

博士論文（要約）

論文題目 **A study on Graft-type Sulfonated**

Polybenzimidazoles for Fuel Cell Applications

(燃料電池用途に向けたグラフト型スルホン化ポリベンズ
イミダゾールに関する研究)

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Polymer electrolyte membrane fuel cells (PEMFCs) are considered as one of the most promising solutions to environmental and energetic aspects, because of its applications for clean electric sources of vehicles. Polymer electrolyte membranes (PEMs), a key-material for PEMFCs, require high proton conductivity (10^{-2} S/cm) and thermal durability (120 °C). Perfluorinated polymers having side chain sulfo groups such as Nafion® have been widely studied because they show outstanding physicochemical stability with high proton conductivity. However, their application for fuel cells is restricted because of low operation temperatures.

To overcome this problem, sulfonated polybenzimidazoles (sPBI) were recently developed as alternative membranes because of their excellent thermal durability. However, the reported sPBIs indicate too low proton conductivity in the magnitude from 10^{-5} to 10^{-3} S/cm regardless of the degree of ion exchange capacity (IEC). It is considered to be due to intra-, intermolecular acid/base reactions between sulfonic acid (SA) and imidazole (Im) groups. Concerning this, Kreuer has shown that the molar balance of SA and Im strongly affect the proton conductivity in solution phase. For the mixtures of SA and Im, maximum conductivity was realized at imbalanced regime rather than 1:1 molar ratio. This means that high proton conductivity of sPBI should be attained at highly localized states of SAs.

In order to realize such a situation, the author proposed graft-type sPBIs, which might adopt highly localized SA groups in PBI matrix. In this study, the author has tried to develop highly proton conducting PEMs, which is proposed on the thermally stable sPBIs by using grafting strategy.

In Chapter 2, radiation-induced graft polymerization, a unique method for polymer modification, was carried out. In this method, the graft chains grow from radicals on the main chain of PBI, hence hereafter this is named as a grafting-from method. This process consists of 1) radiation-induced formation of radical species on the main chain of the base polymer, and 2) radical polymerization of externally added vinyl monomers starting from the radiation-generated radicals. For successful grafting, base polymers must fulfill two requirements; the first one is high sensitivity to radiation, and the second one is stability of radical for grafting polymerization. Concerning this, the author had experienced that an alicyclic polyimide is one of good base polymer for radiation-induced grafting because of its radiation-sensitive chemical structure and crystallinity for trapping radicals. Accordingly, I designed an alicyclic PBI (APBI) as a base polymer.

APBI could be prepared by treating 3,3'-diaminobenzidine and *t*-1,4-cyclohexanedicarboxylic acid in the presence of polyphosphoric acid. The APBI was characterized by $^1\text{H-NMR}$, IR, DSC and TGA analyses. At the stage of preparing *N,N*-dimethylacetamide (DMAc) solution of APBI, it was found that the use of LiCl as a stabilizer considerably increased the solubility of APBI. In addition, the APBI solution

showed lyotropic phase behaviors on the concentration-viscosity plot. Polarized microscope observation of the APBI film indicated the presence of domains with size of several tens of micrometers, in which the APBI chains are considered to be highly oriented. When the film was prepared from non-LiCl-containing APBI solution, such an anisotropic pattern was not observed. The films were irradiated by γ -ray from ^{60}Co (220 kGy) and subjected to ESR analysis. The film prepared from LiCl-containing solution indicated generation of sufficient amount of long-lived radicals, while the one from non-LiCl-containing solution gave very weak ESR signals.

Then, the pre-irradiated APBI films were subjected to radical polymerization. The films were immersed in styrene (St) / solvent (50/50 v/v) at 80 °C for grafting. In bulk of St, grafting polymerization did not proceed at all. Among various solvents tested, 1-PrOH showed highest grafting degree (GD) which is defined as the weight of the grafted polymer over the weight of the starting polymer. This might be due to the fact that the difference between solubility parameters of 1-PrOH and APBI is smaller than that between St and APBI; the solvent 1-PrOH effectively soaked into the film with accompanying St molecules. GD of polystyrene into APBI films could be controlled up to 100%. Polystyrene grafted APBI films (APBI-g-PSt) were successfully characterized by $^1\text{H-NMR}$ and GPC.

Subsequently, APBI-g-PSt films were sulfonated by 0.01 M ClSO_3H in $\text{ClCH}_2\text{CH}_2\text{Cl}$ at 0 °C. A sulfonation degree (SD) was determined by titrimetric analysis. APBI-g-PSt films with the GD of 53 and 100% were sulfonated to give the APBI-based PEMs (APBI-g-PSSA) with the SD of nearly 100% after 3h. In contrast, the SD value for pristine APBI film was found to be almost 0%. From these results, it was concluded that the sulfonation selectively occurred to PSt grafts. In FTIR of APBI-g-PSSA (GD = 100%, SD = 100%), several new peaks at 1005 and 1033, 1215, and 1126 cm^{-1} and the very strong peak observed from 1450 and 1500 cm^{-1} were assigned to $\nu_{\text{sym}}(\text{SO}_3\text{H})$, $\nu_{\text{asym}}(\text{SO}_2)$, and $\nu_{\text{asym}}(\text{SO}_3\text{H})$, and strong coupling between $\nu_{\text{asym}}(\text{NH})$ and $\nu_{\text{sym}}(\text{CN})$, respectively.

