

Polymer Electrolyte Membranes for Fuel Cells Prepared by Radiation-Induced Graft Polymerization of Vinyl Monomers onto Polybenzimidazoles

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ABSTRACT

To prepare the high proton conductivity PEMs based on polybenzimidazole (PBI) substrates, well-established radiation-induced graft polymerization of various vinyl monomers onto PBIs and subsequent sulfonation were carried out. A combination of styrene with an alicyclic polybenzimidazole (APBI) were exhibited high grafting degree, and the resulting PEMs showed much higher proton conductivity (ca. 10^{-1} S/cm at 25 °C, RH = 100%) than those of linear sulfonated PBIs.

INTRODUCTION

Polymer electrolyte membranes for fuel cells (PEMFC) have received considerable interests due to their paramount potentials for the new clean energy sources. Polymer electrolyte membranes (PEMs) are considered to be the most important key in PEMFC, which are directly related to efficiency and longevity under hostile conditions (i.e., temperature and relative humidity). For that purpose, sulfonated perfluoro polymer membranes such as Nafion[®] are known to show high electrochemical stability under 80 °C. However, their stability is rather restricted at higher temperatures. [1]

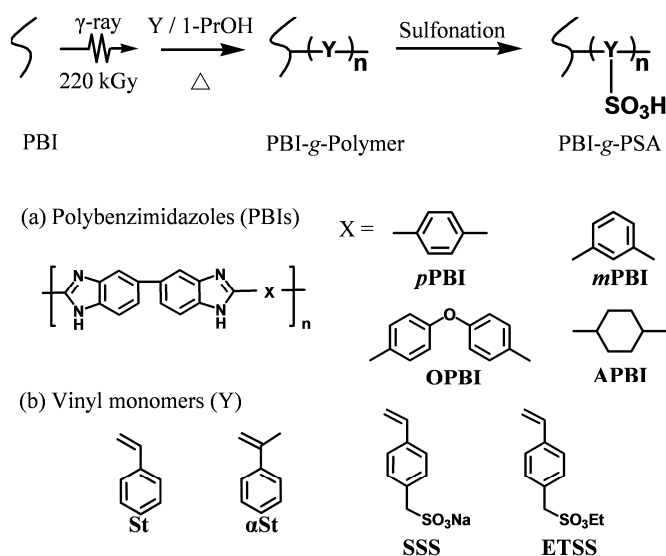
On the other hand, sulfonated hydrocarbon polymer membranes such as polyimides [2], polysulfones [3], poly(ether ether ketone)s [4], and polybenzimidazoles (PBI) [5] are being intensely studied as alternative membranes. In particular, PBI is one of the most attractive polymer backbones due to its excellent durability at high temperature. [6] The approaches concerning the synthesis of sulfonated PBIs (sPBI) are mainly divided into following two types. The first method is the polymerization of monomers having sulfonic acid groups. [7] The second one is post-sulfonation by means of N-alkylation of the imidazole ring with sultones. [8] Unfortunately, sPBIs prepared by both approaches show too low proton conductivity ($\sigma = \text{ca. } 10^{-3}$ S/cm) even though the problems of Nafion[®] are partially cleared.

This low σ of sPBIs is considered to be due to the intra- and/or intermolecular interactions between sulfonic acid (SA) groups and imidazole (Im) units. [9] Kreuer et al. have significantly pointed out that the molar balance of SA and Im, strongly affect the σ in the solution phase. [10] Their result indicates that high σ can be realized at imbalanced regime of the two components rather than equimolar mixture. This means that highly localized SA groups in the PBI membrane is expected to show high σ value.

In order to realize such a microstructure in the PBI membrane, graft polymerization of sulfonated vinyl monomer onto PBI chain might be a choice. Alternatively, graft polymerization of vinyl monomer having reactivity toward sulfonating agents and the subsequent sulfonation is also possible. For that purpose, well-established radiation-induced graft polymerization might be advantageous. Vinyl monomers available for the graft polymerization processes are styrene, α -methyl styrene (α St), sodium styrene sulfonate (SSS), and ethyl styrene sulfonate (ETSS). [11] Herein, we describe preparation of the graft-type sPBIs and evaluation of them as PEMs.

