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Polysulfone with Different Degrees of Sulfonation: Simple Method with Acetyl Sulfate

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In this work, the authors present as an innovation, the homogeneous sulfonation of Udel® polysulfone (PSU) with acetylsulfate (ACS) under reflux at 45°C in dichloromethane and inert N_2 atmosphere (g) for 1.5 h. Different proportions of ACS were used, obtaining sulfonated products with varying degrees of sulfonation (DS). Confirmation of sulfonated polysulfone (PSU-S), denominated as PSU-S_A (high degree of sulfonation) and PSU-S_B (low degree of sulfonation), was carried out by FTIR and ^{1}H NMR. Determination of DS was carried out through thermogravimetric analysis (TGA/DSC), varying indexes between 0.883 and 3.022, which correspond to a sulfonated polymer with ion exchange capacity (IEC) from 1.720 to 4.400 meq/g. The evolution of DS related to methods used was monitored and confirmed by ^{1}H NRM. Sulfonation is undertaken to enhance the suitability of this polymer for future applications in the production of biofuels, targeting its utilization in catalytic processes for esterification and transesterification mechanisms of oils and fats.

Graphical abstract

Keywords

Degree of sulfonation
Homogenous sulfonation
Ion exchange capacity
Kopf method
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1. Introduction

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Some polymers have received special attention in the last years due to their characteristics and properties, becoming the target of study and applications in various sectors, searching for solutions in the health sector, environment, and energy. Among those with great prominence is Udel® polysulfone (PSU), the high-performance polymer used as raw material in the preparation of carbon nanotubes, and nanowires for industrial and biomedical ultrafiltration processes; as well as in the formation of membranes for fuel cells, among many other technological applications [1-6].

The diversification of PSU application is due to its excellent chemicals and mechanical characteristics, for example, good resistance to acids, bases, and other chemical agents in a wide range of pH; like oxidation and mechanical and thermal tension; as well as its good solubility in solvents normally used in preparations of membranes and the possibility of being chemically medicated due to its aromatic rings in its structure [7-10].

Among the possibilities for structural modification of polymers, sulfonation by aromatic electrophilic substitution (AES) is one of the synthetic paths used [11,12]. In it, sulfonic groups are attached to organic molecules by replacing a hydrogen atom in the aromatic ring [13]. In general, polymer sulfonation methods are derived from those used for small organic molecules, however, adjustments in reaction conditions need to be adapted according to the chemical characteristics of the polymer to be sulfonated [12].

The introduction of sulfonic groups has been one of the PSU functionalization tools, due to the possibility of increasing hydrophilicity and improving its permeability, porous size, and other fundamental characteristics for ion exchange membrane in electrolysis processes, electrodialysis, dialysis, fuels cells, reverse electrolysis, sensors, and catalysts for various purposes [14-20].

Over time, lots of reactants have been employed in PSU sulfonation, being able to highlight the sulfur trioxide-triethyl phosphate complex (SO_3/TEP) [21-23], fuming and concentrated sulfuric acid [24], trimethylsilyl chlorosulfonate (TMSClS) [25-32] and chlorosulfonic acid (HSO_3Cl) [14,19,20,29-31,33-36]. These reaction conditions need more careful handling compared to the method proposed in this work.

Even though acetylsulfate (ACS) has been known for some time [37,38], this reagent has not been used to sulfonate the PSU, due to a lack of work in the literature. It is mentioned by Smitha *et al*. [33] as a reaction that does not occur due to its incompatibility between PSU and ACS. Nielsen *et al*. [39] PSU was functionalized with pendant (chloromethyl)benzoyl groups in a previous reaction to then be able to direct the reaction between PSU and ACS, a fact that was not necessary in this work.

Highlighting the importance of sulfonation, Lima *et al*. [40] obtained very promising results in the preparation of electrospun membranes formed by PSU in association with sulfonated polystyrene (PS-S). This electrospun blend is exclusively suitable for catalyzing the esterification of oleic acid, owing to the incorporation of sulfonic groups into the polymer's chemical structure.

Expanding these studies investigated a new methodology with low cost under wide reactional conditions for PSU sulfonation using ACS. Different PSU-S samples were obtained, which were denominated as PSU-S_A (high sulfonation index, i.e., DS > 1) and PSU-S_B (low sulfonation index, where DS ≤ 1). These PSU could be used in the future in a variety of applications, whether as catalysts to produce biofuels or even as a precursor in the production of electrospun catalyst membranes, as discussed by Lima *et al* [40].

2. Material and Methods

Udel® polysulfone (Mw = 35.000 g/mol; MM = 442 g/mol) was acquired with Sigma-Aldrich (USA); acetic anhydride, sulfuric acid, and 95% ethanol were purchased from Acros and utilized as received; as well as dichloromethane provided from Tedia (USA). Deuterated chloroform and deuterated dimethyl sulfoxide were manufactured by CIL (USA).

2.1 Obtaining ACS for the preparations of PSU-S_A

The ACS was prepared just before using it as a reagent in the sulfonation reaction to obtain PSU-S in a high sulfonation degree. The experiments were carried out in a continuous exhaust fume hood.

In a beaker (150 mL) with 24 mL (251 mmol) of acetic anhydride, kept in an ice bath, temperature between 3 and 5°C under magnetic stirring, concentrated sulfuric acid was slowly added (12 mL, 228 mmol) so that the temperature of reaction medium did not exceed the pre-established 5°C. The mixture was kept under magnetic stirring for 30 minutes.

