

# Synchronous Crosslinking Imidized Polymer Electrolytes Having Fully Interpenetrating Polymer Networks (Full-IPNs) Structure for Application in Membrane Fuel Cell

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**Summary:** Polymer electrolyte films having fully interpenetrating polymer networks (Full-IPNs), composed of styrene-maleic anhydride alternating copolymer (PSMAN) and isobutylene-maleic anhydride alternating copolymer (PisoMAN), have been prepared by using 2,2'-benzidinedisulfonic acid (BDSA) as the imidizing crosslinker. The resulting films were characterized by using TGA, EA, IEC, water uptake, and proton conductivity. The purpose of this work deals with the synchronous crosslinking imidization reaction of between polymers as a synthetic method, in order to prepare novel heat-resistant polymer electrolytes for application in membrane fuel cell.

**Keywords:** crosslinking; high temperature materials; interpenetrating networks (ipn); polyelectrolytes; polyimides

## Introduction

Polymer electrolyte fuel cells (PEFCs) are among the most promising electrochemical devices for applications in clean-energy fields because of their high efficiency and low pollution levels, and the proton conducting membrane is a key component of the system. Currently, perfluorosulfonic acid polymers such as Nafion, Felemion, and Aciplex, are of great interest as the representative proton conducting materials for fuel cell applications because of their high proton conductivity and excellent physico-chemical stability.<sup>[1]</sup> However, they are not available for high-temperature because the conductive and mechanical properties deteriorate above 100 °C. The high cost of these materials is also a serious

drawback for practical applications of fuel cells. On the other side, high temperature operation was proposed as one of the ways to reduce CO poisoning, as well as to increase the oxidation rate of fuels, thus resulting in a higher efficiency of the fuel cell. As a result, intensive researches have been focused on developing new partially fluorinated and nonfluorinated polymers, especially sulfonated hydrocarbon polymers, such as sulfonated polyimides, sulfonated polysulfones and polyethers, stabilized polystyrene sulfonic acids, and phosphoric acid doped polybenzimidazole.<sup>[2–4]</sup> Among the sulfonated hydrocarbon polymers, we considered that the sulfonated polyimide (SPI) membranes are one of the promising candidates for fuel cell applications because of their high thermal stability, good mechanical strength and modulus, superior chemical resistance, and excellent film forming ability. However, they have a drawback of poor hydrolytic water-stability especially at higher temperatures due to hydrolytic decomposition of imide rings. Accordingly, we have designed a new structure based on

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the concept of incorporating synchronous crosslinking imide linkage and fully interpenetrating polymer networks (full-IPNs) to SPI as an alternative way for improving the physico-chemical properties. In the present work, the synchronous crosslinking imidized membranes (SCIMs) were prepared with fully interpenetrating polymer networks, by combining styrene-maleic anhydride alternating polymer as a hard segment with isobutylene-maleic anhydride alternating polymer as a soft segment, using an imidizing crosslinker with sulfonate groups. We report the synthesis and electrolyte properties (IEC, water uptake, and proton conductivity) of SCIMs with a full-IPN structure.

## Experimental Part

### Materials

Styrene-maleic anhydride (PSMAN; Mw 350,000) and isobutylene-maleic anhydride (PisoMAN, Mw 325,000) alternating copolymer were purchased from ALDRICH Chemical Co., Milwaukee, 2,2'-Benzidinedisulfonic acid (BDSA) was purchased from the Tokyo Chemical Industry Co., Tokyo, Japan and was purified by dissolution in a triethylamine aqueous solution and then recrystallized twice from ethanol solution prior to use. Dimethyl sulfoxide (DMSO, Aldrich, 99.5%) and triethylamine (TEA, Aldrich, 99.5%) were used as a solvent without further purification.

