

Preparation and evaluation of ionomeric membranes based on sulfonated-poly(styrene_isobutylene_styrene) membranes for proton exchange membrane fuel cells (PEMFC)

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Abstract Sulfonated polystyrene-block-poly-(ethylene-ran-butylene)-block-polystyrene membranes with different sulfonated levels have been prepared and evaluated as proton exchange membrane for polymer electrolyte membrane fuel cell. The polymer was sulfonated by chlorosulfonic acid. Homogeneous membranes were prepared by solvent casting method. Ion exchange capacity, degree of sulfonation, absorption, and solubility of the membranes were studied. The membranes were characterized by Fourier transform infrared, thermogravimetric analyzer, differential scanning calorimetry, and impedance spectroscopy.

Keywords Ionomers · Ion exchangers · Polymer membranes · Fuel cell · Proton conductivity · Ion exchange capacity

Introduction

Fuel cells convert the chemical energy of fuel into electrical energy with high efficiency and no emission of pollutants. Nafion® (DuPont) is the only efficient membrane commercially available for fuel cell application. It is a per-fluorinated membrane. It shows superior performance in fuel cell because of their high proton conductivity, and

chemical and mechanical stability. It is very suitable for hydrogen fuel cells [1], but not suitable for direct methanol fuel cell application because of their high methanol permeability [2, 3]. Methanol crossover from the anode to cathode reduces columbic efficiency and cell voltage, leading to an overall efficiency reduction.

Use of Nafion membranes is limited by loss of conductivity at high temperature, humidification requirements, methanol crossover, high cost of manufacture, and recycling problems. These limitations have already stimulated the development of alternatives for polymeric proton exchange membrane (PEM). The development of new membrane requires polymer with outstanding properties. Nowadays, several alternative PEMs have been investigated for fuel cell applications, which include sulfonated forms of polystyrene, polysulfone, polycarbonate [4], polyether ether ketone (PEEK) [5–9], poly-arylene ether sulfone [10–12], poly(styrene-isobutylene-styrene)[13, 14], polyphenylene oxide [15], polyether ketone (PEK) [16], polyimide [17], and polybenzimidazole [18, 19].

One of the alternatives for Nafion is sulfonated form of polystyrene-ethylene-butylene-polystyrene tri-block polymer (S-PSEBS). This ionomer, which is based on a hydrocarbon polymer, polystyrene-block-(ethylene-ran-butylene)-block-polystyrene (PSEBS), is a thermostable polymer with an aromatic non-fluorinated backbone. It is sulfonated using chlorosulfonic acid (CSA) in the medium of chloroform. Sulfonation is a powerful and versatile process, which makes the polymer suitable for fuel cell application.

In this paper, we have reported the synthesis of sulfonated PSEBS using CSA. The sulfonated ionomer exhibits a number of desirable properties such as ionic conductivity, good mechanical strength, and low affinity to methanol, which is required to suit the direct methanol fuel cell (DMFC) application.

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Sulfonation was confirmed by Fourier transform infrared (FTIR). Properties of sulfonated membranes like ion exchange capacity (IEC) and degree of sulfonation (DS) were investigated by volumetric methods. Water and methanol absorption of membranes were also studied by gravimetry. Conductivity measurements were made by impedance spectroscopy. Membranes were characterized by thermogravimetric analysis (TGA) to understand the thermal behavior and stability.

Experimental

Materials

Polystyrene-block-(ethylene-ran-butylene)-block-polystyrene (PSEBS) ($M_v=89,000$; 29% styrene) was obtained from Aldrich (Germany). CSA was purchased from Spectro-chem, India, and used without further purification. Tri-butyl phosphate (TBP; Lancaster) and methanol (SRL) were purchased and used as received. The solvents used for membrane casting, tetrahydro furan (THF) and dimethyl sulfoxide (DMSO), were purchased from Merck.

Sulfonation

Polystyrene-block-(ethylene-ran-butylene)-block-polystyrene (PSEBS) was sulfonated using CSA as a sulfonating agent. The weighed amount of polymer was dissolved in chloroform. The solution was allowed to cool in an ice bath ($10\text{ }^\circ\text{C}$). Then, the required amount of TBP (to moderate the reaction), followed by CSA, was added drop-wise with continuous stirring. The reaction was carried out in nitrogen atmosphere. The reaction proceeded for 3 h, and it was terminated using methanol. The polymer was dried by solvent evaporation method. Then, the polymer was washed

with water several times until the pH was neutral. Then, the polymer was dried at $75\text{ }^\circ\text{C}$ overnight. Polymers with various DS were prepared. The chemical structure of PSEBS and S-PSEBS are shown in Fig. 1.