2.1.2 Obtaining PSU-S_A

In a three-necked flask (500 mL) containing PSU polymer (5.0110 g; 0.0113 mol) dissolved in CH_2Cl_2 (100 mL), under an inert N_2 atmosphere, magnetic stirring, and a temperature of 45°C, PSU was sulfonated using ACS previously prepared as described in item 2.1. After 1.5 h of reaction, the mixture was poured into a beaker (2 L) containing an ice bath (5°C)/deionized water (500 mL) under mechanical stirring. The mixture was left under mechanical stirring for 30 minutes until the complete formation of a white precipitate (PSU-S). After that, the precipitate was filtered to start the purification step.

The precipitate was washed with 350 mL of deionized water within each step, repeating it three times, and always preheating the water to 55°C to force the evaporation of the phase rich in dichloromethane. There was a complete solubilization of the polymeric material in this step. This solution was then concentrated in a water bath (80°C) and the polymer precipitated. This polymer was dissolved in 95% ethyl alcohol (200 mL), and the new polymer solution was transferred to 10 Petri dishes (100x20 mm) and kept at room temperature (25°C) until almost complete evaporation of the alcohol (approximately 2 days). The PSU-S_A (8.2025 g) was crushed in a blender, sieved through a 1 mm mesh, dried in an oven at 55°C for 15 h, and stored in a desiccator.

2.2 Obtaining ACS for the preparation of PSU-S_B

Once more, the ACS was prepared moments before being used as a reagent in the sulfonation reaction to obtain PSU-S low sulfonation degree.

In a beaker (150 mL) with 6 mL (62.8 mmol) of acetic anhydride, kept in an ice bath, temperature between 3 and 5°C under magnetic stirring, concentrated sulfuric acid was slowly added (3 mL, 57 mmol) so that the temperature of reaction medium did not exceed the pre-established 5°C. The mixture was kept under magnetic stirring for 30 minutes.

2.2.1 Obtaining PSU-S_B

In this experiment, the procedure was similar to item 2.1.2, only with some changes in volumes, masses, and the purification step.

In a three-necked flask (500 mL) containing PSU polymer (5,0022 g; 0,0113 mol) dissolved in CH_2Cl_2 (100 mL), under an inert N_2 atmosphere, magnetic stirring, and a temperature of 45°C, PSU was sulfonated using ACS previously prepared. After 1.5 h of reaction, the mixture was poured into a beaker (2 L) containing an ice bath (5°C)/deionized water (500 mL) under mechanical stirring. The mixture was left under mechanical stirring for 30 minutes until the complete formation of a white precipitate (PSU-S). After that, the precipitate was filtered to start the purification step. Phases were separated and then the precipitate was washed using 500 mL of deionized water, repeating this process three times, the water was preheated to 55°C to discard CH_2Cl_2 and eliminate impurities. In sequence, it was washed with 1 L of cold water, the polymer was filtered and left to dry in an oven at 55°C for 15 h. The PSU-S_B (6,2001 g) was crushed in a blender, sieved into 1 mm meshes, dried in an oven at 55°C, and stored in a desiccator.

2.3 Characterization

2.3.1 FTIR

The characterizations of the raw material (PSU) and its products PSU-S_A and PSU-S_B were done through Fourier Transform Infrared Spectroscopy (FTIR). The FTIR analysis was performed on an IRPrestige-21 device (Shimadzu) using the Attenuated Total Reflectance (ATR) accessory from PIKE Technologies. The measurements were in the region between 4000 and 600 cm^{-1}, with 20 scans and a resolution of 2.0.

2.3.2 Hydrogen Nuclear Magnetic Resonance (NMR) ^1H

The characterization by Hydrogen Nuclear Magnetic Resonance (NMR) of ^1H was performed on Bruker(R) – Model DRX400 – Ultra Shield (R), with 9.4 T magnet and multinuclear direct detection probe (^1H: 400.13 MHz and ^{13}C: 100.61 MHz) for 5 mm diameter tubes, with deuterium "lock" system and Z field gradient generator coil (maximum field of 53.5 Gauss cm^{-1}).

The determination of DS was performed through the Equation 1 [26]:

$$DS_{NMR} = (12-4R) / (2+R); R = A_B/A_A \quad \text{(Eq. 1)}$$

Where **R** provides the relationship between the integrals of the aromatic hydrogens of the sulfonated polymers; $\mathbf{A_A}$ is the area given by the integral of the peaks in region **A** (between 7,65 and 7,95 ppm) and $\mathbf{A_B}$ is related to the region **B** (between 6,83 and 7,35 ppm), presented on Figure 6.

PSU ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (4H, d, J=8.8Hz), 7.24 (4H, d, J=8.7Hz), 7.00 (4H, d, J=8.8Hz), 6.94 (4H, d, J=8.7Hz), 1.69 (6H, s).

PSU-S_A ^{1}H NMR (400 MHz, DMSO): δ 7.95-7.77 (4H, m), 7.70 (0.6H, bs), 7.27 (3.4H, bs), 7.05 (5.5H, bs), 6.93 (1,9H, d), 1.63 (6H, s).

