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Synthesis and Characterization of Sulfonated Poly(styrene-*co*-acrylic acid) for Applications as Pronton Exchange Membranes

Luciano Da Silva,[*1,2] Renato P. Pedrosa,[1] Fernanda Coelho,[1] Luana F. Vieira,[1] Roberto Benavides,[2] Alexandre G. Dal-Bó,[1] Tiago E. Frizon,[1] Marcos M. S. Paula[1]*

Summary: Polymeric membranes were prepared using the mass copolymerization of styrene/acrylic acid (St/AA) at 90/10, 92/8 and 94/6 ratios. Divinyl benzene (DVB) was also added at concentrations of 0.1 and 0.001% weight for each St/AA ratio. The obtained copolymers were sulfonated by treating the materials with concentrated sulfuric acid for 0, 30 and 85 minutes to enhance their ion exchange capacities. The materials were characterized by Fourier transform infrared spectroscopy (FTIR), thermal analysis by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), cross-linking level by gel percentage and acidity through sodium hydroxide titration. The FTIR spectra of the membranes before sulfonation showed the existence of traditional bands that corresponded to the polymer components; some homopolymer main bands were lost, whereas two new bands appeared during the copolymerization reaction. The TGA analyses showed a higher decomposition temperature for the DVB cross-linked membranes, while DSC did not provide much information due to the hygroscopic nature of the membranes. The gel percentage was effectively related to the DVB level. The membranes acidity increased with increasing acrylic acid content, sulfonation time and DVB percentage; however, the acidic values are highly dependent on the solubility of the materials.

Keywords: fuel cell; membrane; polystyrene

Introduction

Fuel cell systems are an economically attractive and clean alternative for electrical energy production. Compared with conventional systems of energy production, fuel cells are more efficient due to the electrochemical principle and lack of combustion reactions, which in turn produce higher yields with less pollution. Fuel cells are essentially batteries that produce direct current through the oxidation of a gaseous fuel, usually hydrogen.[1]

One of the three traditional fuel cells technologies investigated around the world is the proton exchange membrane fuel cells (PEMFC). Such technology uses a polymer membrane to permit diffusion of protons from the anode to the cathode and is intensively used in static and mobile systems. One of the best known materials used as membranes in PEMFCs contains a polymeric structure based on perfluorosulfonic acid (Nafion®).[2] Such prepared membranes exhibit excellent proton- exchange properties and durability, on the order of 10 yr, for use as fuel cells.[3] However, membranes based on Nafion have some significant limitations, including the required low working temperature and high fabrication expense. Thus, the development of novel polymeric materials for PEMFC applications has been of interest to

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[1] Laboratório de Pesquisa em Materiais LAPEM – Universidade do Extremo Sul Catarinense, 88806–000, Criciúma, Brasil

[2] Centro de Investigación en Química Aplicada, Blvd. Enrique Reyna H. 140, Saltillo, Coahuila, México
Fax: +55 48 3431 2750;
E-mail: luciano.silva@unesc.net

Table 1.
Synthesis of Copolymers.

Styrene/Acrylic acid (% molar)	DVB (% molar)	SulfonationTime (min.)
90/10	0.1	30, 85 and 120
92/08	0.1	30, 85 and 120
94/06	0.1	30, 85 and 120
90/10	0.001	30, 85 and 120
92/08	0.001	30, 85 and 120
94/06	0.001	30, 85 and 120

the chemical community.[4] In recent years, Abate el al. has described a wide investigation of aromatic thermoplastic polymers containing ether, ketone and sulfone groups.[1,5–12] These polymers usually show good thermal and mechanical properties, and they have reported that a wide spectrum of characteristics can be obtained by balancing the various groups.[10] Moreover, these polymers are of increasing technological importance: in particular, poly(arylene ether sulfone)s (PAES)s have importance and are used in many fields, for instance as adhesives for metal-to-metal bonds,[13] as membranes in the separation of gases and solids from solutions,[14] as membranes for ultrafiltration and pervaporation[15–18] or electrodialysis[19] and, recently also, as toughening agents for brittle thermosets.[20]

We have previously investigated polymeric materials for applications as sensors and electrolytes for fuel cells.[21–23] In this paper, the synthesis and characterization of sulfonated copolymers of poly(styrene-co-acrylic acid) cross-linked with divinyl benzene is described. The aim of this work was to improve the synthesis and optimize the composition of the polymeric films with the goal of improving their electrolyte, thermal and mechanical properties for use as fuel cells membranes.

