



**SYNTHESIS AND CHARACTERIZATION OF SULFONATED
HFA-co-DABS/ISO COPOLYAMIDES FOR POLYMER ELECTROLYTIC
MEMBRANES**

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ABSTRACT

A series of sulfonated copolyamides with different sulfonation degrees were synthesized from 4,4'-(hexafluoroisopropylidene)dianiline, *HFA* and 2,4-diaminobenzenesulfonic acid, *DABS*, by direct polycondensation using Isophthalic acid, *ISO*, as comonomer. Thin films of the sulfonated copolyamides were prepared by the solution method using dimethylacetamide, DMAc. The structure of the resulting sulfonated polyamides was confirmed by ¹H RMN, which evidenced the presence of amide and sulfonic groups in the proposed concentrations. Their Mechanical properties, inherent viscosities, Ionic Exchange Capacity, IEC, water uptake, W_u and proton conductivity, σ , are also reported. The results showed that membranes present good Ion Exchange Capacity and water uptake. The value of proton conductivity was similar to the one of Nafion tested under the same conditions.

Key words: *sulfonated copolyamides, membranes, water uptake, ion exchange capacity, proton conductivity*



1. INTRODUCTION.

The development of proton exchange membranes (PEM) for fuel cells has received extensive attention lately, because they are known to be one of the most promising clean energy conversion technologies. PEM fuel cells are regarded to be the next step into producing efficient and clean energy since they offer many advantages such as high efficiency, high energy density, quiet operation, environmental friendliness and they can be used in generation of power for laptops, cell phones, transportation and residential use. Perfluorosulfonate ionomer membranes, such as Nafion[®] membranes, are the standard membranes used in fuel cells presently. Although Nafion[®] shows superior performance, the application of these membranes is limited by their high cost, loss of proton conductivity at high temperature and loss of humidity and poor barrier properties to methanol crossover [1-6].

The most successful alternative (PEM) membranes studied to date are based on high performance polymeric backbones containing sulfonic acid groups, such as polysulfones [2, 5, 7-9], polyimides [10-15], poly(arylene-ether)s [16-19] and poly(ether-ether-ketones) [20, 21]. Sulfonation of these polymers is achieved by introducing sulfonic groups ($-SO_3H$); either by treating an existing polymer with sulfonating agents (postsulfonation) or by synthesizing polymers with monomers containing sulfonated moieties, which render these polymers proton conductive. The hydrophobic backbones enhance physical properties and the sulfonic acid groups provide the ionic conductivity and the resulting polymers exhibit high ionic conductivity, good mechanical strength and high temperature resistance [1-5, 8-11]. Aromatic polyamides are considered a class of engineering polymers that are thermally stable, with excellent mechanical properties. The incorporation of ionic groups into the structure of these polymers could impart them ion exchange properties [22]. Because of the presence of amide groups, aromatic polyamides tend to retain water. Amorphous aromatic polyamides particularly those containing fluorine groups such as poly(hexafluoroisopropylidene)isophthalamide, HFAISO, are reported to absorb 4 to 10% water, they are also reported to have a high fractional free volume due to the presence of the lateral $-CF_3$ groups that hinder rotation and increase chain rigidity [22-25].

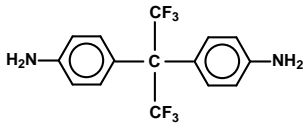
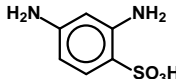
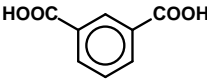
Depending on their chemical composition, water absorption and proton conduction capacity may be enhanced in these polyamides by the introduction of sulfonic acid side groups [22, 26, 27].

