SYNTHESIS OF A NEW POLYMER POLY(STYRENE SULFONIC ACID-CO-4-VINYLPYRIDINE) FOR PROTON EXCHANGE MEMBRANE FOR FUEL CELL

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Several types of poly(styrene sulfonic acid-co-4-vinylpyridine) polymer were realized using as monomers 4-styrenesulfonic acid sodium salt and 4-vinylpyridine. The copolymerization took place through free radical polymerization using different initiators as potassium metabisulfite, ammonium persulfate and sodium persulfate. The aim was the synthesis of a copolymer with a structure and characteristics suitable for creating a Proton Exchange Membrane (PEM) through haloalkyl crosslinking , this having a content of pyridine favorable for crosslinking.

Keywords: initiator, 4-Styrenesulfonic acid sodium salt, 4-vinylpyridine, fuel cell

1. Introduction

In order to improve the performance of proton exchange membrane, an efficient and simple method to reduce the degrees of methanol diffusion and water uptake while enhancing the mechanical properties and dimensional stability is the crosslinking. Several reports were written exploiting the methods for crosslinking polymer-electrolyte membranes and techniques which include the sulfonation of polysulfone/polybenzimidazole (SPSF/PBI) [1], sulfonation of poly(phthalazinone ether ketone) (SPPEK) [2], covalent crosslinked SPEEK [3,4], ionic crosslinking of acid/base blend membranes [5], UV-assisted photo-crosslinking of SPEEK [6–9] and covalent crosslinked polyvinyl alcohol (PVA) [10,11]. These crosslinked polymer-electrolyte membranes display losses in proton conductivity due to the low water uptake values caused by the crosslinking structure.

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The present study describes the synthesis of poly(styrene sulfonic acid-co-vinylpyridine) (NaSS-4VP) with the aim of forming a copolymer with a structure and characteristics suitable for creating a Proton Exchange Membrane (PEM) through haloalkyl crosslinking. The crosslinking agent is used to make the membrane water insoluble, while using suitable monomeric/polymeric material endowed with ion-exchange properties.

Vinyl monomers may be polymerized via free-radical polymerization, a type of chain growth reaction.

One of the most common free radical generation methods is achieved by redox reaction of organic or inorganic compounds. This method is well known for its high effectiveness in mild conditions [12]. Also because components of the redox couple are stable when they are separate, initiator feed can be controlled very easily and catalyst can be delivered in a long period of time if needed.

There are varieties of inorganic redox couples that can initiate free radical polymerizations. For example ammonium persulfate (initiator) and sodium metabisulfite/potassium metabisulfite (oxidizing agent) redox couple is a common pair in this group.

Redox initiators are mostly water soluble and used in emulsion polymerizations very extensively. Redox initiators are dissolved in the aqueous phase of the emulsion and monomers are emulsified in the non-aqueous phase. Polymerization occurs at the interface between the emulsions and solvent [12].

Ammonium persulfate ($(NH_4)_2S_2O_8$) and sodium metabisulfite ($Na_2S_2O_5$) are commonly used as redox pair for free radical polymerization. The reaction is often described as in Eq. (1)

$$S_2O_5^{-2} + S_2O_8^{-2} \rightarrow S_2O_5^{-\bullet} + S_2O_4^{-\bullet} + S_2O_4^{-2} \quad (1)$$

Also, in some studies ammonium persulfate is used as initiator by itself. [13] Similarly Cutié et al. [14] used sodium persulfate and Ye et al. [15] used potassium metabisulfite as radical initiator.

All polymers have some advantages and disadvantages for certain applications. Copolymerization of more than one monomer in free radical polymerization is a highly versatile method in order to balance the polymer properties as needed. It provides flexibility to polymer engineers and scientists. Copolymers can be classified as random, alternating, block and graft copolymers [16]. Each of them has their own unique properties. We can balance the polymer properties by changing the copolymer type in different ways and monomer ratios. Mostly the type of copolymer that we can produce is governed by nature of the co-monomers.

Polymers derived from 4-vinylpyridine (4VP) have been quaternized with alkyl halides [17,18] to form crosslinked polymers for use in anion-exchange membranes [19, 20].

