Long-lived Intermediates in Radiation-induced Reactions of Alicyclic Polyimides Films

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1. Introduction

Since polyimides (PI) have been widely accepted as the membranes with excellent thermal and mechanical properties, the PI films can be applied for fuel cells as a thermally and mechanically stable substrate of polymer electrolyte membrane (PEMs). There have been several reports about sulfonated PI membranes for a state-of-the-art fuel cell PEMs to replace the commercially available Nafion® membranes [1].

Recently, we have been investigating alicyclic polyimides (A-PI) films consisting of aromatic tetracarboxylic acid dianhydrides and alicyclic diamines, which have excellent optical properties such as transparency with similar thermal and mechanical properties to those of aromatic PI films such as Kapton® [2]. On the other hand, we have been developing fuel cell PEMs using the well-established radiation-induced graft polymerization (grafting) and subsequent sulfonation techniques because this technique makes possible to introduce electrolyte polymer into thermally and mechanically stable polymer substrates such as poly(tetrafluoroethylene) (PTFE) and poly(ether ether ketone) (PEEK) [3, 4].

Since the alicyclic PI films should be a good substrate for grafting because of higher efficiency of radical formation at the aliphatic hydrocarbon units, which is the initiating species of radiation-induced grafting. In this paper, we report the first successful preparation of A-PI-based fuel cell PEM (A-PI-PEM) by radiation-induced graft polymerization of styrene to A-PI as a substrate (Scheme 1). The long-lived intermediates in irradiated A-PI films, some of which were only observed as a transient species in pulse radiolysis in solution, were observed in the UV-VIS spectra. Thus, we would also discuss about the relationship between radical species for initiating graft polymerization and long-lived intermediates detected by UV-VIS Spectroscopy.

2. Experimental

A-PI films with 25 µm in thickness prepared from pyromellitic dianhydrides (PMDA) and 4,4'-Diamino dicyclohexyl methane (DCHM) were provided from Teraoka Seisakusho Co., Ltd., JAPAN. A-PI films were irradiated with doses ranging from 50 to 1000 kGy (dose rate : 10 kGy/hr) using γ-rays from 60Co source (Takasaki, JAEA) under argon atmosphere at room temperature.

The pre-irradiated films were immersed in bulk styrene (Wako Pure Chemical Industries, ltd., 99%) or the solutions of styrene in organic solvents (50 vol. %) at temperatures ranging from 50 to 70 °C for grafting. Subsequently, the films having styrene grafts were sulfonated in 0.05 M CISO3H in C2H4Cl2 at 30 °C. A grafting degree (GD) was calculated from following equation, (Wg – W0) / W0 x 100, where W0 and Wg are

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the film weights before and after grafting, respectively. A sulfonation degree (SD) was calculated by titrimetric analysis with 0.02 M NaOH. A-PI-PEM was characterized with a JEOL JSM-5600 scanning electron microscope (SEM) with energy distribution X-ray spectrocope (EDS) as a sulfur probe on the A-PI-PEM [4, 5].

A-PI films were irradiated with a dose of 10 MGy using electron beam of Cockcroft-Walton Circuit (Takasaki, JAEA) under argon atmosphere at room temperature. The irradiated A-PI films were measured with UV-VIS Spectroscope (HITACHI, U-3310 spectrometer).

### 3. Results and discussion

#### 3-1. Preparation of PEMs

In order to prepare the graft-type PEMs consisting of poly (styrene sulfonic acid) (PSSA) grafts and A-PI, the radiation-induced graft polymerization of styrene into the A-PI substrates are first examined in terms of pre-irradiation doses, and grafting solvents and temperatures [6]. Figure 1 shows the plots of GD in bulk styrene at 60 ºC as a function of grafting time with different pre-irradiation doses ranging from 50 to 1000 kGy. The GD of the irradiated films with doses of 220 and 1000 kGy increased and gradually leveled off at around 10 hours, and reached to 70%, which was higher than that with a dose of 50 kGy. PI films are well-known as a radiation resistance material and previously, A-PI films were also observed no appreciable mechanical deterioration at least up to 1000 kGy. Thus, the absorbed dose of the films are fixed 220 kGy for further grafting experiments.

Table 1 shows the GD of styrene into A-PI films pre-irradiated with a dose of 220 kGy and grafted for 24 hr in various solvents at 60 ºC. Consequently, the poly styrene grafted A-PI (PI-g-PSt) with the controlled GD up to 70% were obtained by pre-irradiation with a dose of 220 kGy and changing
showed that polystyrene grafts accelerated the sulfonation reaction. Higher sulfonation degree in PI-g-PSt films with higher GD and the convergence to a quantitative yield of SD indicates the selective sulfonation to the polystyrene grafts. Thus, the PEM consisting of poly (styrenesulfonic acid) grafts and A-PI substrates (A-PI-PEM) with ion exchange capacity (IEC) of 0.54 ~ 2.6 mmol/g can be prepared by controlling SD in the range of 20 ~ 95%.

The PEM with IEC of 1.7 mmol/g was showed the proton conductivity of 0.061 S/cm and the water uptake of 41 %, which are comparable to those of Nafion®. Furthermore, the A-PI-PEM with IEC of 2.6mmol/g showed the highest proton conductivity of 0.26 S/cm with water uptake less than 100%. It should be noted that the A-PI-PEM was kept in mechanical and thermal properties from original A-PI films with excellent those properties even after the grafting and sulfonation processes. Thus, A-PI-PEM prepared by radiation-induced grafting and subsequent sulfonation reaction would be a promising candidate for fuel cell membranes.

3-2. Long-lived intermediates

When A-PI films were irradiated with a dose of 10 MGy in air at room temperature, the new absorption bands were appeared at the wavelengths in the range from 350 to 800 nm in UV-VIS spectra, as shown Figure 2.

The new absorption bands in the spectrum can be separated into four peaks with λmax at 380 (A), 420 (B), 600 (C), and 720 (D) nm. Under air atmosphere at room temperature, three peaks at 420, 600, and 700 nm were decayed nearly 100%, while the peak at 380 nm did not change after 3 hours. Aromatic PI films such as Kapton® have intrinsic color due to intra- and intermolecular of charge transfer, the new persistent peak at 380 nm should be olefin of alicyclic diamine units, which has already been characterized in the model compound [7].

Judging from the result of pulse radiolysis study of model compounds in solution, the long-lived intermediate at 720 nm is assigned to radical anion of the electron-accepting pyromellitic imide moieties in the aromatic PI films [8]. The other peaks at 420 and 600 nm decayed simultaneously within 3 hours. These peaks should be assigned to the radical species, which initiate the graft polymerization of styrene in the films because the decay speeds are almost the same as the grafting speeds and the decay speed of ESR signals of irradiated A-PI films at room temperature. It should be noted that longer lifetime of these species causes the higher probability of the contact with styrene monomer. As the results, the graft polymerization of A-PI films proceeds with grafting degrees up to 70%.

In summary, A-PI films were utilized as a substrate of radiation-induced polymerization to prepare PEM for fuel cells. We successfully prepared the A-PI-PEM by radiation-induced grafting of styrene into A-PI films and subsequent sulfonation. The obtained A-PI-PEM has higher ion conductivity and mechanical and thermal properties, compared with conventional PEM (Nafion®). Furthermore, the long-lived intermediates in irradiated A-PI films were observed in the UV-VIS spectra. In comparison with the decay profile of ESR spectra of irradiated A-PI films, the initiation radicals (B, C) and radical anion (D) can be characterized in terms of the graft polymerization mechanism of A-PI films.

References