Effect of concentration of sulfonating agent

Experiments were carried out by varying the quantities of CSA; the corresponding IEC, DS, water, and methanol absorptions were determined for all the products. Also, all the membranes obtained from the various concentrations of sulfonating agent were analyzed by IR, TGA, and differential scanning calorimetry (DSC).

Membrane preparation

The sulfonated polymer was dissolved in THF and DMSO solvents. The polymer membrane was cast by solvent evaporation method. All the membranes were subjected to IEC, water, and methanol absorption studies.

Membrane purification

The purification test is generally conducted before the membranes were fed into the fuel cell. The membranes were allowed to boil in 3% H_2O_2 , then it is allowed in boiling water for 15 min and then for half an hour in 10% H_2SO_4 . Then, it was washed with boiling water.

Solubility

It should be pointed out that not all sulfonated polymers can be dissolved, and although when they can be, the dissolution process may take up to several days or weeks. According to Rosen [20], there is an assembly of general rules for polymer solubility, based on experimental obser-

Fig. 1 Structure of PSEBS and S-PSEBS

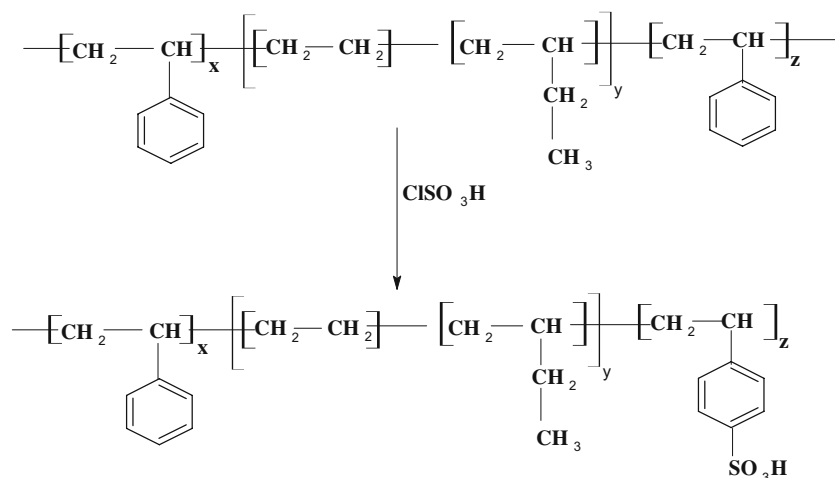


Fig. 2 IEC as a function S/P ratio

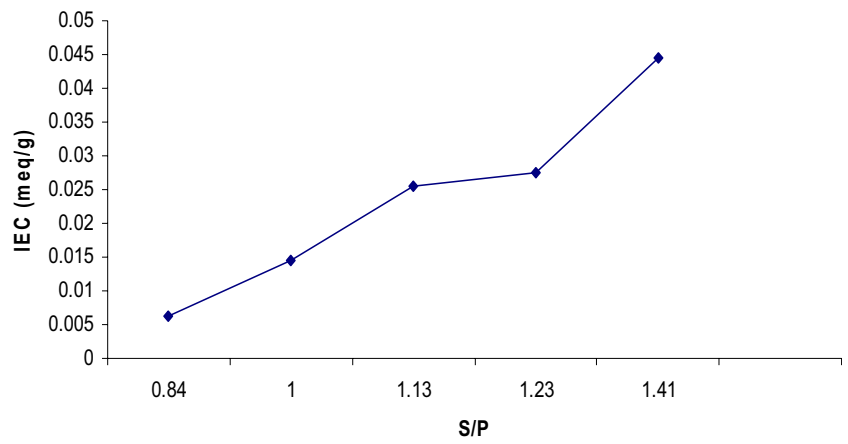
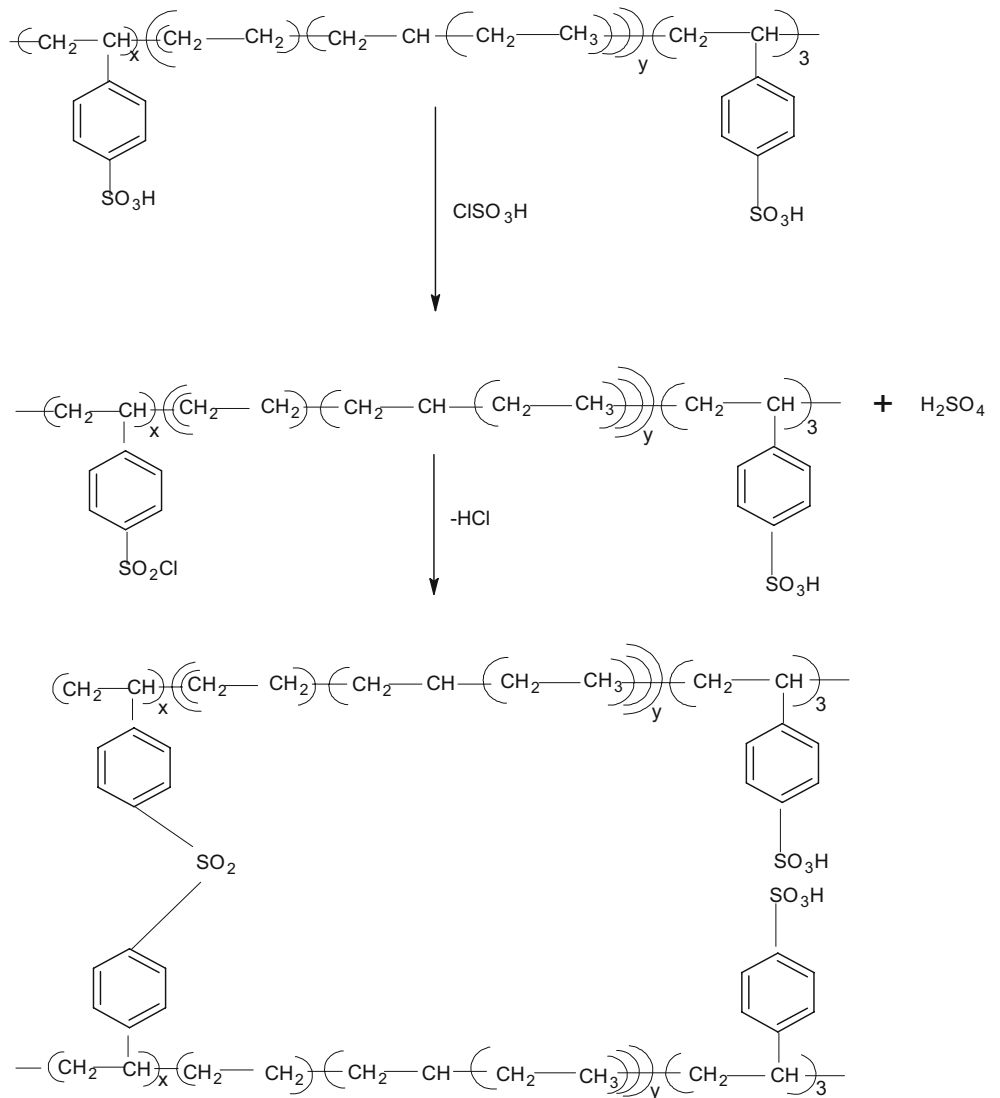