Direct polymerization of sulfonated monomers provides the possibility of control over the position, number, and distribution of proton conducting groups along the polymer backbone than polymer sulfonation.

Styrene sulfonic acid is a styrene derived monomer which creates water soluble polymers [21]. The proton conductivity is primarily dependent on the concentration of sulfonic groups or on the value of IEC so it increases with IEC. Poly-4-vinylpyridine (P4VP) is a polymer of interest due to its high electrical conductivity, though it suffers from low thermal and mechanical stability [22].

Trying to obtain a polymeric crosslinked membrane for fuel cell I prepared a copolymer that can be easily crosslinked, which is inexpensive and easily to prepare.

2. Materials and methods

2.1 Materials

The raw materials are presented in Fig. 1.

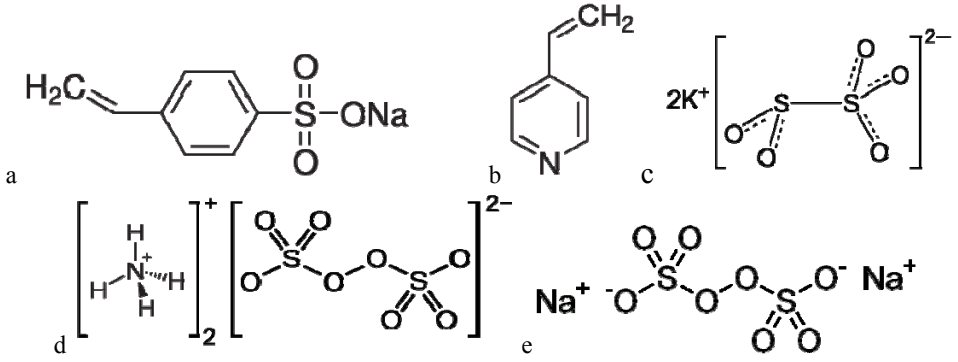

Fig.1. Chemical structures of raw materials: a) 4-Styrene sulfonic acid sodium salt (NaSS); b) 4-vinylpyridine (4VP); c) potassium metabisulfite; d) ammonium persulfate; e) sodium persulfate

The materials used in experiments are 4-Styrene sulfonic acid sodium salt ($H_2C{=}CHC_6H_4SO_3Na$) from Alfa Aesar; 4-vinylpyridine (C_7H_7N) containing 100 ppm hydroquinone as inhibitor, 95% from Aldrich and as initiator were used potassium metabisulfite ($K_2S_20_5$), ammonium persulfate ($(NH_4)_2S_2O_8$), sodium persulfate ($Na_2S_2O_8$).

2.2 Sample preparation

Poly(styrene sulfonic acid-co-4-vinylpyridine) copolymer was synthesized using a free radical polymerization in distillated water at 70ºC under a nitrogen

atmosphere and continuous mixing for 8h in presence of an initiator. The resulting solution was precipitated in acetone and filtered and washed three times with acetone. The precipitated solution was put to the vacuum drier at 80 ºC for 12h.

The scheme of polymerization is shown in Fig. 2 and the monomers feed ratio and the initiator used are summarized in Table 1.

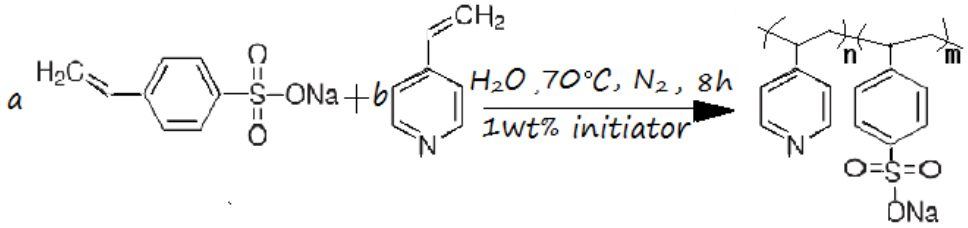

Fig.2. Synthesis of poly(styrene sulfonic acid-co-4-vinylpyridine) copolymer through free radical polymerization ; a-mol of 4-NaSS, b-mol of 4-VP

