

**SYNTHESIS, CHARACTERISATION AND EVALUATION OF
SULPHONATED POLYMERS FOR POTENTIAL APPLICATIONS AS
MEMBRANES FOR FUEL CELLS**

by

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Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

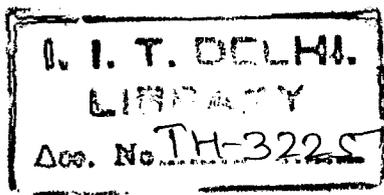
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Sulfonated polymers



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CERTIFICATE

This is to certify that the thesis entitled “**Synthesis, Characterisation and Evaluation of Sulphonated Polymers for Potential Applications as Membranes for Fuel Cells**” submitted by **Ms. Muthu Lakshmi. R.T.S.** to the **Indian Institute of Technology, Delhi** for the award of degree of Doctor of Philosophy, in Polymer Science and Technology is a record of bonafide research work carried out by her. Ms. Muthu Lakshmi has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis.

The results contained in this thesis are original and have not been submitted in partial or full, to any other university or institute for the award of any degree (or) diploma.



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To
Matha, Pitha, Guru, Theivam...

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Strength is Life, weakness in Death

- Swami Vivekananda

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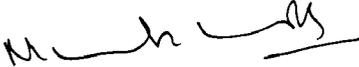
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ABSTRACT

Solid polymer based fuel cells have reached a technological stage where they offer a real challenge to conventional power generating technologies, particularly for transportation. Unlike internal combustion engines (ICE), fuel cells offer potential to generate energy very efficiently without the emissions usually associated with combustion. The possibility of using sulphonated poly (ether ether ketone) (SPEEK) or poly (ether sulphone) (SPES) as solid polymer electrolytes for fuel cells has increased the interest in the sulphonation of these polymers.

The main objective of the present studies was to synthesise and characterise SPEEK and SPES and to evaluate their performance as proton exchange membranes for fuel cells. Two approaches were used for the preparation of sulphonated polymers. These were (a) post sulphonation of polymers available commercially or prepared in laboratory and (b) synthesis of sulphonated polymers using sulphonated monomers.

The thesis has been divided into seven chapters. Chapter 1 is a comprehensive review of the work reported in the literature on post sulphonation of commercially available PEEK & PES using different sulphonating agents. Synthesis of sulphonated polymers from monomers and the techniques used for the characterization and properties evaluation of sulphonated polymers along with their applications are also described in this chapter.

The general procedure adapted for the synthesis of sulphonated polymers by post sulphonation technique or by using sulphonated monomers and the techniques used for characterization and evaluation of properties of sulphonated polymers are described in Chapter 2 of the thesis.

The details of sulphonation of PEEK (Gatone™) (Gharda Chemicals Ltd., India) using conc. H₂SO₄ is reported in Chapter 3 of the thesis. The effect of reaction parameters i.e. temperature, duration of reaction and concentration on the extent of sulphonation was

determined. From elemental analysis, (sulphur content) the degree of sulphonation (DS) was calculated and was found to be in the range of 56-75%. In the FT-IR spectra of sulphonated samples, additional absorption bands associated with sulphonic acid groups were observed at $\sim 3440\text{ cm}^{-1}$, 1252 cm^{-1} , 1080 cm^{-1} , 1024 cm^{-1} and 709 cm^{-1} . The aromatic C-C absorption band of PEEK at $\sim 1490\text{ cm}^{-1}$ was split upon sulphonation. In sulphonated PEEK, ^1H - NMR signal of the proton attached to the α - carbon (i.e. next to the carbon having sulphonic acid group) showed a downfield shift. The ratio of the peak intensity of this signal vs. rest of the protons in the repeat unit therefore was used to estimate SO_3H content and DS calculated was found to be 47-81%.

