{-1}.

3. ANALYTICAL TECHNIQUES

3.1. Nuclear magnetic resonance (^{1}H NMR)

The ^{1}H NMR spectrum of the St-co-BuA ionomer was obtained using a Bruker instrument operating at a frequency of 400 MHz. The analysis conditions were a temperature of 25°C and the central peak of $CDCl_3$ assigned at ≈7.26 ppm (^{1}H) relative to TMS (Internal standar).

3.2. Thermogravimetric analysis (TGA)

The TGA of the St-co-BuA ionomer was performed using a TA Instruments Q500 system. The study was conducted over a temperature range of 25 to 700°C, with a heating rate of 10°C/min, under a nitrogen atmosphere. Prior to the analysis, the ionomer was subjected to intensive drying by increasing the system temperature to 120°C to ensure the complete removal of any solvent/humidity interference.

3.3. Ion exchange capacity (IEC)

The IEC was determined by an indirect titration method, using a Metrohm Titrino 848 automatic potentiometric titrator. Before measurement, the membranes were dried in an oven at 40°C for 24 hours to obtain a constant weight.

The membranes were immersed in a 1 M HCl solution for 24 hours, then rinsed with deionized water and subsequently immersed in a 1 M NaCl solution for another 24 hours, followed by an additional rinse with deionized water. The number of protons displaced in the membranes was determined from the equivalence point obtained during the titration of the NaCl solution with a 0.005 M NaOH solution. The IEC was calculated using the following equation:

$$IEC = \frac{V_{NaOH} \cdot N_{NaOH}}{M_s}$$

Where V_{NaOH} is the volume of the NaOH solution used (ml), N_{NaOH} is the concentration of NaOH (mmol/ml or meq/ml), and M_s is the weight of the dry membrane (g). IEC is generally expressed in millimoles per gram of dry membrane, since the fixed charges (SO_3^-) are monovalent [19]. IEC of sPS ionomers can usually range from less than 1 to 5 mmol/g. However, in the case of copolymers, this value will depend on the comonomer composition.

4. RESULTS AND DISCUSSION

This section presents the results obtained using different analytical techniques to determine the DS in the ionomer (sSt-co-BuA) and its membranes. Additionally, the mathematical arrangements and implemented formulas used for DS calculation are included.

4.1. RMN ^1H

The characteristic signals of protons in the ortho, meta and para positions of the sulfonated aromatic rings were identified in a commercial sPSNa resin from Sigma-Aldrich used as a model. Similarly, the corresponding signals of these protons were observed in the sSt-co-BuA ionomer prepared, either for sulfonated or non-sulfonated structures. The characteristic chemical shifts of these materials are presented in Figure 3.

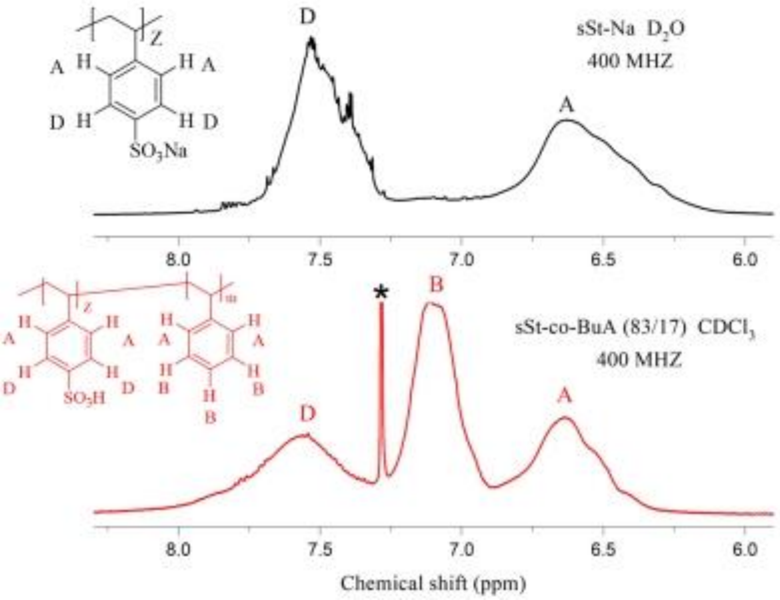


Figure 3. ^1H NMR spectrum of the ionomer sSt-co-BuA, region 8.0-6.0 ppm ($CDCl_3$).*

