Graft-type Sulfonated Polybenzimidazoles for Fuel Cell Applications

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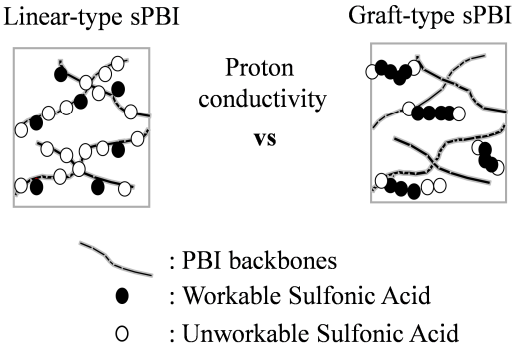
ABSTRACT

To prepare the high proton conductivity PEM based on sulfonated polybenzimidazole (sPBI), grafting strategies of grafting-from and grafting-to were proposed. In our previous report, it was known that the former had limits such as unavoidable damage in sulfonation and precise control of graft chains. In this novel study, it was challenged that these limits were cleared by the latter technique.

INTRODUCTION

Polymer electrolyte membrane fuel cells (PEFCs) are considered as one of the most promising solutions to apply for electrical vehicles. Polymer electrolyte membranes (PEMs) are key-material for PEFCs, whose proton conducting polymers have strongly acidic groups (-SO_3H) to transport protons. Perfluorinated polymers such as Nafion® have been widely studied as a substrate of PEMs due to their outstanding physicochemical stability with high proton conductivity. However, their applications for fuel cells are restricted because of low gas-barrier properties and low operation temperatures. [1]

On the other hand, sulfonated hydrocarbon polymer membranes such as polyimides, polysulfones, poly(ether ether ketone)s, and polybenzimidazoles (PBI) 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. [2] 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. The second one is post-sulfonation by means of N-alkylation of the imidazole ring with sultones. Unfortunately, the reported sPBIs indicate too low proton conductivity (σ) in the magnitude from 10^{-5} to 10^{-3} S/cm regardless of the amount of ion exchange capacity (IEC). These low proton conductivities are considered to be due to intra- and intermolecular acid/base reactions between sulfonic acid (SA) and imidazole (Im) groups. [3]



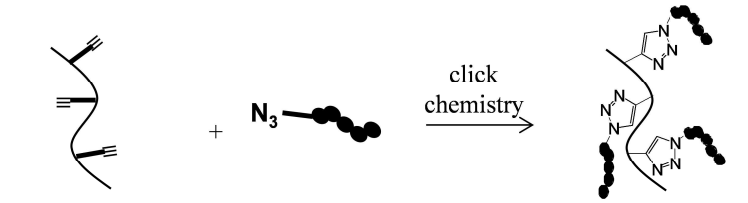
Scheme 1 2D comparison of proton conductivity between linear-type and graft-type sulfonated polybenzimidazoles (sPBI).

Kreuer et al. have significantly pointed out that the molar balance of SA and Im, strongly affect the σ

in the solution phase. [4] 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. (Scheme 1)

In order to realize such a microstructure in the PBI membrane, grafting-from by radiation-induced graft polymerization were proposed, which it was confirmed that graft strategy is effective for increasing σ (up to 10^{-2} S/cm) of sPBI. [5] However, the grafting-from technique showed several problems, which strongly restrict in aspects of both unavoidable damage in sulfonation even though under mild conditions and precise control of graft chains.

To overcome these problems, the author conceived “grafting-to” method in which PSSA chains are introduced to PBI chain by a certain reaction of atom transfer radical polymerization (ATRP) of ethyl styrenesulfonate (ETSS; a monomer needless sulfonation). In addition, the author chose well-defined Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition between alkynylated PBI and azide-functionalized PSSA derivate (PETSS-N_3), or so-called click chemistry. [6] (Scheme 2)



Alkynyl PBI PETSS-N_3 Graft-type sPBI

Scheme 2 Procedures of grafting-to method by click chemistry between alkynyl PBI and azide-functionalized poly (styrene sulfonic) acid derivate (PETSS-N_3).

EXPERIMENTAL SECTION

Materials 3,3’,4,4’-Tetraaminobiphenyl (TAB) from Sigma-Aldrich Chemical was purified by re-crystallization just before using. polyphosphoric acid (PPA) and 2-bromoterephthalic acid (BTA) were purchased from Sigma-Aldrich Chemical and Tokyo Chemical Industry (TCI), respectively, and used as received. [4-(Trimethylsilyl)ethynyl] phenyl boronic acid pinacol ester purchased from Sigma-Aldrich Chemical, and Pd catalyst ($Pd(PPh_3)_4$), bases including cesium carbonate (Cs_2CO_3), sodium azide (NaN_3), and solvents (DMAc, DMF, NMP, DMSO) purchased from Wako were used. N,N,N’,N’’,N’’-Pentamethyldiethylenetriamine and copper(I), (II) bromide were purchased from Sigma-Aldrich Chemical and TCI, resepectively. 1-(Bromoethyl)benzene and ETSS were purchased from TCI and Tosoh, and used without any purification.

