Hindawi Publishing Corporation
Journal of Applied Chemistry
Volume 2013, Article ID 386903, 7 pages
http://dx.doi.org/10.1155/2013/386903

*Research Article*

# Modification of Poly(ether ether ketone) Polymer for Fuel Cell Application

**Devesh Shukla,[1] Yuvraj Singh Negi,[1] and Vijai Kumar[2]**

[1] *Department of Polymer and Process Engineering, Indian Institute of Technology, Roorkee 247001, India*
[2] *Central Institute of Plastic Engineering and Technology, Lucknow 226008, India*

Correspondence should be addressed to Yuvraj Singh Negi; yuvrajnegi@gmail.com

Received 10 April 2013; Accepted 1 October 2013

Academic Editor: Luqman Chuah Abdullah

Polyelectrolyte membrane (PEM) is an important part of PEM fuel cell. Nafion is a commercially known membrane which gives the satisfactory result in PEM fuel cell operating at low temperature. Present research paper includes functionalization of Poly(ether ether ketone) (PEEK) polymer with phosphonic acid group. The functionalization was done with the help of nickel-based catalyst. Further, the polymer was characterized by the FTIR, EDAX, DSC, TGA, and $^1$H NMR, and it was found that PEEK polymer was functionalized with phosphonic acid group with good thermal stability in comparison to virgin PEEK. Finally, the thin films of functionalized polymer were prepared by solution casting method, and proton conductivity of film samples was measured by impedance spectra whose value was found satisfactory with good thermal stability in comparison to commercially available Nafion membrane.

## 1. Introduction

PEEK is a semicrystalline aromatic polymer having high melting temperature (335°C) and very low or no solubility in ordinary solvents at room temperature. Sulfuric acid is the common solvent which dissolves and also sulfonates PEEK at room temperature. Dilute solutions at high temperatures can also be obtained in hydrofluoric acid, trifluoromethanesulfonic acid, dichlorotetrafluoroacetone monohydrate, phenol 1,2,4-trichlorobenzene, and benzophenone [1]. Therefore, modification of PEEK is typical to some extent but desired for many applications such as polymer electrolyte membrane fuel cell (PEMFC) where acid functionalized polymer is required. In case of PEEK, functionalization in polymer stage is mostly reported on sulfonation and nitration [2]. Phosphonation of polymer is one of the methods to modify their properties such as proton conductivity, mechanical and thermal stability, and in polymer stage it was reported by various groups. Alexandratos et al. [3] reported the phosphonation of polystyrene using $PCl_3$ which gave the cross-linked polymer. However, Jakoby et al. [4] reported that the highly substituted phosphonic acid derivative of polyphenylsulfone (PPS) was achieved via the Pd-dibenzylideneacetone (dba) complexed catalyst in solvent diphenyl ether. Increase of reaction temperature from 90°C to 120°C also enhanced the substitution level. Bock et al. [5] reported phosphonation of the polysulfones (PSU) using nickel chloride and silylated phosphonates. The route was found less expensive and gave the halogen free product in comparison to palladium-based catalytic route. Lafitte and Jannasch [6] reported a phosphonation of polysulfones via the lithiation of polymer and subsequent conversion of lithiated sites in to phosphonate unit. The substitution level in lithiation route was found very low.

The above efforts have been done on polysulfones polymer. However, in present paper we have done phosphonation of PEEK polymer by utilizing the well-known Michaelis-Arbuzov Reaction route [7]. Various characterization techniques such as FTIR, EDAX, and NMR supported the phosphonation PEEK with high thermal stability in comparison to PEEK polymer. The proton conductivity of P-PEEK film was also compared with Nafion at >100°C which showed slightly lower value than Nafion.

## 2. Experimental

*2.1. Materials and Methods.* The commercial available Gatone-TM PEEK polymer was obtained by Gharda Chemical India;

Table 1: Calculated wt% of elements in Br-PEEK.

| Element | PEEK | Br-PEEK | $(Br)_2$-PEEK |
|---|---|---|---|
| C | 82.61 | 64.06 | 52.32 |
| O | 17.39 | 13.48 | 11.01 |
| Br | 0 | 22.45 | 36.66 |

Table 2: Measured wt% of elements in Br-PEEK.

| Element | wt% | | | | |
|---|---|---|---|---|---|
| | PEEK | 3 h | 6 h | 9 h | 24 h |
| C | 86.63 | 66.71 | 59.48 | 54.33 | 48.27 |
| O | 13.37 | 12.86 | 11.73 | 10.8 | 8.31 |
| Br | — | 20.43 | 28.79 | 34.87 | 43.42 |

however, reagent grade $NiCl_2$ and Triethyl phosphate were purchased from Sigma-Aldrich, India. Liquid bromine was obtained from MERK India Ltd, India. Dimethyl acetamide (DMAC) and *N*-Methyl-2-pyrrolidone (NMP) were purchased from HiMedia Laboratories, India.

*2.2. Synthesis of Brominated PEEK (Br-PEEK).* All glass wares and PEEK polymer were completely dried at 110°C overnight before use. The reaction assembly was established in fumehood with help of three necks round bottom flask, mechanical stirrer and gas washing bottle attached with nitrogen supply. 15 g (0.052 mol.) of completely dried PEEK powder were charged in flask containing a mixture of 4 mL (0.156 mol.) liquid bromine and 150 mL of concentrated $H_2SO_4$. The reaction mixture was stirred at ambient temperature for 24 h. The brominated samples were collected at 3 h, 6 h, 9 h, and 24 h time intervals and attributed as 3 h, 6 h, 9 h, and 24 h respectively. The polymer was precipitated into ice cold distilled water and further washed with several portions of distilled water, methanol, respectively. To ensure bromine free sample, the polymer was extracted with methanol for 8 h. A white modified polymer was obtained which was finally dried in vacuum oven. To obtain the powder sample, the polymer was grinded in Retsch MM 400 Mixture Mill. Modified polymer was readily soluble in a common organic solvent such as Dimethyl sulfoxide (DMSO), DMAC, Chloroform, and Tetrahydrofuran (THF).

