SYNTHESIS OF NOVEL POLY(PHENYLENE) DERIVATIVES AS PROTON CONDUCTING MEMBRANES FOR FUEL CELLS

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Recently, we focused on sulfonated hydrocarbon polymers as inexpensive materials for proton conducting membranes of PEFC.[1] We reported on high proton conductivities and mechanical properties of sulfonated poly(4-phenoxybenzoyl-1,4-phenylene) (S-PPBP).[2] However, it is difficult to handle S-PPBP membranes for fuel cell applications owing to its rigidity. In this study, we synthesized the novel copolymers, poly (4-phenoxybenzoyl-1,4-phenylene-*co*-*m*-toluene) (PPBP-*co*-PMT), using Ni(0) catalysts to prepare more flexible films. The proton conductivity and fuel cell performance of S-PPBP-*co*-PMT were also investigated.

Experimental

PPBP-*co*-PMTs were synthesized from various feed ratio using the Ni(0)-catalyzed coupling of aryl chlorides, as shown in Scheme.[3] The PPBP-*co*-PMT was sulfonated with sulfuric acid in order to convert it to a proton conducting polymer electrolyte. Sulfonated PPBP-*co*-PMT (S-PPBP-*co*-PMT) was characterized by elemental analysis, ^{1}H-NMR, and FT-IR measurements. Molecular weights of S-PPBP-*co*-PMT were determined by the gel permeation chromatography relative to poly(ethylene oxide) standards in DMF. Proton conductivity of the S-PPBP-*co*-PMT cast films were evaluated by the complex impedance method with a humidic chamber. Fuel cell performance was measured by using hydrogen and air gases as the fuel and oxidant, respectively.

Result and discussion

The 10PPBP-*co*-1PMT represents that the feed molar ratio of monomers was 2,5-dichloro-4'-phenoxy-benzophenone (DPBP) : *m*-dichlorotoluene (MDCT) = 10 : 1. The weight-average molecular weight of S-10PPBP-*co*-1PMT was 135,000 and the sulfonation level of S-10PPBP-*co*-1PMT was estimated to be 85 mol% by elemental analysis and the ion exchange capacity was 2.45 meq/g.

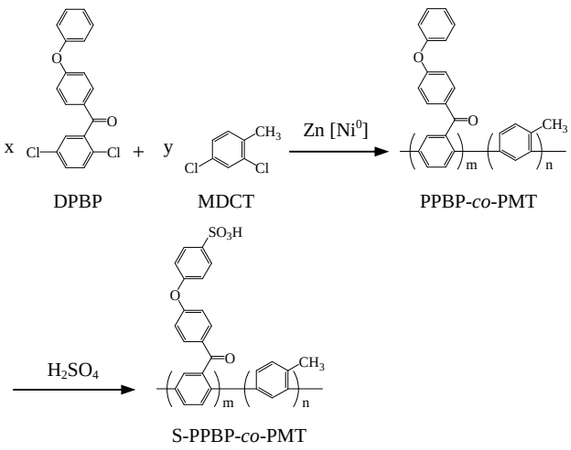
The thermal stability of S-10PPBP-*co*-1PMT was investigated by TG-DTA. The thermal decomposition temperatures of S-PPBP-*co*-PMT were observed between 200 ºC and 390 ºC. These decompositions are due to the elimination of the sulfonic acid and methyl groups respectively, as determined by FT-IR spectroscopy.

Figure 1 shows the mechanical properties of S-10PPBP-*co*-1PMT membranes hydrated with various humidities (30~100 %R. H.) prior to the measurements. The tensile strength of the S-10PPBP-*co*-1PMT membranes decreased with increasing water uptake. Even at 100 %R.H., the S-10PPBP-*co*-1PMT membrane showed tensile strength of about 25 MPa.

To measure conductivity of S-10PPBP-*co*-1PMT membranes in similar condition to actual PEFC operating systems, the impedance was measured in a humidic chamber. Figure 2 shows the Arrhenius plots of conductivity for S-10PPBP-*co*-1PMT (2.45 meq/g) and S-PPBP (2.60 meq/g) at 90 %R. H. The conductivity of the S-10PPBP-*co*-1PMT membrane achieved 10^{-1} S/cm in the range of 30 ºC to 80 ºC at 90 %R. H., which was slightly lower than those of the S-PPBP membrane. This is because the ion exchange capacity of S-PPBP is higher than that of S-10PPBP-*co*- 1PMT.

Reference

[1] M. Rikukawa and K. Sanui, *Prog. Polym. Sci.*, **25**, (2000) 1463.
[2] T. Kobayashi, M. Rikukawa, K. Sanui, and N. Ogata, *Solid State Ionics*, **106**, (1998) 219.
[3] I. Colon and D. R. Kelsey, *J. Org. Chem.*, **51**, (1986) 2627



Scheme Synthesis of S-PPBP-*co*-PMT.

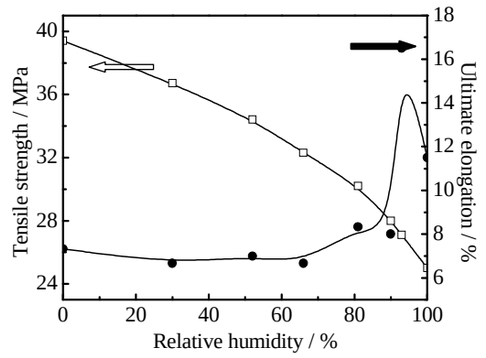


Figure 1 Mechanical properties for S-10PPBP-*co*-1PMT films (2.45 meq/g) as a function of relative humidity.

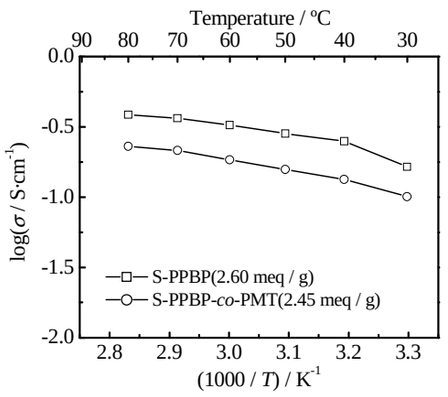


Figure 2 Arrhenius plots of conductivity for S-PPBP (2.60 meq/g) and S-PPBP-*co*-PMT (2.45 meq/g) membranes at 90 %R. H.