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# Sulphonated Poly(ether ether ketone): Synthesis and Characterisation

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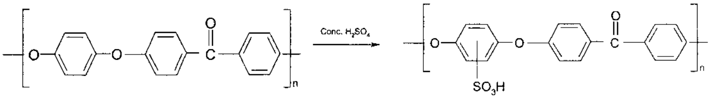
**Summary:** The paper describes the sulphonation of commercially available poly(ether ether ketone) PEEK (GATONE™, Gharda Chemicals Limited, India and VICTREX®, ICI Limited, UK) by using concentrated sulphuric acid. The concentration of GATONE in conc. $H_2SO_4$ was varied from 4-10 % (w/v) whereas in VICTREX® the concentration was 4 % (w/v). The temperature was varied from 35-55°C and the duration of reaction was 3-7 h. Structural characterisation of sulphonated polymers was done by elemental analysis, FT-IR and $^1$H- NMR spectroscopy. On the basis of elemental analysis, the extent of sulphonation of GATONE was found to be 57-75%. The extent of sulphonation as determined by $^1$H-NMR in case of GATONE was in the range of 53-80% and for VICTREX 58-87 %. Thermal analysis, proton conductivity and water uptake of these samples were also studied. Proton conductivity of the films was comparable to the perflourinated polymer (Nafion).

**Keywords:** fuel cells; membranes; poly(ether ether ketone); proton conductivity; sulphonation

## Introduction

Poly (ether ether ketone)s (PEEK) are engineering plastics and find applications in electrical and electronic parts, automotives, aerospace, oil and chemical industries and military equipments.[1] Since PEEK is hydrophobic in nature, it cannot be used for certain applications. Hydrophilicity of these polymers can be increased by sulphonation. The possibility of using these ionic materials as proton exchange membranes (PEM) or direct methanol fuel cell membranes has generated considerable interest in the past. Membranes based on sulphonated PEEK have been reported earlier for fuel cell applications.[2-4]

Jin et al [5] reported that sulphonation takes place only on the phenyl flanked by two ether groups of the PEEK repeat unit. The extent of sulphonation is controlled by the reaction time, acid concentration, and temperature, which can provide a sulphonation range of 30- 100% per repeat unit.



PEEK SPEEK

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A series of novel sulphonated poly (aryl ketone)s have been developed by Hoechst AG for potential application in PEM fuel cells. The sulphonation of PEEK has been carried out by using 98% sulphuric acid [5-9], mixture of sulphuric acid and methane sulphonic acid[10], sulphur trioxide- triethyl phosphate complex and chlorosulphonic acid.[11] A crosslinked structure was formed by using 100% sulphuric acid due to sulphone formation[12], which is negligible in aqueous sulphuric acid i.e. 97.4% because water decomposes the postulated aryl pyrosulphonate intermediate which is required for sulphone formation. Chlorosulphonated PEEK is also formed when chlorosulphonic acid was used. Sulphonated PEEK (SPEEK) is soluble in dimethyl formamide (DMF), dimethyl acetamide (DMAc), dimethyl sulphoxide (DMSO), pyridine and N- methyl- 2 – pyrrolidine (NMP).[13]

Considerable work has been reported on sulphonation of commercially available PEEK (VICTREX ICI product) but no reports are available on sulphonation of other commercially available poly(ether ether ketone)s such as GATONE of Gharda Chemicals Limited, India. There is a difference in the properties of these polymers (Table 1), which may be attributed to the structural difference. This variation may affect the sulphonation behaviour. Therefore, it was considered of interest to carry out the sulphonation of GATONE and evaluate the properties of sulphonated GATONE and compare with the sulphonated VICTREX.

## Experimental

The concentration of GATONE in conc. $H_2SO_4$ was varied from 4-10 % (w/v) whereas in VICTREX® the concentration was 4 % (w/v). The temperature was varied from 35-55°C and the duration of reaction was 3-7 h. The reaction mixture was stirred using mechanical stirrer & the resulting sulphonated polymers (SPEEK) were precipitated by dropwise addition of solution to 500 ml of ice cooled distilled water. The samples were washed till the excess acid was removed and dried in oven overnight at 70°C. The details of sulphonation along with the letter designations are given in Table 2. The films were obtained by casting a DMF solution of SPEEK (3.3 % (w/v)) on a glass plate.