In TG traces, a single step mass loss was observed in PEEK above 400°C , whereas three-step degradation was observed in SPEEK samples i.e. from $50\text{-}250^\circ\text{C}$ (both absorbed and chemically bound water), $250\text{-}450^\circ\text{C}$ (decomposition of sulphonic acid group) and $450\text{-}800^\circ\text{C}$ (breakdown of the polymer backbone). Water uptake of 47 % was observed in SPEEK having $\text{DS} = \sim 80\%$. Tensile strength (TS), tensile modulus (TM) and % elongation of samples having DS less than 70% were in the range of 47-66 MPa, 900-1148 MPa & $\sim 33\text{-}64\%$ respectively. In the samples with higher degree of sulphonation ($\sim 80\%$), the mechanical properties were significantly lower (TS = $\sim 20\text{ MPa}$, TM = 700 MPa and elongation = 10%). The proton conductivity depended on the extent of sulphonation and was in the range of 0.034×10^{-2} - $0.235 \times 10^{-2}\text{ S/cm}$ for samples having $\text{DS} = 46\text{-}81\%$. The conductivity of Nafion117® was $4.91 \times 10^{-3}\text{ S/cm}$ under the similar experimental conditions. However, proton conductivity was higher than Nafion at 100°C in samples having $\sim 80\%$ DS.

Synthesis of SPEEK copolymers carried out using silylated bisphenols is described in Chapter 4 of the thesis. This is a new approach for the synthesis of SPEEK (26 samples). These copolymer samples were prepared by the condensation of 0.01 moles of silylated bisphenol-A (BA)/ (or) silylated phenolphthalein (P): silylated hydroquinone (H)/ (or)

silylated resorcinol (R)/ (or) silylated biphenol (B) (3:1, 1:1, 1:3) and 0.01 moles of desired molar ratio of disulphonated 4,4'-difluorobenzophenone (SDFBP) and 4,4'-difluorobenzophenone (DFBP) (1:1, 1:3). Most of the samples could be dissolved in solvents like DMAc, DMF and DMSO. The samples based on silylated phenolphthalein: silylated biphenol were white beads or flakes while precipitating in ethanol and films could be easily made. Films produced from the other samples were very brittle and so the evaluation of film properties could not be carried out.

Reduced viscosity of all these polymers was found to be above 0.6 dL/g except the polymers synthesised using resorcinol where it was in the range of 0.2-0.3 dL/g. Number average molecular weight (\bar{M}_n) of the samples prepared using silylated biphenol was in the range of $20-35 \times 10^3$ g/mol and weight average molecular weight (\bar{M}_w) was in the range of $40-148 \times 10^3$ g/mol. While in all other polymers, molar mass (\bar{M}_n) of the samples was in the range of $54-116 \times 10^2$ g/mol.

In the $^1\text{H-NMR}$, the proton α - to SO_3H group in SDFBP moiety appeared at $\delta = 8.20$ ppm. Other proton signals due to the protons of SDFBP were at 6.86 and 7.64 ppm and DFBP were at 7.06 and 7.76 ppm. The protons present in the phenolphthalein moiety appeared at 7.70, 7.88 & 7.94 ppm (protons in the benzene ring which is deactivated because of COO group). The characteristic isopropylidene group present in bisphenol-A units appeared at 1.67 ppm. Other proton signals due to bisphenol-A moiety appeared at 6.99 ppm and 7.30 ppm. In case of samples based on hydroquinone, the corresponding signal appeared at 7.16 ppm. Similarly characteristic resorcinol proton signals appeared at 6.89, 7.15 & 7.46 ppm. On the basis of ATR-FTIR and $^1\text{H-NMR}$, it could be concluded that copolymer composition was in good agreement with the feed ratio (with an error in the range of 2-10 %).

As mentioned earlier for SPEEK (chapter 3), the TG traces showed a three-step degradation for all the samples. Amorphous nature of polymers was indicated by DSC and X-ray studies.