EXPERIMENTAL SECTION

Materials 3,3',4,4'-Tetraaminobiphenyl (TABP) from Sigma-Aldrich Chemical Co. was used after purification. Dicarboxylic acids (DCA) and polyphosphoric acid (PPA) were purchased from Tokyo Chemical Industry and Sigma-Aldrich Chemical Co., respectively, and were used as received. *N,N*-Dimethyl acetamide (DMAc), lithium chloride (LiCl) and 1-propanol (1-PrOH) were purchased from Wako. Vinyl monomers such as St, α St and SSS, and ETSS were purchased from Wako, Sigma-Aldrich, and Tosoh, respectively. Chlorosulfonic acid (ClSO₃H) and 1, 2-dichloroethane were purchased from Wako and used as received.



Scheme 1 The preparation of graft-typed PEMs consisting of poly (sulfonic acid) (PSA) grafts and polybenzimidazoles (PBIs) by radiation-induced grafting polymerization of various vinyl monomers (b) onto PBIs (a).

Synthesis and fabrication of polybenzimidazoles (PBIs) PBIs were synthesized by typical condensation polymerization of TABP and DCA using PPA, which acts as not only polymerization solvent but also condensation agent. [12] The obtained PBIs were dissolved in DMAc/LiCl solution, filtered through a whatman 5 μ m filter, and then casted onto a clean glass substrate. The solvent was evaporated at 60 °C overnight under nitrogen flux, and then at 200 °C for 1h. After cooling back to room temperature, membrane were immersed in water and 1-PrOH, and then dried under vacuum for 5 h at 120 °C.

Preparation and evaluation of graft-type sulfonated polybenzimidazoles (sPBIs) A PBI film under argon gas in glass ampoule was irradiated by γ -ray of ⁶⁰Co source with 220 kGy at room temperature, and then they were immediately immersed in vinyl monomers / 1-PrOH (1/1 vol%) solution at 80 °C for grafting. Grafting degree (GD) was calculated as $(W_g - W_0) / W_0 \times 100$, where W_0 and W_g are the film weights before and after grafting, respectively. Subsequently, the film having the graft chains was sulfonated by immersing in 0.01 mol ClSO₃H/CICH₂CH₂Cl at 0 °C. A sulfonation degree (SD) and ion

exchange capacity (IEC) were calculated by titrimetric analysis. Proton conductivity (σ) and water uptakes (WU) were measured under fully hydrated states at room temperature.

RESULTS AND DISCUSSIONS

Synthesis and fabrication of polybenzimidazoles (PBIs) Various PBIs were successfully prepared by condensation polymerization as listed in Table 1, and characterized by FTIR, $^1\text{H-NMR}$, and GPC. Through the intrinsic viscosity measurements, it was found that all PBIs exhibited lyotropic behaviors in DMAc. Tough and flexible membranes were obtained from polymer solution casting in wide concentration ranges. [13] PBIs exhibited excellent mechanical properties (tensile strength of ca.

150 MPa and elongation of ca. 25%) and high thermal stability ($T_d > 500\text{ }^\circ\text{C}$). It might be due to the intermolecular hydrogen bonds and π - π stacking between benzimidazole ring units in the polymer matrix.

Table 1 Synthesis conditions and characterization of various PBIs.

PBI Abbreviation	Reaction time at 200 $^\circ\text{C}$ (h)	Yield (%)	Solubility in DMAc ^b	M_n by GPC (kDa)
<i>p</i> PBI	12	99	+	120
<i>m</i> PBI	2	98	++	88
OPBI	12	97	+	300
APBI	2 ^a	99	++	150

^a 160 $^\circ\text{C}$, ^b ++: Soluble at ambient temperature, +: Soluble at reflux temperature.

