Molecular Structure of Poly(phenylene oxide-g-styrenesulfonic acid) and the Conductivity and Methanol Permeability of the Membrane

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Introduction

For proton exchange membrane (PEM) for direct-methanol fuel cell (DMFC) applications, many hydrocarbon based polymers are studied as possible alternatives to Nafion® which has a critical drawback of high methanol permeation through the membrane. Among many engineering plastics, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is a very hydrophobic polymer with very high glass transition temperature and hydrolytic stability. Application attempts to membranes have been mainly limited to separation membranes after bromination of aromatic protons of PPO [1]. Several attempts [2, 3] have been reported in fuel cell membrane area in the form of sulfonated or other acid containing copolymers, but little has been known with the form of well-defined graft or block copolymers. In this work, well-defined poly(2,6-dimethyl-4,4'-phenylene oxide -g-styrenesulfonic acid) (PPO-g-PSSA) graft copolymer was prepared by ATRP [4, 5]. The branching numbers and branching length of PPO-g-PSSA graft copolymer were controlled and their properties for fuel cell membranes were investigated.

Experimental

Synthesis of PPO-g-PSSA. Brominated PPO macroinitiator (PPO-Br) was prepared by bromination of PPO. The synthesis of PPO-g-PSSA was carried out via ATRP [5]. Macroinitiator (2 g), SSNa (3 g), 120 ml of NMP were introduced into a 250 ml round-bottom flask and flushed with nitrogen for 1 h. Then, copper(I) chloride (CuCl) and 2,2'-dipyridyl were added and flushed with nitrogen for another 30 min. The flask was placed in a preheated oil bath at 120 °C. After 48 h or 72 h, the copolymer was recovered by precipitation in methanol, filtered, stirred in boiling water for 1 h, filtered again, and dried under vacuum at 80 °C. The obtained block copolymer was put into 1M HCl solution and stirred for 24 h to change the salt form (PPO-g-PSSNa) to acid form (PPO-g-PSSA). The copolymer was washed with water, and dried under vacuum at 80 °C. The synthetic scheme is illustrated in **Figure 1**.
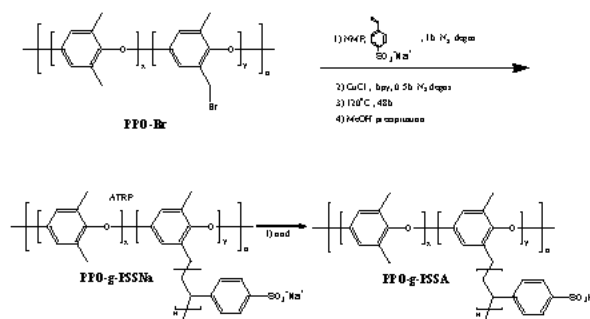

Figure 1. Synthetic scheme of PPO-g-PSSA.

Membrane preparation and characterization. PPO-g-PSSA copolymer was transformed into membrane. Ion exchange capacity (IEC) and % water uptake of the membrane were measured. The impedance of the membranes was determined by A.C. impedance spectroscopy two probe electrode system, which was connected with a HP4192A LF Impedance Analyzer at 30 °C. The methanol permeability of the membranes was determined by diaphragm glass diffusion cell at 30 °C following a previously reported procedure. The glass cell was composed of two chambers, each with a capacity of approximately 100ml, and the membrane was placed between the two chambers. The diffused methanol through the membrane was measured using Waters 2410 RI detector.

Results and discussion

Water uptake, conductivity, and methanol permeability of PPO-g-PSSA. Table 1 shows the synthetic results of the PPO-g-PSSNa, and also the properties of the membrane, in terms of water uptakes as well as theoretical IEC of acid form membranes. Water uptake was less than that of Nafion (~19 wt %) for all membranes probably due to very hydrophobic nature of the PPO matrix. Theoretical IECs were calculated based on the wt % of the PSSNa grafts in the graft copolymer. Measured IEC values showed quite fluctuation probably due to the partial utilization of the ionic phases in the graft copolymers.

Table 1. Molecular Characteristics and Properties of PPO-g-PSSNa

Sample	-Br /PPO Chain[a]	SSNa Wt% in polymer	DP /graft[b]	Water Uptake (%)	IEC (Theo) (meq/g)	IEC (Titr) (meq/g)
1	1.5	31	41	3.6	1.7	0.80
2	1.5	52	98	5.6	2.4	1.24
3	4.7	31	13	6.0	1.7	0.61
4	4.7	48	26	12	2.4	1.20
5	4.7	58	40	15	2.9	2.23
6	6.2	34	11	12	1.6	0.30
7	10.6	31	5.7	5.2	1.7	0.80
8	10.6	50	13	11	2.4	1.15
9	10.6	57	17	17	2.9	1.16

[a] Number of bromomethyl groups per PPO main chain in PPO-Br
[b] Degree of polymerization per graft was calculated by the SSNa wt % in polymer and the number of Br in PPO-Br
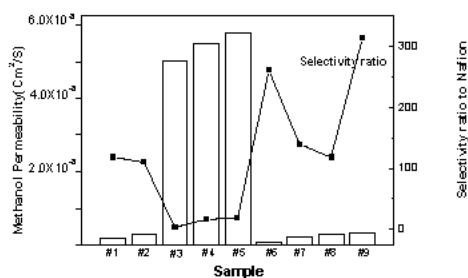

Figure 2. Methanol permeability (bar) and selectivity ratio (line) of PPO-g-PSSA.

Figure 2 shows the methanol permeability and the selectivity ratio of the membranes. The selectivity ratio is defined as the ratio of the proton conductivity to methanol permeability compared to that of Nafion 117 (selectivity = 1 for Nafion). The membrane sample # 5 shows poor methanol barrier property compared to other graft copolymers although the methanol barrier of sample is still up to 21 times of that of Nafion 117 (2.38×10^{-6} cm³ cm/(cm² s)). The methanol barrier of the sample # 9 is more than 700 times of that of Nafion 117, giving selectivity ratio value more than 300.

Conclusions

The membrane showed low MeOH permeability and good proton conductivity, so the membrane can be a good candidate for DMFC or PEMFC membrane. The water uptake, IEC, proton conductivity, and methanol permeability of the membranes are related with the molecular structure of the graft copolymer. The grafting frequency as well as the length of each graft seems to be important factors in determining graft copolymer's phase morphology, and its related properties, and this study is still under investigation.

References

[1] Tongwen X., and Weihua Y *J. Membr. Sci.* **2001**, *190*, 159
[2] Kim B., and Jung B *Macromol. Rapid Comm.* **2004**, *25*, 1263
[3] Miyatake K; Zhou H; Watanabe M *J. Polym. Sci.: Part A: Polym. Chem.* **2005**, *43*, 1741
[4] Matyjaszewski K., Ed *Advances in Controlled/Living Radical Polymerization. ACS Symp. Series 854* (Washington, DC: Amer. Chem. Soc.), **2003**
[5] Cho C G; Jang H Y; You Y G; Li G H; An S G *High Perform. Polymers* **2006**, *18*, 000