The area of the protons in the ortho position (A) of the aromatic ring (6.9–6.3 ppm) remains unaffected before and after sulfonation at best. To further discuss the signal in the 7.8–7.40 ppm region, it is necessary to understand that the chemical environment of the sulfonated aromatic rings is altered when SO_3H groups are grafted. The inductive effect caused by the SO_3H molecules shifts the neighboring aromatic protons downfield due to a decrease in electron density in the aromatic region [20]. Considering the observed decrease in the signal area between 7.1 and 6.9 ppm in materials with high sulfonation degrees, along with an increase in the signal area in the 7.80–7.40 ppm region (figure 4), it is possible to monitor the sulfonation level.

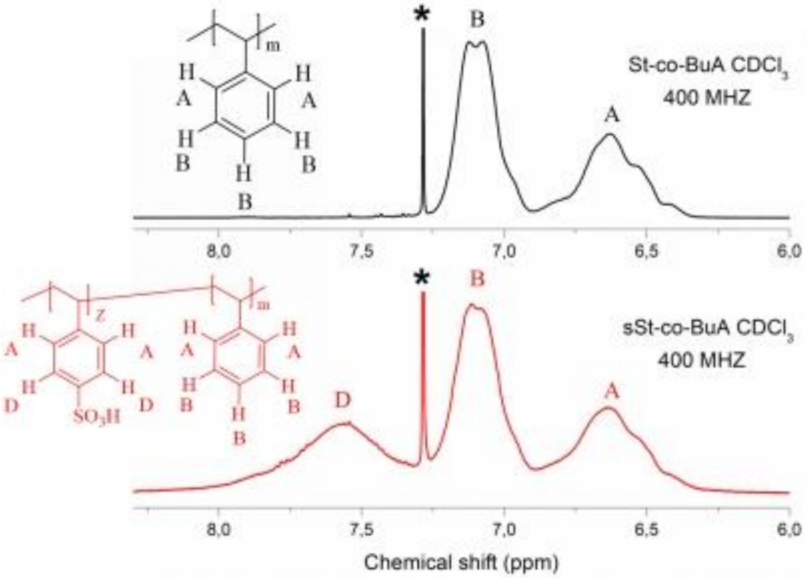


Figure 4. Chemical shift region of aromatic ring protons in the St-co-BuA before and after sulfonation (*$CDCl_3$).

This agrees with the procedures of Baigl D. et al. [13], who observed that as the signal corresponding to meta-positioned protons in sulfonated aromatic rings increased, the meta and para signals of non-sulfonated aromatic rings progressively decreased, until complete disappearance.

The DS of the sulfonated material was calculated using ^1H NMR signals, following the next procedure: the area under the curve of the signal corresponding to the protons in orto position was obtained by normalizing the first integral, followed by the protons in the meta position (adjacent to the grafted SO_3H group). Table 1 presents the normalized areas of each integral obtained.

Table 1. Characteristic integral values of each signal in the sulfonated material.