Fig. 3 Possible interchange cross-linking during sulfonation of PSEBS



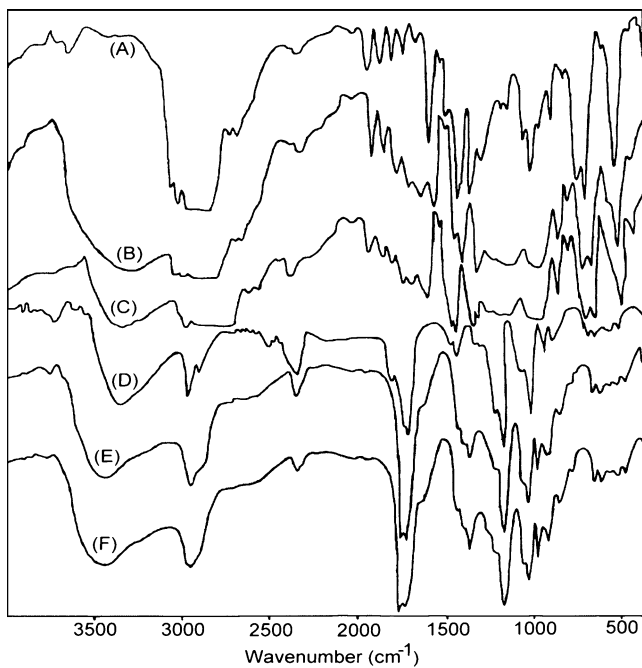


Fig. 4 FTIR spectra of (A) unsulfonated PSEBS; (B) to (F) sulfonated PSEBS with increasing degrees of sulfonation

variations, from which interesting conclusions can be obtained. Thus, it is well-known that the dissolution of polymers depends not only on their physical properties, but also on their chemical structure, such as polarity, molecular weight, branching, cross-linking degree, and crystallinity.

Characterization of polymer

Fourier transform infrared (FTIR) spectra of sulfonated and unsulfonated polymers were obtained. DSC measurements were carried out at a heating rate of 20 °C/min with a SDT Q600 US analyzer. The midpoint of the slope change of the heat capacity plot was taken as the T_g . The TGA analyzer was used to analyze the stability of the polymer with the heating rate of 20 °C/min.

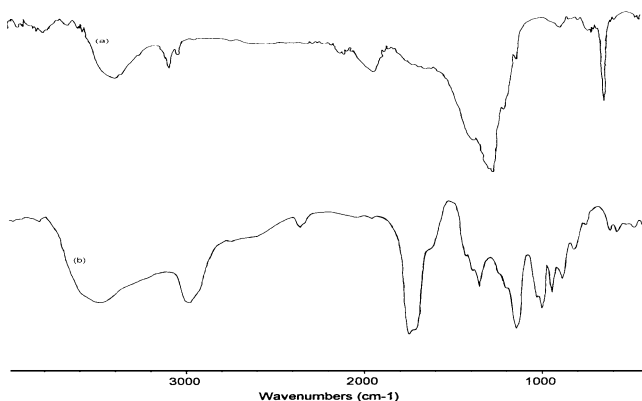


Fig. 5 FTIR spectrum of sulfonated PSEBS by casting (a) DMSO and (b) THF

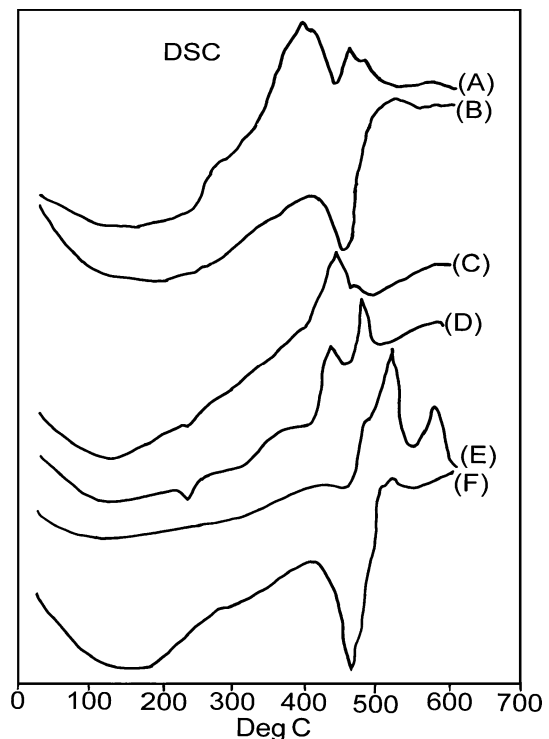


Fig. 6 DSC curves of (A) to (E): sulfonated PSEBS with IEC 0.0062, 0.0146, 0.0254, 0.0273, and 0.0446 meq/g and (F), unsulfonated PSEBS

Water and methanol absorption

The dry polymer membrane was weighed and soaked in respective solvents. After several hours it reached the equilibrium state. Then, the wet weight was measured. The absorption percentage of water and methanol were calculated using the equation,

$$\text{Absorption} = \left\{ \frac{M_w - M_d}{M_d} \right\} \times 100\%$$

M_w = wet Weight of the polymer membrane
 M_d = dry Weight of the polymer membrane

