Preparation of highly porous heat-resistant polybenzoxazole network films and their electrical conductivities

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Abstract

Highly porous rigid polybenzoxazole (PBO) network films were prepared using a precursor-mediated fabrication method. The obtained PBO network films possessed high porosities of ~40%, as calculated from their apparent densities. In addition, the 5%-weight-loss temperatures of the films were ≥570°C under nitrogen atmosphere, demonstrating an excellent thermal stability. The electrical conductivities of the obtained PBO network films and phosphoric-acid-doped PBO network films were also evaluated. In addition, PBO network films containing pyridine rings were prepared and subjected to phosphoric acid doping. The resultant films were found to exhibit the highest conductivities of the films considered in this study owing to proton conduction both between phosphate groups and between the pyridine rings. The highest conductivity was found for a film prepared from a phosphoric-acid-doped PBO network containing pyridine rings, i.e., 2.09×10^{-1} S/cm at 150°C, which was higher than that of Nafion™. Therefore, these films can be used at higher temperatures than that of Nafion™.

Keywords:
rigid polymer network; heat resistance; proton; phosphoric acid; conductivity

Running head:
Highly porous heat-resistant polybenzoxazole network films

Introduction

Polybenzoxazole (PBO) is a representative rigid polymer and widely used for high-performance fibers owing to their high strengths, high elastic moduli, and high thermal and chemical resistances.[1] Incorporating a certain amount of a trifunctional monomer during the synthesis of a PBO allows the formation of a three-dimensional crosslinked polymer network (PBO network).[2,3] As the crosslinked chains in the PBO network are rigid, they do not aggregate, forming nanometer-scale voids. The sizes of these voids can be controlled by changing the ratio of trifunctional and bifunctional monomers (Fig. 1). However, PBO networks cannot be dissolved or melted, leading to intractability, and thereby making them difficult to process into thin films. As a strategy to overcome the

poor moldability of linear PBOs, the polymerization of precursors containing amide bonds has been reported.[4-9] Here, the precursor imparted some flexibility owing to rotation of the amide bond, and PBO films could be produced by the heat treatment of the precursor films. This technique has been used to prepare PBO network films. In our previous study,[3] PBO network films were prepared via two-step polymerization using trimethylsilane as a protecting group for monomers. However, the time for gelation was short using this method; therefore, it was difficult to prepare a uniform and defect-free PBO network film. Hence, a two-step polymerization of PBO network film using bulky tert-butyldimethylsilane as a protective group for monomers (Fig.2) was developed in this study. This procedure increased the time for gelation and resulted in the creation of a uniform, defect-free PBO network film.

A fuel cell is a composed of a fuel electrode (anode) that supplies hydrogen as a fuel, an electrolyte that transfers protons, and an air electrode (cathode) that supplies oxygen.[10] The advantages of fuel cells include their non-generation of unwanted gases such as CO_2 and SO_x, high energy efficiency, and largely silent operation. Accordingly, they are attracting growing attention as a clean energy source. Fuel cells are classified into various types according to their structures and operational conditions. Solid-state polymer fuel cells (PEFCs) have proton-conductive solid polymer membranes as electrolytes.[11] PEFCs show promise as energy sources for automotive applications because of their advantages in terms of miniaturization and weight reduction, short start-up time, and high-power density.[12,13] Currently, Nafion™ is typically used as the electrolyte membrane material in PEFCs as it is chemically stable and has high proton conductivity. However, it requires humidification to maintain its proton conductivity.[14] Therefore, at temperatures of ≥80°C, its conductivity and mechanical stability are decreased because of moisture evaporation.[15,16] Consequently, Nafion™-based PEFCs are operated at lower temperatures, resulting in poisoning of the platinum catalyst and lower power-generation efficiency. These issues are known to be prevented by operating PEFCs at temperatures higher than 100°C.[17,18] Therefore, polymer electrolyte membrane materials that can be used at high temperatures and without humidification are in high demand. Phosphoric-acid-doped polymer electrolyte membranes can be used at high temperatures. This type of electrolyte membrane relies on phosphoric acid, which has a boiling point of ~213°C, for proton conduction.[19] In addition, because phosphoric acid can be impregnated into the voids of PBO network films, phosphoric acid doping is a viable strategy for increasing the proton conductivities of such films.[20,21] Phosphoric-acid-doped polybenzimidazoles (PBIs) have been reported as practicable polymer electrolyte membranes. PBIs have excellent mechanical strength, heat resistance, and proton conductivity upon phosphate

doping.[22] However, PBIs have crystalline regions in which proton conductivity is inhibited.[23]