Signal (ppm)	Area (Normalized)
≈7.8-7.40	0.54
≈6.80-6.40	1

Then, the calculation of the signals area/meta position protons correspondence of the sulfonated aromatic ring (7.8–7.40 ppm), which is divided by 2, as it corresponds to two neighboring protons in the meta position. Similarly, the area of the signals in the 6.88–6.40 ppm region is divided by 2 protons, corresponding to the protons in the ortho position of the non-sulfonated aromatic rings. The results obtained are detailed below.

$$\frac{\int \#H\'s\ META}{2} = \frac{0.54}{2} = 0.27 = D$$

$$\frac{\int \#H\'s\ ORTO}{2} = \frac{1}{2} = 0.5 = A$$

Where D corresponds to the number of hydrogens in meta position, neighbor to SO_3H group and A corresponds to the hydrogens number in ortho position in the aromatic ring (sulfonated or non-sulfonated). The sum of these two values represents the total protons for both sulfonated and non-sulfonated aromatic rings, that is, the total number of aromatic rings present in the material.

$$D + A = \beta$$

$$0.27 + 0.5 = 0.77$$

Therefore, the ratio between the area of the signals corresponding to the sulfonated aromatic rings and the total area will provide the percentage of aromatic rings with SO_3H group grafts, which is equivalent to the DS.

$$Ds = \frac{D}{\beta}\ x\ 100\ \%$$

$$DS = \frac{0.27}{0.77}\ x\ 100\ \% = 35.06\ \%$$

Highlight that the calculated chemical environment corresponds to the DS express in mol%. The ^1H NMR characterization only determines the number of SO_3H species but not side reactions, like crosslinking events (insoluble components) through sulfonic groups.

4.2. Thermogravimetric analysis (TGA)

In Figure 5, the TGA thermogram of the sSt-co-BuA ionomer clearly shows a two-step decomposition, corresponding to the degradation of the sulfonic groups and the thermal stability of the polymer backbone, in contrast to the non-sulfonated copolymer, which exhibits a single weight loss event.

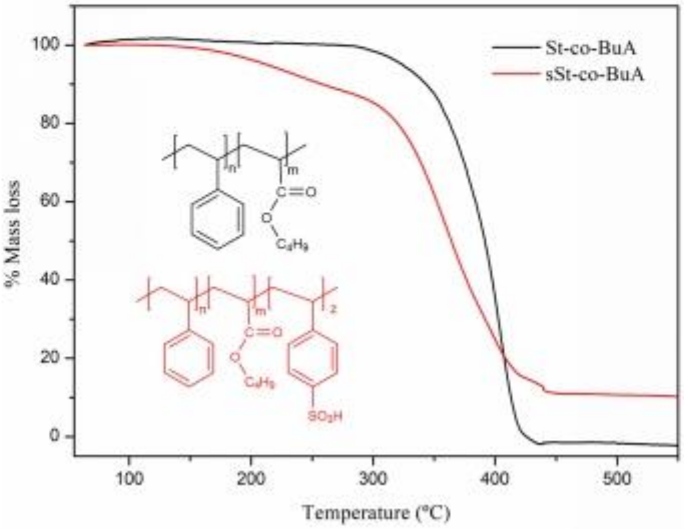


Figure 5. TGA Thermogram of sSt-co-BuA.

As can be observed, two weight loss steps are seen, corresponding to the degradation profile of sSt-co-BuA ionomer. The first weight loss begins around 170°C, by the presence of sulfonic groups species (SO_3H) with complete decomposition up to approximately 280°C [21]. During the sulfonation of aromatic rings a sulfone, crosslinking event ($Ar–SO_2–Ar$), may also form [22]. However, for the purposes of this interpretation, only the events related to the sulfonic groups present within this interval will be considered.

Beata T. Koziara et al. [23], reported a decomposition range of the sulfonic acid groups between 150 and 400 ºC in SPEEK material. Additionally, they demonstrated that the material in its acidic form (SO_3-H) promotes degradation via proton desulfonation, within this temperature range. The second weight loss begins around 300°C and ends around 450°C, related to the thermal stability of the polymer chain or the hydrophobic section of the ionomer [9].

Regarding the first weight loss (170–280°C), a desulfonation reaction occurs (loss of -SO_3H species), according to the reaction $4SO_3H \rightarrow 4SO_2\uparrow+2H_2O\uparrow+O_2\uparrow$ reported [24-25].

