

STYRENE/ACRYLIC ACID COPOLYMERS MODIFIED BY CROSSLINKING AND SULFONATION REACTIONS FOR THEIR USE AS MEMBRANES IN FUEL CELLS

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Abstract

Proton permeation membranes used in hydrogen fuel cells need to have mechanical resistance, hydrophilicity to work in a humid environment but insoluble to water and ability to transport protons from the anode to the cathode side of the cell. Such properties are almost covered by Nafion (DuPont), which has some disadvantages as high cost, and unsatisfactory proton conductivity, as well as some permeation to oxygen and hydrogen. In this work styrene/acrylic acid copolymers were prepared for their use as economic membranes for fuel cells expecting to have mechanical and proton permeation properties through several concentrations of crosslinking and sulphonation and sulphonation reaction time.

Introduction

Aromatic polymers are thermally and chemically stable and are therefore potentially useful for making membranes due to its excellent mechanical properties¹. However it is also necessary that the membrane contains a certain degree of moisture in order to perform the proton conduction phenomenon². One way to achieve this moisture is by copolymerization of acrylic acid with styrene, the carboxylic groups help the swelling of the membrane on contact with water. Subsequently the copolymer is subjected to sulphonation reactions to incorporate -SO₃H groups to the benzene ring, which readily ionize it and thus provide the proton conductivity³. The

water absorbed by the membranes decreases mechanical properties acting as a plasticizer, reducing T_g and modulus of the membrane⁴. However, this phenomenon can be compensated by decreasing the molecular mobility of the material by crosslinking, e.g. divinyl benzene (DVB) for the formation of networks⁵.

It is also advisable to select carefully the conditions and agents to prevent crosslinking through sulphone formation^{6,7}, from sulphonic acid groups, as well as undesired side reactions, especially when using strong sulphonation agents¹.

Experimental

Polymerization. The radical copolymerization in solution of crosslinked styrene-co-acrylic acid was carried out under a nitrogen atmosphere in a glass reactor. Reaction involved introducing the styrene, acrylic acid, benzoyl peroxide (BPO) and divinylbenzene (DVB) into the reactor with diethyl benzene. Considering stirring (200 rpm) and reaction temperature of 90 °C, the polymerization was performed during 120 min. The reaction was stopped and the copolymer recovered by precipitation into methanol. The copolymer was purified dissolving it in acetone and recovered by precipitation into boiling distilled water and finally dried under vacuum at 65-70 °C for 48 h. Copolymers were confirmed by FTIR and RMN.

Copolymer sulphonation. The styrene/acrylic acid copolymer sulphonation was carried out at 40 °C in dichloromethane using an equivalent molar quantity of H₂SO₄ conc. or fresh acetyl sulfate as sulphonation agents, at 1 and 2 hr of reaction time.

Membrane preparation. The copolymer and sulphonated copolymer solutions were dissolved in THF and passed through a 0.45 µm filter. Films were cast from solutions onto a glass mold. The resulting films possessed thicknesses of about 83-93 µm.

Characterization. Gel permeation chromatography (GPC) was carried out with a Hewlett Packard chromatograph, using copolymer solutions of 1mg/1mL. The instrument had three Ultrastyrigel columns (105, 104, 103 Å) with THF as eluent at a flow rate of 1 mL/min (40 °C) and polystyrenes as standard. Glass transition temperatures of the copolymers were measured by differential scanning calorimetry (DSC) using in a 2920 TA Instruments. Samples were first heated up to 170 °C, cooled rapidly to room temperature and then scanned again at a rate of 20 °C/min. Dynamic

mechanical analysis (DMA) was carried out with a TA instruments Q800 using a tensile mode, heating ramp of 2 °C/min and frequency of 1 Hz. Samples were heated from ambient to 130 °C.

Results and discussion

Table 1 lists experimental conditions, T_g , molecular weights and PDI of the copolymers obtained as well as the E' obtained by DMA.

Table 1. Experimental conditions and characterization results from the non-sulphonated styrene/acrylic acid copolymers.