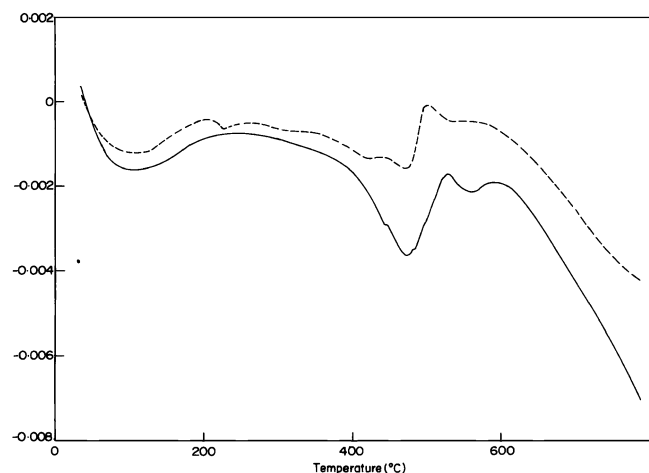


Fig. 7 DSC curves for S-PSEBS in DMSO and THF

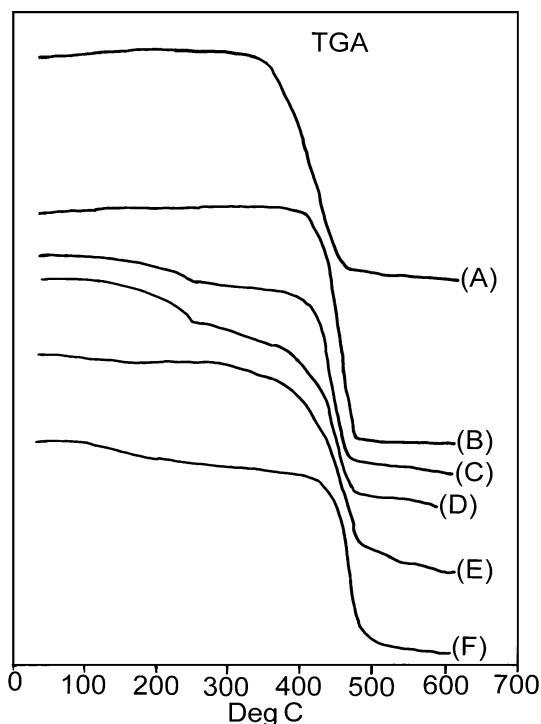


Fig. 8 TGA curves of (A) unsulfonated PSEBS; (B) to (E): sulfonated PSEBS with IEC 0.0062, 0.0146, 0.0254, 0.0273, and 0.0446 meq/g

Ion exchange capacity (IEC)

The ion exchange capacity (IEC) of the membranes were determined by titration method. The dry polymer was weighed and soaked in saturated KCl solution. After several hours the solution was titrated against 0.001 N sodium carbonate solution, using phenolphthalein as an

indicator. The IEC was calculated from the consumed volume of sodium carbonate solution.

The IEC values were expressed as meq/g. The DS values were also calculated. DS is the number of sulfonated units per 100 monomer units, and it is expressed as percentage. Both the IEC and DS indicate the capacity of the membrane to conduct protons through the membrane.

Proton conductivity

Proton conductivity of samples was measured in a measurement cell using complex impedance spectra obtained using Volta lab dynamic-EIS voltammetry model PGZ 301. Studies were carried out using a two-compartment electrochemical cell using platinum foil electrodes and 1 M sulfuric acid solution as the electrolyte.

Result and discussion

Sulfonation analysis

Sulfonation of PSEBS was carried out using CSA. The DS of PSEBS was controlled by the concentration of CSA. The physical and chemical property of a sulfonated PSEBS depends on the DS. In general, DS increases with the increase in the concentration of CSA. The IEC depends on sulfonation reaction conditions, including the polymer concentration, the reaction temperature, the amount of sulfonating agent, and the reaction time. In this study, under the same reaction conditions of temperature (10 °C), time (3 h), and polymer concentration (2.7×10^{-2} mol/l),

