

## 술폰화 폴리이미드의 전도도와 가수분해 안정성을 높이기 위한 새로운 접근

### Novel approach to increase the conductivity and hydrolytic stability of sulfonated polyimides

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#### INTRODUCTION

Fuel cells are identified as the most feasible energy source with minimal amount of noxious emissions. Among the various kinds of fuel cells, PEMFC is the forerunner in the field of fuel cell research<sup>1</sup>. In PEMFC, the polymer membranes are used as the electrolyte. Commercially predominant ionic membrane Nafion<sup>®</sup>, has few drawbacks. Hence many arylene main chain polymers like poly sulfones<sup>2</sup>, PEEK<sup>2</sup>, polybenzimidazole<sup>2</sup>, polyimides<sup>2</sup> were tried in fuel cells. Among other polymers, polyimides has many advantages, still, the main drawback associated with polyimides is their hydrolytic stability, which is very sensitive to their chemical structure. Hence a detailed study on the various aspects of the hydrolytic stability is much warranted.<sup>3</sup>

In this study a series of six-membered polyimides were synthesized by altering the non-sulfonated diamine monomers with increase in the number and size of substituent groups and their effect on properties are studied in detail.

#### EXPERIMENTAL

##### *Synthesis of random copolyimides*

A series of six membered polyimides using NTDA, PTDA as anhydrides, BDSA as sulfonated diamine and non-sulfonated diamine comonomers with different chemical structure (cf. Figure 1) were synthesized by chemical

imidization method.

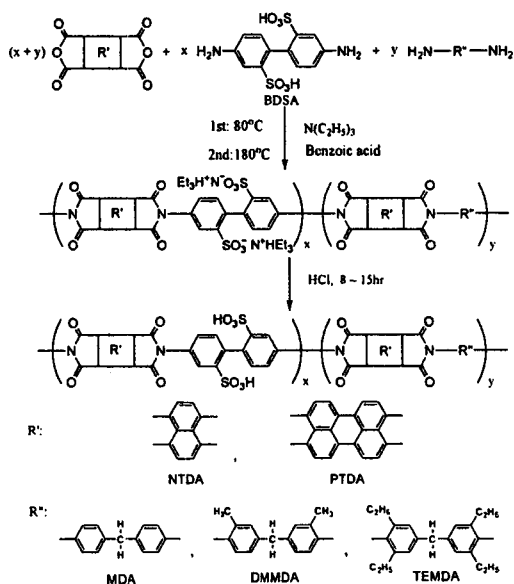


Figure 1. Synthetic scheme of sulfonated polyimides in naphthalenic systems.

## RESULT AND DISCUSSION

### *Spectral analyses*

The chemical structures of synthesized polyimides were confirmed by FT-IR, which is shown in Figure 2.

### *Solubility of sulfonated polyimides*

All the polyimides are soluble in m-cresol. The solubility increased with increase in the number and bulkiness of substituent group. The increase in the size and the number of substituent groups prevent the close packing of polymer chains and thus increase the solvent polymer interaction accounting for the increased solubility. Moreover the substitution in the ortho position to diamine prevent the formation of hydrogen bridges between the carbonyl group of the anhydride and the hydrogen of the diamine phenyl ring which increase the flexibility of the system and thus leading to increased solubility. (Table 1)

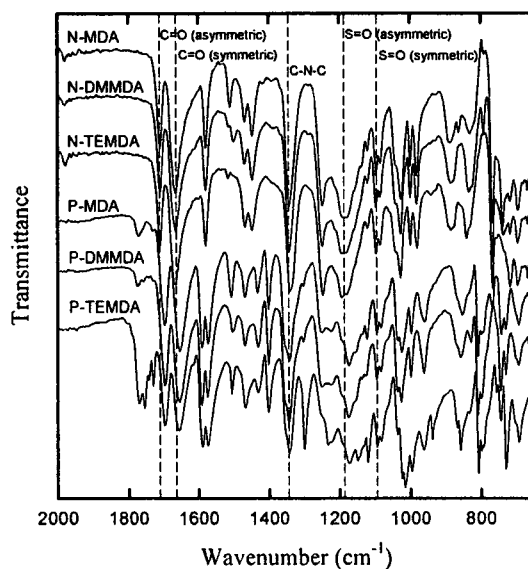


Figure 2. FT-IR spectra of sulfonated polyimides.