In this project, we report sulfonated copolyamides with sulfonation degrees, *SD*, between 20 and 50 mol % that are synthesized from the diamines 4,4'-(hexafluoroisopropylidene)dianiline, HFA, and 2,4-diaminobenzenesulfonic acid, DABS. The mixture of diamines is reacted by polycondensation with isophthalic diacid, ISO, in order to produce random copolymers poly(hexafluoroisopropylidene-co-2,4-diaminobenzenesulfonic) isophthalamides (HFA-co-DABS/ISO). Membranes from the sulfonated polyamides were prepared using solvent evaporation. Their structure is characterized ^1H NMR spectroscopy. Their water up take was assessed as well as their ionic exchange capacity (IEC) and proton conductivity in order to determine the effect of an increased concentration of sulfonic acid groups on these properties. At the same time, we would like to assess if sulfonated HFA-co-DABS/ISO as prepared membranes present characteristics similar to those membranes used in PEM cells.

2. EXPERIMENTAL.

Polyamide poly(hexafluoroisopropylidene)isophthalamide, HFAISO and the sulfonated copolyamides were synthesized by direct polycondensation following a procedure described first by Yamazaki, [28, 29] with some small modifications. The polycondensation reaction was performed with equimolar amounts of the diamine, HFA, and diacid, ISO, for the HFAISO, or a controlled combination of non sulfonated and sulfonated diamines, HFA and DABS with isophthalic diacid, ISO, for the copolymers, HFA-co-DABS/ISO adjusting the concentration of diamine monomer HFA to monomer DABS (HFA/DABS) as shown in Table 1 which in turn adjust the sulfonation degree, *SD*. The reaction was carried out using calcium chloride, CaCl_2 , N-Methyl-2-Pyrrolidone, NMP, as a solvent, with pyridine, Py, and triphenyl phosphate, TPP, as the transfer reactants.

Table 1. Molar concentration of monomers used for synthesis of HFAISO polyamide and copolyamides HFA-co-DABS/ISO.

Polymer	Diamines		mmol of Diacid ISO
	mmol of HFA	mmol of DABS	
			
HFAISO	1.25	-	1.25
HFAS82	1.00	0.25	1.25
HFAS73	0.875	0.375	1.25
HFAS64	0.75	0.5	1.25
HFAS55	0.625	0.625	1.25

Thin membranes of the polyamide and sulfonated copolyamides were cast using dimethylacetamide, DMAc, as the solvent by the solution method. ^1H NMR spectra for HFAISO and HFA-co-DABS/ISO copolyamides were obtained in a Bruker 400 MHz NMR spectrometer using deuterated dimethyl sulfoxide (DMSO- d_6) as the solvent and tetramethylsilane (TMS) as an internal standard. Inherent viscosities (η_{inh}) of all polymers were determined in DMAc using a Cannon-Ubbelohde viscometer No. 50 at 30°C at a polymer concentration of 0.2 g/dL. Mechanical properties under uniaxial tension for wet membranes were determined at 25 °C in a micro tensile machine Minimat (Rheometrics Inc.) at a testing speed of 1 mm min $^{-1}$ with a 100 N load cell. The ability of the membranes to absorb water was estimated by gravimetric analysis. It was immersed in deionized water for 48 h at a fixed temperature (at 25, 45, 65 and 75 °C). At the end of this time the membrane was extracted, wiped with blotting paper and immediately weighed to determine their wet membrane weight. The next step was to dry the membrane at 120°C under vacuum for 48 h and weight is again to determine the dry membrane weight. The water uptake, W_U was calculated according to the following equation:

$$W_U (\%) = \frac{ww - wd}{wd} \times 100 \quad (1),$$

where ww (g) and wd (g) are the weight wet and weight dried respectively.

Water uptake for polyamides and copolyamides is reported as the average value of at least two measurements. A potentiometric titration technique was used to determine the Ion Exchange Capacity (IEC) of the membranes at room temperature. The dry membrane was weighed and immersed in 1M HCl solution for 24 h and then was washed with de-ionized water until the pH was neutral. The membrane in the acid form, H^+ , was then converted to the sodium form, Na^+ , by immersing the membrane in NaCl 2 M solution for 24 h. The exchanged H^+ ions were titrated using NaOH 0.01 M solution. The IEC of the membranes was determined by [21]:

$$IEC\left(\frac{mmol}{g}\right) = \frac{V \times M}{wd} \quad (2),$$

where V (ml) and M (M) are volume consumed and the molar concentration of NaOH, respectively. wd (g) is the weight dried of the membrane. IEC is reported as the average of at least two measurements.

