World Applied Sciences Journal 32 (11): 2239-2244, 2014
ISSN 1818-4952

DOI: 10.5829/idosi.wasj.2014.32.11.14561

Characterization and Sulfonation Degree of Sulfonated Poly Ether Ether Ketone Using Fourier Transform Infrared Spectroscopy

[1]R. El-Araby, [1]N.K. Attia, [1]G. Eldiwani, [2]M.G. Khafagi, [3]S. Sobhi and [3]T. Mostafa

[1]Chemical Engineering and Department of Pilot Plant, National Research Centre, Dokki, Giza, Egypt
[2]Spectroscopy Department, Physics Division, National Research Centre, Dokki, Giza, Egypt
[3]Department of Chemical Engineering, Faculty of Engineering, Cairo University, Giza, Egypt

Abstract: Poly ether ether ketone containing sodium sulfonate groups with high molecular weight were successfully prepared by aromatic nucleophilic reaction between three different monomers; 4,4'-difluorobenzophenone and 5,5'-carbonylbis (2-fluorobenzene sulfate) (sulfonated monomer) with bisphenol A in the presence of potassium carbonate anhydrous in dimethyl sulfoxide as a solvent. The polycondensation process is achieved at 170°C and the sulfonated poly ether ether ketone is produced at various degree of sulfonation by controlling the percentage of the sulfonated monomer. The composition and incorporation of the sulfonated repeating unit into the copolymer are determined by Fourier Transform Infrared (FTIR) spectroscopy which has been demonstrated to be a very powerful technique for the analysis of commercial polymeric materials. The analysis allows the precise and rapid determination of the degree of sulfonation (DS) of the produced sulfonated copolymer which is promising candidate for proton exchange membrane fuel cell.

Key words: Proton exchange fuel cell · Sulfonation · FTIR spectroscopy · Degree of sulfonation · Nucleophilic reaction.

INTRODUCTION

Proton exchange membrane (PEM) fuel cells are becoming increasingly important as alternative energy sources for stationary, automobile and portable power. Environmental concerns such as increasing amount of toxic emissions into the atmosphere when fossil fuels are used to produce electricity and gasoline for vehicles has led to extensive research and development on renewable alternative energy sources. Fuel cells have been proposed to have potential to provide reliable future energy sources. (PEM) fuel cells are very promising due to their, high power density and high efficiency. PEMs must have good mechanical, thermal and chemical stabilities and still have high proton conductivity. Engineering thermoplastics based on wholly aromatic poly (arylene thioether sulfone)s, poly (arylene ether phosphine oxide) and poly (arylene ether sulfone)s have been modified for use as proton exchange membranes for fuel cells by directly copolymerizing up to two pendent sulfonate groups per repeat unit as stated by Maria *et al*. [1]. Mechanical, chemical and thermal resistance are inherent properties of most types of poly(arylene)s, Liu *et al*. [2] stated that high proton conductivity can, in principle, be obtained by either post sulfonation or direct copolymerization using disulfonated monomers.

Directly copolymerized sulfonated poly (arylene sulfone)s have shown comparable or better proton conductivity than state of the art NafionTM based PEMs [3]. Precise control of the ionic concentration, well-defined ionic locations and enhanced stability due to the deactivated position of the -SO3H group are some of the advantages of direct copolymerization of sulfonated monomer. Direct copolymerization where the disulfonated monomer is copolymerized with other suitable comonomers to synthesize disulfonated copolymers has been developed [4]. Disulfonated poly (ether ether ketone) copolymers from the disulfonated monomer have been synthesized directly and characterized using FTIR which was used also in quantitative technique to determine the degree of sulfonation of the produced copolymers [5]. In the current study, sulfonate groups

Corresponding Author: Reham El-Araby, Chemical Engineering & Pilot Plant Department, National Research Centre, Dokki, Giza, Egypt. E-mail: rehamelaraby@hotmail.com.