Experimental Part

Materials

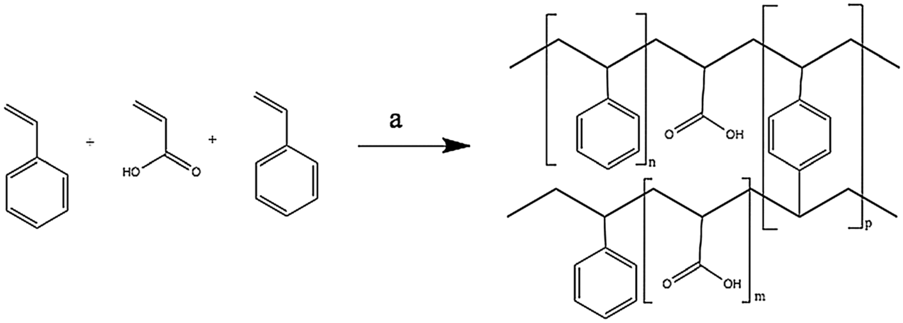
Comonomers and chemicals were obtained from following sources and used without further purification. Styrene, acrylic acid and divinyl benzene were purchased from Aldrich Chemical Co. (USA), benzoil peroxide from Vetec Química Fina-Brazil and sulfuric acid from Carlo Erba-Brazil.

Synthesis

Copolymers were synthesized at three different molar ratios of styrene/acrylic acid, each cross-linked with two different divinyl benzene (DVB) ratios and treated for three different durations with sulfuric acid for sulfonation. Table 1 shows the preparation recipes using such variables.

Synthesis of Copolymers (Scheme 1)

The appropriate amounts of comonomers and DVB were added to a 150 mL glass reactor that was equipped with a mechanical stirring, heating and condensing system. The mixture was stirred, heated to 100 °C,



Scheme 1.
Reaction scheme used for the preparation of the copolymers. a = benzoyl peroxyde, 100 °C, 2h.

initiator benzoyl peroxide was added. These conditions were maintained for 2 h and then cooled to room temperature. Acetone (200 mL) was then added to the stirred solution until the material was dissolved. Finally, excess methanol was added to precipitate the desired copolymer. The solid was dried in a vacuum oven for 24 hours.

Sulfonation of Copolymers (Scheme 2)

Five grams of the appropriate copolymer and 30 mL of dichloromethane were added to a 150 mL flask provided with mechanical stirring, heating and a reflux condenser. The mixture was heated to 40 °C, maintained under an argon atmosphere and stirred until complete dissolution; then 25 mL of concentrated sulfuric acid was added drop wise. After the appropriate time interval was reached (Table 1) the mixture was added to 600 mL of deionized water. The yellowish solid was separated by filtration and thoroughly washed with deionized water until the washing liquid had a pH value of 3. The solid was then dried in a vacuum oven for 24 hours.

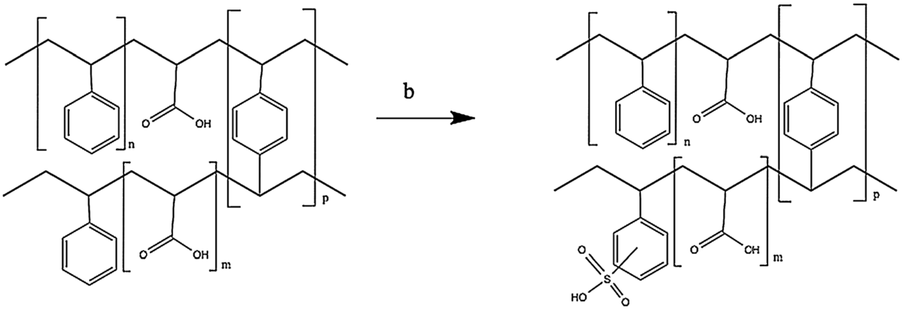
Membrane Preparation

The membrane were made by casting (w/w) solutions in chose solvent onto a glass plate and dried at 40 C for about 1 day, 60 C for another day and further evaporated at 100 C under vacuum for 2 days. The final product was transparent membrane with a thickness of about 35 um. The membrane preparation procedure in this work was similar to the methods described by other researches [24,25]

Characterization

The sulfone group content was monitored by titration with sodium hydroxide (NaOH). A specific amount of the sulfonated copolymer was first dissolved in acetone. A 0.1 M NaOH solution was then added drop wise and the pH was monitored until a neutral solution was obtained. The NaOH consumption divided by the resin mass added was calculated as an indirect measurement of the SO_3H groups neutralized. The sulfonated copolymers were also characterized by FTIR to observe the sulfone bands formations in the spectra. The sulfone index was calculated by dividing the peak height of the absorbance band at 1170 cm^{-1} (axial deformation of S=O bond) by the acrylic acid reference band using peak height at 1452 cm^{-1}, using specific software included in the instrument. Infrared spectra were recorded on a Shimadzu Prestige 21 spectrometer (Japan) from samples prepared as thin films.