Proton conductivity was measured by electrochemical impedance spectroscopy using a Potentiostat-Galvanostat AUTOLAB Model PGSTAT12/30/302 with the *EIS* module over a frequency range of 10^6 to 1 Hz with oscillating voltages of 50 mV. Prior to the measurement, and in order to test their stability, the membranes were immersed in water for 96 h at room temperature, then they were immersed in HCl 1 M for 12 h to activate them, and finally they were washed with deionized water until neutral pH. Nafion[®] 115 was also subjected to the same treatment and their proton conductivity measured under the same conditions. The proton conductivity (σ) of each membrane was calculated from the impedance data according to the follow equation:

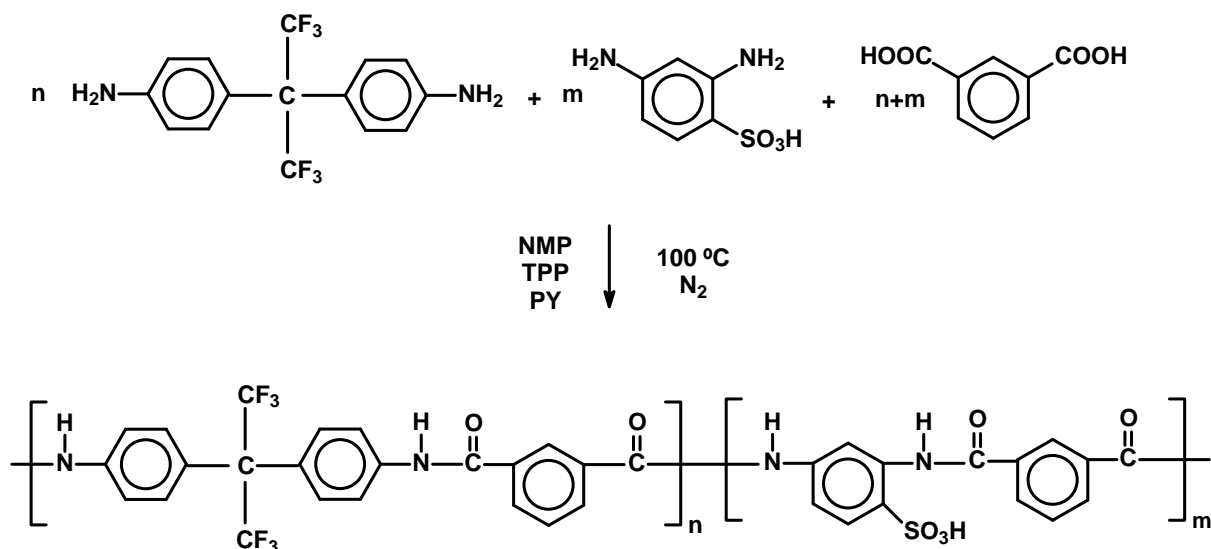
$$\sigma(S\,cm^{-1}) = \frac{l}{RA}$$

(3),

Where σ is the proton conductivity ($S\,cm^{-1}$), l the membrane thickness (cm), R the membrane resistance (Ω) and A is the membrane area (cm^2).