Radiation-induced graft polymerization of various vinyl monomers onto polybenzimidazoles (PBIs) The result for radiation-induced graft polymerization of St and α St onto various PBIs are shown in Figure 1. Phenylenedicarboxylic acid-derived PBIs, namely, *p*PBI and *m*PBI, showed no grafting reactivity due to their high radiation resistance. OPBI with ether groups in the main chain showed increased grafting reactivity than the aromatic PBI. The mechanism for the grafting might be similar to those of poly(ether ether ketone)s. [14] In the case of alicyclic-structured APBI, graft polymerization of St occurred with GD up to 100% by elongating grafting time to 30 h. Such a high grafting reactivity of APBI might be derived from relatively sensitive alicyclic structure to irradiation. The grafting of α St in acetonitrile at 60 $^\circ\text{C}$ onto APBI, however, exhibited much lower GD of 30%. [15] This result coincides known difference in the reactivity of St and α St. Unfortunately, *p*-substituted St such as SSS and ETSS showed no grafting reactivity to all PBIs.

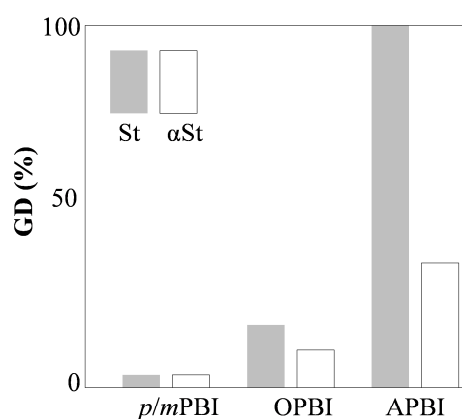


Figure 1 Grafting degree (GD) of St and α St onto various PBIs by radiation-induced graft polymerization.

Preparation and evaluation of graft-type sulfonated polybenzimidazoles (PBIs) The highly polystyrene-grafted PBI, hereafter called APBI-g-PSt, was sulfonated with ClSO_3H to prepare graft-typed PEMs. It was revealed that the sulfonation selectively proceeded on polystyrene grafts but not on APBI main chains. When APBI-g-PSt with GD of 53% was sulfonated for 3 h, the PEMs with

an SD of 100% was obtained. (Figure 2) The PEMs showed proton conductivity as high as 0.12 S/cm (IEC = 2.9 mmol/g, WU = 100%), which is comparable with perfluorinated PEMs such as Nafion[®]. The large σ value might be due to the formation of macro ion-channels of the grafted poly(styrenesulfonic acid) to transport protons which can be hardly realized by hitherto reported linear sulfonated type sPBIs.

CONCLUSIONS

We described the preparation and evaluation of graft-typed PEMs based on PBI polymer substrates. The combination of alicyclic PBI and St showed high grafting reactivity. By means of selective sulfonation to polystyrene grafts of APBI-g-PSt, graft-type PEMs with high proton conductivity were successfully prepared for the first time.

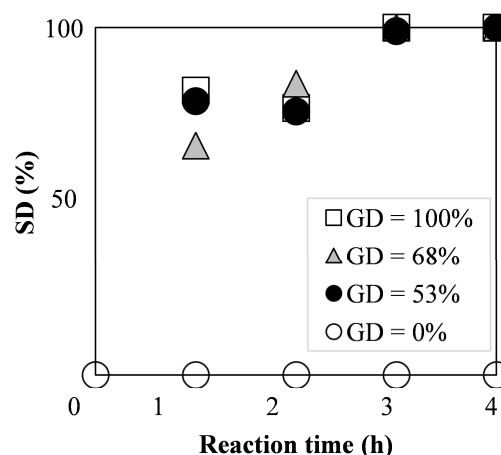


Figure 2 Sulfonation degree of APBI-g-PSt.

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