

Semi-alicyclic sulfonated polyimide thin film with organized structure for high proton conductive electrolyte

○Yuze Yao¹, Hayato Watanabe², Mitsuo Hara², Shusaku Nagano³, Yuki Nagao¹
(¹*School of Materials Science, Japan Advanced Institute of Science and Technology,
1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan.*

²*Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8601, Japan.*

³*Venture Business Laboratory, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8601, Japan.)*

¹*Tel: +81-761-51-1541, Fax: +81-761-51-1149, E-mail: ynagao@jaist.ac.jp*

Abstract

Alkyl sulfonated polyimide (ASPI) thin films with a molecular ordered structure can exhibit high proton conductivity because of a lyotropic liquid crystalline property. Based on previous studies, the proton conductivity and molecular order of ASPI increase with increasing the average molecular weight.^[1] However, our newly synthesized semi-alicyclic sulfonated polyimide thin film composed of 1,2,3,4-cyclopentanetetracarboxylic dianhydride (CPDA) and 3,3'-bis-(sulfopropoxy)-4,4'-diaminobiphenyl (3,3'-BSPA) showed high proton conductivity and an organized structure. The obtained polymer was characterized by ¹H NMR spectrum. The average molecular weight, which was measured by GPC, was 9300. The thin film achieved a high conductivity of $2.1 \times 10^{-1} \text{ S cm}^{-1}$ under 25 °C and 95% relative humidity (RH). We compared this value with other ASPI with comparable molecular weight and found this work showed highest conductivity. Grazing-incidence small-angle X-ray scattering (GISAXS) revealed that apparent scattering was observed in the out-of-plane direction as the humidity increased. The scattering position shifted toward the higher d value. This indicates that a lamellar structure was formed in a high RH region by a lyotropic liquid crystalline property. Although a π - π interaction reduces by the introduction of the semi-alicyclic CPDA from the aromatic backbone, we could observe the formation of an organized structure. This formation of the organized structure could improve proton conductivity

1. Introduction

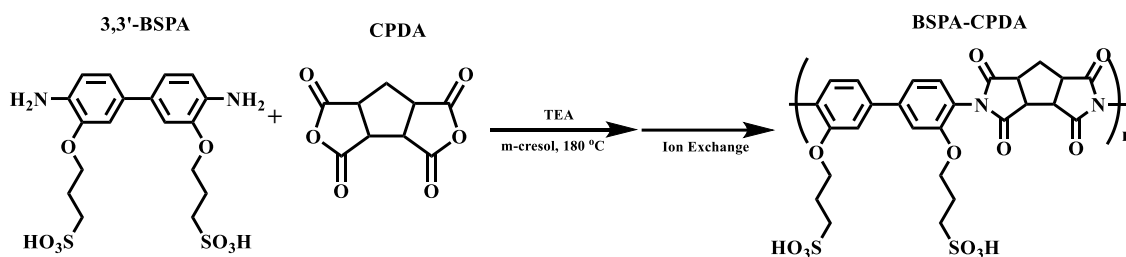
Polymer electrolyte fuel cells (PEFCs) are widely regarded as a new generation of energy conversion systems owing to their advantages such as high efficiency, high energy density, and environment friendly, which can replace fossil fuels in automotive applications and civilian power sources^[2]. Polymer electrolyte membranes (PEM) are important components of PEFCs which originated from their excellent proton conductivity, prevention of electron transport, and penetration of fuels and oxidants^[3]. Nafion, perfluorosulfonic acid (PFSA) has been extensively acted as electrolyte material for PEFCs due to their remarkable proton conductivity, excellent chemical and physical stability with a wide range of humidity and temperature. However, some defects such as high cost and methanol permeability triggered us to design suitable electrolyte material, which can replace Nafion to establish next generation system by PEFCs^[4-5]. Comparing other reported materials, alkyl sulfonated polyimides (ASPI) can be elected as most promising candidates because of their good chemical stability and high proton conductivity. ASPI has a hydrophobic main chain and a hydrophilic side chain, when it interacts with water molecules, it can form a liquid crystal structure and even forming an ion channel which can facilitate proton transport^[6]. The formation of ordered structure for fully aromatic ASPIs depends on higher molecular weight. However, studies on the effects of introducing aliphatic ring structures into polyimide backbones on molecular order and proton conductivity are still relatively rare. With these in mind, we design a new semi-alicyclic sulfonated polyimide to investigate those properties.

2. Experimental

2-1. Polymer synthesis

The monomer, 3,3'-bis(sulfopropoxy)benzidine (3,3'-BSPA), can be synthesized according to previous report^[7]. The polycondensation reaction between diamine monomer (3,3'-BSPA) and another dianhydride monomer 1,2,3,4-Cyclopentanetetracarboxylic Dianhydride (CPDA) was performed by a typical one-step polymerization method to afford sulfonated polyimide (BSPA-CPDA) in scheme 1. The synthesis of BSPA-CPDA can be considered successful after confirming the obtained product by NMR and FT-IR. The molecular weight of the final product was measured by gel permeation chromatography (GPC), which are $M_n = 4300$ and $M_w = 9300$, respectively.