3. RESULTS AND DISCUSSION.

Sulfonated copolyamides HFA-co-DABS/ISO with different sulfonation degrees, *SD* were synthesized through the high temperature polycondensation reaction of the monomers: HFA, DABS and ISO in the presence of NMP, TPP, and Py. The sulfonation degree, *SD*, was controlled by adjusting the ratio of diamines HFA and DABS (HFA/DABS). A schematic of the reaction is given in Scheme 1. The HFAISO polyamide and HFA-co-DABS/ISO copolymers obtained were white rigid fibers. The fiber size increased with decreasing concentration of sulfonated diamine in the copolymer. The amount of CaCl_2 used in the reaction had a great effect on the polymerization, as it was necessary to add a larger amount (8 to 10% more) of CaCl_2 as the amount of sulfonated diamine increases in the copolymer polymerization reaction. It was also necessary to increase the reaction times described in the literature from 8 a 24 hours [29], during the synthesis of sulfonated copolyamides; otherwise a yield reduction in the reaction or low molecular weight products were obtained. The resulting polyamides showed moderated inherent viscosities which decrease with increasing concentration of sulfonated monomer and they are in the range of 0.35-0.18 dL/g in DMAc. The inherent viscosity is a relative measure of polymer molecular weight, therefore can be considered, the polymer molecular weight decreases when the amount of sulfonated monomer was increased in the copolyamide. This effect had been observed in several sulfonated polymers [22].



Scheme 1. Schematic reaction to obtain the sulfonated copolyamides, HFA-co-DABS/ISO.

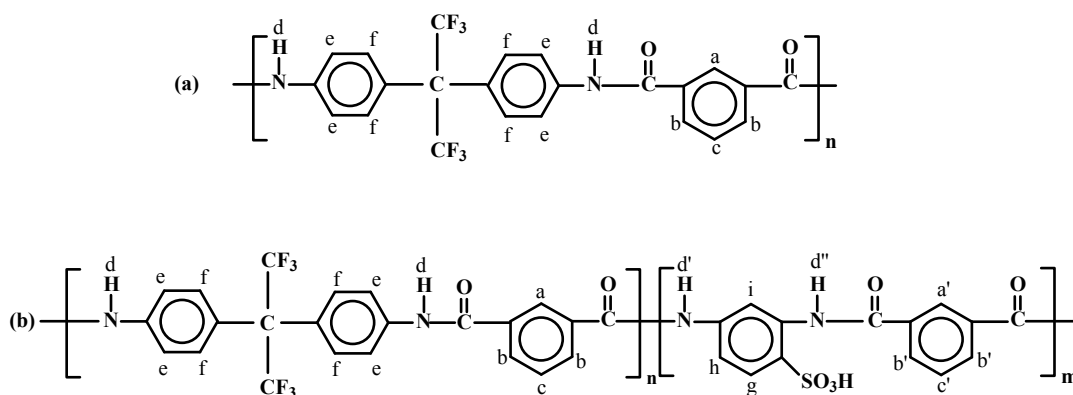
Films of copolymers elaborated using the solution evaporation method were translucent with a yellowish coloration that intensified as *SD* increased. The rigidity of the films also increased with increasing sulfonation degree. The thickness of all membrane films was in the range 0.08-0.15 mm.

Figure 1 shows the ^1H NMR spectra of (a) HFAISO polyamide, and (b) HFA-co-DABS/ISO sulfonated copolyamides respectively. The integration area ratio of each proton agrees with the structure of HFAISO polyamide, Figure 1(a), and HFA-co-DABS/ISO copolyamides, Figure 1(b). Initially there appear two new proton interactions when the sulfonic acid groups are introduced to the polyamide, the peak at 8.95 ppm only appears in the spectra of sulfonated copolymers. This signal corresponds to the ortho proton H_g respect to the sulfonic acid group, appearing at downfield due to the electron-withdrawing effect of the sulfonic acid group. The aromatic hydrogen atoms H_h and H_i near the $-\text{SO}_3\text{H}$ group were detected at 8.63 and 7.54 ppm, respectively. We also observed that with increasing amount of sulfonated monomer there is an increase in the intensity of the signal of these protons. All the other peaks correspond to other aromatic hydrogen atoms of the chemical structure of the sulfonated copolyamides that are also present in the homopolyamide HFAISO.

Table 2. Sulfonation degree determined by ^1H RMN and inherent viscosity of sulfonated copolyamides.