In this study, PBO network films were fabricated using a new polymerization method with tert-butyldimethylsilyl (TBS)-4,6-diaminoresorcinol dihydrochloride (DAR) (Fig.2) and their structural and mechanical properties and heat resistances were evaluated using thermogravimetric and dynamic viscoelasticity analyses. In addition, phosphoric acid doping of the films was performed, and the acid uptake and electrical conductivities of the resultant films were evaluated using impedance measurements. In phosphoric-acid-doped polymer electrolyte membranes, proton conduction occurs both between phosphoric acid groups and between basic groups and phosphoric acid groups.[19] Therefore, to increase their proton conductivity, PBO network film having pyridine rings was prepared using a pyridine-based monomer, and its heat resistance and conductivity were evaluated in the same way as those of the other PBO network films.

Experimental
Reagents
DAR and tert-butyldimethylsilyl chloride (TBS-Cl) were obtained from Tokyo Chemical Co., Ltd (Tokyo, Japan). *N*, *N*-Dimethylformamide (DMF) was supplied by Wako Pure Chemical (Osaka, Japan). Triethylamine (TEA) was supplied by Kishida Chemical (Osaka, Japan). 1,3,5-Benzentricalbonyl trichloride (TMC) and chloroform were supplied by Aldrich (St. Louis, USA). Pyridine-2,5-dicarbonyl chloride (PYCC) was supplied by Matrix (South Carolina, USA). Terephthaloyl chloride (TPC) was manufactured by Tokyo Chemical Co., Ltd (Tokyo, Japan).

Synthesis of TBS-DAR
TBS-Cl (35.370 g) was added to an excess of DAR (5 g) dissolved in DMF (234.8 mL) containing TEA (88 mL) in 500-mL eggplant flask and stirred at 25°C for 24 h under a nitrogen atmosphere (Fig. 2). The resulting precipitate was collected by filtration and washed with distilled water until the washings became neutral. Then, the product was dried under vacuum for 12 h at 80 °C.[4]

Preparation of PBO and Pry-PBO network films
TBS-DAR, bifunctional TPC, and trifunctional TMC were mixed in chloroform to prepare TBS-prePBO network gels. Molar ratios of TPC/TMC were 9:1, 8:2, and 7:3, respectively. Chloroform was volatilized from the gels to produce TBS-pre PBO network films. The prepared TBS-pre PBO network film was press-molded at 300°C and 5 MPa,

and subjected to heat treatment for 8 h at 450°C (Fig. 3a). In the case of the preparation of Pry-PBO network films, PYCC was used instead of TPC at PYCC/TMC molar ratios of 8:2 and 7:3 to produce TBS-Pry-prePBO network gels, and the following treatment was conducted in the same manner as TBS-pre PBO network films (Fig. 3b).

Preparation of phosphoric-acid-doped PBO and Pry-PBO network films

The PBO network films were immersed in 99% phosphoric acid at 100°C for 2 days. To remove excess phosphoric acid, the resultant PA-PBO network films were washed in methanol and vacuum dried at 80°C. PA-Pry-PBO network films were fabricated in a similar manner using 99% phosphoric acid at 80°C. The thickness of the resulting film was ~100 μm.

Evaluation of the physical properties of PBO and Pry-PBO network films

The apparent densities of the PBO network and Pry-PBO network films were calculated with the weight and volume of the films. The porosity of the PBO network film was calculated with reference to the density of PBO fiber (1.54 g/cm^3)[25] and the apparent densities using the following Equation (1). For Pry-PBO network films, no information for the density of Pry-PBO fiber was available. However, formula weight of the repeating unit of Pry-PBO (237.2) is similar to that of PBO (236.2). Therefore, using the density of PBO fiber, porosity of the Pry-PBO network film was calculated similar to that of PBO network film.