### Measurements

The chemical structures of the prepared membranes were characterized with a FTIR spectroscope (Digilab FTS-80; Bio-Rad, Richmond, CA). Thermogravimetric analysis (TGA) was performed to estimate the thermal stability of the membrane with DuPont 951 thermogravimetric analyzer at a heating rate of 10°C/min under a continuous nitrogen flow of 50 ml/min in a temperature range of 30°C to 800°C. All the specimens were dried in vacuum for 24 hr before measurement. The ionic-exchange capacity (IEC) was mea-

sured by classical titration using NaOH and HCl solutions. The proton conductivity was measured using four-point probe electrochemical impedance spectroscopy over the frequency range from 1 Hz to 1 MHz (Model IM6e, Zahner). The membranes ( $2.0 \times 2.0 \text{ cm}^2$ ) and two blackened platinum plate electrodes were set in a Teflon cell. The distance between the two electrodes was 2.0 cm. The cell was placed in a thermocontrolled humidity chamber to measure the temperature dependence of the proton conductivity. The water uptake was gravimetrically measured from the dried and humidified membranes as follows. The membranes were dried in a vacuum oven at 60°C for 12 hr and then immersed in liquid water at room temperature. After 24 hr, the membrane was then wiped dry and quickly weighed. The water uptake (W) was calculated from

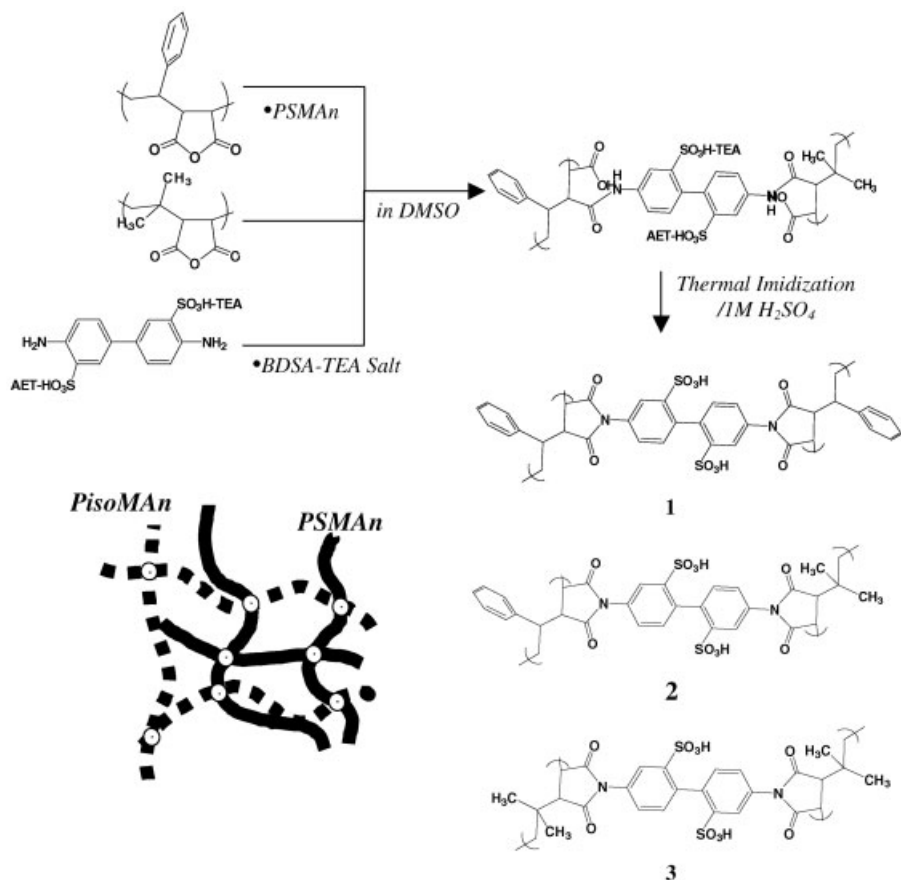
Water Uptake (%)

$$= ((W_s - W_d)/W_d) \times 100$$

where,  $W_s$  and  $W_d$  are the weights of the wet and dry membranes, respectively.