PSU-S_B ^{1}H NMR (400 MHz, DMSO): δ 7.97-7,76 (4H, m), 7.72 (0.4H, s), 7.26 (3.7H, bs), 7.14-6.75 (7.7H, m), 1.62 (6H, s).

2.3.3 Thermal Analysis: TGA/DSC

The thermal analysis was performed on a thermal analysis system TA Instruments Q-600-Simultaneous DTA/TGA/DSC, where the TGA and DSC curves were done simultaneously, and the samples were heated at room temperature until 800 °C at a rate of 10°C/min under N_2 atmosphere.

The DS determination of the sulfonated polymers was done through the Equation 2 [29]:

$$DS_{TGA} = 442 / (EW - 81); EW = 1 / [(W_{2\ step} / 100) / 81] \quad \text{(Eq 2)}$$

Where 442 and 81 refer to the PSU molar mass and the group $-SO_3H$, respectively, and the $W_{2\ step}$ is related to the mass lost on the second step, it means, in the thermal desulfonation of the sample.

2.3.4 Relationship between DS and IEC of sulfonated polymers (PSU-S_A and PSU-S_B)

The DS and IEC quantities are related through Equation 3 [26]:

$$IEC = (DS \times 1000) / [442 + (DS \times 81)] \text{ meq of } H^+/\text{g of dry polymer} \quad \text{(Eq 3)}$$

Where 442 is referred to the mere PSU molar mass and 81 refers to the molar mass of the group $-SO_3H$.

2.3.5 Scanning Electron Microscopy

A morphological evaluation of PSU-S_A and PSU-S_B was performed by scanning electron microscopy using a Carl Zeiss model EVO MA 10. Samples were sputter-coated with 20 nm of gold layer and then examined on the microscope at 20 kV.

3. Material and Methods

In this work, the synthesis methods for sulfonated polymers used permitted that two types of polymers were synthesized with excellent results. The choice of sulfonation conditions was based on the work of Martins *et al.* [41]. A material with a moderate degree of sulfonation was desired since low degrees of sulfonation could not present low catalytic efficiency. A high degree of sulfonation could result in the loss of favorable properties of the catalysts, such as low mechanical resistance and a high degree of swelling. In this way, the sulfonation conditions were based on those conducted by Martins *et al.* [41], achieving desirable properties for the catalyst using cited reaction conditions for polystyrene sulfonation.

Prolonged temperature and reaction time favor parallel reactions, such as desulfonation and crosslinking [11,12], so preliminary tests indicated a time of 1.5 h, as optimal for the study. We will discuss the results obtained during the experimental work in the syntheses of the sulfonated polymers PSU-S_A (DS > 1) and PSU-S_B (DS ≤ 1) through the AES reaction using ACS as a source of SO_3H (electrophilic reagent). The proposed mechanism is described below, taking Pinto *et al.* as a reference [38], in Figure 1.

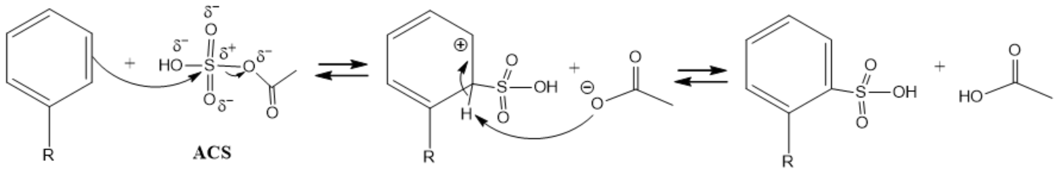

Fig. 1. Proposed mechanism for sulfonation using acetyl sulfate (ACS) as the sulfonating agent.

The reactivity of the sulfonating reagent depends, according to Khomein *et al*. [12], mainly on the ability to form sulfonic ions and the presence of good leaving groups in the structure. In the case of ACS, while it can make sulfur sufficiently deficient in electrons, providing the electrophilic species, -SO_3H group (active site), for the electrophilic attack on the aromatic ring, this sulfonant has in its structure a good leaving group, in this case, the acetate group.

In the reactions with AES, in structures like bisphenol A (poly(arylene ethers), as the one contained in the PSU, the insertion of the group -SO_3H occurs preferably in the ortho position related to the C-O bonds of the ether group of the monomeric part of bisphenol A, that is, in the meta position to the alkyl group (position 2 in Figure 2), due to the lower steric hindrance and the mesomeric effect, predominant in this case, the inductive effect caused by the alkyl group in this activated aromatic ring, exactly by the alkyl group [22,26,29,30,42]. In the case of PSU, the deactivating group (sulfone) causes the reaction rate to be lower, however, both the orientation position of the sulfone group and the C-O group are coincident, that is, sulfonation occurs in position 7 (Figure 2) [42].

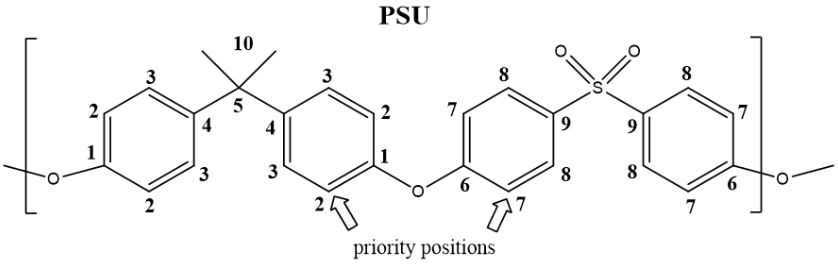

Fig. 2. PSU structure and priority position to occur AES.