## Structural Characterisation

A Carlo ERBA, EA 1108 elemental analyzer (CHNSO) was used for elemental analysis. FT-IR spectra of polymer samples either in film or in KBr pellets were recorded on NICOLET FT-IR spectrometer. A BRUKER AC300 spectrometer was used to record $^1$H- NMR using tetramethyl silane as an internal standard and DMSO-$d_6$ as a solvent.

Table 1. Properties of Polymers (as given in Manufacturers Data Sheet)

| S. No | Property | Test method | GATONE$^{TM}$5200P | VICTREX® 450P |
|---|---|---|---|---|
| 1. | Density | ISO1183 | 1.32 g/cc | |
| Mechanical properties | | | | |
| 2. | Tensile Strength | ISO527 | 95 MPa | 97 MPa at 23°C<br>12 MPa at 250°C |
| 3. | Tensile Modulus | ISO527 | 3800 MPa | |
| 4. | Elongation at Break | ISO527 | >50 % | Up to 60 % |
| 5. | Flexural Strength | ISO178 | 160 MPa | 53 MPa at 23°C |
| 6. | Flexural Modulus | ISO178 | 3800 MPa | 4100 MPa |
| 7. | Izod Impact | ISO179 | 6.0 kJ/m$^2$ (notched) | - |
| | | ISO180/1A | - | 6.4 (notched) and no break (unnotched) |
| Thermal properties | | | | |
| 8. | HDT at 1.82 MPa | ISO75 | 150°C | 152°C |
| 9. | Glass Transition temperature | DSC | 148°C | 143°C |
| 10 | Melting Point | DSC | 338°C | 340°C |

## Thermal behaviour

Thermal characterisation was done using a TA 2100 thermal analyzer having a 951 TG module. Thermogravimetric analysis was carried out in the temperature range of 50°C-850°C in $N_2$ atmosphere (flow rate = 60cm$^3$/min) using a heating rate of 20°C/min. A sample weight of 10 ± 2 mg was used.

## Water uptake

SPEEK film samples were first dried at 120°C for 20 h. The dried films were weighed and kept immersed in water at 35 ± 2°C. The films surface was dried by a filter paper and the hydrated polymer was weighed after definite time intervals. From the knowledge of difference in weight of dried and wet samples, water uptake was calculated.

Table 2. Reaction Conditions and Sample Designations for the preparation of Sulphonated PEEK Samples in 98% $H_2SO_4$

| S. No | Reaction Time (h) | Reaction temp (°C) | Conc. of PEEK (w/v %) | Sample designation |
|---|---|---|---|---|
| 1 | 3 | 35 | 6.25 | G-1 |
| 2 | 3 | 40 | 6.25 | G-2 |
| 3 | 3 | 45 | 6.25 | G-3 |
| 4 | 3 | 45 | 5.00 | G-4 |
| 5 | 3 | 55 | 4.00 | V-1 |
| 6 | 5 | 55 | 4.00 | V-2 |
| 7 | 7 | 55 | 4.00 | V-3 |

* $G_1$-$G_4$ were obtained by using GATONE$^{TM}$ while $V_1$-$V_3$ were from VICTREX

## Proton conductivity measurements

Proton conductivity of all the samples was measured by impedance spectroscopy using an EG&G PARC potentiostat/galvanostat (model 273) and a Schlumberger 1255HF frequency response analyser unit.

## Results and Discussion

VICTREX® used for sulphonation was flaky in nature whereas GATONE was in powder form. The dissolution of GATONE in $H_2SO_4$ was faster than VICTREX. The sulphonation within the sample (both GATONE and VICTREX) is not homogeneous.

The sulphonated samples obtained after 5h of reaction were either completely soluble in water (when the reaction temperature was 45°C) or were highly swollen (at a reaction temperature of 35°C). Isolation of such samples in dry form was difficult, therefore the results of sulphonated samples obtained after 3h of reaction are given in Table 2. Sulphonated samples were flaky in nature and pinkish in color. The films obtained were transparent with yellowish tinge.

## Elemental analysis

The elemental composition of some GATONE samples is given in Table 3. The degree of sulphonation could be calculated from the % sulphur content and was found to be in the range of 57-75%. Higher sulphur content as well as degree of sulphonation was found for samples prepared at 45°C.