### 2.3. Aryl Phosphonation of Monobrominated PEEK (Br-PEEK)

*(a) Tetrakis(triethy1phosphite)nickel(0).* Tetrakis(triethy1phosphite)nickel(0) compound was synthesized by the previously reported method [7]. About 4.0 g of Tetrakis(triethy1phosphite)nickel(0) (melting point 106–109°C) was obtained.

*(b) Phosphonation of Br-PEEK.* Solution of 12 g (0.033 mol) 3 h Br-PEEK in 150 mL DMAC was prepared in a reactor equipped with oil bath, gas inlet and outlet, thermometer, condenser, and dropping funnel. A cold trap was attached to the head of the reflux condenser. The temperature of solution was raised up to 100°C. Subsequently, a solution of freshly prepared tetrakis(triethylphosphite)nickel(0) in DMAC was transferred in to the reaction flask and finally raised the temperature up to 180–200°C. The concentration of catalyst was varied as 5, 10, 15, and 20 mol% and attributed as 5 m, 10 m, 15 m, and 20 m. Application of nitrogen stream provides the inert medium and simultaneously drives off evolved vapors. A homogeneous, brownish solution was obtained. Above the 160°C, 2–4 drops of triethylphosphite were added in the reaction flask. Further, the batch was kept under slow stirring at 180–200°C for 8–10 h. The reaction mixture was turned black as the reaction proceeded. A solid polymer was obtained by precipitation of reaction mixture into methanol. Polymer content was decanted and subsequently suspended in water. For removal of catalyst residue, the water-suspended polymer was sonicated in Ultrasonicator (UTS-120, Unitech Ultrasonics) for 15 min. Polymer was filtered and dried at 100°C. Hydrolysis of phosphonated polymer (P-PEEK) was carried out by refluxing with concentrated HCl for 50 h. After complete washing with distilled water and drying in vacuum oven, the white solid polymer was obtained.

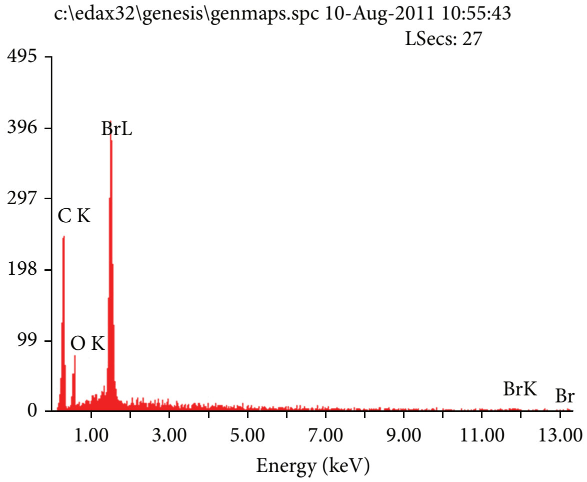


Figure 1: EDAX of 3 h Br-PEEK.

The characterizations of polymers were done by the following equipment—elemental analysis by EDAX detector equipped in FEI Quanta 200FC SEM system, IR spectra by Thermo-Nicolet Nexus FT-IR spectrometer, $^1H$ NMR by Bruker AC500 MHz NMR spectrometer, and thermal analysis by EXSTAR TG/DTA 6300. Proton conductivity of P-PEEK film sample was determined by Impedance Gain Phase Analyzer (Solartron SL1260) in which Julabo S25 was equipped for temperature variation.

## 3. Results and Discussion

### 3.1. Characterization of Brominated PEEK (Br-PEEK)

*3.1.1. Elemental Analysis of Br-PEEK by EDAX.* The wt% of C, O, and Br in mono- and dibrominated PEEK was calculated theoretically (Table 1) and also measured by EDAX system (Figure 1 and Table 2). EDAX system attached with SEM was unable to measure the hydrogen weight. Therefore, during theoretical calculation we have eliminated the hydrogen

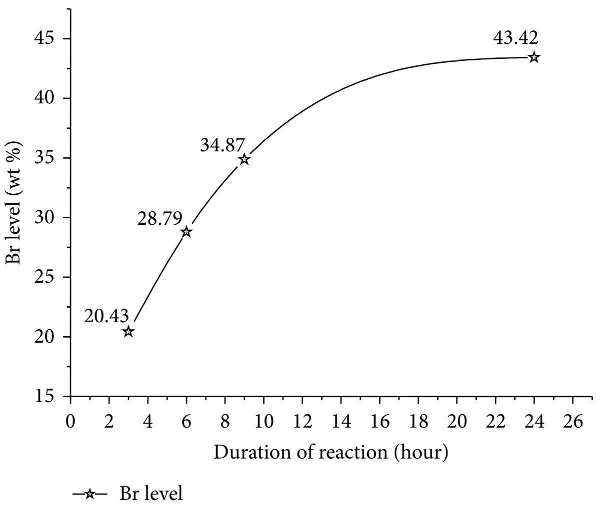


Figure 2: Bromine level in Br-PEEK polymer.