Polymer	SD(%)		η_{inh}
	Theoretical	H NMR	
HFAISO		-	0.35
HFAS82	20	18.00	0.27
HFAS73	30	28.60	0.25
HFAS64	40	39.71	0.18
HFAS55	50	49.26	0.19

In order to determine the sulfonation degree, from figure 1 (b) the relationship between the areas of protons which does not change in HFAISO or the copolymers, H_f , and the proton ortho to the $-SO_3H$ group in the copolymer H_g , was calculated [27]. The resulting concentration of sulfonated moieties using the ratio of the areas for protons H_f and H_g for sulfonated copolyamides agrees well with the concentration of sulfonated monomer initially charged for the synthesis, with a minimum drift, indicating that the structures proposed with different sulfonation degrees, SD , were obtained, as described in Table 2.



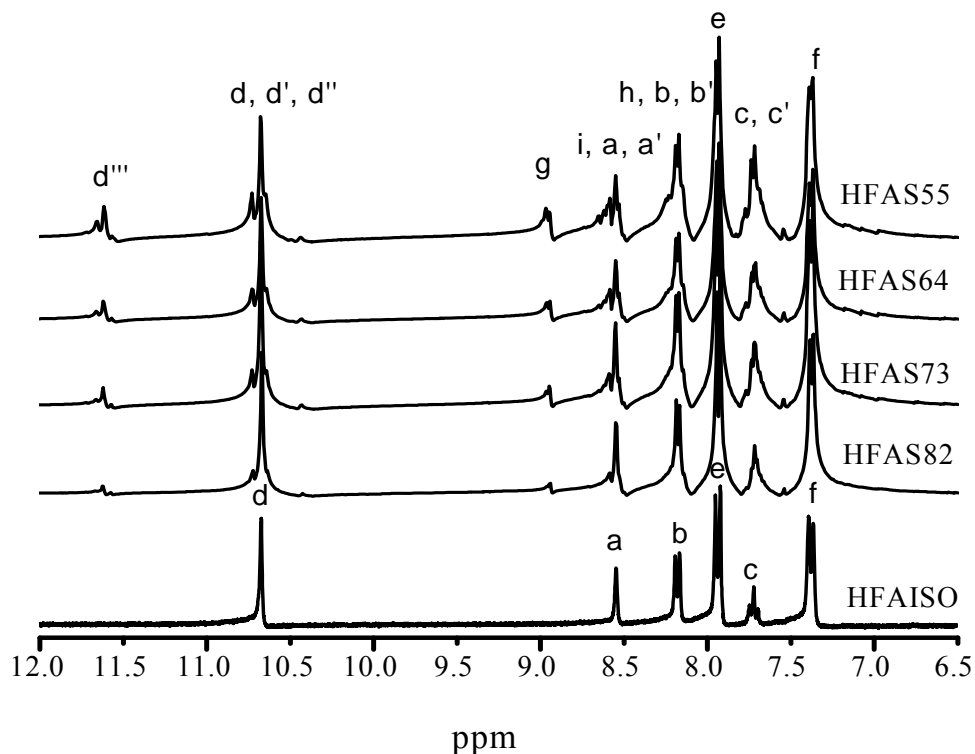


Figure 1. ^1H NMR of polyamide and sulfonated copolymers.

Since ionic membranes tend to be used in environments with high humidity such as PEM cells or in contact with water solutions, it is important to determine their mechanical properties when they are hydrated. Table 3 lists the thickness, tensile strength, elastic modulus and elongation at break of HFAISO and HFA-co-DABS/ISO membranes. As a reference, Nafion[®] 115 was also subjected to the same test. The values of elastic modulus are between 280 and 494 MPa and tensile strength between 20 and 34 MPa, they also do not show a general trend with increasing sulfonation degree. Since water uptake at 25°C is already equilibrated at 48 h in the membranes, the mechanical tests values dispersion is attributed to differences in the plasticization of the test samples particularly for HFAS55 which shows higher mechanical tensile modulus and strength. It is also found that the values for tensile strength and elastic modulus are at least 2 times larger than those found in Nafion[®] 115 at the same testing conditions.

Table 3. Thickness and mechanical properties under tension of polyamide HFAISO, Nafion[®] 115 and sulfonated copolyamides HFA-co-DABS/ISO.