Table 3. Results of Elemental Analysis and Degree of Sulphonation (DS %)

| S. No. | Sample designation | Carbon (%) | Hydrogen (%) | Sulphur (%) | Empirical formulae | DS (%) |
|---|---|---|---|---|---|---|
| 1 | G-1 | 62.96 | 3.98 | 4.94 | $C_{34}H_{26}O_{11}S_1$ | 57 |
| 2 | G-2 | 63.37 | 4.44 | 5.83 | $C_{29}H_{24}O_9S_1$ | 67 |
| 3 | G-3 | 62.94 | 4.62 | 6.11 | $C_{55}H_{48}O_{17}S_2$ | 70 |
| 4 | G-4 | 59.68 | 4.79 | 6.54 | $C_{49}H_{47}O_{18}S_2$ | 75 |

## FT-IR

In sulphonated samples, additional absorption bands associated with sulphonic acid groups were observed at 3440, 1252, 1080, 1024 and 709cm$^{-1}$. The broad band at ~3440 cm$^{-1}$ is assigned to the O-H vibration of ~$SO_3H$ as well as to the absorbed moisture. The other bands are due to sulphur-oxygen vibrations; asymmetric O=S=O stretch (1252 cm$^{-1}$), symmetric O=S=O (1080 cm$^{-1}$) stretch, S=O stretch (1024 cm$^{-1}$), and S-O stretch (709 cm$^{-1}$).

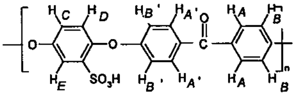
The aromatic C-C absorption band of PEEK at ~1490 cm$^{-1}$ and 1414 cm$^{-1}$ were split and new bands 1472 and 1402 respectively appeared upon sulphonation. The intensity of the new absorption peak~1472 cm$^{-1}$ increased while that of 1492 cm$^{-1}$ decreased with increase in temperature of the reaction.

Both PEEK and sulphonated PEEK samples had an absorption peak at ~840 cm$^{-1}$ which is characteristic of the out-of-plane bending of two hydrogens of 1,4-disubstituted benzene ring. In addition, the sulphonated samples had a new band at ~867cm$^{-1}$ which is characteristic of the out-of-plane C-H bending of an isolated hydrogen in a 1,2,4-trisubstituted phenyl ring. So, the changes observed in the IR spectra indicate the presence of –$SO_3H$ groups

## $^1$H-NMR

The $^1$H- NMR spectra of SPEEK samples are shown in Fig. 1. In the $^1$H- NMR spectra of SPEEK samples, the aromatic proton resonance signals were observed in the range of $\delta$ = 7-

7.75 ppm. In sulphonated samples, $H_B$ and $H_D$ appear as a doublet at 7.12 ppm & triplet at 7.27ppm respectively. The doublet at $\delta$ = 7.87 ppm and triplet at $\delta$ = 7.92 ppm correspond to $H_A$ and $H_{A'}$ protons. Presence of sulphonic acid group in the hydroquinone ring of SPEEK leads to a downfield shift of $H_E$ protons compared to $H_C$ or $H_D$ protons. Therefore the observed signal at 7.50 ppm should correspond to $H_E$ protons. The labeling of various magnetically non-equivalent protons in SPEEK samples is shown as,



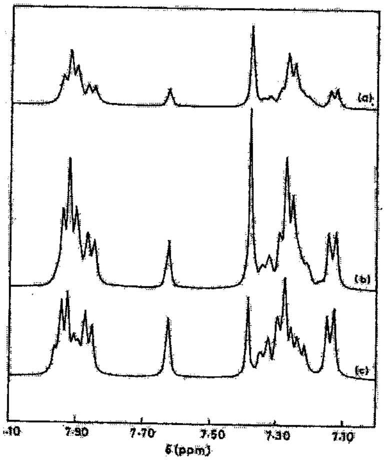


Figure 1. $^1$H-NMR Spectra of SPEEK Samples (a) G-1 (b) G-3 and (c) G-4

The intensity of $H_E$ signal therefore may be used to estimate for the $SO_3H$ content.[13] The ratio between the peak areas of the signals corresponding to all other aromatic hydrogen atoms may be expressed as,

$$\frac{H}{12-2n} = \frac{AH_E}{\Sigma\, AH_{A,\,A',\,B,\,B',\,C,\,D}}$$

Where 'n' is the number of $H_E$ per repeat unit. An estimate of degree of sulphonation (DS) expressed is = n x 100 (%).