Designating the PSU-S_A when occurs AES in more than one ring and can involve both positions (2 and 7) and PSU-S_B when occurs the substitution in only one single ring (mainly in position 2)

3.1 FTIR Analysis

The PSU sulfonation (PSU-S_A and PSU-S_B), was confirmed due to the FTIR spectra, as can be seen in Figure 3-a,b.

Comparison of the two signals (in the region from 600 to 4000 cm^{-1}) between three FTIR spectra (PSU, PSU-S_A, and PSU-S_B) allowed us to verify the signals referring to the basic chemical structure of PSU at 2930 cm^{-1} for the CH in the aromatic ring/ the signals at 1237, 1140 and 1102 cm^{-1} referred to S=O of the sulfone group; 1585 and 1014 cm^{-1} stretches referring to the C-O bond (in aromatics) and phenyl ether, respectively. These signals were maintained in the sulfonated polymers, the evidence that sulfonation occurred is given by the appearance of signals in the range between 3556-3421 cm^{-1} referring to SO_2OH stretching; 1237, 1144, 1104, and 1040 cm^{-1} (with small variation between the PSU-S samples), referring to the S-O stretching (highlighted in Figure 3-b) through the amplification of the peaks in the region between 600 and 1500 cm^{-1}). These data agree with those of Ryu *et al*. [35], and Avci *et al*. [14]. Dourado [24], Eroglu *et al*. [31], Martos *et al*. [29], and Smitha *et al*. [33].

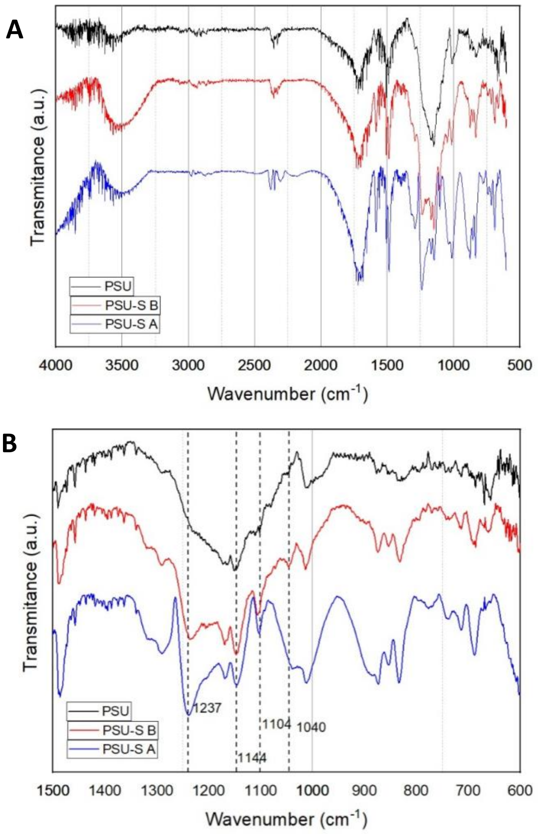

Fig. 3. FTIR spectra of PSU, PSU-S_A, and PSU-S_B samples. (A) entire spectral range. (B) magnification of the region between 600 and 1500 cm^{-1}.

3.2. PSU analysis by ^{1}H NMR

Initially, data from ^{1}H NMR analysis of Udel® PSU (Figure 4) will be shown, searching to show the changes (the insertion of sulfonic groups) that occurred in its structure after sulfonation.