Table 1. Solubility of sulfonated polyimides

Polyimide	m-Cresol	NMP	DMAc	DMSO
NTDA-BDSA/MDA (1/1)	○	×	×	△
NTDA-BDSA/DMMDA (1/1)	○	△	○	○
NTDA-BDSA/TEMDA (1/1)	○	○	○	○
PTDA-BDSA/MDA (1/1)	○	×	×	△
PTDA-BDSA/DMMDA (1/1)	○	×	×	×
PTDA-BDSA/TEMDA (1/1)	○	△	△	○

#### *Thermal property*

All the polyimide thin films exhibited three-step degradation pattern. The first weight loss was due to the loss of absorbed moisture. The second step of degradation corresponds to the degradation of aromatic sulfonyl groups. The third step indicates the decomposition of the polyimide backbones. All the polyimides

showed thermal stability upto 500 °C. The thermal stability decreased with increase in the bulkiness and the number of substituent groups

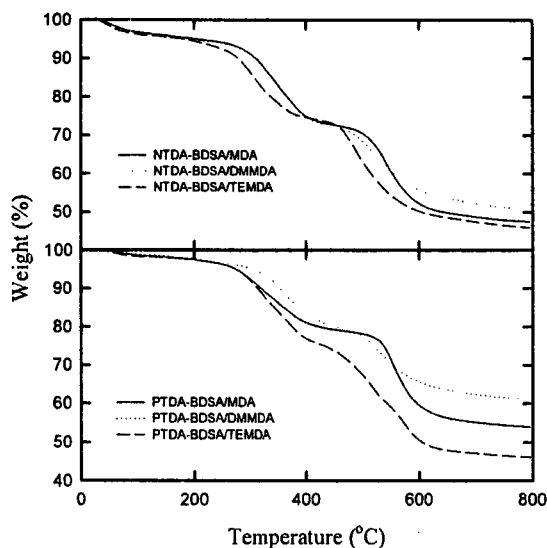


Figure 3. Thermal properties of sulfonated polyimides.

#### *IEC and Water uptake of sulfonated polyimides*

The water uptake and IEC values depend on the amount of sulfonyl groups present in the polymer. Both water uptake and IEC decreased with increase in the molecular weight of the non-sulfonated diamine which increases with the size and the number of substituent groups. With increase in the molecular weight number of sulfonyl groups in a particular weight fraction will decrease leading to low IEC and water uptake. Polyimides based on PTDA exhibited lower IEC and water uptake due to the higher molecular weight of PTDA than the NTDA.

#### *Hydrolytic stability*

The polyimides with more substituents showed increased hydrolytic stability. (Table 2) This must be due to flexibility of the polymer chain rendered by the substituents. As reported, flexibility increases the molecular relaxation and hence

increases the membrane stability<sup>4</sup>. Moreover the alkyl substituents are electron donating groups and hence it increases the nucleophilicity of the diamine which counter the nucleophilic attack of OH groups which lead to degradation.

Table 2. Water uptake, IEC and hydrolytic stability of sulfonated polyimides

Polyimide	thickness ( $\mu\text{m}$ )	water uptake (%)	IEC (mequiv/g)	hydrolytic stability		
				temp. ( $^{\circ}\text{C}$ )	time (h)	stability
N- MDA	13.87	38.5	1.76	80	80	brittle
N-DMMDA	27.85	32.3	1.72	80	110	good
N-TEMDA	34.10	23.7	1.12	80	110	good
P- MDA	35.00	35.1	1.64	80	110	Somewhat brittle
P-DMMDA	25.32	27.8	1.58	80	110	good
P-TEMDA	30.64	23.3	1.13	25	-	brittle

### Conductivity

Nafion<sup>®</sup>115 showed high conductivity at low temperatures than polyimides due to high swelling and hydrophilic/hydrophobic phase separation. With increase in temperature the conductivity rapidly increased in the case of polyimides with more substituent groups. (Table 3) These substituents lead to irregular packing thus increasing the free volume. Free volume in the non-sulfonated segment augment the water uptake in turn the conductivity of the polymer<sup>5</sup>. Moreover water gets trapped in these voids and the evaporation of these trapped water is suppressed by rigid polyimide chains<sup>6</sup>. These trapped water account for the proton conduction at high temperature. This result is significant because the high conductivity is achieved despite low water uptake and IEC compared to MDA based polyimides. In polyimides having substituents, due to the increased free volume water molecules can easily diffuse and this accounts for high conductivity. This can be inferred from the slope of polyimides and Nafion<sup>®</sup>115 systems.

Table 3. Proton conductivity of sulfonated polyimides

Polymers	conductivity (S/cm)						
	30°C	40°C	50°C	60°C	70°C	80°C	90°C
N-MDA	-	-	0.0259	0.0538	0.0702	0.0790	-
N-DMMDA	0.0092	0.0101	0.0173	0.1213	0.2320	0.3137	0.3777
N-TEMDA	0.0044	0.0065	0.0087	0.0195	0.0210	0.1265	0.1403
Nafion <sup>®</sup> 115	0.0810	0.0989	0.1157	0.1338	0.1463	0.1606	0.1759

## CONCLUSIONS

The number and size of the substituent groups in the non sulfonated diamine was systematically varied, for the first time to increase the free volume and these polyimides showed increased conductivity despite low water uptake and IEC and also showed very high conductivity than Nafion<sup>®</sup>115. The substituent groups rendered high hydrolytic stability due to imparted flexibility and increased nucleophilicity. All the polyimides exhibited characteristic high thermal stability (> 470 °C) and hence these polyimides can be used in high temperature PEMFC.

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