were incorporated into the copolymer structure by direct aromatic nucleophilic substitution polycondensation of disodium 3,3'-disulfonate-4,4'-difluorodiphenylketone, 4,4'-difluoro benzophenone and bisphenol A in the presence of anhydrous potassium carbonate. In this study FTIR spectroscopy was used to confirm the chemical structures of the sulfonated poly ether ether ketone by means of conveniently determining the functional groups and the successful introduction of the sulfonic acid groups was confirmed by the FTIR spectra of sulfonated poly ether ether ketone (SPEEK).Relative band intensities in FTIR spectra are correlated with the composition of copolymer which allowed for both qualitative and quantitative determination of the functional groups of the synthesized copolymers as well as determination of the sulfonation degree.

MATERIALS AND MOTHODS

Experimental: 4, 4'-difluorobenzophenone was purchased from Aldrich Chemical Co. and used as received. Fuming sulfuric acid (20% SO3)purchased from Kanto Chemical Co. Bisphenol A, used as a monomer received from Aldrich Chemical 99% purity; Dried till constant weight prior to use in polymerization reactions.

Potassium carbonate anhydrous, dried at 60°C till constant weight prior to use. Other reagents and solvents were obtained commercially and used without further purification. FTIR (FT/IR-6100 type A Jasco Japan TGS detector with the absorbance technique ranging from 400 to 4000 cm^{-1} with scanning speed of 2 $mmsec^{-1}$) was utilized. Samples for (FTIR) were prepared by blending 198 mg of IR spectroscopic grade KBr and 2 mg of sulfonated salt.

Synthesis of SPEEK Copolymers: Sulfonated poly ether ether ketone copolymers were synthesized with various degrees of sulfonation via direct co-polymerization of 5, 5'- carbonylbis (2-fluorobenzene-sulfonate) monomer (SDCDPS) and 4,4'-difluorobenzophenone and bisphenol A. Fig. 1 shows the equation of (SPEEKS) formation, while Fig. 2 is a flow diagram for that copolymer synthesis. Flow diagram copolymerization was carried out in a 250 ml round bottom flask reactor equipped with an overhead mechanical stirrer, nitrogen inlet, Dean-Stark trap and a condenser. The reactor was charged with 4.5658g (20 mmol) of bisphenol A, followed by 1.15 equivalent of potassium carbonate. Dry DMSO (dimethyl sulfoxide) was introduced to afford about 20% solid concentration and toluene was used as an azeotropic agent with the ratio of (1:2) toluene: DMSO. The reaction solution was stirred heated at 150oC for four hours, during which time, phenolate salt formation was observed by watching the removal of water azeotropically with toluene. The azeotropic solvent was completely removed after four hours. Then the sulfonated monomer which was synthesized as in the previous study reported by El-Araby *et al*. [6] added with 4, 4'-difluorobenzophenone (DFBPH) by different molar ratios into the flask reactor and with excess of DMSO. The reaction solution was stirred while heating at (~170oC) for 16 hours.

The viscous reaction product was cooled and precipitated in distilled water. After being washed several times with distilled water, the precipitated copolymers were transferred to boiling distilled water where salts were extracted. The copolymers were then washed several times with distilled water and dried in a vacuum oven at 120°C for 24 hours. Each experiment was carried out under various reaction conditions and periods. Samples were