## Results and Discussion

The synchronous crosslinking imidized membranes (SCIMs) with fully interpenetrating polymer networks (Full-IPNs), composed of styrene-maleic anhydride alternating polymer (PSMAN) and isobutylene-maleic anhydride alternating polymer (PisoMAN), have been prepared by using 2,2'-benzidinedisulfonic acid-triethylamine (BDSA-TEA) salt. The synthesis of SCIMs was performed by two-pot system as shown in Scheme 1. First, the polyamic acid (PAA)/DMSO mixtures, composed of two polymers (PSMAN/PisoMAN) and BDSA-TEA salt, were carefully cast on a glass plate, and then the plates were placed in a vacuum oven at 60°C for 48 hr to slowly remove most of the solvent. SCIMs with different Full-IPNs were synthesized by changing the molar ratio of PisoMAN to PSMAN added. The films were thermally



### Scheme 1.

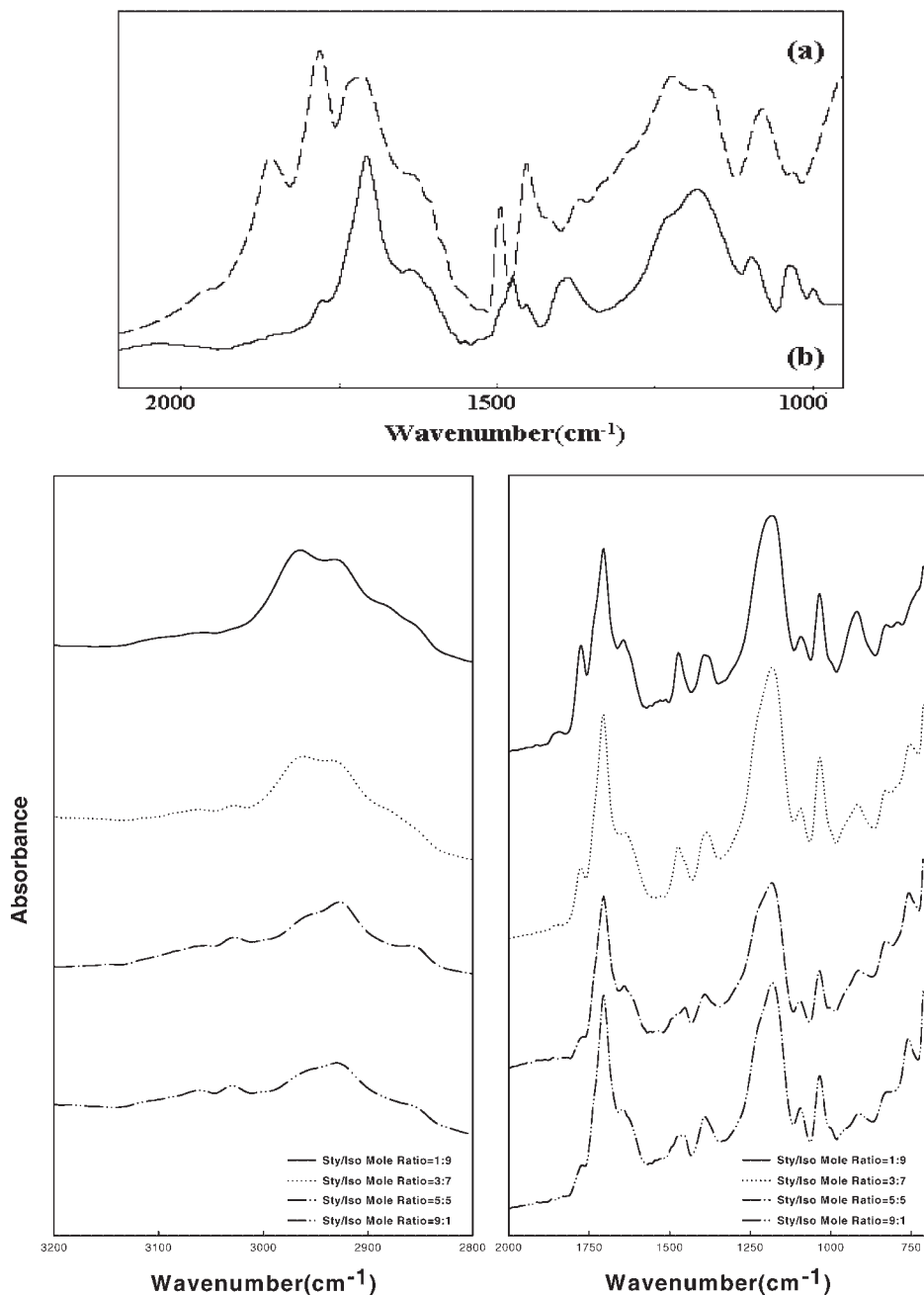
Syntheses route of synchronous crosslinking imidized membrane (SCIM) of fully IPNs composed of (1) styrene-styrene crosslinked imide segments, (2) styrene-isobutylene crosslinked imide segments, and (3) isobutylene-isobutylene crosslinked imide segments.

