

# Synthesis of New Sulfonated Copolyimides in Organic and Ionic Liquid Media for Fuel Cell Application

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**ABSTRACT:** New sulfonated copolyimides containing ether, carbonyl, and bulky naphthyl group in backbone were synthesized in two reaction media: organic solvent and ionic liquid media. For this purpose a new sulfonated diamine (BANBPDS) and an unsulfonated diamine (BANBP) was prepared through reactions of 4,4'-dichlorobenzophenone-3,3'-disulfonic acid, and also 4,4'-dichlorobenzophenone with 5-amino-1-sodium naphthoxide, respectively. Three series of sulfonated copolyimide with different sulfonation contents (40–80%) were prepared by reaction of the sulfonated diamine (BANBPDS) in companion with three unsulfonated diamines including BANBP, 4,4'-oxydianiline (ODA), and 1,8-diamino-3,6-dioxaoctane (DADO) with 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA). Two media were selected for preparation of copolyimides. Copolyimides synthesized in ionic liquid had

higher inherent viscosity and higher molecular weight in comparison with similar copolyimides that were synthesized via common organic solvent method. Incorporation of flexible groups in polyimide structures increased solubility and processability of the copolyimides. After characterization of polymers with common methods, their water uptake, water stability, ion exchange capacity (IEC), thermal behavior and stability, crystallinity, and morphology were studied. The polymers showed suitable properties including high thermal stability and ion exchange capacity, which were the basic requirements for application as fuel cell membranes. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1981–1992, 2012

**Key words:** polyimides; thermal properties; membranes; fuel cell; ionic liquid

## INTRODUCTION

During the past decades, significant attentions have been paid to polymer electrolyte membrane (PEM) fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) as clean energy sources for transportation, stationary, and portable power applications due to their high efficiency and low pollution to environment. PEM is a key constituent in PEMFC and DMFC systems and serves as a proton conductor and a fuel separator between anode and cathode. Among different candidates, perfluorosulfonate ionomers such as DuPont's Nafion membranes are the state-of-art commercially available PEMs with features of high proton conductivity and outstanding chemical stability.<sup>1,2</sup> However, some disadvantages such as large fuel crossover, lower operating temperature (less than 80°C), and the high cost critically limit their industrial application. Because of these deficiencies extensive efforts have been devoted to develop alternative PEMs based on sulfonated aromatic polymers.

Sulfonated polyimides (SPIs) with six-membered imide rings are one of the promising candidates of PEMs for fuel cell applications.<sup>3–15</sup> Polyimides have become one of the most important classes of high performance polymers due to their high thermal stability, good chemical resistance, and excellent mechanical properties. Among different high-performance polymers, polyimide materials are noted for their high thermal stability, solvent resistance, excellent insulating integrity, good mechanical strength, excellent dimensional stability, low coefficient of friction, high dielectric strength, low dielectric constant, low out gassing, and resistance to creep and wear. According to the mentioned properties, one of the recent usages of polyimides is as membrane for fuel cell and for gas separation. However, the commercial use of these polymers is often limited because of their poor solubility and too high softening or melting temperatures.<sup>16–23</sup>

One approach to increase the solubility and processability of polyimides is the introduction of flexible linkages or bulky units into their polymer chains. It has been commonly recognized that aromatic ether linkages inserted in aromatic main chains provide them a significantly lower energy of internal rotation. Generally, such a structural modification leads to lower glass transition temperature and crystalline-melting temperatures as well as major improvement

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in solubility and other processing characteristics of the polymers without greatly sacrificing other valuable polymer properties.<sup>24–29</sup>

On the other hand, six-membered ring polyimides are more difficult to prepare and cast into membranes because of their lower solubilities in common organic solvents. Six-membered ring anhydrides are more stable, but less reactive toward an amine group in respect to their five-membered analogs. Therefore, it is necessary to use catalysts in the reaction of such dianhydrides with diamines.<sup>30</sup> An acidic catalyst such as benzoic acid (BA) has been added in the first step, and it may promote the formation of the *trans*-isoimide. It has been proposed that a basic catalyst is then needed to convert the *trans*-isoimide into final imide.<sup>31</sup>