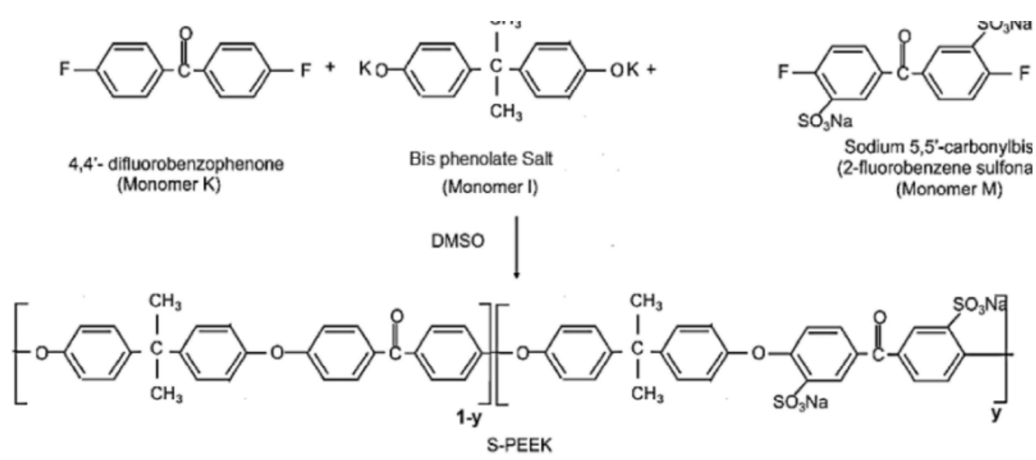

Fig. 1: Formation of S-PEEKs through Co-poly Condensation Reaction.

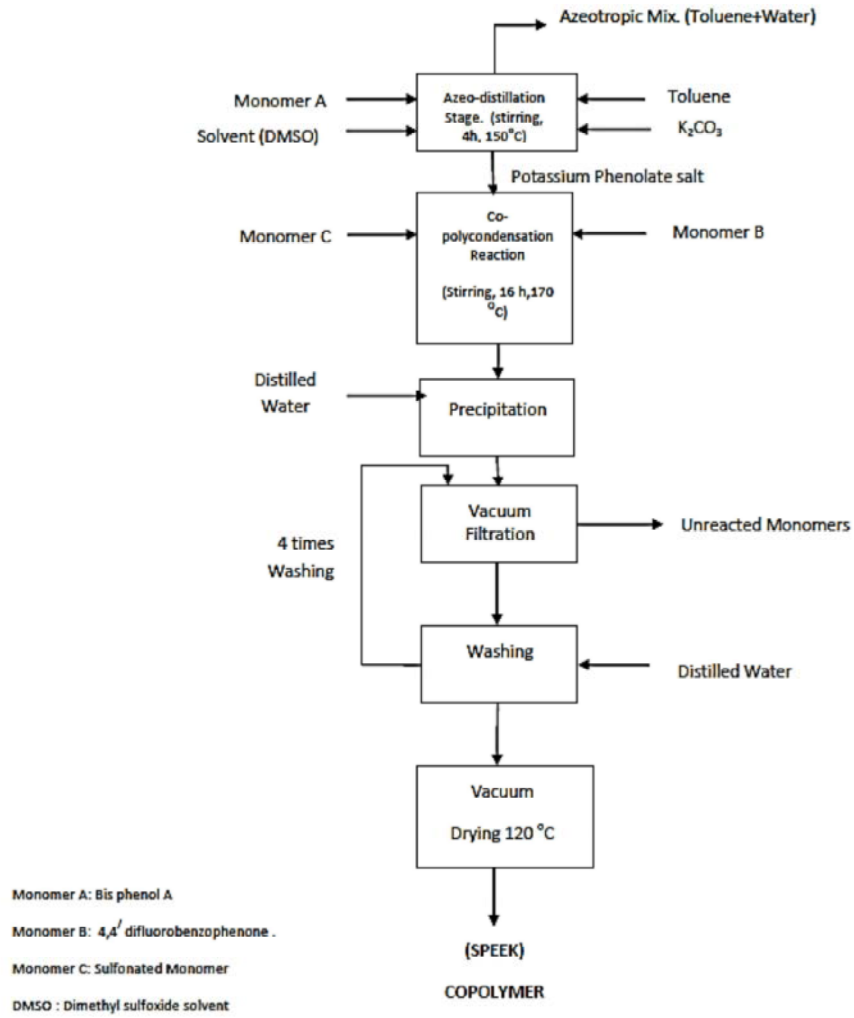

Fig. 2: SPEEK Copolymers Synthesis Flow Diagram.

withdrawn at pre-determined time intervals and subjected to titration for degree of sulfonation determination as mentioned as by Sultan *et al*. [7] and Mistri *et al*. [8]. Extent of reaction (conversion percent) was experimentally determined and the number of reacted moles of each monomer in the produced copolymers was calculated.