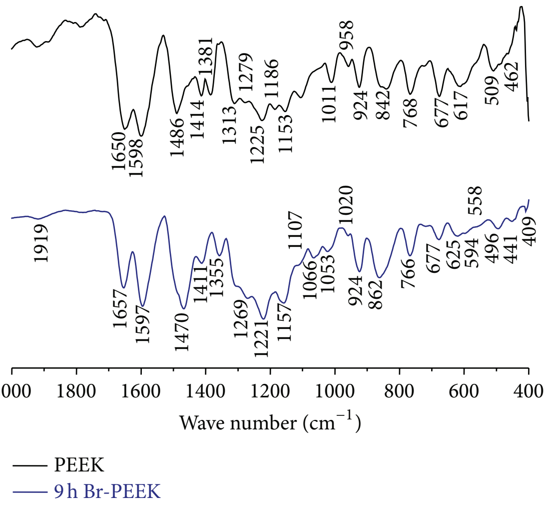


Figure 3: FTIR of PEEK and 9 h Br-PEEK.

weight and assumed the total weight as 100%. Br level increased with increasing the duration of reaction (Figure 2). The wt.% of Br in sample 3 h was found equal to the calculated wt% of monobrominated PEEK, while in sample 9 h it was found to be close to the calculated wt.% of dibrominated PEEK that is about 37% (Table 2). The wt% was correlated with degree of substitution (DS) by using [12, 13].

$$\mathrm{DS} = \frac{mY}{(100W - W_s Y)}, \tag{1}$$

where $m$ is molar mass of repeat unit, $W$ is the formula weight of the substituent group, $W_s$ is the net increase in formula weight due to the introduction of substituent group per unit, and $Y$ is the wt.% of substituent. The value of DS was found to be 0.89 (3 h), 1.60 (6 h), 1.85 (9 h), and 2.65 (24 h).

*3.1.2. FTIR Analysis of Br-PEEK.* FTIR spectrum of pure PEEK polymer was reported by the Nguyen and Ishida [14], Varsanyi [15], and Bellamy [16]. The typical absorption band reported in PEEK polymer was found almost same as Br-PEEK (Figure 3). In general, the C-Br stretching vibration in organic compound was reported in the range of 700–500 cm$^{-1}$ while in [17] it was reported that aliphatic hydrocarbon showed the C-Br stretching in the range of 700–500 cm$^{-1}$ whereas aromatic hydrocarbon showed the C-Br stretching in the region of 1200–1000 cm$^{-1}$ (strong multiple bands). A new doublet band was observed near 1066–1053 cm$^{-1}$ in Br-PEEK which may be due to C-Br stretching vibration. Since pure PEEK has many absorption bands in the region of 700–500 cm$^{-1}$ therefore it is very difficult to assign the specific bands for C-Br stretching in this region.

*3.1.3. $^1$H NMR Spectra of Br-PEEK.* Since pure PEEK is insoluble in organic solvents except in strong acids, therefore its $^1$H-NMR spectrum could not be recorded. The $^1$H NMR of brominated sample is shown in Figure 4. Br-PEEK (3 h) showed signal between the region 7.78–7.85 (m) ppm, 7.40 (d) ppm, 7.26–7.28 (dd) ppm, 7.17–7.24 (m) ppm, and 7.12–7.14 (dd) ppm. These signals were observed in the aromatic region and associated with Ar-H. The signal 7.40 (d) ppm was found due to substitution of bromine group in the hydroquinone segment.

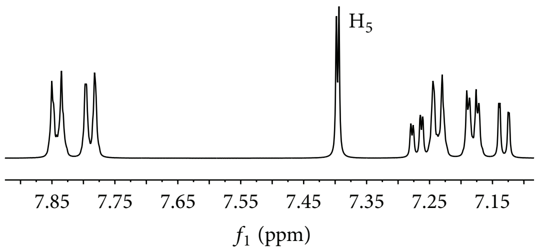


Figure 4: $^1$H NMR of 3 h Br-PEEK.

Further, a distinct signal at 8.00 (d) ppm and 7.62 (dd) ppm was obtained in 9 h and 24 h samples which may be associated with the neighbouring proton of substituted benzophenone segment of Br-PEEK. The substitution in benzophenone segment of PEEK polymer was also reported by the Conceição et al. [18]. The DS in Br-PEEK was also determined by measuring the ratio of intensity of the distinct signal with integrated intensity of the signals corresponding to all the other aromatic hydrogens [10]. The DS obtained by the NMR was found lower in comparison to the DS obtained by the elemental analysis (EDAX data) (0.74 (3 h), 1.23 (6 h), 1.65 (9 h), 2.38 (24 h)).

### 3.2. Characterization of Phosphonated PEEK (P-PEEK)

*3.2.1. FTIR Spectra of P-PEEK.* P-PEEK was characterized by the FTIR spectrometer. The main reported absorption bands are as follows. González et al. [19] assigned the P=O stretching in the range of 1240–807 cm$^{-1}$. Trotta et al. [20] assigned the P=O stretching at 1240 cm$^{-1}$. According to Stuart [21] the characteristic infrared bands in phosphonated aromatic compounds are as follows: (1) aromatic P=O stretching in

Table 3: Element % in P-PEEK ester by EDAX.

| Element | Calculated wt% | Measured wt%<br>P-PEEK ester<br>5 m | <br><br>10 m | <br><br>15 m | <br><br>20 m |
|---|---|---|---|---|---|
| C | 68.49 | 65.94 | 67.34 | 70.41 | 72.01 |
| O | 23.82 | 13.69 | 15.06 | 18.46 | 19.93 |
| P | 7.69 | 1.73 | 2.98 | 4.15 | 6.02 |
| Br | — | 18.46 | 13.86 | 6.07 | 0.82 |
| Ni | — | 0.18 | 0.76 | 0.91 | 1.22 |

