Mild side-group sulfonation of polyetherketones for proton exchange membranes

Liu, Baijun; Robertson, Gilles P.; Guiver, Michael D.

Publisher's version / Version de l'éditeur:

Polymeric Materials: Science & Engineering, 95, pp. 206-207, 2006

Mild Side-Group Sulfonation of Polyetherketones for Proton Exchange Membranes

Baijun Liu, Gilles P. Robertson, and Michael D. Guiver*

Institute for Chemical Process and Environmental Technology, National Research Council, Ottawa, Ontario K1A, 0R6, Canada

INTRODUCTION

Fuel cells are regarded as promising future clean power sources. Proton exchange membrane fuel cells (PEMFC)s and direct methanol fuel cells (DMFC)s using proton conductive polymer membranes as one of the components are drawing growing attention for their automotive and portable applications.[1] Significant efforts are being made to develop new high-performance membranes as alternatives to Nafion®. Aromatic PEKs are well known as high performance thermoplastics for their overall combination of chemical, physical and mechanical properties Most of the sulfonated PEK membranes were developed based on sulfonated commercial polymers or sulfonated commercial monomers.[2,3]

Recently, several sulfonated polymers prepared by stereo-controlled post-sulfonation have been reported, with the sulfonated groups attached to side groups.[4] In this work, PEKs with pendant (4-sulfonic acid)phenyl and (3-methyl-4-sulfonic acid)phenyl groups were prepared by a very mild stereo-controlled post-sulfonation method, and their schematic structures are depicted in Figure 1. Their properties related to PEM applications were well characterized.

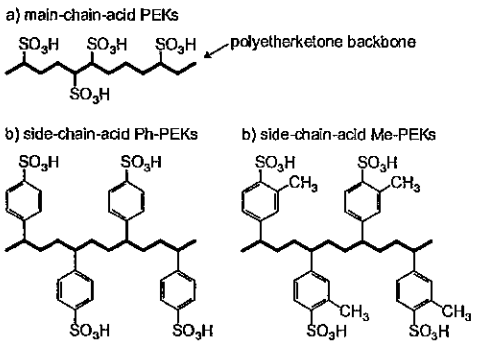

Figure 1. Representation of PEKs by post-sulfonation.

EXPERIMENTAL

Characterization and Measurements. FTIR spectra were measured on a Nicolet 520 Fourier transform spectrometer. ^1H and ^{13}C NMR spectra were obtained on a Varian Unity Inova NMR spectrometer operating at frequencies of 399.95 MHz for ^1H and 100.575 MHz for ^{13}C. A TA Instruments thermogravimetric analyzer (TGA) instrument model 2950 was used for evaluating thermal stability. A TA Instruments differential scanning calorimeter (DSC) model 2920 was used for measuring T_g. The water uptake and swelling ratios of the polymers were measured by immersion of the polymer films in deionized water for 24 h. They were calculated from the differences of weight and length before and after this procedure, respectively. Inherent viscosities (η_{inh}) were measured using an Ubbelohde viscometer in DMAc solutions of polymers at 0.5 g/dL at 30 °C. Oxidative stabilities of the membranes were evaluated by immersing the films into Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 °C. The proton conductivities at 100% RH were estimated from AC impedance spectroscopy data, obtained over a frequency range of 1 to 10^7 Hz using a Solartron 1260 gain phase analyzer. Mechanical properties were evaluated at room temperature on an Instron 5565 instrument at a strain rate of 10 mm/min, and a 500 N load cell was used. Methanol permeability was measured using a simple two compartment glass diffusion cell.

Preparation of Starting Polymers. The synthesis of the starting polymers was accomplished by a nucleophilic aromatic substitution polycondensation.[5]

Preparation of Sulfonated Polymers. An example of a typical reaction is as follows: 2 g of Me-PEEK and 40 ml of concentrated sulfuric acid were added into a 100 ml flask. After stirring at room temperature for 3 h, the resulting homogeneous viscous solution was poured into a mixture of water and ethanol to get a silk-like solid. The solid was washed with water until the water reached neutral pH. The sulfonated Me-PEEK was dried in a vacuum oven at 100 °C for 2 d.

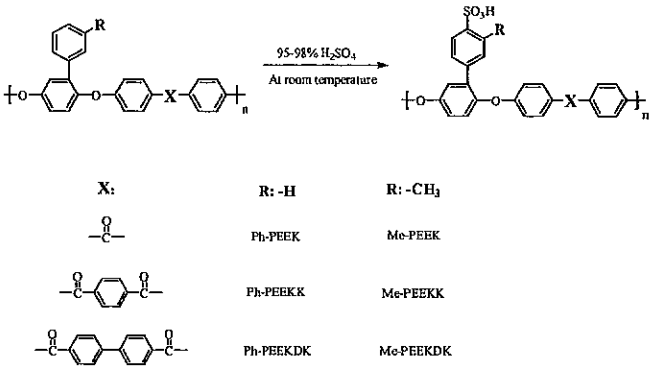

Figure 2. Structures and abbreviations of sulfonated PEKs based on the homopolymers.