Ionic liquids (ILs) are fascinating solvents and their potential to substitute organic solvents in different areas of chemistry has been definitely established.<sup>32</sup> In some studies, polycondensation catalytic effect of ILs was observed, for instance, relatively high molecular weight polyimides were obtained in the absence of any added catalyst, and it was concluded that ILs act not only as solvents but also as catalysts.<sup>33,34</sup> In polycondensation of aromatic dianhydrides with aromatic diamines, solubility of starting materials could be enhanced by addition of imidazolium-type zwitterion which led to higher molecular weights of resulting polyimides.<sup>35</sup>

This article reports the synthesis of a novel sulfonated diamine, 4,4'-bis(5-amino-1-naphthoxy) benzophenone-3,3'-disulfonic acid (BANBPDS) and an unsulfonated diamine, 4,4'-bis(5-amino-1-naphthoxy) benzophenone (BANBP). Polycondensation reactions of 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) with combination of BANBPDS and one of the unsulfonated diamines (BANBP, or ODA, or DADO) with different molar ratios resulted in preparation of sulfonated copolyimides with different sulfonation content. These copolyimides containing carbonyl, flexible ether, and naphthyl bulky groups were prepared using common solvent method as well as ionic-liquid method to study the role of IL in imidization. Investigation of the properties of sulfonated copolyimides showed their basic capability for application as membranes of fuel cells.

## EXPERIMENTAL

### Starting materials

The 1-ethyl-3-methylimidazolium bromide (purity > 97%) was purchased from Fluka Company. The 4,4'-Oxydianiline (ODA), 1,8-diamino-3,6-dioxaoctane (DADO), 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA), 5-amino-1-naphthol (AN), 4,4'-dichloro benzophenone (purity > 99%), and other

chemical materials were purchased from Merck or Aldrich Chemical Company. DADO (purity > 98%) was used as received, while the ODA (purity > 99%) and AN (purity > 97%) were recrystallized with ethanol. NTDA (purity > 98%) was dried under vacuum at 170°C overnight. Dimethyl sulfoxide (DMSO) and *N*-methyl-2-pyrrolidone (NMP) were distilled over CaH<sub>2</sub> under reduced pressure and *m*-cresol over anhydrous P<sub>2</sub>O<sub>5</sub> as well.

### Monomer synthesis

Synthesis of 4,4'-dichlorobenzophenone-3,3'-disulfonic acid disodium salt (DCBPDS)

A typical procedure is as follows: 12.55 g (49.50 mmol) of 4,4'-dichlorobenzophenone and 30 mL of fuming sulfuric acid (30% SO<sub>3</sub>) were placed in a two-necked, round-bottomed flask equipped with a condenser, a nitrogen inlet tube, and a magnetic stirrer. The mixture was stirred at 110°C for about 30 h. The reaction mixture was cooled to room temperature and dissolved in 200 mL of ice water, and 90 g of sodium chloride was added to produce a white precipitate of the product. The powder was filtered, redissolved in 200 mL of deionized water, and neutralized to the pH = 6–7 with aqueous 2N sodium hydroxide. An excess of sodium chloride (90 g) was added to salt out the sodium form of the disulfonated monomer. The resulting white precipitate was filtered off, washed with saturated sodium chloride solution, and dried at 130°C in vacuum for 10 h. The crude product was dissolved in DMSO and filtered to remove the insoluble inorganic salt. The filtrate was distilled under reduced pressure and the residue was thoroughly washed with acetone and dried at 140°C in vacuum for 20 h. About 22.0 g of white product was obtained, yield: 97%. FTIR (KBr pellet, cm<sup>-1</sup>): 1021 (S=O, sulfonic acid, symmetric), 1068 (S=O sulfonic acid, asymmetric), 1241 (C—O—C), 1667 (C=O). <sup>1</sup>H-NMR spectrum (400 MHz, DMSO-d<sub>6</sub>, ppm): 8.20 (d,2H), 7.61 (dd,2H), 7.55 (d,2H).

Synthesis of 4,4'-bis(5-amino-1-naphthoxy)benzophenone 3,3'-disulfonic acid (BANBPDS)

To a dry three-necked flask equipped with a dropping funnel, a Dean-Stark trap and a condenser 10.55 g of AN (63 mmol), 2.52 g (63 mmol) of NaOH, 95 mL of DMSO, and 41 mL of chlorobenzene were charged. The reaction mixture was magnetically stirred and heated to 160°C for 4 h, and then 15 mL of chlorobenzene was added and reflux was continued for another 4 h to remove water from the reaction mixture completely. DCBPDS (12.74 g, 28 mmol) and 6.5 mL of DMSO were added to the reaction mixture, and it was heated to 170°C for about 30 h. After cooling to room temperature, the

mixture was filtered and the filtrate was precipitated in a large excess of acetone. The obtained product was filtered and washed with acetone for several times. It was then vacuum dried at 120°C overnight. The yield of reaction was about 72%.