Polymer	Thickness (mm)	Tensile strength (MPa)	Elastic Modulus (MPa)	Elongation at break (%)
HFAISO	0.08	27.43±8.55	494.32±23.4	6.53±3.4
HFAS82	0.11	34.81±8.01	427.05±38.2	11.89±5.7
HFAS73	0.15	19.98±5.62	277.45±13.6	10.93±1.6
HFAS64	0.12	20.91±9.91	286.76±11.8	9.14±3.5
HFAS55	0.14	29.67±1.45	410.83±11.8	12.62±1.7
Nafion 115	0.12	13.17±0.13	89.31±11.6	181±54.0

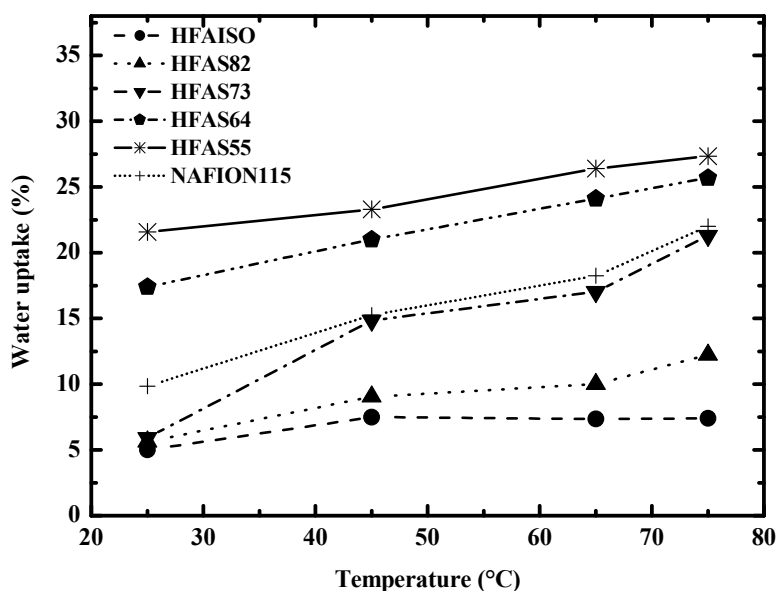


Figure 2. Water uptake as temperature increase for membranes of HFAISO polyamide and HFA-co-DABS/ISO sulfonated copolyamides.

As can be seen in Figure 2, HFA-co-DABS/ISO membranes with higher sulfonation degree values, HFAS64 and HFAS55, tended to have larger water uptake at all temperatures and the water uptakes increase with increasing *SD*. It is also seen that the hydrophylicity in HFAS64 and HFAS55 is larger than the one observed in Nafion[®] 115 which is attributed to a larger free volume due to the presence of $-CF_3$ groups and swelling of the membrane due to the water bonded by the $-SO_3H$ groups. Those two effects combined are credited for the increase in water uptake even though the aramide polymer backbone is less flexible than that of the Nafion[®] 115. It also seen that at low temperatures (25°C) there is a jump in the water uptake between copolymers containing 30 and 40 mol % sulfonic acid groups, it is taken as an indication that there is a critical concentration of $-SO_3H$ groups that given the opening of the structure and vicinity of them allows for an increase in water uptake, as have been reported in other similar polyamides [22].

Table 4. IEC of polyamide HFAISO and sulfonated copolyamides HFA-co-DABS/ISO.

Polymer	IEC (mmol/g ór mequiv/g)	
	^a Theoretical	Experimental
HFAISO	-	0.15
HFAS82	0.59	0.58
HFAS73	0.87	0.49
HFAS64	1.02	0.83
HFAS55	1.39	1.6
Nafion® 115		1.28

^a Theoretical IEC values was obtained as in ref. 1 $IEC = \frac{SDX1000}{318+80SD}$.