The materials were further characterized by DSC using a calorimetric cell (Shimadzu DSC-50, Japan) over a temperature ranging from ambient to 250 °C, heating ramp of 10 °C/min and under an argon atmosphere, traces correspond to second run. The thermal resistance was also evaluated using a thermobalance (Shimadzu TGA-50, Japan) over a temperature ranging from



Scheme 2.
Sulfonation reaction. b = CH_2Cl_2, H_2SO_4.

ambient to 600 °C, heating ramp of 20 °C/min. and under a nitrogen atmosphere.

The cross-linking level was evaluated by calculating the insoluble material percentage. Two grams of the material were weighed and extracted continuously in dichloromethane by refluxing in a Soxhlet apparatus for 6 hours. The undissolved material was weighed for the cross-linking percentage calculation, W/W_0 where W is the final weight and W_0 the initial weight.

Results and Discussion

The copolymer exhibited good solubility in dichloromethane. The sulfonation step, sulfuric acid was added after complete solubilization of the copolymer.

Sulfonic groups titration is a convenient method for evaluating the sulfonation process, also because in acetone as solvent, the sulfonic acid groups of the copolymer have sufficient affinity to interact with NaOH. However, in the case of our copolymers there were two acidic groups that consume the neutralizing NaOH: sulfonic groups and acrylic acid. Figures Figure 11(a) and (b) show the consumption of NaOH with respect to sulfonation time for each of the prepared membranes. At sulfonation time zero, some NaOH consumption was apparent, due to the presence of acrylic acid, and higher material values that possess a higher amount of acrylic acid. Such values were greatly increased with increasing sulfonation time; this trend represents the consumption of NaOH by the sulfonic group.

The NaOH consumption increment was not always directly proportional to higher acrylic acid percentage, especially for the 92/8 ratio membranes containing the higher amount of cross-linking agent (0.1%DVB). Such St/AA ratio promotes a noticeable difference in NaOH consumption, since it has the highest values for 0.001% DVB but the lowest for 0.1% DVB, while 90/10 and 94/6 ratios were very similar independently of cross-linking level. This result is presumably due to the links occupied by DVB within the copolymer chains and secondary reactions after sulfonation. Additionally, for high NaOH consumption traces there seems to be a limit at 85 min of sulfonation, apparently as a consequence of secondary reactions promoted by sulfonation and enhanced by DVB level.

Figure 2 shows part of the FTIR spectra for the sample 94/06 with 0.001%DVB for different sulfonation times, with the sulfonic S=O and C=O reference bands highlighted. The latter is a mixture of signals corresponding to the acrylic acid

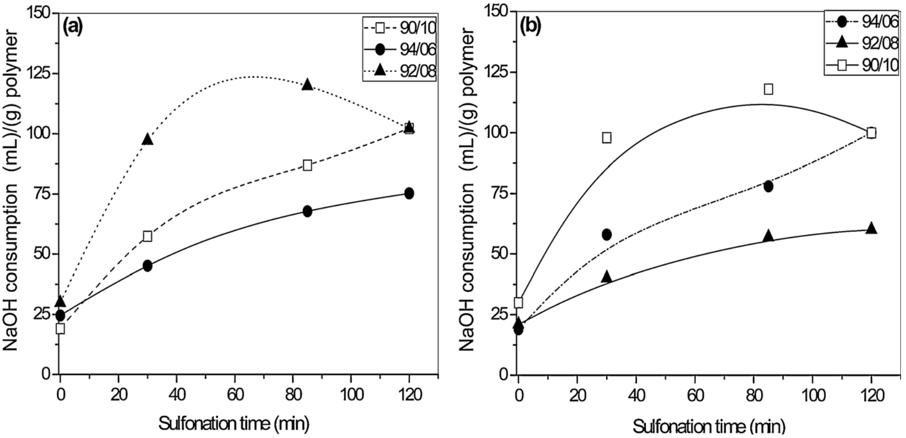


Figure 1.
NaOH consumption per polymer mass for membranes sulfonated at different times. (a) 0,001% DVB (b) 0,1% DVB.