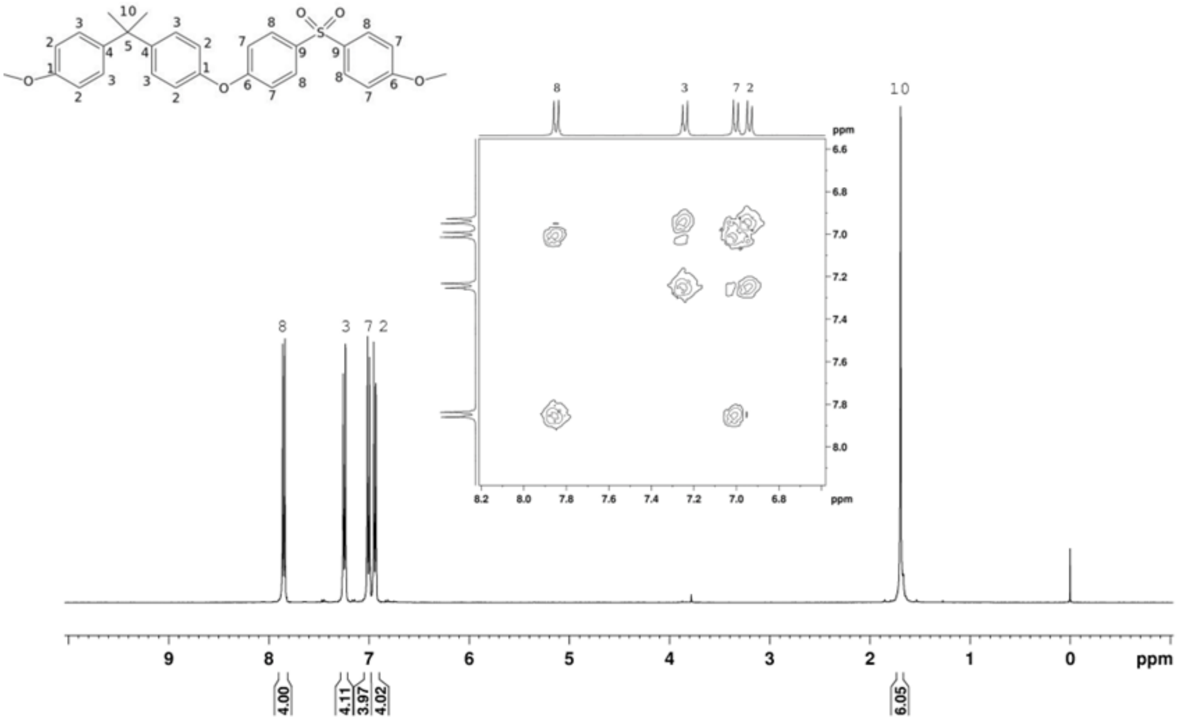

Fig. 4. ^{1}H NMR and ^{1}H-^{1}H COSY spectrum (400 MHz, $CDCl_3$/TMS) of the Udel® PSU.

The ^{1}H NMR spectrum of PSU presents well-defined signals. The possibility of it being a symmetric compound is evidenced by the small number of observed signals. The protons in position 8 have their electronic density reduced by the 'sulfonyl' group, resulting in their positioning in a lower field. The positive mesomeric effect of the ether group shields the aromatic protons 2 and 7, leading to an observable upfield shift. This attribution is based on Noshay and Robenson [21]. Martos *et al*. [29] and Eroglu *et al*. [31] present inversion between protons 7 and 2, however, the ^{1}H-^{1}H COSY spectrum (homonuclear Correlation Spectroscopy), highlighted in Figure 4, confirmed the attribution proposed here, with the coupling of 7 with 8 and 2 with 3.

3.3 PSU-S$_A$ and PSU-S$_B$ analysis by ^{1}H NMR

Examples of PSU-S$_A$ and PSU-S$_B$ structures can be seen in Figure 5. In these examples, to facilitate understanding of the discussion, it is considered that the substitutions occur in the priority positions (2 and 7) of the PSU, but in practice, the possibilities for insertion of the -SO_3H group are much more diverse, complex, and capable of other combinations. The numbering of protons followed the model presented by Eroglu *et al*. [31] and Avci *et al* [14].

Due to the difference in sulfonation in the preparation step of the PSU-S$_A$ and PSU-S$_B$, it is possible to notice the differences between the ^{1}H NMR spectrum of each sample in the aromatic protons region (Figure 6).

The ^{1}H NMR spectra of both sulfonated polymers exhibit significant differences compared to the non-sulfonated polymer. Sulfonation proceeds via a non-uniform process, resulting in the coexistence of moieties that remain unsubstituted, moieties with -SO_3H groups inserted at position 2, moieties with -SO_3H groups inserted at position 7, and moieties with -SO_3H groups inserted at both positions 2 and 7. This leads to broadening of the observed signals. The polymer shows different mere units throughout its structure, therefore the spectrums seen in Figure 6 result in that diversity with chains with the group -SO_3H inserted in position 2 in one of its meres in position 7 and so on. That diversity and complexity make it hard to make an individual assignment for each proton [26, 29, 42].

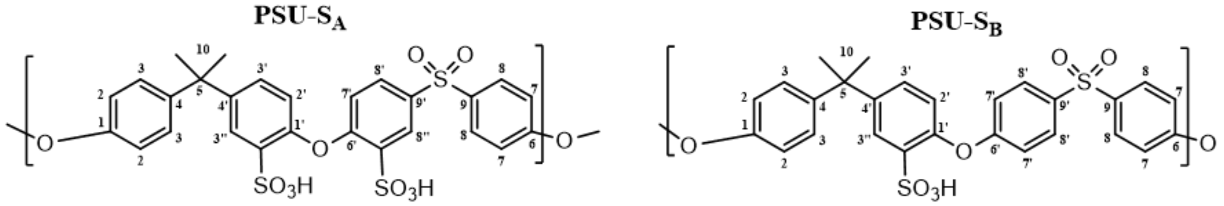

Fig. 5. Possible representation of PSU-S$_A$ (left) and PSU-S$_B$ (right) structures.