RESULTS AND DISCUSSION

Comparison of Sulfonation Reactivity. Sulfonated PEEK (Victrex) has been widely studied based on its high performance. Bishop et al.[6] and others reported that it took up to 33 days in 97.4% sulfuric acid at room temperature to obtain the fully sulfonated PEEK. To increase the sulfonation reaction rate of PEEK, high temperature and strong sulfonation reagents (e.g. fuming sulfuric acid) must be used. That leads to the possibility of polymer decomposition or side reactions. Above all, it is difficult to precisely control the degree of sulfonation (DS), which is a key parameter for proton conductivity and dimensional stability of membranes. In contrast with the sulfonation of commercial PEEK, the phenylated and 4-methyphenylated PEEKs had a distinct advantage for the sulfonation rate. For both of them, the reaction proceeded rapidly in 96-98% sulfuric acid at room temperature, with fully sulfonated polymers (DS~100%) being obtained within 3 h. It is also interesting to note that only one substitution site occurred on the pendant benzene ring per repeating unit of Me-PEEK and Ph-PEEK, as shown by NMR spectroscopy.

Table 1. Viscosity and Thermal Properties of the Polymers Before and After Sulfonation.

polymer	η (dL/g)		T_g (°C)		TD_{onset} (°C)	
	unS	S	unS	S	unS	S
Me-PEEK	0.96	2.16	147	190	453	207
Me-PEEKK	--	3.42	159	167	462	206
Me-PEEKDK	--	1.20	170	182	454	214
Ph-PEEK	0.62	1.50	158	185	512	210
Ph-PEEKK	--	3.10	166	174	496	204
Ph-PEEKDK	--	3.35	186	--	502	212

Thermal Properties. Only one transition temperature was found in the DSC curve before decomposition temperature for all the samples, which indicated their amorphous nature. For unsulfonated polymers, their T_g values ranged from 147 to 186 °C. In general, polymers had higher T_g values after sulfonation because of the

introduction of polar sulfonic acid groups. They were in the range of 167~190 °C. All the unsulfonated polymers showed excellent thermal stabilities as judged by their TGA curves. After sulfonation, the onset of thermal decomposition decreased to around 204~214 °C because of the introduction of sulfuric acid groups. The first decomposition stage around 210 °C is associated with the loss of the $-SO_3H$ groups and the second decomposition stage around 500 °C is related to the degradation of the main chains. There were no weight losses below 180 °C for all the materials.

Mechanical Property. Good mechanical properties of the PEMs in either anhydrous or hydrous states are one of the necessary demands for their applications. A comparison of the novel membranes with side-chain sulfonic acid substituents and Nafion 117 are listed in Table 2. The samples in dry state had tensile stress at maximum load of 79.6~110.0 MPa, Young's moduli of 1.53~2.15 GPa, and elongation at break of 9.9~52.0%. In the wet state, the samples showed excellent mechanical properties with tensile stress of 42.6~64.5 MPa and Young's moduli of 0.32~0.85 GPa. In particular their elongations at break were up to 114.7~204.5%, which showed they were very flexible materials. These materials showed a much higher tensile strength and the lower elongation than Nafion 117. The tensile strength results in both dry and wet states undoubtedly showed they were strong and flexible membrane materials.

Table 2. Mechanical Properties of the Sulfonated Polymers in Their Dry and Wet States

Sulfonated Polymer	Tensile Stress (MPa)		Young's Modulus (Gpa)		Elongation at Break (%)	
	dry	wet	dry	wet	dry	wet
Me-PEEK	79.6	64.5	1.53	0.72	22.3	159.0
Me-PEEKK	110.0	42.6	2.03	0.40	20.9	204.5
Me-PEEKDK	98.0	59.5	1.92	0.85	13.3	114.7
Ph-PEEK	87.0	45.6	1.76	0.32	9.9	183.8
Ph-PEEKK	103.2	63.6	2.15	0.60	10.4	145.1
Ph-PEEKDK	88.6	64.1	2.12	0.70	52.0	128.3
Nafion 117	38.0	28.4	0.18	0.10	301.5	329.2

Water Uptake and Swelling Ratio. Water uptake and swelling ratios of PEMs are closely related to DS, proton conductivity, dimensional stability, and mechanical strength. The water within the membrane provides a carrier for the proton, and maintains high proton conductivity. However, excessive water uptake in a PEM will lead to unacceptable dimensional change or loss of dimensional shape, which could lead to weakness or a dimensional mismatch when incorporated into a Membrane Electrode Assembly (MEA). Therefore, the preparation of sulfonated polymers with ideal water uptakes and dimensional stability are one of the critical demands for their application as PEMs. As shown in Table 3, Me-PEEKK, Me-PEEKDK, Ph-PEEKK and Ph-PEEKDK had low water uptake and swelling ratios.