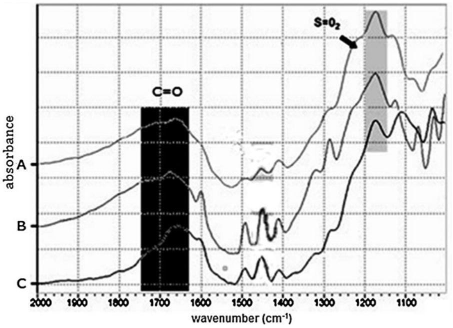


Figure 2.
FTIR spectra for copolymer 94/06 (St/AA) and 0.001% DVB sulfonated during 30 (C), 85 (B) and 120 (A) minutes.

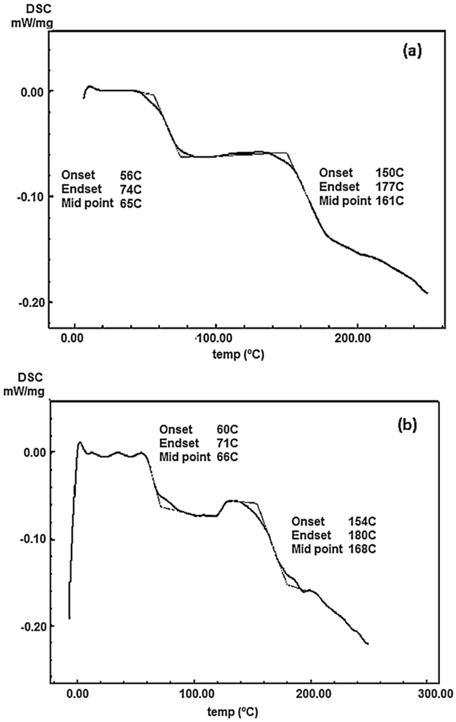


Figure 4.
DSC thermograms for copolymer 92/8 with 0.1 **(a)** and 0.001% **(b)** DVB.

(1705 cm^{-1}) and a saturated ketone (1678 cm^{-1}) formed between carbonyl and sulfonic acid as a secondary reaction. The sulfone band enhancement within the copolymer molecular structure of the copolymers is clear throughout the treatment time. When the absorbance values of the 1170 cm^{-1} band were measured and divided by the reference band at 1452 cm^{-1}, the sulfone index was obtained. Figure 3 shows the values for this sample. The obtained trend corroborates the one observed during the NaOH titration, clearly indicating the sulfonation groups increment with treatment time. All samples showed a similar trend.

Figure 4 shows the DSC thermograms for copolymers 92/08 with 0.1 (a) and 0.001%DVB (b) at second run. The thermograms show two thermal transitions (Tg) for the copolymers with positions that are quite different than those for the individual homopolymers (PS = 100 °C, PAA = 106 °C). Apparently two species were formed during the copolymerization reaction, the most stable giving a high Tg (160 °C) but a less stable copolymer which could be absorbing humidity and showing a plasticizing effect, having a lower Tg transition (60 °C). Considering during first run the material was heated only until a temperature of 150 °C, it is possible that part of the water retained into the structure was not removed and plasticized species remained.

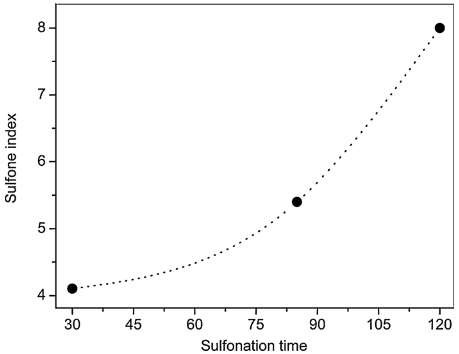


Figure 3.
Sulfone index obtained for the copolymer 94/06 and 0.001% DVB for different sulfonation time.