Chenliang Gong et al [26] found that sulfonated polystyrene and other chemicals with sulfonic acid (SO_3-H) and sulfonate salt groups (SO_3-X), in the temperature range of 200 to 275°C, release water molecules and sulfur dioxide, for the sulfonic acid groups.

To determine the DS using the information from the TGA thermogram of sSt-co-BuA, it is necessary to know the molar percentage relationship between the sulfonating agent and the aromatic rings (100%), the theoretical molecular weight of the repeating unit calculated based on the composition determined by ^{1}H NMR, which is equivalent to 5 units of St per 1 unit of butyl acrylate (BuA) (83/17) (Figure 6).

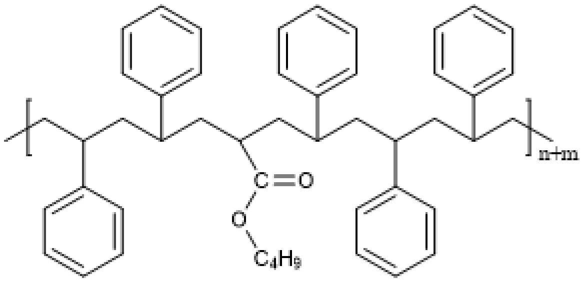


Figure 6: Real composition of St-co-BuA (83:17) determined by ^{1}H NMR

The theoretical molecular weight of the St comonomer is 104 g/mol, while that of BuA is 128 g/mol. Therefore, to correctly interpret the molecular weight of the repeating unit, it is necessary to divide the weight of BuA by 5 and add it to the weight of St, which allows for an appropriate relationship between both components, as determined in the composition. This relationship is interpreted as follows:

St-co-BuA(83/17) = 104 g/mol + (128/5) g/mol = 129.6 g/mol.

Finally, to determine the molecular weight of the repeating unit of the ionomer, the sum of the SO_3H groups should be considered, with a molecular weight of 81 g/mol (129.6 g/mol + 81 g/mol = 210.6 g/mol). This is necessary to calculate the maximum percentage of SO_3H groups that can be grafted onto the polymer matrix. This value is obtained using the following relationship:

$$\%SO_3H = \frac{(100\ \%)(81\ \frac{g}{mol})}{(210.6\ \frac{g}{mol})} = 38.46\ \%$$

Considering that the maximum percentage of SO_3H groups is 38.46%, and calculating the % loss obtained, relative to the weight loss signals corresponding to the SO_3H group, it is possible to determine the DS. The TGA thermogram shows a weight loss of 14.57%, then:

$$DS = \frac{(100\%)(14.57\%)}{(38.46\%)} = 37.88\%$$

4.3. IEC

IEC for membranes from the sulfonated copolymer was determined using an indirect method of titration, as detailed in the experimental section. The IEC values were obtained for two membranes, prepared with MEK and solvent/non-solvent mixture of THF/Toluene in a 1:1 ratio. The results, presented in Table 2, represent the average of three repetitions for each test

Table 2. Ion exchange for membranes prepared with different solvents

Ionomer-solvent	IEC (mMol/g)
sSt-co-BuA/MEK	1.857
sSt-co-BuA/THF/Toluene (1:1)	0.373

It is important to highlight that the IEC is related to the DS, or the number of ionic species grafted onto the ionomer, but only for those sites available for ion exchange. Material shows a significant difference between the cation exchange membranes (CEMs) prepared with polar solvents and those prepared with solvent/non-solvent mixtures. Although both come from the same material, with the same DS, there are notable differences in the ion exchange values. This is because the type of solvent used to mold the membranes affects the freedom and availability of the ionic sites [27], [28], [29]. The CEMs made with MEK show a higher number of available ionic sites compared to those prepared with non-polar solvent mixtures The DS can also be calculated from the IEC values and directly compared with those previously obtained through ^1H NMR and TGA. The ^1H NMR and TGA techniques involve the magnetic moment and mass of the component without transforming the ionomer. On the other hand, IEC directly depends on the solvent's ability to solve the polymer chain used in membrane preparation. This includes the ionomer-solvent interaction, the solvent's ability to solvate both hydrophobic and hydrophilic regions, phase inversion conditions, the counterion, and other factors. These aspects ensure that the ionic groups are as available as possible for exchange reactions.