For the evaluation of APBI-based PEMs, proton conductivity (σ) and water-uptakes (WU) of fully hydrated states at room temperature were measured and plotted as a function of ion exchange capacity (IEC). The σ values for APBI-g-PSSAs at $\text{IEC} \leq 2.5$ were in the order of 10^{-3} S/cm, which is similar to the σ of reported linear-type sPBIs. On the other hand, APBI-g-PSSA showed 10 times higher σ ($\sim 10^{-2}$ S/cm) than those of linear-type sPBIs at the same IEC (2.9 mmol/g) even though their water uptakes were similar to each other. It was considered that workable SA of graft-type sPBI was highly localized in the film, hence contributed to the increased high proton conductivity rather than linear-type sPBIs. Moreover, it was observed that the obtained graft-type sPBI showed excellent thermal durability in water at 120 °C until 600 h.

SEM images of low and high σ samples showed distinct difference; the high σ sample had

sea-island structure, while well-dispersed morphology was observed in low σ sample. EDX analysis of the former revealed that the nitrogen content of the island was significantly lower compared to the sea. This means that the islands are rich in PSSA content. Therefore, plausible transportation of proton in the radiation-induced graft-type sPBI was considered to be as follows: The protons in the island part move quickly through the well-contacted SA moieties, while their motion should be slower in the sea part because the proportion of available SA is smaller due to intra- and intermolecular interactions between SA and Im. The difference in the σ value between the two samples should arise from the presence/absence of the highly proton conducting island region.

The sPBI made by grafting-from method successfully showed high σ value and high thermal stability. However, there remains a problem. The film with high σ value showed high IEC (>2.9) and this usually accompany high water uptake of >100%. This means that the membrane should considerably swell resulting in large mechanical stress of the film. In order to suppress this swelling, IEC should be reduced.

Moreover, the grafting-from technique was strongly restricted in aspects of both precise control of graft chains and unavoidable damage during sulfonation reaction. To overcome these problems, the author conceived “grafting-to” method in which poly(styrenesulfonic acid) chains are introduced to PBI chain through the polymer reaction. For this purpose in Chapter 3, the author chose well-defined Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition between alkynes and azides, or so-called click reaction.

According to the above plan, PBI having alkynyl group was synthesized: First, brominated PBI (BrPBI) and sequenced brominated PBI (APBI-*seq*-BrPBI) were prepared by typical polycondensation. Suzuki Coupling between BrPBI or APBI-*seq*-BrPBI and [4-(trimethylsilyl)ethynyl] phenyl boronic acid pinacol ester proceeded with the conversions of up to 50%.

Concerning the preparation of poly(styrenesulfonic acid), atom transfer radical polymerization (ATRP) is thought to be advantageous in two aspects; 1) ATRP gives polymers of narrow distribution of molecular weight, and 2) the terminal of the polymer chain has halide functional group, which can be readily converted to other functional groups. Poly(ethyl styrenesulfonate) was prepared under conventional ATRP reaction conditions to give terminally brominated poly(ethyl styrenesulfonate) (Br-PETSS), and this polymer was subsequently treated with sodium azide to give terminally azide functionalized PETSS (N₃-PETSS). Here the sulfonate ester instead of sulfonic acid was used because the strongly acidic nature of the sulfonic acid is known to be harmful for ATRP reaction. Unfortunately, the obtained N₃-PETSS showed broader molecular weight distribution (PDI = 1.2). Nevertheless, N₃-PETSS with known molecular weight of 20 kDa was successfully obtained.

Click reaction between alkynated PBIs and N₃-PETSS was carried out in DMAc/LiCl without additional catalyst. The obtained graft-type sPBI presented high solubility in common organic solvents. However, when additional catalyst was used, the obtained polymers showed extremely low solubility to any solvents due to autocatalysis for cross-linking between alkyne, azide, and Cu(I). Finally, side-chain of EtOSO₂ was hydrolyzed. Inspection of the ¹H-NMR for graft-type sPBIs indicated the increasing of aromatic structure from 7 ppm to 8 ppm. In addition, FTIR and GPC also confirmed to no azide (2098 cm⁻¹) residues and increased molecular weight profiles in the final graft-type sPBI, respectively.

The effect of graft density under fixed PETSS graft length to 8 kDa was evaluated aspect for proton conductivity of PEMs. It was found that the polymer blend which consists of BrPBI and APBI-*seq*-BrPBI-based graft-type sPBIs showed almost constant σ value throughout the IEC range of 3 to 1. The lowering of IEC value while holding σ at nearly constant value could be interpreted as successful phase separation of the component polymers resulting in the efficient formation of proton conducting path.

In Chapter 4, it was concluded that sPBIs made by grafting strategy resulted in significant advance in the field of hydrocarbon-based PEM in the viewpoint of high proton conductivity, high thermal stability, and low IEC by keeping high order σ , blend copolymers with various aromatic PBIs were employed. Because aromatic PBIs showed extremely low and no GD, more highly localized SA could be afforded. Actually, the obtained graft-type blend sPBIs showed to be slightly reduced IEC and water uptakes. Even though morphological changes on blend effect should be pursued in detail, it was indicated that reduced IEC of graft-type sPBI could be prepared by blend with more hydrophobic aromatic PBIs.