Table 1

Conditions used for copolymerization

Sample	Monomer feed ratio [mol]: [mol]		Initiator (1wt%)	Content of H_2O	Copolymer	
	4-NaSS	4-VP	Monomers	wt%	Appearance	Color
Sample 1	3	2	$K_2S_20_5$	36	Powder	Light brown
Sample 2	3	2	75% $(NH_4)_2S_2O_8$/ 25% $K_2S_20_5$	81	Powder	Yellow
Sample 3	3	2	$(NH_4)_2S_2O_8$	75	Glassy	Yellow
Sample 4	1	1	$Na_2S_2O_8$	44	Glassy	Dark yellow
Sample 5	1	2	$Na_2S_2O_8$	44	Glassy	Light brown
Sample 6	3	2	$Na_2S_2O_8$	89	Glassy	Yellow

The copolymer was characterize using a MIR spectrometer (PerkinElmer spectrophotometer) using 32 scans with a spectral resolution of 1 cm^{-1} and by the content of vinylpyridine.

3. Results and discussions

Infrared spectra were collected using MIR spectrometer (PerkinElmer spectrophotometer) using 32 scans with a spectral resolution of 1 cm^{-1}. IR samples were prepared by mixing a small amount of powder sample (about of 0.1-2% of the KBr amount) with KBr powder and pressing into a transparent pellet.