RESULTS AND DISCUSSION

Determination of the Degree of Sulfonation of SPEEK Copolymer Using Back Titration: The degrees of sulfonation were determined by titration as stated by Khanh Ngan and Dukjoon Kim [9] and Jianli Wang *et al.* [10], are consistent with the calculated values, which clearly suggested that degrees of sulfonation can be readily manipulated by controlling the amount of sulfonated monomer added. The degree of sulfonation (Ds) as illustrated in Table 1, which is the number of sulfonated groups per repeating unit, was controlled by adjusting the ratio of monomer m to monomer k.

Characterization of Sulfonated Poly Ether Ether Ketone (SPEEK): In this study FTIR spectroscopy was used to confirm the chemical structures of the sulfonated poly ether ether ketone by means of conveniently determination of the functional groups. Characteristic absorptions observed are listed in Table 2. The successful introduction of the sulfonic acid groups was confirmed by the FTIR spectra of sulfonated poly ether ether ketone SPEEK as illustrated in Fig. 3, where the strong characteristic peak at 1020 cm^{-1} was assigned to the symmetric stretching of S=O in the (- SO_3Na) group, the characteristic absorption peaks at 1079 and 1020 cm^{-1} correspond to asymmetric and symmetric

Table 1: Produced Sulfonated Copolymer.

Sample	Monomer m (mmol)	Monomer k (mmol)	m:k	% Sulfonated monomer	Calculated degree of sulfonation
SPEEK-1	2	18	1:9	10	0.2
SPEEK-2	4	16	1:4	20	0.4
SPEEK-3	8	12	2:3	40	0.8
SPEEK-4	16	4	4:1	80	1.6

m:sulfonated monomer. K: diflourobenzophenone monomer (DFBPH). % SM =m/(m+k) x100 (where S.M.is a sulfonated monomer).
Ds =2x % S.M (where 2 is the # of SO3Na in each monomer).

Table 2: Infrared Absorption Bands Frequencies (cm^{-1}) of SPEEK.

Absorption Band cm^{-1}	Intensity*	Origin
1661	s	C=O
1653	s	
830	s	C-H
679	m	
927	vs	
771	s	
624	m	C=S
1486	vs	C-C
1592	s	C=C
862	m	
685	s	S-O
1079	m	S=O
1020	s	
1028	s	O=S=O
1252	s	
1084	m	
1093	m	$Ar\text{-}SO_3Na$
621	m	
1217	s	Ph-CO-Ph
929	s	

*vs =very strong, s = strong and m =medium.

O=S=O stretching vibrations of sodium sulfonate groups, respectively. The characteristic band around 1490 cm^{-1} from tri substitution of benzene rings is caused by the introduction of sodium sulfonate groups and that around 1652 cm^{-1} is due to aryl carbonyl groups which was confirmed by Chengji Zhao *et al*.[11] and Chalida Klaysom *et al*.[12]. These results confirmed that the sodium sulfonate groups were surely incorporated into the copolymers as expected.