Porosity
$$= (1 - \text{PBO network apparent density/ PBO fiber density (1.54 g/cm}^3)) \times 100 \quad (1)$$

For thermogravimetric analysis (Thermo Plus TG8 120/SD, Rigaku Co., Ltd.), samples were heated to 800°C at a temperature increase rate of 10 °C/min under a nitrogen flow (100 mL/min). Viscoelasticity analyses were performed (DMA1, Mettler Toledo Co., Ltd.) with heating in air from 40°C to 450°C at a temperature increase rate of 10 °C/min.

Evaluation of the physical properties of phosphoric-acid-doped PBO and Pry-PBO network films

The phosphoric acid contents of the PA-PBO network and PA-Pry-PBO network films were calculated with reference to the original film weight, using Equation (2). Phosphoric acid doping levels were calculated with molar ratio of phosphoric acid and benzoxazole unit using the following Equation (3).

The phosphoric acid contents

$$= \frac{The\ phosphoric\ acid\ doped\ film\ weight\ - The\ original\ film\ weight}{The\ original\ film\ weight} \quad (2)$$

Phosphoric acid the doping level

= molar ratio of phosphoric acid/ molar ratio of benzoxazole unit (3)

A 4294A precision impedance analyzer (Keysight technologies, Co., Ltd., Santa Rosa, CA, USA) was used to perform impedance measurements from 30°C to 150°C in the frequency range from 40 Hz to 10 MHz, with ambient pressure, and without humidification for the PBO network, PA-PBO network, and PA-Pry-PBO network films, with Nafion™ films also being analyzed for comparison. The film was sandwiched between two platinum ribbons. The conductivity was calculated from the following: area of small platinum ribbon, thickness of film and impedance.

Results and Discussion

Films of the preparation of the PBO network film and Pry-PBO network film are shown in Fig. 4. By volatilizing chloroform in the polymerizing solvents from TBS-pre PBO network gel and TBS-Pry-pre PBO network gel, a uniform TBS-prePBO network film and TBS-Pry-prePBO network film could be produced. Thereafter, a thin and uniform PBO network film and Pry-PBO network film having a thickness of approximately 100 μm were obtained via drying, heat press molding, and heat treatment. Infrared absorbance (IR) spectra showed characteristic peaks originating from amide bonds, and the peak of tert-butyldimethyl introduced as a protective group could be confirmed in TBS-prePBO network film and TBS-Pry-prePBO network film as shown in Fig. S1 and S2, respectively. However, in the IR spectrum measurement after the heat treatment of TBS-prePBO network film and TBS-Pry-prePBO network film, peaks of the amide bond and the protective group disappeared, and peaks derived from the oxazole ring and C=N were observed as shown in Fig. S1 and S2, respectively. Additionally, as shown in Fig. 5a, no weight loss was observed in the thermogravimetric analyses of PBO network film at 400°C from 350°C, the temperature at which weight loss occurs upon formation of the oxazole ring.[4] These results showed that the PBO network film and Pry-PBO network film could be produced via TBS-pre PBO network film and TBS-Pry-pre PBO network film.

The appearance of the resulting PBO network film and Pry-PBO network films are uniform and no voids of size are present in the visible-light order. In addition, no micron-order and submicron-order voids were observed in the surface and tensile fracture surfaces of the prepared PBO network film using scanning electron microscopy (Fig. S5). Similar results are observed for the Pry-PBO network films. Furthermore, the calculated apparent densities and porosities of the PBO network films are shown in Table 1. An increase in apparent density and decrease in void fraction are observed with decreasing TPC content. Similar results are observed for the Pry-PBO network films, as shown in Table 1.