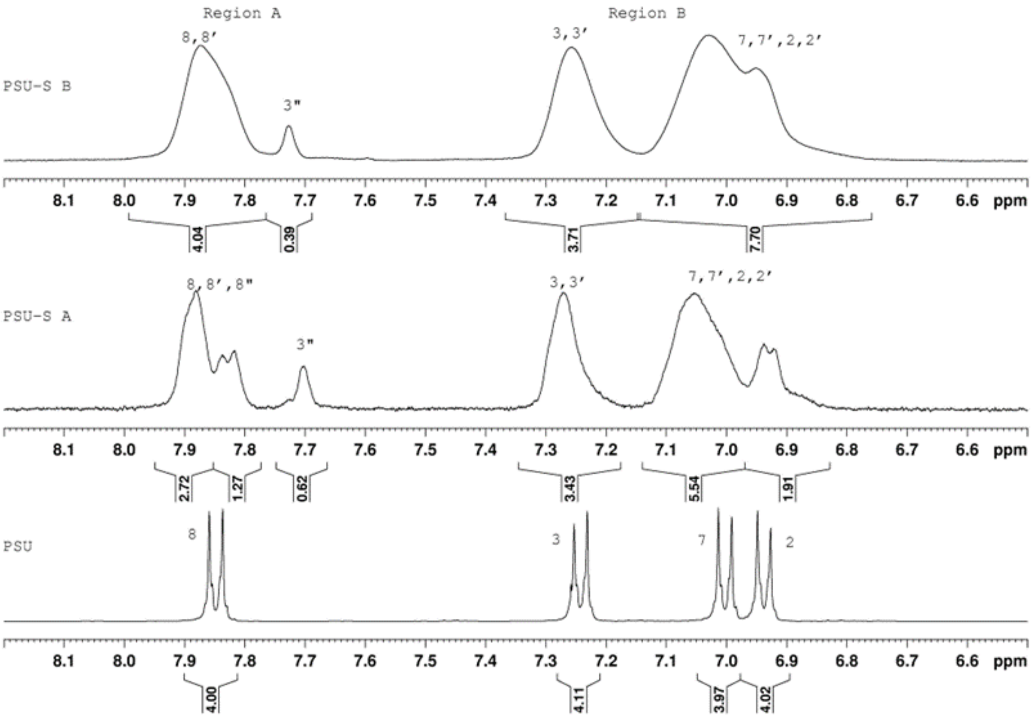

Fig. 6. ^{1}H NMR of PSU, PSU-S$_A$, and PSU-S$_B$ containing the integration of aromatic proton signals.

By observing the integrals of proton 2, it is possible to conclude that sulfonation preferably occurs at this site, as its integration reduces from 4 protons to approximately 1.91 on PSU-S$_A$. The insertion of -SO$_3$H groups in position two directly affects the displacements of the protons adjacent to them. Therefore, as sulfonation occurs in position 2, the integral of the adjacent proton 3 (7.25ppm) is reduced from 4 to 3.43. Simultaneously, a signal at 7.7 ppm becomes observable and is attributable to the 3" hydrogen, which is adjacent to the sulfonated site 2. This attribution is corroborated by the sum of the integrals of 3, 3', and 3", which adds up to 4, thus confirming that 3" is derived from 3.

The same phenomenon occurs when sulfonation happens in position 7. Its adjacent proton 8" appears as a distinctly observable signal in the region of 7.8 ppm. It is also possible to conclude that the signal at 7.8 ppm results from the sulfonation of position 7, as adding integrals of 8, 8', and 8" results in 4, corroborating that part of the 8 protons is now under the influence of the SO$_3$-H inductive effect.

The two PSU-S polymers exhibit the same signals at 7.7 ppm (proton 3"). However, the integral values indicate that the sulfonation of PSU-S$_A$ is significantly higher (0.62 versus 0.39). Additionally, the signals of PSU-S$_A$ in region A are more resolved. So, it is possible to observe that this polymer also underwent sulfonation in position 7, as discussed above.

NMR data agree with the other presented techniques, indicating that both polymers underwent sulfonation to different degrees, with PSU-S$_A$ considerably more sulfonated than PSU-S$_B$. The proton assignments of the PSU-S$_A$ and PSU-S$_B$ were performed according to the literature [14,21,29,31].

3.4 DS determination of PSU-S$_A$ and PSU-S$_B$ by TGA/DSC

The DS determination highlights the difference between each sample of PSU-S$_A$ and PSU-S$_B$, which was performed by TGA/DSC analysis. The thermogram of these samples is presented in Figure 7.

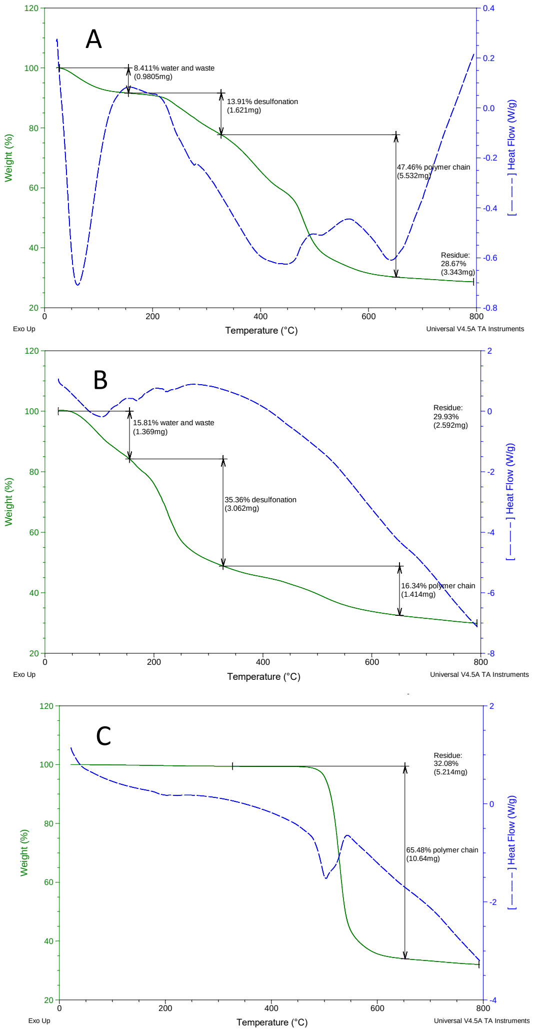

Fig. 7. PSU-S$_B$ Thermograms (A), PSU-S$_A$ (B), and PSU (C).