Table 4 shows theoretical ion exchange capacity, IEC, values for the synthesized copolymers and they are compared to experimentally obtained values. The theoretical IEC values are higher than those found experimentally with the exception of the ones for HFAS55 which presents a IEC value that is larger than the theoretical one. It is important to note that not all sulfonic groups are accessible to apply the technique of titration. An example would be the HFAS73 membrane, which has the lowest value of IEC, because it presents perhaps the greatest membrane thickness. The membranes obtained from copolyamides HFA-co-DABS/ISO showed an increase in IEC with increasing degree of sulfonation, this is attributed to the increase on water concentration and retention of sulfonated polyamides due to the increased concentration of sulfonic groups, which in turn opens the sites available for ionic exchange in the structure, and increases the possibilities of an enhanced proton transfer capacity.

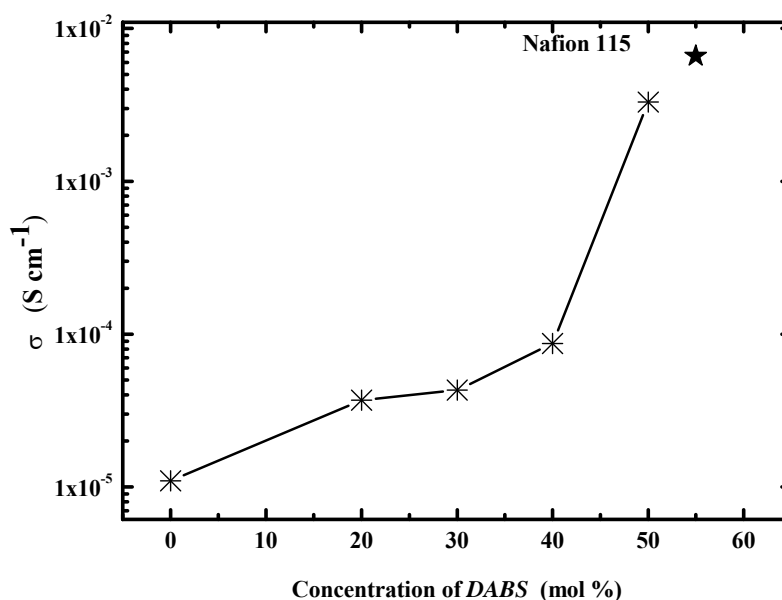


Figure 3. Proton Conductivity of sulfonated polyamides HFA-co-DABS/ISO with increasing *SD*.

The proton conductivity, σ , for membranes at 25 °C is shown in Figure 3. Nafion[®] 115 was used for comparison with the membranes synthesized in this work. Following the trend observed for ion exchange capacity, the proton conductivity of the copolyamides membranes show a trend, of increasing proton conductivity with increasing *SD* as in other reports [4, 30]. As shown in Figure 3, an increase in *SD* from 20 to 50 % results in an increase of up to two orders of magnitude in proton conductivity values. These results indicate that it is possible to render proton conductive copolymers based on fluorinated polyaramides such as those prepared in this work.

4. CONCLUSIONS.

Membranes based on rigid fluorinated copolyaramides, HFA and a sulfonated monomer DABS were obtained with increasing degree of sulfonation by direct polycondensation, the resulting poly(hexafluoroisopropylidene-co-diaminobenzensulfonic)isophthalic copolyamide,

HFA-co-DABS/ISO, were cast from DMAc, the thickness of all membrane films were in the range 0.08-0.15 mm and the rigidity of the films increased with increasing sulfonation degree. The mechanical tests showed larger elastic modulus and tensile strength as compared to those presented by Nafion[®] 115. The analysis of water uptake, IEC and proton conductivity, generally show that they increase with increasing concentration of sulfonated diamine in the copolyamides, although there is a threshold where the water uptake and IEC jump to higher values at a concentration between 30 and 40 mole % of sulfonic acid groups. The membrane HFAS55 show values of water uptake and IEC higher than that of Nafion[®] 115 at room temperature. Proton conductivity values at room temperature obtained with the membrane HFAS55 are in the same order of magnitude as those obtained for Nafion[®] 115. Overall membranes prepared from HFAS55 should be considered good candidates for proton exchange membranes with improved thermal stability as compared to the ones used actually, although further testing for oxidative and acid stability should be made.

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