Determination of the Degree of Sulfonation of SPEEK Copolymer Using FTIR Spectroscopy Technique: Fourier transform infrared spectroscopy is a powerful tool used to characterize the functional groups in a material. (FTIR) was used to further verify the incorporation of the sulfonate groups and chemical structure of the sulfonated poly ether ether ketone (SPEEK) copolymers [13]. As illustrated before in Fig. 3 the 626 cm^{-1} and 685 cm^{-1} peak corresponds to (C=S) and (S-O) of the sulfonic acid group. These signal intensities of the bands characteristics of the sulfonic acid groups and by

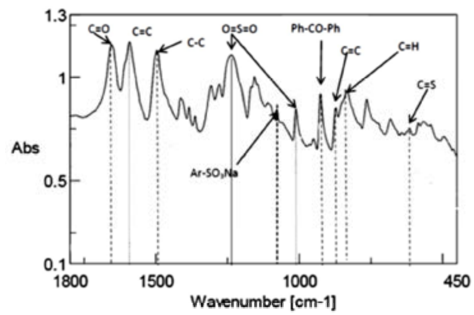

Fig. 3: FTIR Spectrum of SPEEK Copolymer.

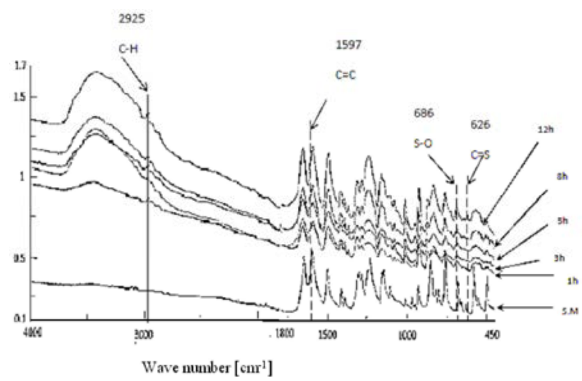

Fig. 4: FTIR Spectroscopy of SPEEK for Different Reaction Time

standardization of absorption for one or more functional groups that are not changing during the reaction. It was demonstrated that the absorption intensity of the sulfonic acid increased with reaction time which is an evident of increasing degree of sulfonation with time as expected and is shown in Fig. 4. FTIR has been successfully utilized to characterize many sulfonated polymers. Wang, *et al*. [14] and Gunduz [15] developed FTIR quantitative techniques to characterize post-sulfonated poly (arylene ether sulfones).

Standardized FTIR spectra allowed for qualitative and quantitative determination of the functional groups of the synthesized copolymers. Fig. 4 shows SPEEK copolymer FTIR spectra as a function of reaction time. The IR peak at 626 cm^{-1} is characteristic of the C=S linkage, which was selected for normalizing each of the sulfonated copolymer

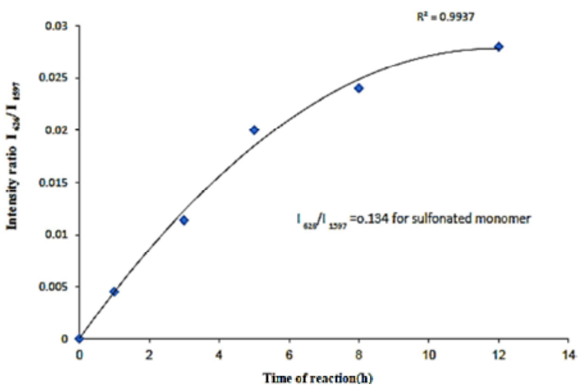

Fig. 5: Intensity Ratio I 626/I 1597 Versus Time of Reaction using FTIR Spectroscopy.

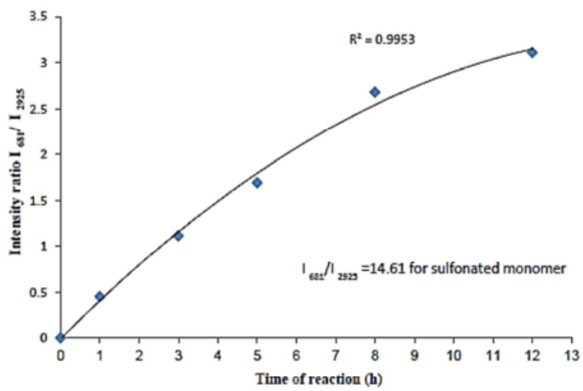

Fig. 6: Intensity Ratio I 681/I 2925 Versus Time of Reaction using FTIR.