The PSU polymer is well known for its thermal stability, presented only in one step of mass loss around 500°C that corresponds to the decomposition of the main chain, confirmed by literature values [29.32]. Different of PSU, its sulfonated derivates, PSU-S_A and PSU-S_B, show TGA/DSC thermograms presenting three separate steps, the first stage corresponding to the loss of hydration water and solvents; the second stage corresponding to the thermal desulfonation and the third indicates the degradation of the main chain [29,31,32]. In Table 1, it's possible to verify the data of weight loss on the three highlighted bands of the samples represented in Figure 7; and the values of DS_{TGA} and IEC_{TGA}.

The relationship between the masses lost in the second stage (desulfonation) and third stage (degradation of the main chain) confirms that there is a difference in the amount of -SO_3H groups between PSU-S_A and PSU-S_B, with the DS calculated for each of them in the values of 3.022 and 0.883, corresponding to sulfonated products with IEC of 4.400 and 1.720 meq/g respectively.

Table 1. Mass loss values (%), sulfonation degree, and IEC determined for PSU-S_A and PSU-S_B.

Sample	Mass loss (%)			relationship between 3 step and 2 step	DS_{TGA}[a]	IEC_{TGA}[b] (meq/g)
	1 step (27 to 155 °C)	2 step (155 to 327 °C)	3 step (327 to 650 °C)			
PSU-S_A	15.81	35.36	16.34	0.46	3.022	4.400
PSU-S_B	8.41	13.91	47.46	3.41	0.883	1.720

[a] Equation 2: $DS_{TGA} = 442 / (EW - 81)$; $EW = 1 / [(W_{2\ step} / 100) / 81]$ [29]. [b] Equation 3: $IEC = (DS \times 1000) / [442 + (DS \times 81)]$ meq of H^+/g of dry polymer [26].

3.5 DS Determination of PSU-S_A and PSU-S_B by ^{1}H NMR

^{1}H NMR is a technique that allows obtaining qualitative and quantitative parameters relating to the presence of the -SO_3H group in polymeric structures [21]. The quantitative analysis is based on the method proposed by Kopf (Union Carbide Corporation) initially described in the work of Noshay and Robenson [21] and adapted over time by other authors [14,26,29,30].

The basis of this analysis is that in sulfonation, the substitution promotes a change in the ^{1}H spectrum, because, as already mentioned, the introduced sulfonic group strongly influences the hydrogen of its neighboring carbon**,** moving it to a lower field. This shift allows the quantification of DS through the integration of this peak, as the proton in question is isolated in the spectrum [30]. In Figure 6 it is possible to see the examples of PSU-S_A and PSU-S_B in this specific position and notice the displacement and isolation of the proton in question, in this case, marked as 3'' at 7.72 and 7.70 ppm. The DS value of the PSU-S_A and PSU-S_B samples are represented in Table 2.

Table 2. Sulfonation degree and IEC values obtained for PSU-S_a and PSU-S_b samples.

Sample	A_B (Protons 2,2',3,3',7,7')	A_A (Protons 3'',8,8',8'')	R = (A_B/A_A)	DS [a]	IEC [b] (meq/g)
PSU-S_A	10.88	4.61	2.36	0.587	1.199
PSU-S_B	11.41	4.43	2.58	0.371	0.786

[a] Equation 1: $DS_{NMR} = (12 - 4R) / (2+R)$; $R = A_B/A_A$ [26]. [b] Equation 3: $IEC = (DS \times 1000) / [442 + (DS \times 81)]$ meq of H^+/g of dry polymer [26].

The result by NMR confirms that there is a difference between the DS for the samples PSU-S_A and PSU-S_B prepared with ACS. The data obtained, however, 0.587 for PSU-S_A and 0.371 for PSU-S_B are lower than the ones obtained by TGA/DSC in a proportion of 3.4 times to the PSU-S_A (DS_{TGA} = 3.022) and 2.4 times to PSU-S_B (DS_{TGA} = 0.883). The determination of the DS using the NMR technique considers the sulfonation occurring mainly in the theoretically most favorable position of the mere (in proton 2) and disregards the substitution in other positions and rings. This allows us to infer that the results are, therefore, partial, and smaller than what the real replacement promotes.

In the work of Martos *et al* [29], the comparison between the DS values obtained through NMR and TGA for PSU-S samples sustains this hypothesis. These authors, when preparing the sulfonated polymer in the PSU/TMSCIS (1:6) condition, showed values of DS_{NMR} = 0.96 and DS_{TGA} = 1.84 (proportion of 1.9 times). Using PSU/$ClSO_3H$ (1:3) they reach higher values of DS_{NMR} = 0.86 and DS_{TGA} = 2.10 (proportion of 2.4 times).

3.6 Morphological characterization of PSU-S_A and PSU-S_B by SEM

The PSU-S_A and PSU-S_B samples were morphologically characterized by scanning electron microscopy. The micrographs are presented in Figure 8.

The micrographs suggest that different syntheses led to different aggregation states of samples. The escape of dichloromethane bubbles can lead to the morphological differentiation observed on the PSU-S_B surface, that is, an apparent lower arrangement compaction compared to the PSU-S_A micrograph. The smooth surface seen in Figure 8(a) may be due to contact with the support used to dry the material.