Table 4: Solubility of P-PEEK acid and ester in various solvents.

| Solvent | Phosphonated PEEK<br>Room temp. | <br>Temp. > 150°C |
|---|---|---|
| DMSO | C | C |
| DMAC | C | C |
| NMP | C | B |
| DMF | C | B |
| DMSO$^+$ | C | B |
| DMAC$^+$ | C | B |
| NMP$^+$ | C | A |
| DMF$^+$ | C | C |
| 4-Chlorophenol$^+$ | C | C |
| THF$^+$ | C | C |
| Cyclohexanone$^+$ | C | C |

$^+$Solvent and 2-3 drops of acid HBr/$H_2SO_4$, A: soluble, B: Sparingly soluble, C: not soluble.

between 1350–1300 cm$^{-1}$, (2) aromatic P–C stretching in between 1450–1430 cm$^{-1}$, and (3) phosphorus ester P–OH stretching in the region 1040–930 cm$^{-1}$. The spectrum of pristine PEEK shows many absorption bands in the above mentioned region such as asymmetric stretching of diphenyl ether groups in the region of 1227 cm$^{-1}$ and 1190 cm$^{-1}$. Therefore, a clear identification of addition of phosphonate ester group was somewhat difficult. From the comparison of spectra of P-PEEK ester and PEEK (Figure 5), we found the new absorption band at 1250–1233 cm$^{-1}$, 1470 cm$^{-1}$, and doublet at 1036 cm$^{-1}$ which might be due to the presence of P=O stretching, P–C stretching, and phosphorus ester P–OH stretching, respectively. All other characteristics band of PEEK such as presence of carbonyl group at 1651 cm$^{-1}$ remained the same in P-PEEK derivatives.

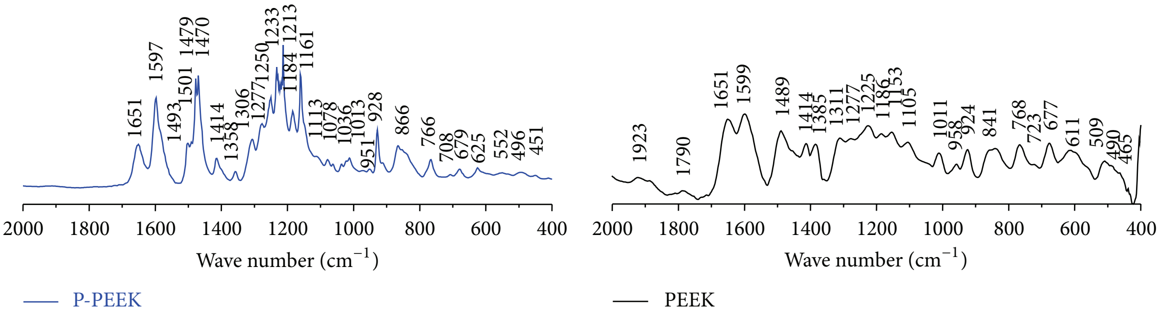
*3.2.2. Elemental Analysis by EDAX.* The wt.% of different elements in P-PEEK ester derivatives were determined by EDAX (Figure 6) and also calculated theoretically by ignoring the hydrogen atom as like in Br-PEEK. Table 3 represented the calculated and measured wt% of different elements in monophosphonated P-PEEK ester. The wt% of phosphorous in different P-PEEK ester samples were found lower than the calculated wt% of monophosphonated PEEK (7.69 wt%). It was observed that P-PEEK samples have some bromine. The DS was calculated according to (1) whose values were ~0.17, 0.30, 0.45 and 0.71 in P-PEEK ester 5 m, 10 m, 15 m and 20 m respectively.

*3.2.3. Solubility of P-PEEK Ester and P-PEEK Acid.* The solubility of P-PEEK ester and P-PEEK acid were determined by visual inspection in various solvent at room temperature and also at high temperature >150°C. It was found that both are insoluble in almost all the organic solvents. NMP sparingly dissolved the P-PEEK acid and ester both only at high temperature. Further, addition of 2-3 drops of acid such as HBr or $H_2SO_4$ fairly dissolved the both form of polymer (Table 4).

*3.2.4. NMR Characterization of P-PEEK.* Solubility of P-PEEK ester was not found in any normal available deuterated solvent. Therefore, characterization of P-PEEK in liquid stage was somewhat difficult. To resolve the problem of solubility, initially a concentrated solution of P-PEEK ester in NMP at higher temperature was prepared which was further utilized in DMSO-$d_6$ to prepare a solution of P-PEEK ester—NMP/DMSO-$d_6$ in the ratio of 1/3. The $^1$H NMR spectra of NMP and P-PEEK ester—NMP in DMSO-$d_6$ were determined, respectively. NMP showed the signal at 3.4 ppm, 2.85 ppm, 2.37 ppm, and 2.30 ppm. The signal near 2.5 ppm was associated with DMSO-$d_6$. These entire signals were also found in P-PEEK ester-NMP sample. P-PEEK ester gave signal in both aromatic and also in aliphatic regions (Figure 7) due to presence of aromatic protons and protons of ethyl ester at 4.46 ppm and 1.19 ppm. Aryl phosphonation effected a downfield shift of proton neighbouring to phosphonic ester group as well as a broadening and splitting of signals into a doublet of doublets [5]. The broadening, splitting of signal, and downfield shifting were also found in case of P-PEEK samples as the degree of phosphonation increases (Figure 7). The degree of phosphonation can be calculated from the signal ratio of the ethyl ester protons and the protons of aromatic region [4] which was observed 0.14, 0.25, 0.42, and 0.68 in P-PEEK ester 5 m, 10 m, 15 m, and 20 m, respectively. Phosphonation in PEEK polymer was also confirmed by the solid state $^{31}$P NMR spectrum of P-PEEK (Figure 8) which showed only a single signal at 12.52 ppm. Single peak was also reported by Bock et al. [5] in case of $^{31}$P NMR spectra of P-PSU acid.