Fig. 9 TGA curves for S-PSEBS in DMSO and THF

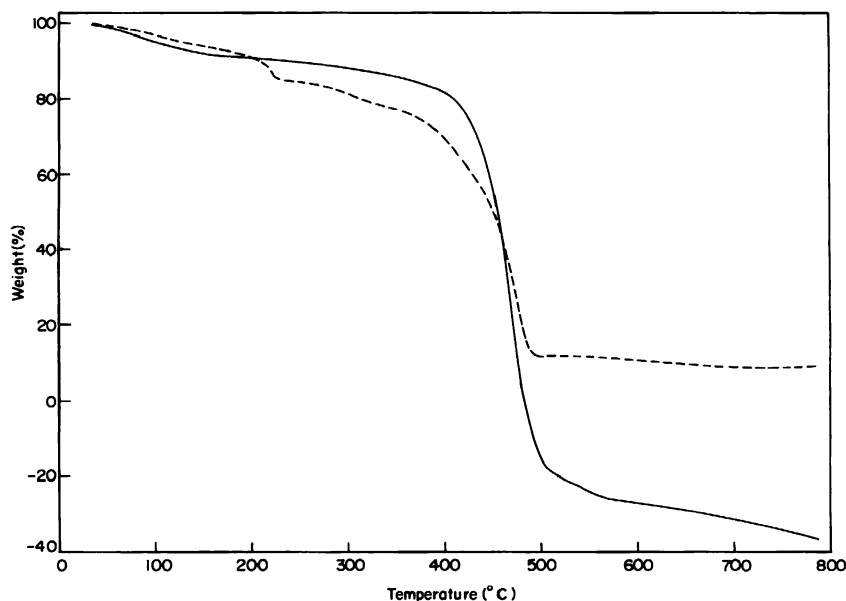
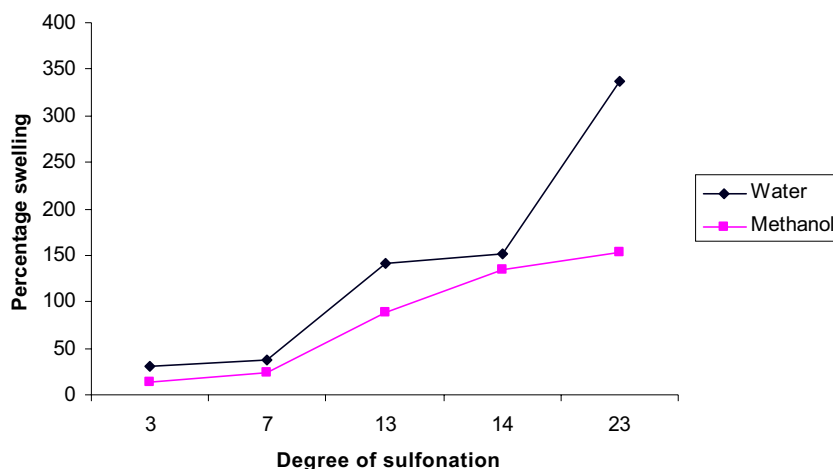


Fig. 10 Equilibrium absorption of water and methanol of S-PSEBS



various DS polymers were obtained by varying the concentration of the sulfonating agent. Figure 2 shows the IEC as a function of the sulfonating agent/polymer mol concentration ratio (S/P). The IEC of the S-PSEBS increased with the increase in sulfonating agent.

Those with high DS did not exhibit film-forming characteristics and showed poor solubility. Hence, the membrane with 13% DS and less was chosen for further studies.

Solubility

Sulfonation is commonly used to modify the polymers to increase their hydrophilicity. The PSEBS polymer is hydrophobic in nature, and when sulfonated it becomes hydrophilic in nature. The incorporation of the sulfonic acid groups causes increase in solubility in high polar solvents such as water and methanol [21, 22]. S-PSEBS, with higher DS, absorbed more and more amount of water and methanol, but did not dissolve in such solvents.

The S-PSEBS was cast into the membrane using DMSO solvent by solution casting method. The sulfonated polymer

was dissolved in DMSO at its boiling point of 189 °C. Then, membranes were obtained by solvent evaporation at 85 °C for 1 day. Cross-linking of sulfonated polymer is expected to occur during this process, as given in Fig. 3. Membranes were also prepared using THF as solvent by casting and evaporation at room temperature for 48 h.