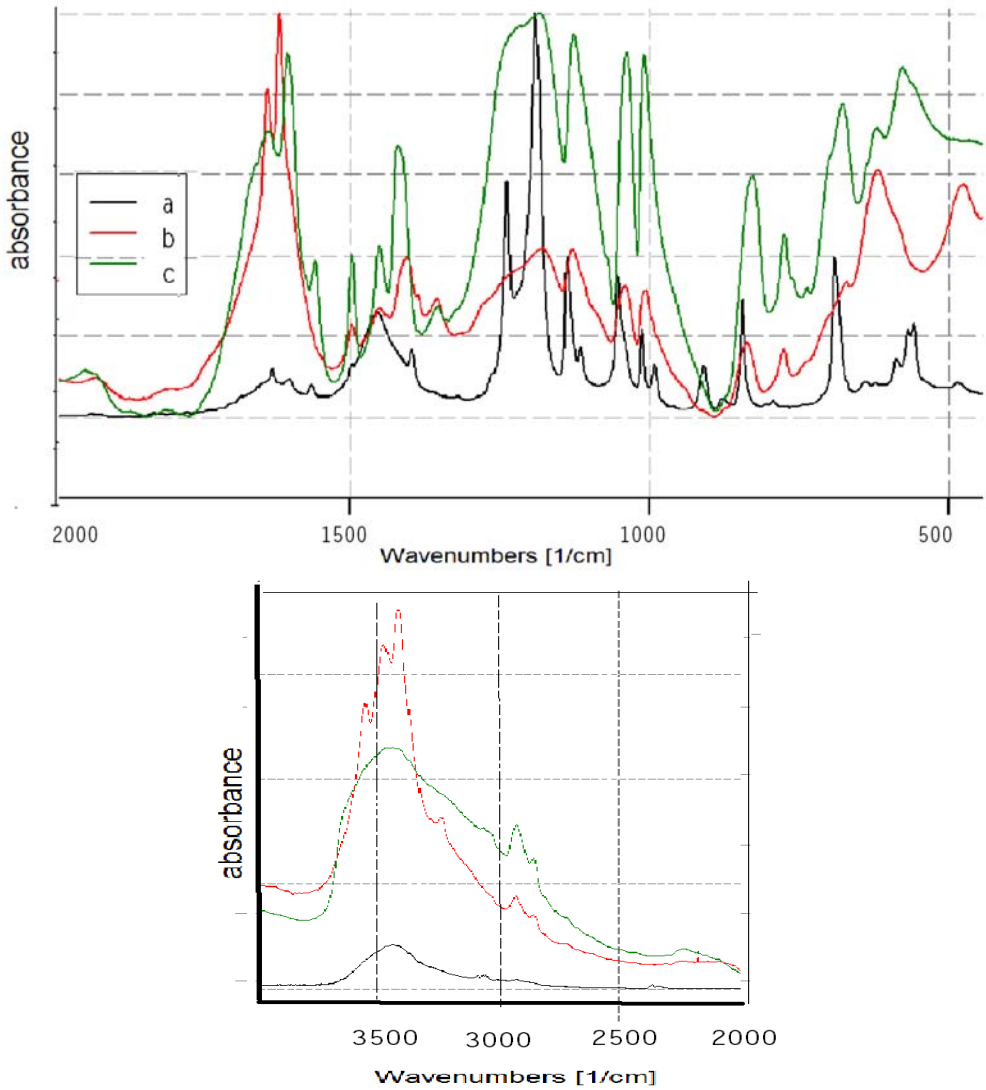

Fig.3. IR spectra a) sample 1; b) sample 2; c) sample 3

A significant peak at the 1638 cm^{-1} C=C bond in the vinyl monomer can be seen. For instance, since they all have C=C double bound, they all have a peak at 1660-1630cm wavenumber range. However to understand whether they polymerized with other monomers we need to determine their characteristic peaks.

Styrene has a series of peaks 2927, 2924 cm^{-1} wavenumbers. These peaks are due to C-H stretches in the phenyl ring. The same peaks on the styrene sulfonic acid spectrum were seen as well, since it has phenyl side group too. Also styrene spectrum shows the most significant peak at 690, 670, 677 cm^{-1}

wavenumber which is due to benzene ring bending. The same peak exists in the styrene sulfonic acid monomer as well but not as significant as styrene. Styrene sulfonic acid shows similar behavior like styrene monomer except it has a series of peaks at the range of 1200-1120 cm^{-1} wavenumber range due to sulfonate group attached to phenyl ring. This side groups the most significant peak of the monomer at 1190 cm^{-1} wavenumber. So using all these characteristic peak position information we will be able to get a very basic idea about addition of the monomers to polymer very quickly.

The SO_3^- group asymmetric and symmetric vibration adsorption peaks can be assigned to the peaks at 1051, 1041, 1038 and 1012, 1006, 1009 cm^{-1}. Peaks 1190, 1180, 1184 and at 1137, 1128, 1126 cm^{-1} can be assigned to the in-plane skeleton vibration of benzene ring and in-plane bending vibration of benzene ring.

A significant peak at the 1558 cm^{-1} was seen. This peak can be assign to the pyridine cation because of C=N bond which have the absorption bands at 1590-1430 cm^{-1} corresponding to the pyridine ring.

The peaks at 1354 and 845, 837, 828 are the bending vibration of CH_3 groups of aliphatic chains.

After comparing the three spectra, it can be observed that sample 1 did not copolymerized due to the absence of pyridine group.

The content of vinylpyridine was determined using a potentiometric titration with HCl 0.05M, and the values are shown in Table 2.

Table 2

Content of vinylpyridine in copolymer

Sample	Content of vinylpirydine in the copolymer [%]
Sample 2	1.00
Sample 3	18.70
Sample 4	29.80
Sample 5	22.20
Sample 6	45.40

After seeing the content of pyridine obtain in the copolymer we can conclude that for the copolymerization of 4-Styrene sulfonic acid sodium salt and 4-vinylpyridine the most suitable initiator is $Na_2S_2O_8$. Moreover, it could be observed as well, that the copolymerization was influenced of the quantity of solvent used in copolymerization, and the optimal quantity of solvent is ~90%.

All obtained copolymers are soluble in water and in dimethylsulfoxide.

6. Conclusions

After trying to copolymerize, in the presence of a few types of initiators ($K_2S_20_5$, 75% $(NH_4)_2S_2O_8$/ 25% $K_2S_20_5$, $(NH_4)_2S_2O_8$, $Na_2S_2O_8$), it was observed that, in the presence of $K_2S_20_5$, 75%$(NH_4)_2S_2O_8$/25% $K_2S_20_5$, 4-styrene sulfonic acid sodium salt and 4-vinylpyridine did not copolymerize, and the most suitable initiator in copolymerization is $Na_2S_2O_8$. In the future, the proton exchange membrane should be obtained by crosslinking the copolymer obtained in this work with a suitable haloalkyl.

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