The DS from the ion exchange capacity, which is related to the available and exchangeable sites, is calculated based on the formula determined by R. Y. M. Huang, et al [30]. Using the molecular weight values of the repeating unit and the sulfonic group weight, the following formula was used:

$$\%DS = \frac{IEC\ x\ Mw\ material}{1 - (IEC\ x\ Mw\ SO_3H)}\ x\ 100$$

Regarding the molecular weight of the material (Mw), it represents the molecular weight of the unmodified repeating unit of the material, without considering the sulfonic groups. This value is calculated based on the composition of the copolymer. In this case, the proportion of styrene is five times greater than that of butyl acrylate (BUA) in the composition. Therefore, the molecular weight of styrene is 104 g/mol, while the molecular weight of BUA (128 g/mol) is divided by 5 to respect this ratio. This ensures that the formula is not altered and that the molecular weight of the material, including the sulfonic groups, is correctly calculated. Thus, the molecular weight of the material is: 104 g/mol + (128/5 g/mol) = 129.6 g/mol. On the other hand, Mw SO_3H represents the molecular weight of the sulfonic group based on the aromatic rings in the material. In this case, assuming complete sulfonation of one aromatic ring unit (derived from the styrene comonomer), the corresponding molecular weight is 81 g/mol. With these values and the previously obtained IEC data (properly converted to mol/g), the DS for each material was determined. To ensure the accuracy of the results, the DS was calculated as the average of three tests conducted per membrane.

Table 3 shows the DS values for membranes obtained from solvents or mixtures with different dielectric constants during the membrane preparation procedure.

Table 3. DS calculated from IEC values

Ionomer-solvent	DS (%)
sSt-co-BuA/MEK	28.3
sSt-co-BuA/THF/Toluene (1:1)	4.9

As expected, a big DS value difference is observed between membranes since the calculation considers not only the presence of sulfonic groups but also their availability for exchange in an ionic environment. The reasons for such big differences will be published soon.

5. CONCLUSIONS

The ionomer sSt-co-BuA, with a molar composition of 83:17 was prepared and characterized, achieving its chemical modification through the grafting of sulfonic groups onto the polymer matrix. Such modification resulted in an average DS ranging from 5-38%, depending on the technique used. ^{1}H NMR was employed to characterize the material and determined an approximate DS value of 35%. Thermal analysis revealed two weight losses: the first corresponding to the sulfonic groups and the second to the stability of the main chain. The DS percentage of the material, determined via TGA, was approximately 38%.

The values obtained for the IEC varied depending on the ionomer's affinity for the solvent, and the calculated DS also reflected these differences, being 28% for membranes prepared with the MEK solvent, but 5% when cast from a mixture of solvent/no-solvent.

The different techniques implemented for determining sulfonic groups in styrene-derived copolymers were successfully correlated, allowing for the characterization of this parameter through various physicochemical techniques. It is also important to remark that DS values are usually reported from IEC results, without considering the big differences in the results from the solvent used to prepare casted membranes.

6. ACKNOWLEDGMENTS

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Author Statement

J.C. Sánchez Hiza - Methodology, Experimental design.

R. Benavides - Experimental design, Conceptualization, Data curating.

D. Morales Acosta - Experimental design, Conceptualization, Data curating.

Luciano da Silva: Supervision, Writing- Reviewing and Editing.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes: The authors declare no competing financial interest

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