Preparation of poly[2,2’-(2-bromo-1,4-phenylene)-5,5’-bibenzimidazole] (BrPBI) A 300 ml two-necked round flask equipped with mechanical stirrer and nitrogen inlet was charged TAB (2.1427 g, 0.0100 mol) in 100 g of PAA. After TAB was completely dissolved, BTA (2.4503 g, 0.0100 mol) was added to the flask. The reaction mixture was stirred at 170 ºC for 5 h, at 200 ºC for 2 h. Then,

BrPBI fibers were washed with water several times, and kept overnight in aqueous $NaHCO_3$ to remove residual PAA. After being washed with water for several times, the fibers were dried in a vacuum oven at 140 ºC for 14 h. Yield: 91%. ^{1}H-NMR (DMSO-*d6*, ppm): 8.64 (s, 2H, amine proton), 8.36 (s, 2H), 8.01 (s, 4H), 7.82-7.66 (br, 3H), FT-IR (KBr, cm^{-1}): 3350-2750 (N-H), 1620 (C=N), 1585, 1445, 1290 (benzimidazole ring), TGA: T_d > 500 ºC, GPC; 104 kDa (M_n), 1.9 (PDI).

Graft-type sPBI prepared by grafting-to Before performing of click chemistry, Suzuki coupling between BrPBI and [4-(trimethylsilyl)ethynyl] phenyl boronic acid pinacol ester was carried out in DMF with Pd catalyst and Cs_2CO_3 base. In addition, ETSS was polymerized under ATRP conditions in DMAc, and PETSS-N_3 could be prepared by its azide modification of terminally brominated PETSS (PETSS-Br). The obtained PETSS-Br and PETSS-N_3 were characterized by GPC and FTIR, respectively. Click chemistry between alkynyl PBIs and PETSS-N_3 was carried out in DMAc without CuBr, which was characterized by ^{1}H-NMR, GPC, and FTIR.

RESULTS AND DISCUSSIONS

PBIs having alkynyl group was synthesized as follows: BrPBI was first synthesized starting from TAB and BTA by typical polycondensation. Then BrPBI was subjected to Suzuki coupling with [4-(2-trimethylsilyl)ethynyl]phenylboronic acid pinacol ester. As summarized in Table 1, Suzuki couplings proceeded with the high conversions up to 90%, as reported in reference. [7] It was confirmed that use of Cs_2CO_3 as a base in DMF resulted in higher conversion to give alkynylated PBI.

Table 1 Suzuki coupling between bromo polybenzimidazoles (BrPBI) and [4-(trimethylsilyl)ethynyl] phenyl boronic acid pinacol ester with 2 mol% Pd catalyst for 8 h at 120 ºC.

Entry	Base	Solvent	Conversion by ^{1}H-NMR (%)
1	Cs_2CO_3	DMF	50 [a)]
2	Cs_2CO_3	DMF	90
3	Na_2CO_3	DMF	N. R.
4	NaOH	DMF	N. R.
6	Cs_2CO_3	NMP	54
7	Cs_2CO_3	DMSO	84

a) 2 h.

Poly(ethyl styrenesulfonate) was prepared under conventional ATRP reaction conditions to give terminally brominated poly(ethyl styrenesulfonate) (PETSS-Br), and this polymer was subsequently treated with sodium azide to give terminally azide functionalized PETSS (PETSS-N_3). Unfortunately, the obtained PETSS-N_3 showed broader molecular weight distribution (PDI = 1.2-1.5) than generally

expected for ATRP products. Nevertheless, PETSS-N_3 with known molecular weight of 8-20 kDa was successfully obtained. It was reported that ETSS monomer decomposes during solution polymerization in DMF due to amine impurities in the solvent, in which these amines and the resulting sulfonate groups poison the copper catalyst and thus influence the polymerization rate. [8]

Click chemistry between alkynylated PBIs and PETSS-N_3 was carried out in DMAc/LiCl. It was found the residual trace copper species contained in PETSS-N_3 worked as a catalyst, and there was no need to add Cu(I) salt for this reaction. [9] ^{1}H-NMR spectrum of the product clearly showed the presence of polystyrene moieties. In addition, FTIR and GPC confirmed the absence of azide group (ν_{N3} = 2057 cm^{-1}) and increased molecular weight profiles in the final graft-type sPBI, respectively.

After the IEC-controlled PEMs were made by blending between graft-type sPBI and non-sulfonated BrPBI, side-chain sulfonate ethyl ester groups were hydrolyzed by alkaline aqueous solution, and then back-acidified by hydrochloric acid to give PSSA graft chains. Evaluation of the resulted PEMs was carried out. Interestingly, the polymer blend using identical sPBI showed almost constant σ value throughout the IEC range of 3 to 1. The non-lowering of σ value at low IEC region could be interpreted as successful phase separation of the component polymers resulting in the efficient formation of proton conducting path. [10]

CONCLUSIONS

It was described that graft-type sPBI was successfully prepared by grafting-to technique of click chemistry. In addition, it was confirmed that the IEC controlled graft-type sPBI could be prepared by blending between graft-type sPBI and non-sulfonated BrPBI.

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