Fourier transform infrared (FTIR)

Figure 4 shows the infrared (IR) spectra of both PSEBS and S-PSEBS samples. Appearance of broad envelope around 3,000–3,600 cm^{-1} was assigned to –OH stretch of the sulfonic acid group. Appearance of peak around 1,177, 1,054, 1,058, and 1,163 cm^{-1} was assigned to the O=S=O (asymmetric stretch), which is because of the presence of SO_2 ; stretching confirms that the polymer PSEBS has been sulfonated. Disappearance of the peak at the frequency of 720 cm^{-1} and 693 cm^{-1} shows that the sulfonic acid group is substituted in the aromatic ring, when compared to the unsulfonated PSEBS [23]. Appearance of the peak at around 869 cm^{-1} shows that the sulfonic acid group is substituted at par position.

Fig. 11 Absorption studies of S-PSEBS membrane prepared with DMSO

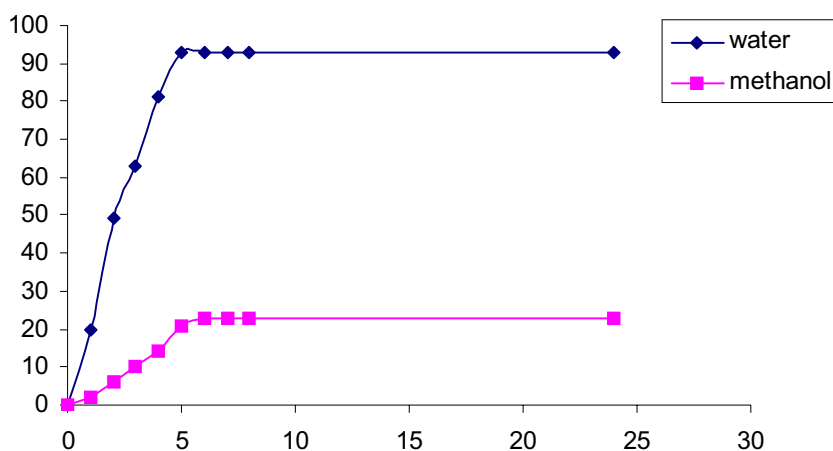


Fig. 12 Absorption studies of S-PSEBS membrane prepared with THF

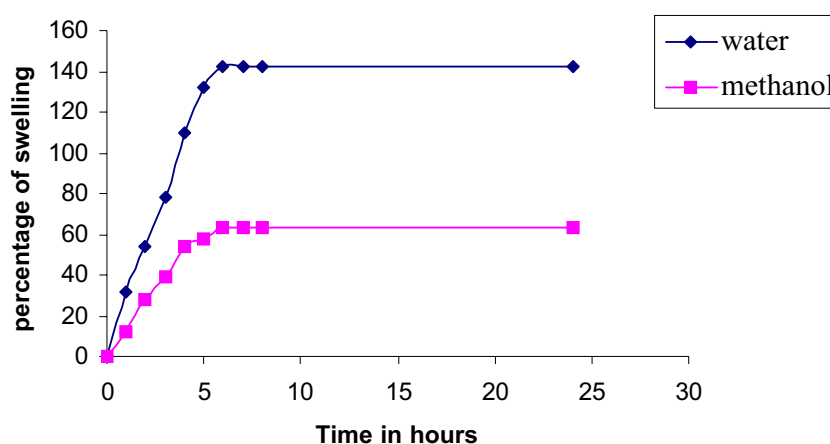


Figure 5 shows the IR spectra of sulfonated PSEBS membrane prepared by casting in (a) DMSO and (b) THF. Appearance of broad envelope at 3,390 and 3,457 cm^{-1} shows the presence of $-\text{OH}$ groups bonded to the sulfonic acid group substituted in the benzene ring in spectra a and b, respectively. Appearance of the peak at 1,177 and 1,097 cm^{-1} was because of the presence of sulfonic acid groups in a and b, respectively. Appearance of a peak in a at 1,598 cm^{-1} confirms the presence of SO_2 cross-linkage in the sulfonated sample membrane cast from DMSO.

Differential scanning calorimetry

Figure 6 shows the DSC curves of S-PSEBS with different DS. The inflection point of the slope change of the heat capacity plot was taken as the T_g , and it was between 110 and 130 $^{\circ}\text{C}$ for the various S-PSEBS. This means that S-PSEBS could be easily fabricated for membrane electrode assembly (MEA) preparation at a relatively lower temperature, conveniently without undergoing any chemical decomposition. In MEA preparation, the membrane is subjected to high pressure and fit in between the electrodes.