The product (14.02 g, 20.02 mmol) was dissolved in 132 mL of water in a beaker with stirring. Then 3.95 g (40.04 mmol) of HCl (37%) was added to the mixture and it was stirred to form a precipitate. It was filtered and purified in a Soxhlet extractor with methanol and acetone consecutively overnight. The resulting brownish diamine dried at 130°C in vacuum oven overnight. The yield of reaction was about 70%. FTIR (KBr pellet,  $\text{cm}^{-1}$ ): 1027 (S=O, sulfonic acid, symmetric), 1085 (S=O sulfonic acid, asymmetric), 1248 (C—O—C), 1593 (C—N), 1651 (C=O), 3060 (CH, Aromatic), 3133–3431 ( $\text{NH}_2$ , OH).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ , ppm): 8.20 (d, 2H), 7.93 (dd, 2H), 7.46 (d, 2H), 7.38 (dd, 2H), 7.33 (d, 2H), 7.14 (dd, 2H), 7.10 (dd, 2H), 6.69 (d, 2H), 6.5 (d, 2H), 5.87 (s broad, 4H).

#### Synthesis of 4,4'-bis (5-amino-1-naphthoxy) benzophenone (BANBP)

Nearly 2.53 g (10 mmol) of 4,4'-dichlorobenzophenone, 25 mL of dry NMP, and 15 mL of dry toluene, and 3.44 g (21 mmol) of AN were placed into a 100-mL two-necked round-bottomed flask equipped with a Dean-Stark trap, a condenser, a nitrogen inlet tube, a thermometer, and a magnetic stirrer. Then 4.442 g (31.5 mmol) of  $\text{K}_2\text{CO}_3$  was added to the mixture and the reaction mixture was heated to 140°C for 6 h with continuous stirring. The generated water was removed from the reaction mixture by azeotropic distillation. The reaction temperature was raised to 165°C by removing more toluene, and kept at the same temperature for 20 h during this time. Then 100 mL of 5% NaOH was added to the reaction mixture and after filtration the mixture was washed repeatedly with a 5% NaOH solution and water. The obtained diamine was dried at 60°C in a vacuum oven overnight (yield 91%). FTIR (KBr pellet,  $\text{cm}^{-1}$ ): 1239 (C—O—C), 1595 (C—N), 1654 (C=O), 3047 (CH, Aromatic), 3363 ( $\text{NH}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ , ppm): 7.96 (d, 2H), 7.73 (d, 4H), 7.38 (d, 2H), 7.19 (dd, 2H), 7.17 (dd, 2H), 7.05 (d, 4H), 6.96 (d, 2H), 6.68 (d, 2H), 5.85 (s, 4H).

#### Synthesis of sulfonated copolyimides in triethylammonium salt forms

Sulfonated copolyimides were prepared in organic solvent (common method) and ionic-liquid media.

*Common method.* A typical procedure for the preparation of BANBPDS-ODA (50) copolyimide was as follows: to a 100 mL completely dried three-necked

flask were added 1.312 g (2 mmol) of BANBPDS, 10 mL of *m*-cresol, and 0.7 mL of  $\text{Et}_3\text{N}$  under nitrogen flow with stirring. After complete dissolving, 0.4 g (2 mmol) of ODA, 1.073 g (4 mmol) of NTDA, and 1 g (8 mmol) of benzoic acid were added to the flask. The mixture was stirred at room temperature for a few minutes and then heated at 80°C for 4 h and 180°C for 9 h. Next, 1.033 g (8 mmol) of isoquinoline was added to the reaction, and it was heated at 180°C for another 9 h. The reaction mixture was cooled to room temperature and precipitated into an excess of isopropyl alcohol. The precipitated copolyimide was collected by filtration and purified in a soxhlet extractor with methanol and then acetone overnight. The resulting polymer was dried in a vacuum oven at 100°C for 6 h and then at 150°C for 24 h. The same procedure was repeated for the synthesis of other copolymers based on ODA, DADO, and BANBP as unsulfonated diamines and with different degrees of sulfonation (40–80 mol %). Yields of the reactions were about 79–86%.