The cross-linking agent concentrations did not exert a significant influence on the transitions temperature but a small effect on the trace resolution for the sample with lower DVB amount, perhaps due to more isolated species, which in turn can suffer rearrangement due to an increased solubility between both phases, before the transition. Additionally, it was difficult to obtain useful thermograms for the material after sulfonation due to high bound water absorption. The thermogram for the copolymer without any crosslinking agent had a Tg temperature about 95 °C, as reported previously.[21,22]

Thermogravimetric analyses (Figure 5) were used to evaluate differences in copolymers with and without 0.1 wt% crosslinking agent. As can be seen, there was an improvement in the thermal stability after DVB addition, as can be usually expected for a partially cross-linked material. There was also noticeable a loss of weight starting at 100 °C, which is due to the volatilization of water from the copolymer, in agreement with the humid structure suggested in the DSC evaluations.

The addition of 0.1%DVB increased the most significant mass loss transition temperature by more than 10 °C for the copolymer. Such an increment will increase the thermal stability of the material for future applications as a membrane for PEMFC. No clear differences were observed for the materials that were crosslinked with 0.1 or 0.001% DVB nor for the materials after sulfonation treatment (not shown here).

The synthesized copolymers also exhibited an improvement in their chemical resistance after being cross-linked with the DVB. The insolubility degree as a result of the sulfonation process was measured as the gel percentage following extraction with dichloromethane in a Soxhlet system. Figure 6 shows the results that were obtained for the materials with the most desired physical properties (as flexibility and stability detected manually) for membranes usages: 92/08, 0.001% DVB and 94/06, 0.1% DVB.

Some degree of degradation was observed for the 92/08 copolymer after 85 minutes of sulfonation because its solubility level was extended during the sulfuric acid treatment, while for the most cross-linked material (0.1%DVB) no such effect was observed. Although both materials were highly insoluble in dichloromethane, they were soluble enough in acetone for the preparation of films to use as membranes.

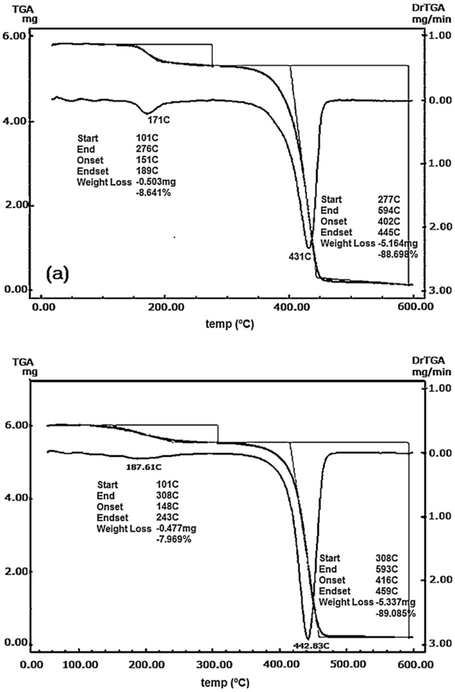


Figure 5.
TGA thermograms for a copolymer 92/08 without crosslinking agent **(a)** and with crosslinking agent (0.1% DVB) **(b)**.

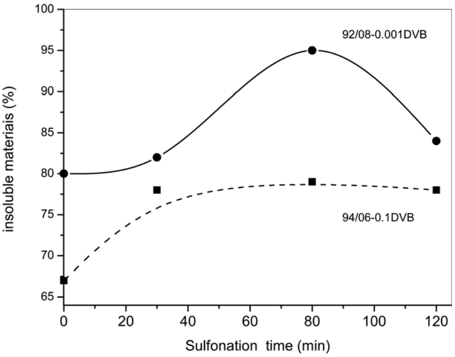


Figure 6.
Insolubility of membranes in dichloromethane for (St/AA) 92/08 with 0.001% DVB and 94/06 with 0.1% DVB at different sulfonation times.

The membrane preparation procedure used in this work allowed to obtain membrane with relatively water swelling and dimensional stability.

Conclusion

Sulfonated copolymers of styrene-co-acrylic acid that were cross-linked with DVB form films and could be useful as polyelectrolyte materials to use as PEMFC membrane. No significant thermal transitions alterations were observed after cross-linking, but some enhanced thermal resistance was observed. The sulfonation process, monitored by titration, and the effect of crosslinking agent was observed using Soxhlet extraction in dichloromethane. With a level of 0.1% DVB, the copolymer insolubility in dichloromethane was reduced and a sulfonation time of 85 minutes would provide the appropriate amount of sulfonic groups/decomposition in the copolymer structure to generate polyelectrolyte behavior. Electrochemical evaluation is underway to test polyelectrolyte behaviour.

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