4. Conclusions

It was possible to obtain sulfonated Udel® PSU using acetyl sulfate from two stoichiometric conditions between sulfuric acid and acetic anhydride under mild reaction conditions. Sulfonation was confirmed by FTIR and ^{1}H NMR. The DS was determined by thermogravimetric analysis, obtaining values of 3.022 for PSU-S_A and 0.883 for PSU-S_B, which is equivalent to IEC values of 4.400 and 1.720 meq/g, respectively. The reaction conditions used in this work demonstrate that it is possible to obtain control over the degree of sulfonation by changing the proportions of the reagents used in sulfonation. Thus, in this work, it was demonstrated that it is possible to sulfonate polysulfone using acetyl sulfate in a homogeneous phase, with short reaction times and at low temperatures.

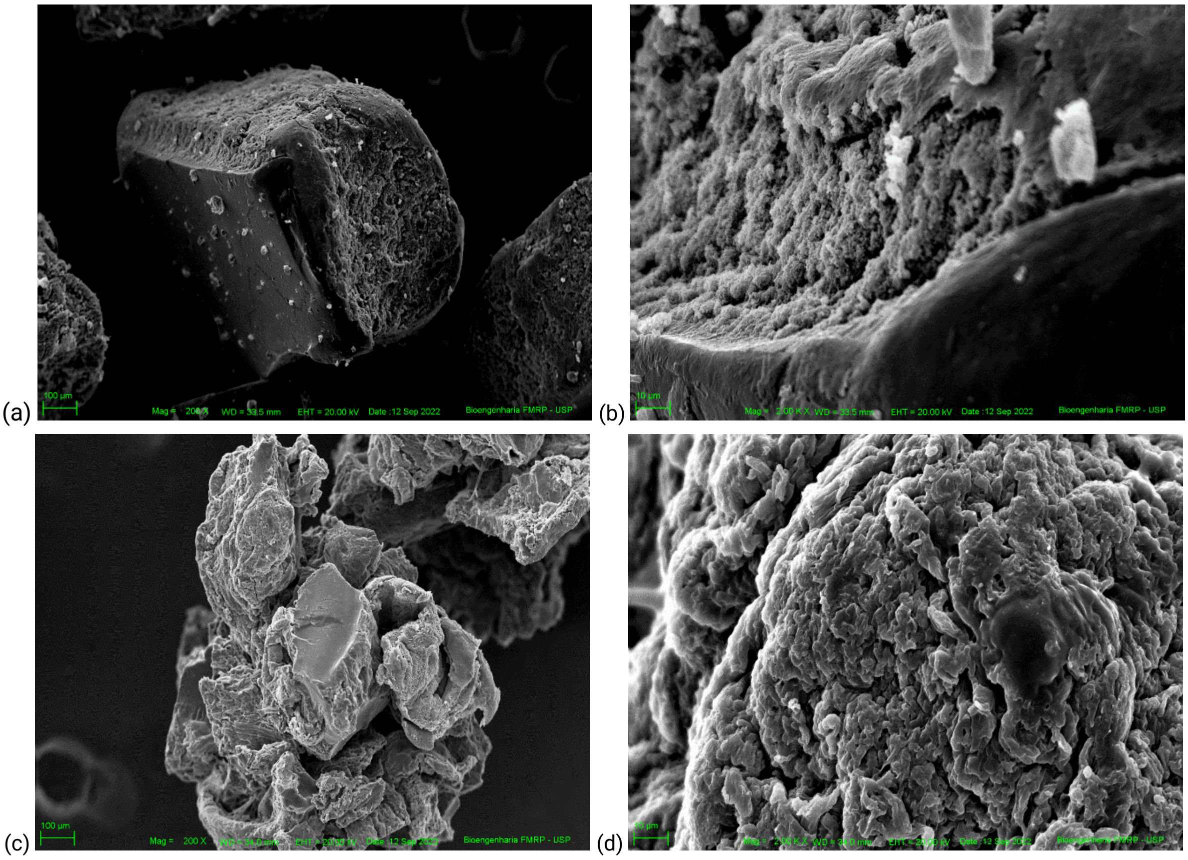

Fig. 8. Micrographs of the PSU-S_A magnified (a) 200x and (b) 2000x and of the PSU-S_B magnified (c) 200x and (d) 2000x.

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Author Contributions

Altamiro Xavier de Souza – Conceptualization; Formal analysis; Funding acquisition; Investigation; Methodology; Resources; Visualization; Writing – original draft; Writing – review & editing. Paulo Donato Frighetto - Formal analysis; Investigation; Visualization. Gabriel Badagnani de Carvalho - Formal analysis; Investigation; Visualization. Henrique de Castro Degiovani – Visualization; Writing – review & editing. Marcelo Firmino de Oliveira - Funding acquisition; Resources. Cláudio Roberto Neri - Formal analysis; Investigation; Visualization; Writing – original draft. Vinícius Palaretti - Formal analysis; Investigation; Visualization; Writing – original draft; Writing – review & editing. Anizio Marcio de Faria - Funding acquisition; Resources; Writing – review & editing. Daniel Pasquini - Funding acquisition; Resources. Luís Carlos de Morais – Conceptualization; Funding acquisition; Investigation; Methodology; Project administration; Resources; Supervision; Visualization; Writing – review & editing.

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