*3.2.5. Thermal Analysis of P-PEEK.* P-PEEK (20 m) showed $T_g$ 220°C and $T_m$ ~ 381°C which was about 44°C higher than the PEEK polymer. It shows that P-PEEK exhibited higher thermal stability than PEEK polymer ($T_g$ 152°C, $T_m$ 337°C) (Figure 9). A significant wt. loss was found at 313°C which may be possible due to the conversion of phosphoric acid segment in to anhydride (Figure 10). P-PEEK also showed the higher residual mass, which may be possible due to presence of incombustible phosphorus oxides.

*3.2.6. Proton Conductivity P-PEEK.* Proton conductivity of P-PEEK was determined by casting the film on Indium-tin oxide (ITO) coated glass sheet using the solvent NMP. Coated



(a) (b)

FIGURE 5: FTIR of P-PEEK ester (20 m).

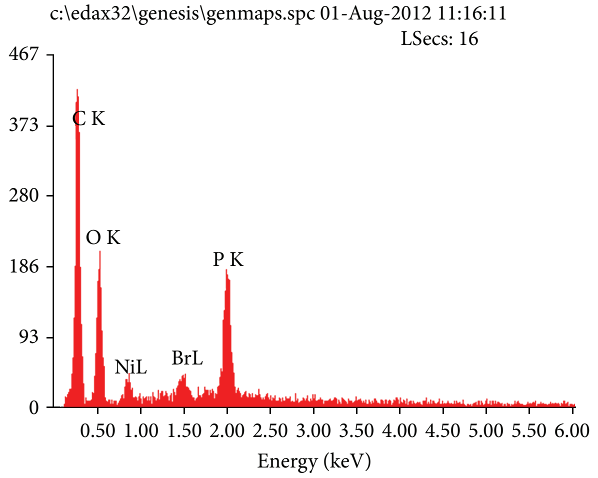


FIGURE 6: EDAX of P-PEEK ester (20 m).

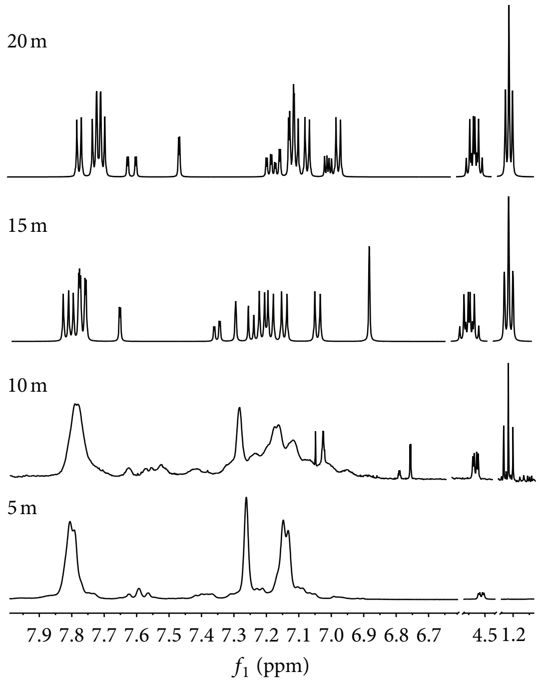


FIGURE 7: $^1$H NMR of P-PEEK ester 5 m, 10 m, 15 m, and 20 m.

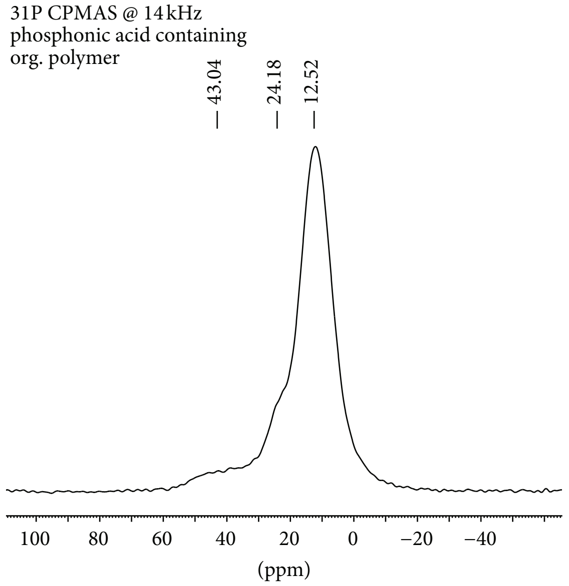


FIGURE 8: Solid state $^{31}$P NMR of P-PEEK acid.