imidized with increasing temperature at 150 °C for 12 hr, 180 °C for 6 hr, and finally 240 °C for 1 hr under vacuum to remove residual solvent. The resulting membranes were detached from the glass plate, and then immersed into 1 M H<sub>2</sub>SO<sub>4</sub> overnight so that the salt form of BDSA was converted into acid form, followed by washing with deionized water several times until it reached neutral pH. Finally, the membrane is composed of three types of crosslinked imide segment of type 3 to 1, as shown in Scheme 1.

To confirm the chemical structure of the SCIMs of Full-IPNs, FT-IR spectroscopic measurements were carried out. A repre-

sentative FT-IR spectrum of the synthesized SCIMs of Full-IPNs is shown in Figure 1. As can be seen in Figure 1, the formation of the imide rings was confirmed by the absorption peaks at 1780 cm<sup>-1</sup> (C=O symmetric stretching), 1721 cm<sup>-1</sup> (C=O asymmetric stretching), and 1380 cm<sup>-1</sup> (C-N stretching), as compared with the nascent anhydride polymer, respectively. In addition, no peaks at 1848 cm<sup>-1</sup> and 1779 cm<sup>-1</sup> related to the anhydride absorption were also observed, which also could be assigned to the formation of imide ring completely.

From the growths of the peaks intensity at 2962 and 2873 cm<sup>-1</sup> (C-H asymmetric

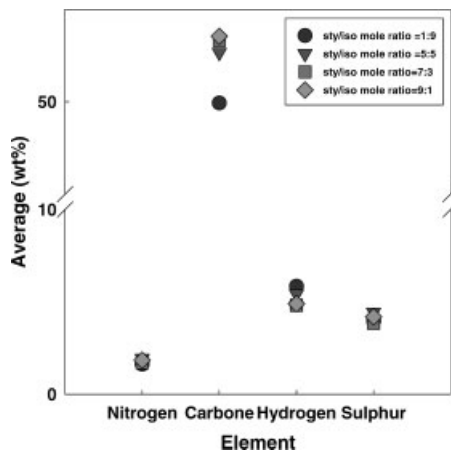


**Figure 1.**

FT-IR spectra of (a) the nascent polymer, (b) SCIM of Full-IPNs, and SCIMs with different IPNs.

and symmetric stretching of C-(CH<sub>3</sub>)<sub>2</sub> group) according to mole ratios of PISO-MAN, it can be considered that the synchronous crosslinking imidized mem-

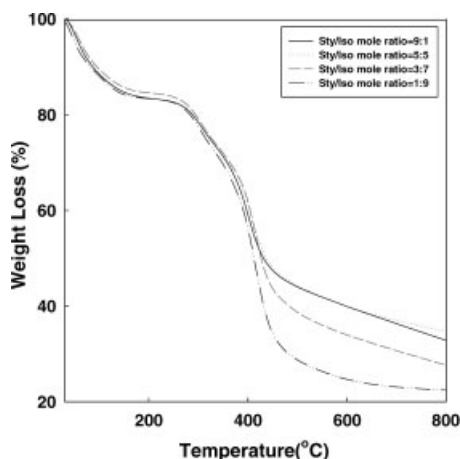
branes (SCIMs) were prepared with fully interpenetrating polymer networks, by combining styrene-maleic anhydride alternating polymer as a hard segment with



**Figure 2.**  
Element analysis of SCIMs with different IPNs.

isobutylene-maleic anhydride alternating polymer as a soft segment, using an imidizing crosslinker with sulfonate groups. This observation is supported by the element analysis result of SCIMs of Full-IPNs in Figure 2. The reason is because the amount of carbon and hydrogen increases gradually with increasing the mole ratio of PISOMan, while that of sulfur and nitrogen remains the same.