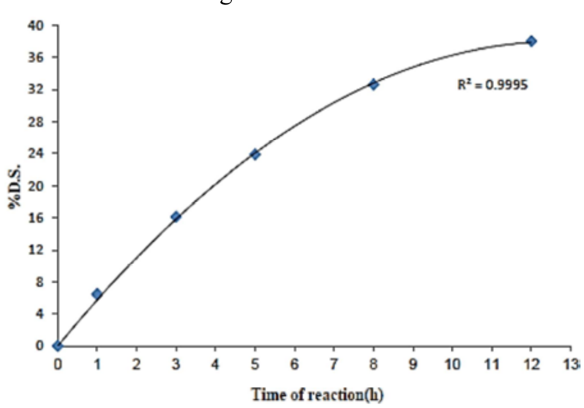

Fig. 7: Degree of Sulfonation of SPEEK using FTIR Spectroscopy.

spectrums and peaks at 686 cm^{-1} corresponded to a vibrational stretching for the sodium sulfonate group. The intensity increased with the amount of the incorporated sulfonated monomer, which was observed for all sulfonated copolymer series in different reaction time.

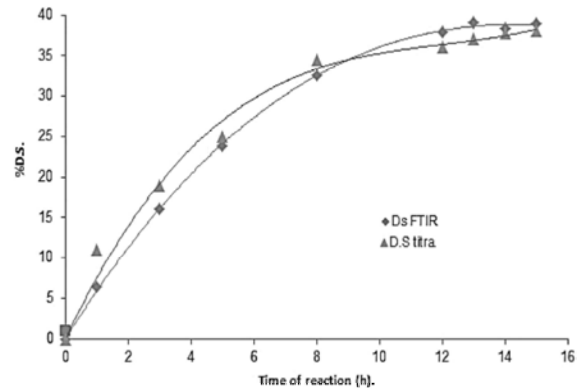

Fig. 8: Comparison between Degree of Sulfonation of SPEEK using FTIR and Titration.

Relative band intensities in FTIR spectra are correlated with the composition of copolymer. In order to track the quantitative change of sulfonated group, the ratio (I626/ I ref1) copolymer: (I626/I ref1) sulfonated monomer and (I685/I ref2) copolymer: (I685/I ref2) sulfonated monomer were calculated, where I ref1 and I ref2 is the intensities of the aromatic C=C peak at 1597cm^{-1} and aliphatic C-H peak at 2925 cm^{-1} which are the references (unchanging) peaks. As in Equation (1), the results proved that the sulfonic functional groups are gradually introduced to the SPEEK polymer (Figs. 5, 6, 7). Quantitative determination of pendent sulfonic acid groups along the copolymer chain via titration confirmed the spectroscopic values FTIR analysis which was illustrated in Fig. 8.

$$D.S. = \frac{(I\ 626/I\ ref.)\ copolymer}{(I\ 626/I\ ref.)\ sulfonated\ monomer} * 2 \quad (1)$$

CONCLUSION

Sodium sulfonate-functionalized poly (ether ether ketone)s with different degree of sulfonation were synthesized by polycondensation reactionvia direct polymerization of the sulfonated difluoro monomers and bisphenol A. The composition and incorporation of the sulfonated repeating unit into the copolymer were confirmed by FTIR spectroscopy which has been demonstrated to be a very powerful technique for the analysis of commercial polymeric materials and allowed the precise and rapid determination of the degree of sulfonation (DS) of the produced sulfonated copolymer.