The tensile test results of PBO network film are shown on Table1. PBO network film was composed of a rigid PBO segment, but its elastic modulus was several GPa because of its crosslinked porous structure. However, flexibility of the molecular chains is increased by rotation of the branching point. As a result, the elongation at break of the PBO network film was exhibited as several percent. The elastic modulus did not improve even when the apparent density increased, and PBO network film with TPC/TMC = 8/2 showed the highest elastic modulus and strength. Although the density of PBO network film increases with increasing composition of TMC, the length of the linear segments decreases and the flexibility of the molecular chains increases. Consequently, PBO network film with TPC/TMC = 8/2 exhibits the highest mechanical properties. This tendency was the same in Pry-PBO is noted in Table 1. Thermogravimetric analysis results for the PBO network films are shown in Fig. 5a. For all the monomer ratios the 5%-weight-loss temperature is ≥570°C, demonstrating the excellent heat resistance of PBO network films. The dynamic viscoelasticity analysis results for the PBO network films are shown in Fig. 6a. Storage moduli above 1 GPa are maintained up to 450 °C, the highest temperature investigated, for all monomer ratios. This demonstrates that the mechanical properties of the PBO network films do not deteriorate at high temperatures. Thermogravimetric analysis results for Pry-PBO network films are shown in Fig. 5b. For both monomer ratios, the 5%-weight-loss temperature is ≥470°C, demonstrating the excellent heat resistance of Pry-PBO network films. The dynamic viscoelasticity results for the Pry-PBO network films are shown in Fig. 6b. Storage moduli above 1 GPa are maintained up to 450 °C for both monomer ratios. This demonstrates that the mechanical properties of Pry-PBO network films do not deteriorate at high temperatures. Furthermore, to examine the durability, cycle tests of heating at 450°C and cooling to 25°C under nitrogen atmosphere were conducted. The results are shown in Fig. S3 and Fig. S4. The elastic modulus of PBO network film did not change even in the repeated heat test as shown in Fig. S3. Tensile strength of PBO network film retained about 80% value in the

repeated heated test as shown in Fig. S4. The results indicated that PBO network film has heat resistance and durability. Pry-PBO network films also had heat resistance and durability as well.

After immersion in phosphoric acid, weight increases of ≥2.8 times based on the original film weight are observed, as shown in Table 1. The PA doping level (molar ratio of phosphoric acid vs. benzoxazole unit) is also shown in Table1. Since voids exist in the PBO network film, it was found that a relatively large PA doping level was obtained when compared with PBI membranes.[26, 27] Thus, phosphoric-acid-impregnated films (PA-PBO network films) were successfully prepared. Furthermore, even after methanol washing, a 1.4-fold (or higher) weight was maintained owing to the phosphoric acid residue. Data for PA-Pry-PBO network films are shown in Table 1. After immersion in phosphoric acid, the weight, increased ≥3.0 times based on the original film weight, is observed. As voids exist in the Pry-PBO network film as well, a relatively large doping level was obtained in the Pry-PBO network films. Thus, phosphoric-acid-impregnated films (PA-Pry-PBO network film) were successfully prepared using this method. Furthermore, even after methanol washing, a 1.2-fold (or higher) weight increase is still observed owing to the retained phosphoric acid.

Impedance analysis results for PBO network and methanol-washed PA-PBO network films are shown in Fig. 7. The conductivities of the PBO network films were as low as 1.0×10^{-9} S/cm at 150°C. This result showed that the PBO network films exhibit poor conductivities prior to phosphate doping. However, after phosphate doping and methanol washing, the conductivity of the film (the methanol-washed PA-PBO network film prepared with a TPC/TMC ratio of 7:3) was 3.65×10^{-3} S/cm at 150°C. This result showed that after phosphate doping and methanol washing, the conductivities enhanced greatly. In addition to the fact that the conductivities do not decrease without humidity control, they also increased with increasing temperature. Furthermore, the conductivities do not decrease even over 80 °C.

Next, the conductivities of PBO network and PA-PBO network films were compared with those of Nafion™ (Fig. 8). Nafion exhibited a drastic reduction in electrical continuity above 80 °C, whereas the PA-PBO network films exhibited no such degradation of conductivity. Thus, film conductivity in the case of the PA-PBO network film prepared with a TPC/TMC ration of 7:3 was improved to 6.53×10^{-2} S/cm by phosphoric acid content, resulting in conductivities comparable with those of Nafion™ at a high temperature of 150 °C. The PA-PBO network film prepared at TPC/TMC of 7:3 showed the highest conductivity both with and without methanol washing. As shown in Table 1, the largest amount of phosphoric acid in the PBO network was observed in TPC/TMC =

9:1, and not in TPC/TMC = 7:3. Similar results have reported for the PA-doped tetrazole-base membranes.[28] PA-doped tetrazole-base membranes studies[30] have reported that not only the PA doping level is large but also pKa values of membranes are small to exhibit high proton conductivity of PA-doped tetrazole-base membranes. Since the pKa of the rigid segment of PBO network in this study is -0.13 [29] and is smaller compared to the value of phosphoric acid (1.85) [30], proton conduction between phosphates and molecular chains was more likely than proton conduction between phosphates. Therefore, the higher proton conductivity is exhibited by PBO network having a higher proportion of PBO segments per unit volume i.e., higher density. Therefore, PBO network with the highest density TPC/TMC = 7/3 exhibited the highest proton conductivity.