Scheme 1. Synthesis of BSPA-CPDA.



2-2. Characterization

The following experiments were performed on the polymer thin film to confirm the properties.

- Proton conductivity measurement: Electrochemical impedance spectroscopy will be used to test proton conductivity
- Water uptake measurement: Quartz crystal microbalance (QCM) will be used to measure water uptake.
- Ordered structure evaluation: Grazing-Incidence Small-Angle X-ray Scattering (GISAXS) will be used to evaluate the ordered structure of thin film.

3. Results and discussion

3-1. Analysis of proton dissociation behavior on sulfonic acid group

The molecular states of the sulfonic acid group of BSPA-CPDA thin film were analyzed by RH controlled in situ FT-IR. The obtained spectra are shown in Figure 3-2 (a). The absorption attributed to the O = S = O asymmetric stretching vibration ($\nu_{\text{asym}}(\text{S}=\text{O}_{\text{asym}})$) of the sulfonic acid group (SO_3^- with protons dissociated (or bonded to oxonium ions)) was observed at 1030-1040 cm^{-1} . The peak area of $\nu_{\text{asym}}(\text{S}=\text{O})$ under different RH conditions was recorded as $S_x(\text{SO}_3^-)$, and the peak area of $\nu_{\text{asym}}(\text{S}=\text{O})$ at 0% RH was recorded as $S_0(\text{SO}_3^-)$. The proton dissociation (PD (%)) rate of the sulfonic acid group under each humidity condition can be calculated by Formula 3-1.

$$\text{PD (\%)} = (S(\text{SO}_3^-) - S_0(\text{SO}_3^-)) / (S_{95}(\text{SO}_3^-) - S_0(\text{SO}_3^-)) \quad 3-1$$

The obtained PD value and water uptake value are made as a function of RH and the image was shown in Figure 3-2 (b). It can be observed that PD showed a clear 2-stage increase trend with increasing RH. When the relative humidity was less than 20%, the rapid growth of PD indicates that the sulfonic acid group starts to absorb water and ionize. When the RH reaches 20%, the PD growth rate decreases and continues to increase at this rate. When RH reaches 40%, PD almost stops increasing until RH reaches 60%. At this time, the ionization rate of the sulfonic acid group was about 70%. When the RH exceeds 60%, the PD starts to increase rapidly in the second stage until the RH reaches 80%, and then remains almost unchanged. At this time, the sulfonic acid group was considered to be completely ionized.

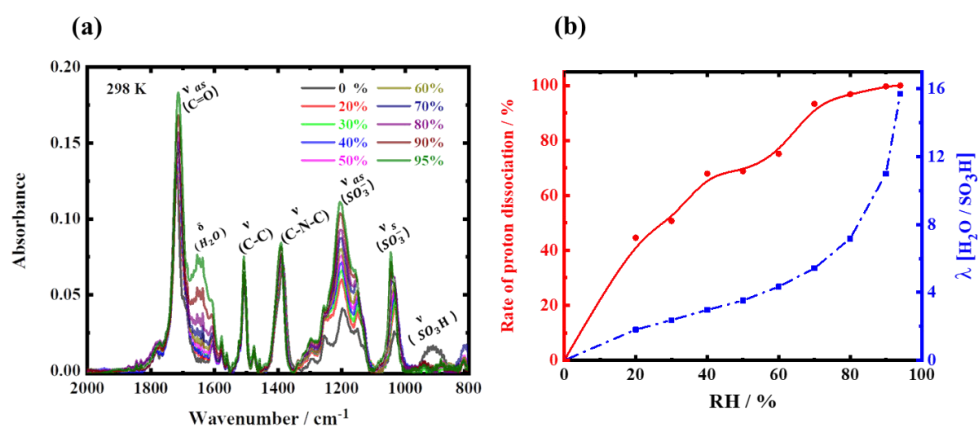


Figure 3-2. (a) *in-situ* FT-IR under humidity control absorption spectra of BSPA-CPDA thin film and (b) Humidity dependent PD value and water content for BSPA-CPDA thin film.

3-2. Structural analysis of BSPA-CPDA thin film

In order to investigate the internal structure of the thin film, structural analysis of BSPA-CPDA thin film in a humidified state was performed by *in-situ* GI-SAXS measurement. Figure 3-3 (a) showed a two-dimensional imaging image of the BSPA-CPDA thin film. One-dimensional plots for in-plane and out-of-plane directions were shown in Figure 3-3 (b). The layer distance (d) value which calculated from this scattering and make it as a function of water uptake value was shown in Figure 3-10 (c). Results indicate that the thin film exhibits a humidity-dependent lamellar structure by a lyotropic liquid crystalline property. No apparent scattering peak was observed in the in-plane direction from 2D profiles. Therefore, the thin film exhibits a nematic lamellar phase. In the previous report, semi-aliphatic backbone of sulfonated polyimide reduced ch-pack interaction compared to the fully aromatic and planar backbone. Comparing to other ASPIs that have been reported, the d value of fully aromatic ASPI changes linearly, however that of semi-alicyclic ASPI changes stepwise. When water uptake value was larger than 7, the d value of the semi-alicyclic ASPI starts to increase linearly. At that time, obvious scattering peaks begin to appear in the 2D image corresponding to GISAXS.