*Ionic-liquid method.* A typical procedure for the preparation of BANBPDS-ODA (50) copolyimide was as follows: into a two-necked flask equipped with magnetic stirrer, nitrogen gas inlet, and condenser 0.79 g (1.2 mmol) of BANBPDS and 0.42 mL of  $\text{Et}_3\text{N}$  under nitrogen flow was stirred for 1 h. After that, 0.24 g (1.2 mmol) of ODA, 0.64 g (2.4 mmol) of NTDA, and 5.24 g of 1-ethyl-3-methyl imidazolium bromide were poured into the flask. Then after 10 min stirring at room temperature, reaction temperature increased to 180°C gradually. After 10 h about 1.05 g of 1-ethyl-3-methyl imidazolium bromide was added to reaction mixture and let reaction stirred for 5 min later. Then reaction was cooled and product was added to excess amount of methanol. Precipitate was filtered and filtrate was soxhleted with methanol, water, and acetone consequently over night. The obtained product was dried at 150°C in vacuum oven for 24 h. The same procedure was repeated for the synthesis of other copolymers based on ODA, DADO, and BANBP as unsulfonated diamines and with different degrees of sulfonation (40–80 mol %). Yields of the reactions were about 82–91%.

#### Conversion of sulfonated copolyimides from triethylammonium salt to acid forms and their film formation

Sulfonated polyimide membranes were prepared by casting their DMSO solutions ( $\approx 5$  wt %) onto glass dishes and dried at 80°C for 10 h. The as-cast films were soaked in methanol at 60°C for 1 h to remove the residual solvent, and then were immersed into 1.0N hydrochloric acid at room temperature for 2 days. The resulting films were thoroughly washed with deionized water till the rinsed water became



neutral followed by drying in vacuum at 150°C for 20 h.

### Measurements

Infrared measurements were performed on a Bruker-IFS48 FTIR spectrometer (Ettlingen, Germany). Spectra of solids were carried out using KBr pellets. The  $^1\text{H}$  NMR spectra were recorded in  $\text{DMSO-}d_6$  solution using a Bruker Avance DPX 400MHz (GmbH, Germany). Tetramethylsilane (TMS) was used as an internal reference. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a Stanton Redcraft STA-780 (London, UK) in air at a heating rate of  $10^\circ\text{C min}^{-1}$ . The dynamic mechanical measurements were recorded on a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA) over a temperature range of 25–300°C at 1 Hz and a heating rate of  $10^\circ\text{C min}^{-1}$  (Surrey, UK). Inherent viscosities were measured by using an Ubbelohde viscometer in a concentration of  $0.5 \text{ g dL}^{-1}$  in NMP at 30°C. Molecular weight was determined by gel permeation chromatography (GPC). It was performed on a Waters 150-C instrument using Styragel columns and a differential refractometer detector. The molecular weight calibration was carried out using polystyrene standards. Calibration and measurements were made at a flow rate of  $1 \text{ mL min}^{-1}$ , DMF was used as solvent, and 1% (w/v) of LiBr was added to each sample before running. Morphological studies were performed using Tescan, SE Detector, model Vega XMU scanning electron microscope (SEM). The X-ray diffraction (XRD) was performed at room temperature on an X-ray diffractometer (Siemens model D 5000) using Ni-filtered  $\text{Cu K}\alpha$  radiation (40 kV, 25 mA) with scanning rate of  $3^\circ \text{ min}^{-1}$ .

IEC was measured by the widely used titration method: 0.2–0.3 g of dry sulfonated polyimides were cut into small pieces and immersed into saturated sodium salt solution with stirring for 2 days. The resulting solution was titrated with 0.01M sodium hydroxide solution using phenolphthalein as an indicator. The ion exchange capacity (IEC) value was calculated according to the following equation<sup>36</sup>:

$$\text{IEC}(\text{meq/g}) = \frac{V_{\text{NaOH}} \times C_{\text{NaOH}}}{W_{\text{dry}}}$$

where  $V_{\text{NaOH}}$  and  $C_{\text{NaOH}}$  refer to the volume and concentration of sodium hydroxide and  $W_{\text{dry}}$  refer to weight of dry membranes.