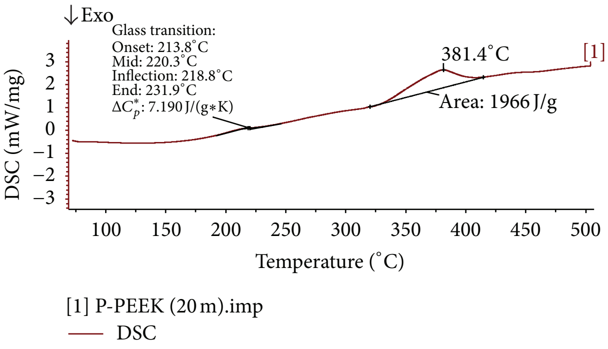


FIGURE 9: DSC of P-PEEK (20 m).

glass sheet was further dipped in water for 24 h. The thickness of polymer film was determined by taking the difference in glass sheet thickness before and after the coating. The polymer coated sheet was sandwiched with ITO coated glass sheet, and impedance was measured by varying the frequency

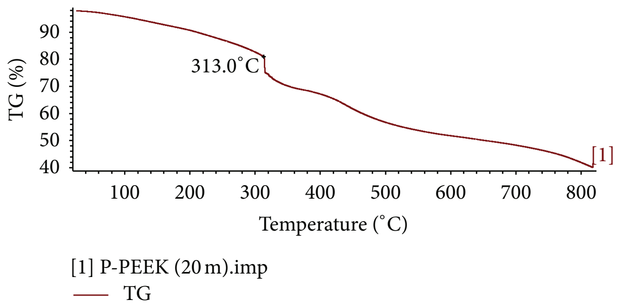


Figure 10: TGA of P-PEEK (20 m).

Table 5: Proton conductivity of polymer membranes.

| Membrane | Proton conductivity (S $cm^{-1}$) | | |
|---|---|---|---|
| Nafion | 0.06–0.100<br>(25–30°C)<br>[8] | 0.19<br>(90°C)<br>[8] | 0.210<br>(120°C)<br>[9] |
| SPEEK | 0.008<br>(25°C)<br>(DS 0.80)<br>[10] | 0.076<br>(100°C)<br>(DS 0.80)<br>[10] | 0.033<br>(120°C)<br>(DS 0.83)<br>[11] |
| P-PEEK (20 m) | 0.0069<br>(25°C) | 0.0550<br>(90°C) | 0.114<br>(120°C) |

100 Hz to 32 MHz, AC voltage 50–500 mV in Impedance Gain Phase Analyzer (Solartron SL1260). Julabo S 25 was used for variation in temperature during the impedance measurement. Proton conductivity was calculated by the following equation $\sigma = L/RA$, where $L$, $R$, and $A$ are the distance between the two electrodes, membrane resistance, and cross-sectional area of the membrane, respectively [22–24]. The value of $R$ was determined by plotting the graph between the impedance of real and imaginary plot (Figure 12). The point of resistance was that where the imaginary part was found to be zero. Conductivity of the P-PEEK samples increases with temperature and degree of phosphonation. The proton conductivity P-PEEK-20 m was found 0.0069 S $cm^{-1}$ at 25°C, 0.055 at 65°C, 0.083 S $cm^{-1}$ at 90°C, and 0.114 $cm^{-1}$ at 120°C (Figure 11 and Table 5). The Nafion membrane has been reported best ionic conductor at low temperature and high humidity [8, 25]. S-PEEK membrane showed comparable proton conductivity with Nafion at high degree of sulfonation and humidity. Both Nafion and S-PEEK membrane exhibited loss of conductivity and physical failure at temperature >100°C. The loss of conductivity was found greater in S-PEEK. Although conductivity of P-PEEK was found to be slightly lower than Nafion at >100°C but its thermal stability was found higher, and it is expected that P-PEEK will show better durability with acceptable proton conductivity in comparison to both Nafion and S-PEEK.

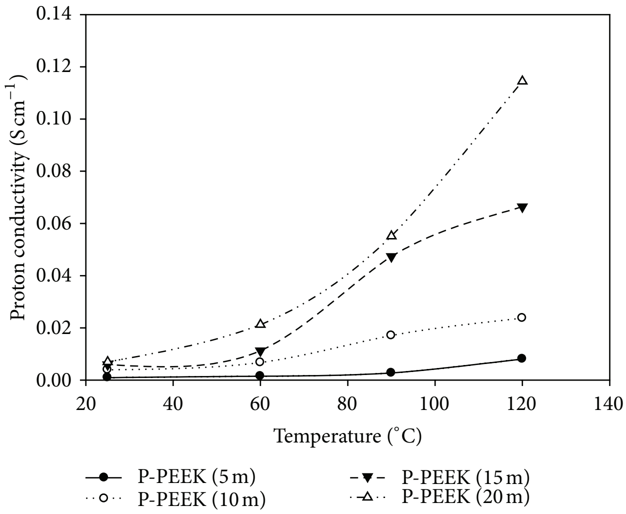


Figure 11: Proton conductivity of P-PEEK samples with temperature.

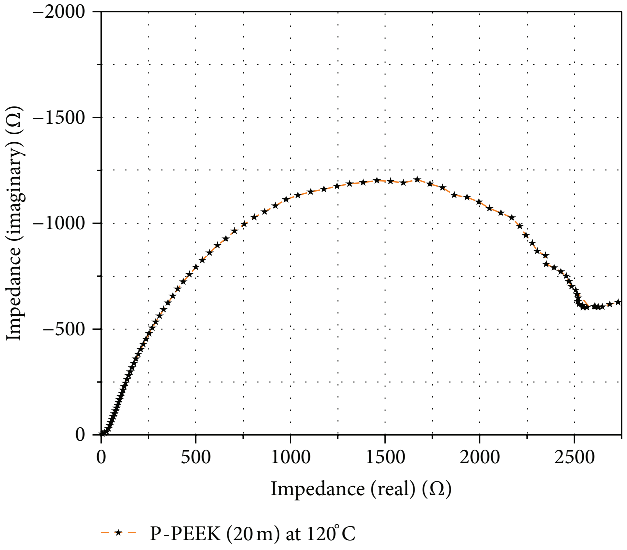


Figure 12: Nyquist plot of P-PEEK (20 m).