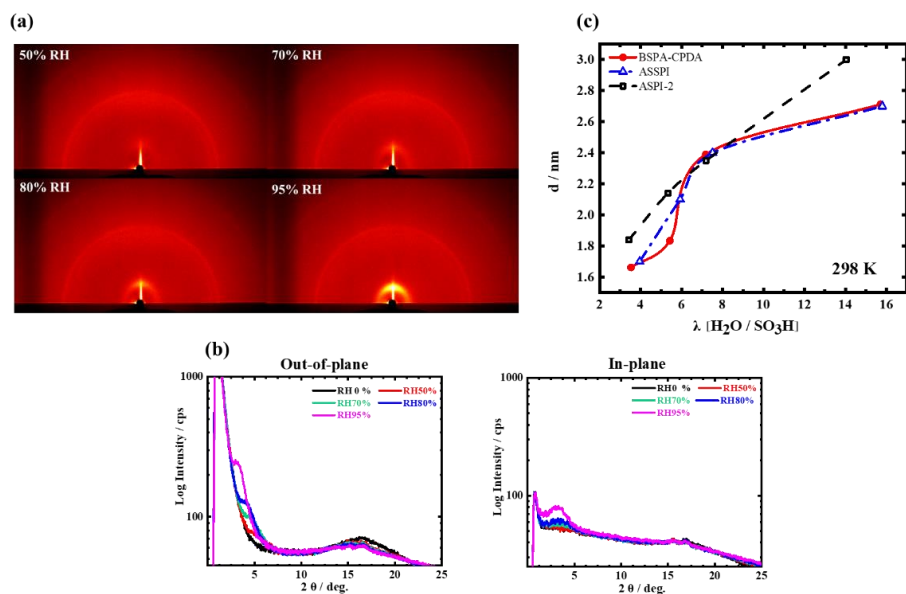


Figure 3-3. Humidity-dependent GI-SAXS results of BSPA-CPDA thin film, (a) 2D patterns and (b) 1D profiles; (c) Humidity-dependent layer distance of BSPA-CPDA, ASSPI and ASPI-2 thin films

3-3. Proton conductivity

For comparison, the humidity dependence of the proton conductivity of BSPA-CPDA and the other two ASPIs with similar molecular weight was shown in Figure 3-4. We have found that the proton conductivity of the BSPA-CPDA increased with increasing RH. Proton conductivity reached 0.2 S cm^{-1} at 95% RH. This value is the highest one among the reported sulfonated polyimide thin films with comparable molecular weight^[8-9]. Comparing the previous work with this work, both used similar semi-aliphatic backbones. Although the trends of water uptake and state of the proton dissociation were similar, the degree of the molecular ordering was different. The present sulfonated polyimide exhibited the apparent lamellar scattering from GISAXS profiles though the previous one did not in the low molecular weight. Therefore, we concluded that the highest proton conductivity of the BSPA-CPDA thin film was derived from the relatively higher degree of molecular ordering.

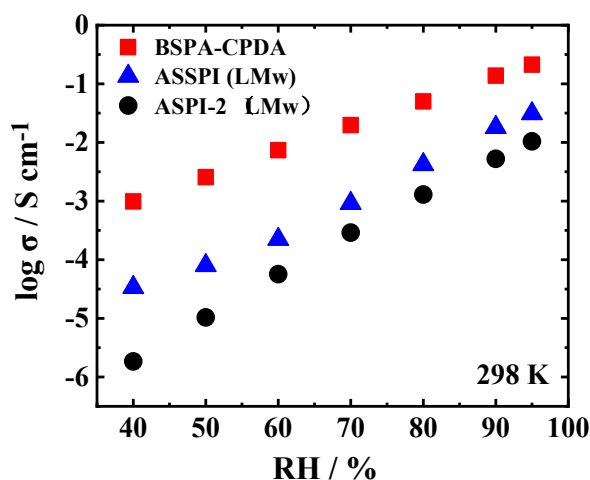


Figure 3-4. Proton conductivity of BSPA-CPDA thin film as a function of relative humidity RH at 298 K

4. Conclusions

Through this study we have reached the following conclusions:

- We have newly synthesized a sulfonated polyimide by using a cyclopentane structure in the molecular skeleton and got a lower molecular weight of 9300.
- The new polymer can exhibit a proton conductivity value of 0.21 S cm^{-1} . This is the highest proton conductivity compare to other ASPIs with comparable molecular weight.
- This is the first time we have observed lamellar organized based on the lyotropic liquid crystal property structure in low molecular weight ASPI.

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