Water uptake (WU) measurements were carried out by immersing the membranes (0.2–0.3 g per sheet) into deionized water at 30°C for 24 h. Then the membranes were taken out, wiped with tissue

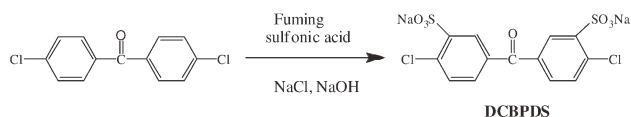
paper, and quickly weighed on a microbalance. Water uptake was calculated from:

$$\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100,$$

where  $W_{\text{dry}}$  and  $W_{\text{wet}}$  refer to the weight of dry and wet membranes, respectively.<sup>37</sup>

## RESULTS AND DISCUSSION

Polyimides derived from naphthalenic anhydrides (NTDA), or in general six-membered ring polyimides, are less strained and have been reported to exhibit better thermal and chemical stability, along with enhanced mechanical strength, in comparison with analogous five-membered ring counterparts. Unfortunately, NTDA exhibits low reactivity and does not form high-molecular-weight polyimides by common two- and one-step procedures in organic solvents including dimethylformamide (DMF), NMP, nitrobenzene, dimethylacetamide (DMAc), and *m*-cresol in the absence of any catalyst even at temperatures as high as 200°C.<sup>38</sup> Thus, the reaction of such monomers is usually carried out at 180–220°C and in the presence of carboxylic acid as a catalyst. Another drawback in syntheses of six-membered ring polyimides is their lower solubilities in common organic solvents. Useful methods and solvents have been developed in the recent years for preparation of chemicals. In polymer science, ionic liquids (ILs) are applied as solvents for polymerization processes and as constituents of polymeric materials. It has been assumed that one of the properties of the ILs that extend their application is their polarity, especially as solvents for ionic polymerization. Based on recent reports, it seems that in spite of their ionic nature, ILs are only moderately polar solvents and their estimated dielectric constant values are lower than some common solvents such as nitromethane or dimethylformamide. However, the high charge density in ILs, existence of hydrophobic (long alkyl chains) and hydrophilic (ionic groups) segments in ILs, ability of certain ILs to break hydrogen bonds and possibility of specific interactions of cationic or anionic components with growing species or monomers may lead to properties that do not exist in solution of common organic solvents. Therefore solubility of starting materials could be improved by performing of polycondensation reaction in ILs media which afford higher molecular weights of resulting polyimides.<sup>39</sup> Also, catalytic effect of ILs has been investigated in polycondensation, for instance high molecular weight polyimides were obtained in the absence of any added catalysts



**Scheme 1** Preparation of sulfonated salt of dichloro benzophenone.

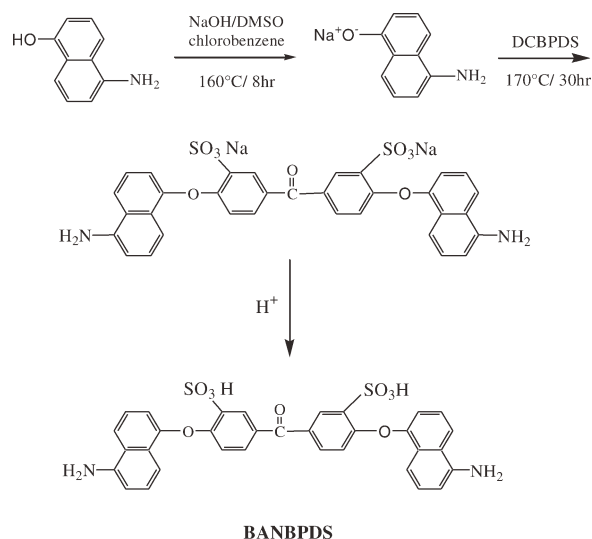
and it was concluded that ILs act not only as solvents but also as catalysts.