Reaction	BPO (% molar)	DVB (% molar)	T_g^a (°C)	M_w (g/mol)	Polydispersity index (PDI)	E'^b (MPa)
A	0.045	0.25	119.4	182,799	3.1	2922
B	0.045	0.30	119.2	245,590	3.6	2061
C	0.050	0.00	91.8	93,662	1.9	N.F.
D	0.050	0.05	111.9	87,155	2.6	N.F.
E	0.050	0.20	120.4	156,048	3.1	1482
F	0.050	0.30	118.8	248,100	3.5	2569
G	0.175	0.15	116.9	100,371	2.3	N.F.
H	0.300	0.00	107.8	44,923	1.7	N.F.
I	0.300	0.05	112.4	41,509	1.9	N.F.
J	0.300	0.10	93.6	47,658	2.0	N.F.
K	0.300	0.30	113.1	128,606	3.4	N.F.

^a T_g by DSC, ^b E' by DMA, value at ambient temperature, NF= Unable to make film

We can observe that there is only one T_g value for each copolymer, indicating that in fact we have a random copolymer, instead of a block copolymer, which would result in two separated T_g values.

Only four copolymers were able to make films (A, B, E and F), which are the ones with the largest molecular weights and PDI from among all samples, except K reaction. The latter suggests the reason for feasibility to make films by casting, unlike the other copolymers with more brittleness. It is also clear that E' values has a linear relationship with M_w ^{8,9}. Figure 1 shows E' traces and the results in a 3D graph showing clearly the effect of the variables evaluate (Concentration of BPO and DVB) into M_w .

Copolymers prepared with 0.05 % BPO were selected for sulphonation reactions with concentrated sulphuric acid and acethyl sulfate. From FTIR data it was observed that long sulphonation time with acethyl sulphate enhances the signal at 1064 cm^{-1} (stretching S=O) corresponding to

sulphonic acid, but reduce it when treating with sulphuric acid. The latter suggests two possibilities: high sulphonic acid formation that make the material highly soluble in water (lost by washing) or decomposition of the structure by the strong acid treatment.

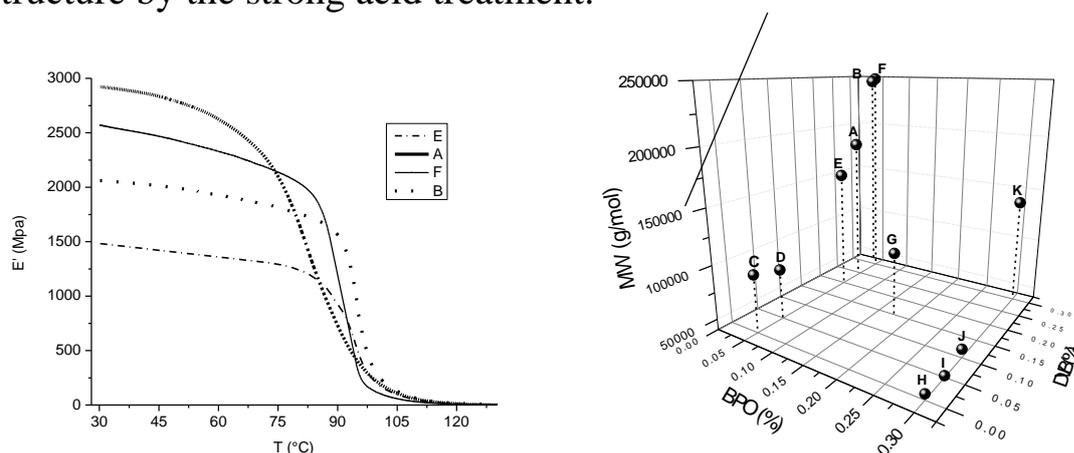


Figure 1. DMA results for films and effect of experimental conditions on M_w .

A noticeable effect observed for long sulphonation time (both agents) is the formation of a cyclic ketone as remanent after nucleophilic aromatic substitution over the carbonile with water elimination.

Conclusion

Copolymers were prepared in a random sequence and high concentration of initiator and low level of DVB reduce M_w and availability to make films as a consequence. Sulphonation reaction can be carried out by using sulphuric acid or acetyl sulphate, specially the latter, with some effect in loosing wettability when loosing acrylic acid through ketone formation.

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