REFERENCES

1. Maria, G., J. Xiangling, L. Xianfeng, N. Hui, J. Eric and L. Yunfeng, 2004. Direct synthesis of sulfonated aromatic poly (ether ether ketone) proton exchange membranes for fuel cell applications. Journal of Membrane Science, 234: 75-81.
2. Liu, Y., A. Bhatnagar, Q. Ji, J.S. Riffl, J.E. McGrath, J.F. Gebel and Kashiwagi, 2000. T. Polymer, 41: 5137-5146.
3. Wang, F., M. Hickner, Q. Ji, W. Harrison, J.B. Mecham, T.A. Zawodzinski and J.E. McGrath, 2001. Effect of Acidification Treatment and Morphological Stability of Sulfonated Poly (arylene ether sulfone) Copolymer Proton-Exchange Membranes for Fuel-Cell use Above 100°C. Macromol. Symp., 175(1): 387-396.
4. Hickner, M., H. Ghassemi, Y. Kim, B. Einsla and J. McGrath, 2004. Alternative Polymer Systems for Proton Exchange Membranes (PEMs). Chem. Rev., 104: 4587- 4612.
5. Sonpingkam, S. and D. Pattavarakorn, 2014. Mechanical Properties of Sulfonated Poly (Ether Ether Ketone) Nanocomposite Membranes. International Journal of Chemical Engineering and Applications, 5(2): 181-185.
6. El-Araby, R., N.K. Attia, G. Eldiwani, S. Sobhi and T. Mostafa, 2012. Preparation of Sulfonated Monomer for PEM Fuel Cell and Solvent Optimization for Recrystallization. World Applied Sciences Journal, 16(8): 1082-1086.
7. Sultan, A.S., A. Al-Ahmed and S.M. Zaidi Javaid, 2012. Viscosity, Rheological and Morphological Properties of Sulfonated Poly (ether ether ketone): PEM Fuel Cell Membrane Material. Macromolecular Symposia, 313(1): 182-194.
8. Mistri, E.A., A.K. Mohanty and S. Banerjee, 2012. Synthesis and characterization of new fluorinated poly (ether imide) copolymers with controlled degree of sulfonation for proton exchange membranes. Journal of Membrane Science, 411-412: 117-129.
9. Khanh Ngan, Do T. and Kim Dukjoon, 2008. "Synthesis and characterization of homogeneously sulfonated poly (ether ether ketone) membranes: Effect of casting solvent. Journal of Applied Polymer Science, 110: 1763-1770.
10. Jianli Wang, Junbin Liao, Lan Yang, Shenggang Zhang, Xuelei Huang and Ji. Jianbing, 2013. "Highly compatible acid-base blend membranes based on sulfonated poly (ether ether ketone) and poly (ether ether ketone-alt-benzimidazole) for fuel cells application. European Polymer Journal, 49: 1673-1681.
11. Chengji Zhao, Li. Xianfeng, Zhe Wang, Zhiyu Dou, Shuangling Zhong and Hui Na, 2006. Synthesis of the block sulfonated poly (ether ether ketone)s (S-PEEKs) materials for proton exchange membrane. Journal of Membrane Science, 280: 643-650.
12. Chalida Klaysom, P., Bradley, G.Q. Ladewig, Lu. Max and Lianzhou Wang, 2011. Preparation and characterization of sulfonated poly ether sulfone for cation-exchange membranes. Journal of Membrane Science, 368(1-2): 48-53.
13. Surya Subianto, Namita Roy Choudhury and Naba Dutta, 2014. Composite Electrolyte Membranes from Partially Fluorinated Polymer and Hyperbranched, Sulfonated Polysulfone. Nanomaterials, 4: 1-18.
14. Wang, F., J. Li, T. Chen and J. Xu, 1999. Synthesis of poly (ether ether ketone) with high content of sodium sulfonate groups and its membrane characteristics. Polymer, 40: 795-799.
15. Nazan Gunduz, 2001. Synthesis and Characterization of Sulfonated Polyimides as Proton Exchange Membranes for Fuel Cells. PhD Thesis, Virginia Polytechnic Institute and State University, USA.