The water uptake of the copolymers was in the range of 11.9 -40 % depending on the extent of sulphonation. The methanol diffusion coefficients (D) of these membranes at different temperatures were in the range of 10^{-6} - 10^{-8} kg/cm²s. The proton conductivity was in the range of 6.4×10^{-4} - 1.2×10^{-5} S/cm at 25°C.

The sulphonation of PES polymers (Gafone™) or copolymers (synthesised in laboratory) form the basis of Chapter 5 of the thesis. Conc. H₂SO₄ or chlorosulphonic acid or fuming H₂SO₄ were used as sulphonating agents. In section A of this chapter, the details of sulphonation of Gafone™ (Gharda Chemicals Ltd., India) are described while in section B the details of synthesis of copolymers and their sulphonation reactions are described. The PEES copolymers were synthesised first by taking the equimolar amounts of 4,4'-dichlorodiphenyl sulphone and bisphenols i.e. bisphenol A: hydroquinone (MH), bisphenol-A: resorcinol (MR) and bisphenol-A: phenolphthalein (MP) (3:1, 1:1 and 1:3) and then sulphonated using fuming sulphuric acid at 0°C for 30 -60 mins. Both the non-sulphonated and sulphonated polymers were characterised by FT-IR and ¹H-NMR. The degree of sulphonation in sulphonated PES (Gafone™) using ¹H-NMR was in the range of 5-46 %. In case of sulphonated copolymers, the extent of sulphonation estimated by elemental analysis (i.e. S content) indicated that in both bisphenol-A as well as other biphenyl units (i.e. H, R or P) were sulphonated when the sulphonation was carried out at 0°C for 60 mins.

The synthesis and characterization of sulphonated PEES copolymers by reacting sulphonated monomers i.e. 4,4'-difluorodiphenyl sulphone and varying molar ratio of silylated hydroquinone sulphonic acid: bisphenols i.e. bisphenol-A(SBA)/ 4,4'-dihydroxybiphenyl (SBP)/ hydroquinone (SHQ)/ phenolphthalein (SPH)/ 2,6-dihydroxynaphthalene (SNA) is reported in Chapter 6. The main purpose of these studies was to evaluate the effect of copolymer structure on the properties of SPEES while keeping the degree of sulphonation fixed i.e. 75 or 60 mol-% of silylated hydroquinone sulphonic acid and varying the

bisphenols (25 or 40 mol-%). All the sulphonated polymers were flaky in nature and were highly soluble in dipolar aprotic solvents such as DMAc, DMF, DMSO and NMP.

The samples had medium to high molecular weights as indicated by the reduced viscosities (0.3 – 2.1 dL/g). The \overline{M}_n was in the range of 7,900 - 18,100 g/mol whereas the \overline{M}_w was ~ 26,100 to 74,600 g/mol. Films prepared from these samples were tough and transparent with a brownish tinge.

In addition to the characteristic absorption bands corresponding to the aromatic skeleton in ATR-FTIR spectroscopy, the characteristic absorption bands of SO₃H & SO₂ groups were also present. The aromatic proton region in ¹H-NMR spectra confirmed the structure of polymers and was also used for quantifying the content of the different structural units.

The glass transition temperature (T_g) could only be determined for few of the copolymer samples and was in the range of 184 -205°C. The proton conductivity of the samples was in the range of 6.4 x 10⁻³ - 1.2 x 10⁻⁵ S/cm at 25°C. SPEES membranes having hydroquinone or bisphenol-A exhibited higher proton conductivity at 100°C compared to Nafion.

In Chapter 7, general discussions and conclusions of the work are given. Higher proton conductivity was observed in samples having SPEEK (~ 80 % DS - prepared by post sulphonation method) and SPEES membranes (synthesised from sulphonated hydroquinone sulphonic acid and hydroquinone or bisphenol-A) than Nafion at 100°C. Methanol permeability was also lower than Nafion and was found to increase with increase in DS of the samples.

Suggestions for future work are also given in this chapter.

References are given at the end of the thesis.

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