The calculated DS values are given in Table 4. Depending on the temperature and duration of sulphonation reaction, DS values ranging from 53-80 % were obtained in case of GATONE and 58-87 % in case of VICTREX.

Table 4. Degree of Sulphonation as Calculated from $^1$H NMR

| S. No | Sample Designation | DS (%) |
|---|---|---|
| 1 | G-1 | 53 |
| 2 | G-2 | 57 |
| 3 | G-3 | 65 |
| 4 | G-4 | 80 |
| 5 | V-1 | 58 |
| 6 | V-2 | 80 |
| 7 | V-3 | 87 |

## Thermal behaviour

### Thermogravimetric Analysis

The TG traces showed multistep mass loss in sulphonated samples while single step decomposition was observed in PEEK above 400°C (Table 5). Three-step degradation was observed in SPEEK samples i.e. from 50-200°C, 200-450°C and 450-800°C. The mass loss from 50-200°C in SPEEK is due to loss of physically and chemically bound water. The observed mass loss between 200-450°C in SPEEK samples may be attributed to decomposition of sulphonic acid group. Breakdown of the polymer backbone takes place above 450°C.

## Water uptake

The presence of water facilitates proton transfer and increases the conductivity of solid-state electrolytes. The enhancement of hydrophilicity by sulphonation of PEEK polymer can be followed by water absorption of SPEEK films as a function of degree of sulphonation (Table 6).

## Proton conductivity

The proton conductivity of thin films (60-100µ) was found to be in the range of 1.3 x $10^{-2}$ S/cm in VICTREX polymers and 0.04- 0.22 x $10^{-2}$ S/cm in GATONE polymers. The conductivity values are comparable with the values reported for Nafion membranes ($\sigma \geq 10^{-2}$ S/cm).[14]

Table 5. Results of TG Analysis of PEEK & SPEEK Samples

| S. No | Sample designation | MASS LOSS (%) | | | |
|---|---|---|---|---|---|
| | | 50-200°C (%) | 200°C-450°C (%) | Above 450°C (%) | Char residue (%) |
| 1 | GATONE™ | - | - | 49.8 | 50.2 |
| 2 | G-1 | 7.6 | - | 39.2 | 53.2 |
| 3 | G-2 | 5.0 | 14.8 | 35.4 | 55.2 |
| 4 | G-3 | 10 | 16.0 | 30.0 | 44.0 |
| 5 | G-4 | 1.0 | 18.0 | 29.6 | 51.4 |
| 6 | VICTREX® | ---- | ---- | 48.9 | 51 |
| 7 | V-1 | 5 | 14 | 33 | 48 |
| 12 | V-2 | 6 | 21 | | 73 |
| 14 | V-3 | 6 | 42 | | 42 |

*Char residue indicate the mass remaining at 800°C.*

Table 6. Results of Water Uptake and Proton Conductivity in SPEEK Samples

| S. No | Sample designation | Water uptake (%) | Proton conductivity x $10^{-2}$ (S/cm) |
|---|---|---|---|
| 1 | G-1 | 23 | 0.22 |
| 2 | G-2 | 24 | 0.04 |
| 3 | G-3 | 28 | 0.14 |
| 4 | G-4 | 47 | 0.15 |
| 5 | V-1 | 15 | - |
| 6 | V-2 | 58 | 0.71 |
| 7 | V-3 | 84 | 0.35 |

## Conclusions

A series of sulphonated PEEK samples were synthesized by varying the reaction time, temperature and the PEEK concentration in 98% sulphuric acid. The sulphonation was confirmed by FTIR spectra of SPEEK where additional absorption bands associated with sulphonic acid groups were present at 3440, 1252, 1080, 1024, and 709cm$^{-1}$. Splitting of C-C aromatic bands on sulphonation was also observed. All these structural characterization results are consistent with each other. The extent of sulphonation (measured by elemental analysis and $^{1}$H- NMR) increased by increasing temperature of the reaction and 80% sulphonation was attained at 45 and 50°C. An increase in moisture absorption of SPEEK films was observed with an increase in degree of sulphonation. Decomposition of sulphonic acid group was indicated by mass loss in the temperature range of 200°C-450°C in thermogravimetric analysis. In unsulphonated PEEK, no mass loss was observed in this region. The proton conductivities were found to be in the range of 0.34 –2.6 x $10^{-2}$ S/cm. The major difference between GATONE and VICTREX was in terms of ease of sulphonation, proton conductivity and moisture absorption.

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