Introduction of sulfonated units into the backbone of six-membered ring polyimides (sulfonated polyimides) induces proton conductivity character to the final polymers while maintaining their suitable physical and chemical properties which are required for the preparation of fuel cell membranes.<sup>40–42</sup>

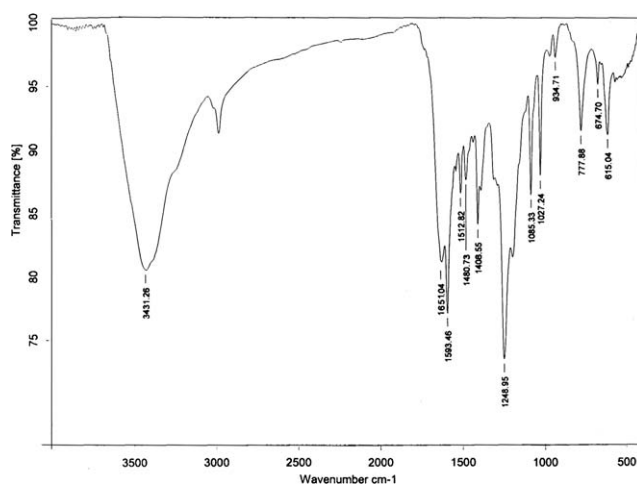
Modification of chemical structure of polyimides via introduction of new sulfonated and unsulfonated monomers into the backbone of polymers, and investigation of their structure–property is our main aim in this article. Therefore, we designed and prepared two diamines, a sulfonated (BANBPDS) and an unsulfonated diamine (BANBP), and polycondensed these monomers with a six-membered ring dianhydride (NTDA) to produce related sulfonated copolyimides. Sulfonic acid units situated in the backbone of these copolyimides are responsible for proton transfer and therefore ion exchange capacity of fuel cells.<sup>43,44</sup>

Thus, 4,4'-dichlorobenzophenone was sulfonated via electrophilic substitution reaction using fuming sulfuric acid and converted to 4,4'-dichlorobenzophenone-3,3'-disulfonic acid. Subsequently, reaction of this diacid with sodium hydroxide resulted sodium salt (DCBPDS) form of this diacid (Scheme 1).

On the other hand, 5-amino-1-sodium naphthoxide was prepared through reaction of 5-amino-1-naphthol with sodium hydroxide in DMSO and



**Scheme 2** Preparation of sulfonated diamine.

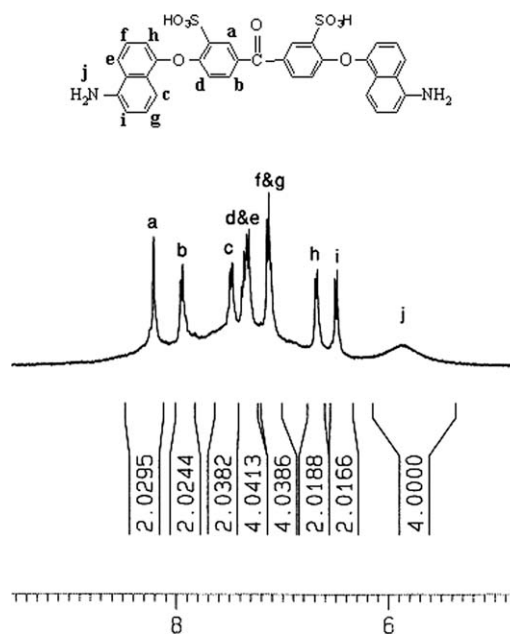


**Figure 1** FT-IR spectrum of BANBPDS.

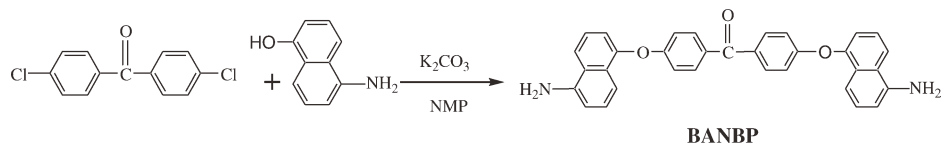
chlorobenzene as an azeotropic agent using Dean-Stark trap. Reaction of DCBPDS and 5-amino-1-sodium naphthoxide and subsequent acidification led to preparation of sulfonated diamine (BANBPDS) according to Scheme 2. The FT-IR and <sup>1</sup>H-NMR spectra of BANBPDS were shown in Figures 1 and 2, respectively.

In another reaction 4,4'-bis (5-amino-1-naphthoxy) benzophenone (BANBP) as the unsulfonated diamine was prepared via nucleophilic substitution reaction of 5-amino-1-naphthol with 4,4'-dichlorobenzophenone (Scheme 3). The FTIR and <sup>1</sup>H-NMR spectra of BANBP are shown in Figures 3 and 4, respectively.