On the other hand, the synthesized SCIMs showed higher thermal stability with increasing styrene segment content, as shown in Figure 3, and they have

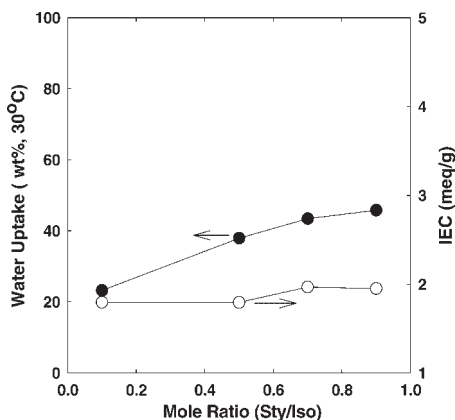


**Figure 3.**  
TGA curves of SCIMs with different IPNs.

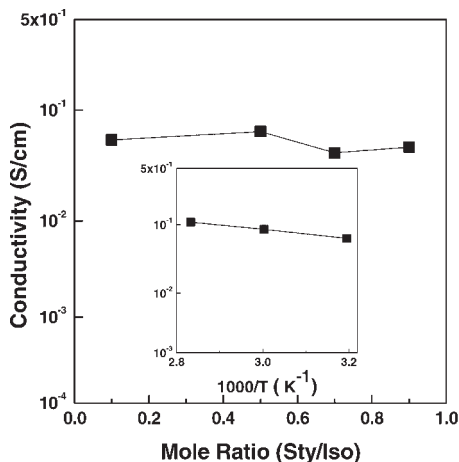
two-step degradation. The first step occurred at around 300 °C and the second step of thermal degradation took place at 400 °C. The degradation of the first step could be assigned to the sulfonic acid decomposition and possibly loss of tightly bound water,<sup>[5]</sup> while the degradation in the second step is due to main chain decomposition. The overall thermal decomposition temperature of the second step for the SCIMs synthesized was slightly lower than that of the conventional polyimides that they are usually decomposed at around 500~600 °C.<sup>[6,7]</sup>

In addition, as can be seen in Figure 4 and 5, SCIM of Full-IPNs showed higher water absorption and IEC values with increasing styrene segment content, whereas the change in the proton conductivity of that was not remarkably.

Generally, the electrolyte properties, such as water uptake, IEC, and proton conductivity, are strongly dependant on temperature, relative humidity, and acidity. In fact, the proton conductivity of the resulting membranes increased from 0.065 to 0.11 S cm<sup>-1</sup> with increasing ambient temperature as can be seen in Figure 3. Therefore, the above results might be due to a variation of physical property such as free volume and bulkiness in the membrane by hindering effect of a bulky styrene segment. Accordingly, it could be con-



**Figure 4.**  
Water Uptake and IEC of SCIMs with different IPNs.



**Figure 5.**

Proton conductivities of SCIMs with different IPNs.

cluded that the electrolyte properties, such as water uptake and IEC, strongly depend on the morphological characteristics as a key variable in determining performance under the same sulfonation condition.

## Conclusions

In our previous work, a series of the synchronous crosslinking imidized membranes (SCIMs) were prepared and evaluated as novel polymer electrolytes. In addition, the membranes showed very good water stability and high proton conductivities of  $2.0 \text{ S cm}^{-1}$  in water at  $120^\circ\text{C}$ , despite their high ionic exchange capacity ( $1.4 \sim 1.9 \text{ mequiv g}^{-1}$ ). Accordingly, we have designed a new structure based on the concept of incorporating synchronous crosslinking imide linkage and fully interpenetrating polymer networks (full-IPNs)

to polymer electrolytes as an alternative way for improving the physico-chemical properties. SCIMs were prepared with fully interpenetrating polymer networks, by combining styrene-maleic anhydride alternating polymer as a hard segment with isobutylene-maleic anhydride alternating polymer as a soft segment, using an imidizing crosslinker with sulfonate groups. By changing the composition ratio of styrene and isobutylene segments, the morphological properties of SCIMs with fully interpenetrating polymer networks have been designated and characterized by using TGA, EA, and electro-physical properties such as ionic exchange capacity, proton conductivity, and water uptake. Experimental results showed that the synthesized membranes showed higher thermal stability and water uptake with increasing styrene segment content, while the electrolyte properties (IEC and proton conductivity) were little difference between them.

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