## 4. Conclusions

Commercial PEEK polymer can be brominated with only a small excess of bromine in $H_2SO_4$. However, no catalyst was used during the reaction. FTIR, EDAX, and $^1$H-NMR indicated that PEEK can be brominated readily. Further, conversion of Br-PEEK in to P-PEEK was carried out in presence of nickel-based catalyst. P-PEEK was characterized by various techniques, and it was found that P-PEEK showed high thermal stability in relation with PEEK polymer and solubility in NMP at higher temperature. The proton conductivity of P-PEEK was compared with Nafion at >100°C which showed slightly low value but thermal stability of P-PEEK was found good. Thus, it is expected that P-PEEK will show better durability with acceptable proton conductivity in comparison to both Nafion and S-PEEK at high temperature.

## Acknowledgments

One of the authors is thankful for financial support from the Ministry of Human Resource Development (MHRD), India, and also for NCL Pune, India, for carrying out solid state NMR.

## References

[1] J. E. Mark, *Polymer Data Handbook*, Oxford University Press, 1999.

[2] D. Shukla, Y. S. Negi, J. S. Uppadhyaya, and V. Kumar, “Synthesis and modification of poly (ether ether ketone) and their properties: a review,” *Polymer Reviews*, vol. 52, no. 2, pp. 189–228, 2012.

[3] S. D. Alexandratos, M. A. Strand, D. R. Quillen, and A. J. Walder, “Synthesis and characterization of bifunctional phosphinic acid resins,” *Macromolecules*, vol. 18, no. 5, pp. 829–835, 1985.

[4] K. Jakoby, K. V. Peinemann, and S. P. Nunes, “Palladium-catalyzed phosphonation of polyphenylsulfone,” *Macromolecular Chemistry and Physics*, vol. 204, no. 1, pp. 61–67, 2003.

[5] T. Bock, R. Mülhaupt, and H. Möhwald, “Halogen-free polyarylphosphonates and polyelectrolyte membranes for PEMFC by Nickel-Catalyzed phosphonylation with silylated phosphates,” *Macromolecular Rapid Communications*, vol. 27, no. 24, pp. 2065–2071, 2006.

[6] B. Lafitte and P. Jannasch, “Phosphonation of polysulfones via lithiation and reaction with chlorophosphonic acid esters,” *Journal of Polymer Science A*, vol. 43, no. 2, pp. 273–286, 2005.

[7] T. M. Balthazor and R. C. Grabiak, “Nickel-catalyzed Arbuzov reaction: mechanistic observations,” *Journal of Organic Chemistry*, vol. 45, no. 26, pp. 5425–5426, 1980.

[8] S. Slade, S. A. Campbell, T. R. Ralph, and F. C. Walsh, “Ionic conductivity of an extruded Nafion 1100 EW series of membranes,” *Journal of the Electrochemical Society*, vol. 149, no. 12, pp. A1556–A1564, 2002.

[9] N. Miyake, J. S. Wainright, and R. F. Savinell, “Evaluation of a sol-gel derived nafion/silica hybrid membrane for proton electrolyte membrane fuel cell applications: I. Proton conductivity and water content,” *Journal of the Electrochemical Society*, vol. 148, no. 8, pp. A898–A904, 2001.

[10] S. M. J. Zaidi, S. D. Mikhailenko, G. P. Robertson, M. D. Guiver, and S. Kaliaguine, “Proton conducting composite membranes from polyether ether ketone and heteropolyacids for fuel cell applications,” *Journal of Membrane Science*, vol. 173, no. 1, pp. 17–34, 2000.

[11] B. Lakshmanan, W. Huang, D. Olmeijer, and J. W. Weidner, “Poly(ether ether ketone) membranes for elevated temperature PEMFCs,” *Electrochemical and Solid-State Letters*, vol. 6, no. 12, pp. A282–A285, 2003.

[12] A. Philippides, P. M. Budd, C. Price, and A. V. Cuncliffe, “The nitration of polystyrene,” *Polymer*, vol. 34, no. 16, pp. 3509–3513, 1993.

[13] “Degree of Substitution,” in *Encyclopedia of Polymer Science and Technology*, John Wiley & Sons, 2002.

[14] H. X. Nguyen and H. Ishida, “Molecular analysis of the crystallization behavior of poly(aryl-ether-ether-ketone),” *Journal of Polymer Science B*, vol. 24, no. 5, pp. 1079–1091, 1986.

[15] G. Varsanyi, *Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives*, Adam Hilger, London, UK, 1974.

[16] J. L. Bellamy, *The Infrared Spectra of Complex Molecule*, Chapman and Hall, London, UK, 3rd edition, 1975.

[17] *Sadtler Handbook of Infrared Spectra*, Bio-Rad Laboratories, Informatics Division.

[18] T. F. Conceição, J. R. Bertolino, G. M. O. Barra, S. L. Mireski, A. C. Joussef, and A. T. N. Pires, “Preparation and characterization of poly (ether ether ketone) derivatives,” *Journal of the Brazilian Chemical Society*, vol. 19, no. 1, pp. 111–116, 2008.

[19] L. González, O. Mó, M. Yáñez, and J. Elguero, “Very strong hydrogen bonds in neutral molecules: the phosphinic acid dimers,” *Journal of Chemical Physics*, vol. 109, no. 7, pp. 2685–2693, 1998.