The DSC curves for S-PSEBS membranes cast in DMSO and THF are compared in Fig. 7. The T_g of the membrane prepared in DMSO was slightly higher than the one prepared in THF, which may be attributed to the possible cross-linking and reduction in few sulfonic acid groups.

Thermogravimetric analysis

The TGA curves of the S-PSEBS samples with various DS are shown in Fig. 8. The thermal decomposition temperature of the membrane is a function of sulfonation. The unsulfonated sample displays thermal stability up to 380 $^{\circ}\text{C}$, but the sulfonated membrane loses its stability beyond 250 $^{\circ}\text{C}$. A small transition around 100 $^{\circ}\text{C}$ in the sulfonated sample is attributed to the presence of moisture. The

transition around 250 $^{\circ}\text{C}$ may be caused by the thermal degradation of the sulfonic acid groups. The transition around 380 $^{\circ}\text{C}$ is attributed to main chain scission. Thus, sulfonation decreases the thermal stability of the polymer because of the degradation of the sulfonic acid groups at lower temperatures. However, the sulfonated hydrocarbon polymer membrane has adequate thermal properties for application in fuel cells, as their thermal decomposition is detected only beyond 200 $^{\circ}\text{C}$.

The TGA curves for S-PSEBS cast in DMSO (a) and THF (b) are compared in Fig. 9. The thermal stability of S-PSEBS membrane cast in DMSO was found to be higher than that cast in THF, which may be because of the cross-linking.

Water and methanol sorption

The water sorption and methanol sorption of the S-PSEBS membranes with different DS, prepared using THF solvent, are compared in Fig. 10. Usually, water and methanol absorption is defined in weight percentage with respect to the weight of the dry membrane. The equilibrium percentage of water and methanol sorption of the membranes at room temperature was found to be increasing with increasing sulfonation level up to a maximum of 337 and 153%, respectively. Increase in the amount of polar sulfonic acid group in the polymer results in a significant increase of absorption level. The maximum water uptake of the samples increases with increasing DS, which leads them to be more hydrophilic [21].

The absorbance of the membrane plays an important role in the conducting phenomena. Figures 11 and 12 show the increase in the solvent absorption of S-PSEBS membranes prepared using DMSO and THF, respectively. Initially, the membrane rapidly absorbs the solvents, and then it gradually increases with time. From visual observations, it was noted that the S-PSEBS membrane increased approximately twice its area after immersion in water but remained completely immiscible in water. The absorption of metha-

nol was relatively lower than the water absorption, in contrast to the Nafion membrane, which absorbs more methanol than water.

In both cases (Figs. 11 and 12), the methanol absorption of S-PSEBS was found to be two to three times less than the water absorption. In the case of DMFC, the methanol is used as a source of hydrogen, and methanol absorption of the membrane is expected to be lower to avoid crossover. This methanol crossover is highly predominant in Nafion, hence, is one of the major limitations of the membrane to use in DMFC. Water absorption of S-PSEBS membrane prepared by THF solvent is found to be more than that prepared in DMSO, as S-PSEBS polymer in THF has more number of $-SO_3H$ group compared to that in the DMSO solvent. This is because of some of the $-SO_3H$ being converted to SO_2 cross-linkages when subjected to higher temperatures.

Proton conductivity

Ion exchange capacity (IEC) provides an indication of the number of acid groups present in a polymer, which are responsible for the conduction of proton and, thus, is an indirect and reliable approximation of the proton conductivity. It is measured by titration method. Proton conductivity of all the membranes with IEC (0.01 to 0.02 meq/g) was determined using impedance spectroscopy and was found to be excellent in the order of 10^{-3} S/cm. The values are highly comparable to the Nafion membrane.

Conclusion

Polystyrene-block-(ethylene-ran-butylene)-block-polystyrene (PSEBS) was sulfonated using CSA as a sulfonating agent. Membranes of various DS were prepared by casting method using THF and DMSO. The solvent absorption properties of membranes were studied. Methanol absorption was found to be lower than water absorption. FTIR spectra confirmed the sulfonation of the polymer and cross-linking of membrane in DMSO solvent. DSC and TGA analysis showed that the thermal stability of the polymer decreases with the increase in sulfonation. The proton conductivity of membranes was found to be excellent in the order of the 10^{-3} S/cm. These results conclude the suitability of the membrane for proton exchange membrane fuel cells (PEMFC) application.

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