Table 3. Water Uptake, Swelling Ratio and Proton Conductivity of the Sulfonated Polymers

Polymer	Water Uptake (%)		Swelling Ratio (%)		σ (S/cm)	
	25 °C	80 °C	25 °C	80 °C	25 °C	80 °C
Me-PEEK	17.1	121.6	9.5	45.5	0.046	0.134
Me-PEEKK	10.3	24.1	3.1	8.7	0.015	0.049
Me-PEEKDK	7.1	10.7	1.7	2.1	0.013	0.040
Ph-PEEK	22.5	-- --	9.7	-- --	0.060	-- --
Ph-PEEKK	15.9	24.1	5.7	13	0.033	0.077
Ph-PEEKDK	12.8	16.3	4.3	5.6	0.012	0.025

Methanol Permeability and Proton Conductivities. One of the drawbacks of Nafion is its high methanol crossover in the DMFC application. This limitation is associated with Nafion microstructure, where interconnected ionic domains strongly contribute to its high proton conductivity, but at the same time contribute to fast methanol diffusion. Sulfonated PEK membranes containing the ketone diphenyl ketone moiety (Ph-PEEKDK and Me-PEEKDK) exhibited extremely low methanol diffusion, which likely arises from their well-defined regular and rigid backbone molecular structure.

The proton conductivities of the membranes are presented in Table 3. All the samples exhibited room temperature conductivities higher than 0.01 S/cm, which is conventionally regarded as the minimum value required for practical PEM application in FC. At 80 °C, proton conductivities of Ph-PEEKK and Me-PEEKK were 0.077 and 0.049 S/cm, respectively. Me-PEEK and Ph-PEEK exhibited still higher proton conductivity, but their applicability in FC is limited by their poor dimensional stability in hot water.

Table 4. Oxidative Stability and Methanol Permeability of the Polymers

Polymer	MethanolPermeability (cm^2/s)	Oxidative Stability	
		W (%)	T (h)
Me-PEEK	7.43×10^{-7}	88	1.1
Me-PEEKK	2.28×10^{-7}	97	2.5
Me-PEEKDK	9.55×10^{-8}	98	>6.0
Ph-PEEK	1.05×10^{-6}	--	0.8
Ph-PEEKK	3.31×10^{-7}	98	2.0
Ph-PEEKDK	2.30×10^{-7}	99	>6.0
Nafion 117	1.55×10^{-6}	98	>6.0

Oxidative Stability. The oxidative stability of the polymers was evaluated in Fenton's reagent at 80 °C, as shown in Table 4. This method is regarded as one of the standard tests to gauge relative oxidative stability and to simulate accelerated fuel cell operating conditions. It is expected that side-chain-acid polymers should have improved oxidative resistance than main-chain-acid polymers. All the polymers except Me-PEEK and Ph-PEEK exhibited excellent oxidative stability. Their retained weight was above 97% after treatment in Fenton's reagent at 80 °C for 1 h, and they did not dissolve after 2.0 h treatment at 80 °C. As expected, the polymers with the lower DS had better oxidative stability. Sulfonated Me-PEEKDK and Ph-PEEKDK, maintained dimensional shape and flexibility even after 6 h treatment, which is indicative of their outstanding oxidative stability. The oxidative resistance of these polymers was much better than reported analogues with similar IEC values and comparable to Nafion 117.

CONCLUSIONS

Several side-group-sulfonated PEKs have been prepared under very mild reaction conditions. Only one site on the pendant benzene ring per repeating unit was susceptible to sulfonation. All the membranes had excellent tensile properties in both wet and dry states. Me-PEEKK, Me-PEEKDK, Ph-PEEKK and Ph-PEEKDK possessed low swelling ratios, excellent oxidative stability, and low methanol permeability. Me-PEEKK and Ph-PEEKK showed proton conductivity of 0.049 and 0.077 S/cm at 80 °C. Combining all these properties, Me-PEEKK and Ph-PEEKK may be promising materials for PEMFC and DMFC applications.

ACKNOWLEDGEMENT

Financial support for this project, provided by the joint research cooperation program between the National Science Council of Taiwan (R.O.C.) and the National Research Council of Canada, is gratefully acknowledged.

REFERENCES

1. Rikukawa, M.; Sanui, K. *Prog. Polym. Sci.*, **2000**, *25*, 1463.
2. Hickner, M.A.; Ghassemi, H.; Kim, Y.S.; Einsla, B.R.; McGrath, J.E., *Chem. Rev.* **2004**, *104*, 4587.
3. Xing, P. X.; Robertson, G.P.; Guiver, M.D.; Mikhailenko, S.D.; Wang, K. P.; Kaliaguine, S., *J. Membr. Sci.*, **2004**, 229, 95.
4. Miyatake, Kenji; Hay, Allan S. *J. Polym. Sci.: Polym. Chem.* **2001**, *39*, 3211.
5. Wang, S.; McGrath, J. E.; In "Step Polymerization", Rogers, M. Long; T. E. (Eds.) Wiley, New York, **2003**.
6. Bishop, M.T.; Karasz, F. E.; Russo, P. S.; Langley, K. H. *Macromolecules*, **1985**, *18*, 86.