[20] F. Trotta, S. C. Mio, K. Martina, E. Drioli, and P. Finocchiaro, “New poly ether ether ketones containing phosphorus for membrane preparation,” *Asia-Pacific Journal of Chemical Engineering*, vol. 5, no. 1, pp. 249–255, 2010.

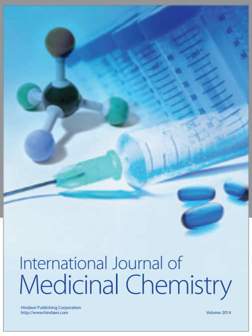
[21] B. H. Stuart, “Organic molecules,” in *Infrared Spectroscopy*, Fundamentals and Applications, pp. 71–93, John Wiley & Sons, 2005.

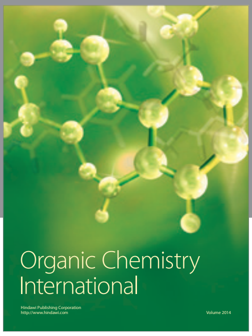
[22] C. Zhao, H. Lin, K. Shao et al., “Block sulfonated poly (ether ether ketone)s (SPEEK) ionomers with high ion-exchange capacities for proton exchange membranes,” *Journal of Power Sources*, vol. 162, no. 2, pp. 1003–1009, 2006.

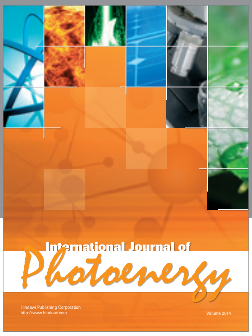
[23] P. Xing, G. P. Robertson, M. D. Guiver, S. D. Mikhailenko, K. Wang, and S. Kaliaguine, “Synthesis and characterization of sulfonated poly (ether ether ketone) for proton exchange membranes,” *Journal of Membrane Science*, vol. 229, no. 1-2, pp. 95–106, 2004.

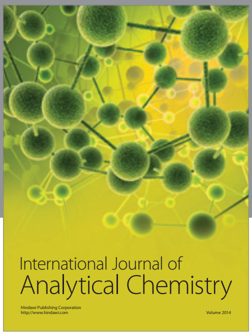
[24] N. Zhang, G. Zhang, D. Xu et al., “Cross-linked membranes based on sulfonated poly (ether ether ketone) (SPEEK)/Nafion for direct methanol fuel cells (DMFCs),” *International Journal of Hydrogen Energy*, vol. 36, no. 17, pp. 11025–11033, 2011.

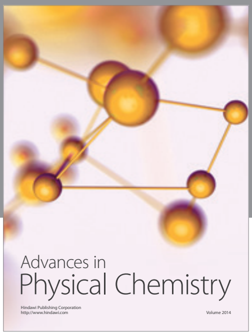
[25] G. Alberti, M. Casciola, L. Massinelli, and B. Bauer, “Polymeric proton conducting membranes for medium temperature fuel cells (110–160°C),” *Journal of Membrane Science*, vol. 185, no. 1, pp. 73–81, 2001.

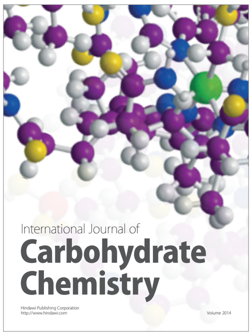

International Journal of
Medicinal Chemistry

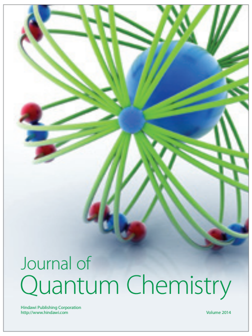

Organic Chemistry
International


International Journal of
Photoenergy

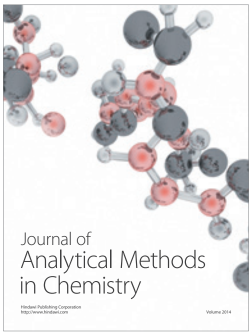

International Journal of
Analytical Chemistry


Advances in
Physical Chemistry

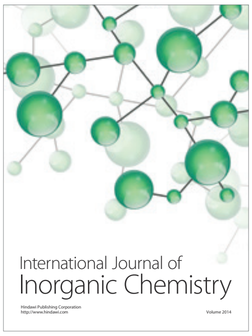

International Journal of
Carbohydrate Chemistry


Journal of
Quantum Chemistry

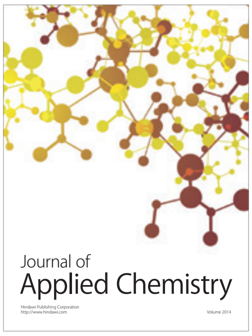

The Scientific
World Journal

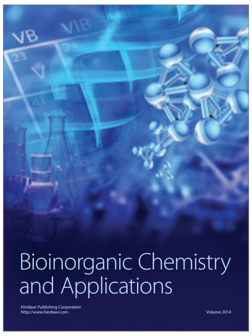

Journal of
Analytical Methods
in Chemistry


Journal of
Spectroscopy

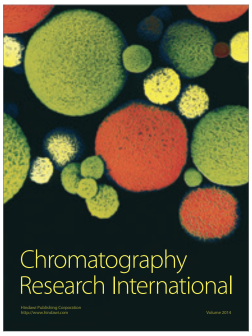

International Journal of
Inorganic Chemistry


International Journal of
Electrochemistry


Journal of
Applied Chemistry


Bioinorganic Chemistry
and Applications


Journal of
Theoretical Chemistry


Chromatography
Research International


Journal of
Catalysts


Journal of
Chemistry


International Journal of
Spectroscopy