The impedance analysis results for the methanol-washed PA-Pry-PBO network films are shown in Fig. 9, and the conductivities of the PA-Pry-PBO network films and Nafion™ are shown in Fig. 10. The introduction of pyridine rings to the network was performed to increase the density of basic moieties. As a result, the PA-Pry-PBO network films exhibit higher conductivities than the PA-PBO network films. In addition, the conductivities of the PA-Pry-PBO network films do not decrease, even above 80 °C. Accordingly, the highest conductivity of 2.09×10^{-1} S/cm is observed at 150 °C for the PA-Pry-PBO network film prepared at PYCC/TMC = 7:3, and it is higher than that of Nafion™. Thus, these results demonstrate that the conductivity of PBO network films can be improved by introducing basic moieties to the structure. Moreover, this result shows that the obtained film can be used at a higher temperature than that at which Nafion™ can be used.

Conclusions

PBO network films were successfully produced using a precursor-mediated strategy, and they were found to exhibit heat resistance irrespective of the monomer ratio employed. The conductivities of the PBO network films were as low as 1.0×10^{-9} S/cm at 150°C but were dramatically improved upon impregnation with phosphoric acid to 3.65×10^{-3} S/cm at 150°C. The PBO network film prepared with a monomer ratio of 7:3 and doped with phosphoric acid exhibited a conductivity of 6.53×10^{-2} S/cm at 150°C, which is higher than that of Nafion™. In addition, a Pry-PBO network film, in which a monomer with a pyridine ring was introduced, impregnated with phosphoric acid exhibited conductivities of 1.05×10^{-2} and 2.09×10^{-1} S/cm at 150°C before and after methanol washing, respectively, which are higher than the corresponding values for the PBO network film.

Data availability statement

The data that supports the findings of this study are available in the supplementary material of this article.

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Table 1 Density, porosity, mechanical properties, phosphoric acid contents and phosphoric acid doping level for PBO network and Pry-PBO network films

	PBO network			Pry-PBO network	
TPC/TMC, PYCC/TMC	9/1	8/2	7/3	8/2	7/3
Apparent density (g/cm^3)	0.80	0.86	0.94	0.83	0.88
Porosity (%)	48	44	39	46	43
Modules (GPa)	1.4±0.4	3.0±0.2	2.2±0.5	1.4±0.2	0.9±0.1
Breaking strength (MPa)	33.1±4.9	83.5±15.7	40.9±10.8	25.5±9.80	32.1±13.9
Breaking elongation (%)	3.3±0.6	4.7±1.4	3.0±1.4	2.7±1.3	5.0±1.9
Phosphoric acid / network[*1]	3.7	3.5	2.9	3.2	3.0
PA doping level[*2]	9.0	8.4	6.9	7.7	7.2
Phosphoric acid / network[*1] of Methanol-washed film	1.5	1.5	1.4	1.6	1.2
PA doping level[*2] of Methanol-washed film	3.6	3.7	3.5	3.9	3.0

*1 The phosphoric acid contents was calculated with reference to the original film weight, using the following Equation.

$$The\ phosphoric\ acid\ contents = \frac{The\ phosphoric\ acid\ doped\ film\ weight\ -\ The\ original\ film\ weight}{The\ original\ film\ weight}$$

*2 The PA doping level was calculated using the following Equation.

$$The\ PA\ doping\ level = \frac{The\ phosphoric\ acid\ content\ weight/98}{The\ original\ film\ weight/236.23\ or\ 237.22}$$

98 : molecular weight of phosphoric acid
236.23 : molecular weight of PBO unit
237.22 : molecular weight of Pry-PBO unit