To investigate the structural effect and the effect of sulfonation content on the final properties of polyimides, in addition to prepared unsulfonated



**Figure 2** <sup>1</sup>H NMR spectrum of BANBPDS.



**Scheme 3** Preparation of unsulfonated diamine BANBP.

diamine (BANBP), two commercially available diamines including 4,4'-oxydianiline (ODA) and 1,8-diamino-3,6-dioxaoctane (DADO) were used for the preparation of sulfonated polyimides. Thus, three series of sulfonated copolyimides with 40–80% sulfonation content were prepared via one-step polycondensation reactions of the sulfonated diamine (BANBPDS) in companion with one of the unsulfonated diamine (ODA, DADO, or BANBP) with NTDA as six-membered ring dianhydride in two media: organic solvent and IL media (Scheme 4). The sulfonation content of the copolymers was controlled by varying the molar ratios of sulfonated diamine (BANBPDS) versus unsulfonated diamines (ODA, DADO, or BANBP).

FTIR and  $^1\text{H}$  NMR spectroscopy were used for the characterization of the copolymers. In Table I the results of characterization data of the polymers (triethylammonium salt) were brought and the representative FT-IR spectrum of BANBPDS-ODA polyimide was shown in Figure 5.

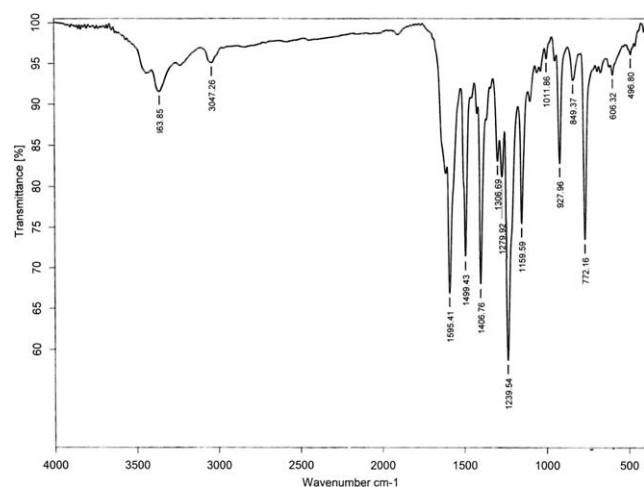
### Molecular weights

The inherent viscosity as a criterion for evaluation of molecular weights in two different methods of polyimide synthesis showed that IL allow to obtain higher-molecular-weight polyimides in the absence of any additional catalyst in comparison with common method (Table II). According to the obtained results, inherent viscosity of the polyimides prepared via IL method ( $0.78\text{--}0.90\text{ dL g}^{-1}$ ) was higher

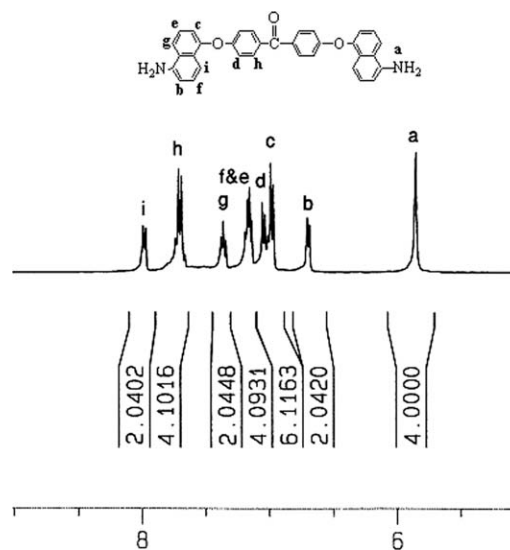
than the same polyimides prepared using common organic solvent method ( $0.46\text{--}0.50\text{ dL g}^{-1}$ ). Molecular weights of polymers were also determined using GPC method. The number-average molecular weights of polymers in common method were in the range of 26,300–31,200 with polydispersity index of 2.3–3.2, while they were about 37,500–44,400 with polydispersity index of 2.1–3.0 for copolyimides prepared via IL method. It was concluded that the ability of IL to act as activating agents has of great importance. Because molecular weight has profound effects on the final properties of polymers, therefore in the rest of the study the properties of copolyimides prepared through IL method were emphasized.

### Solubility

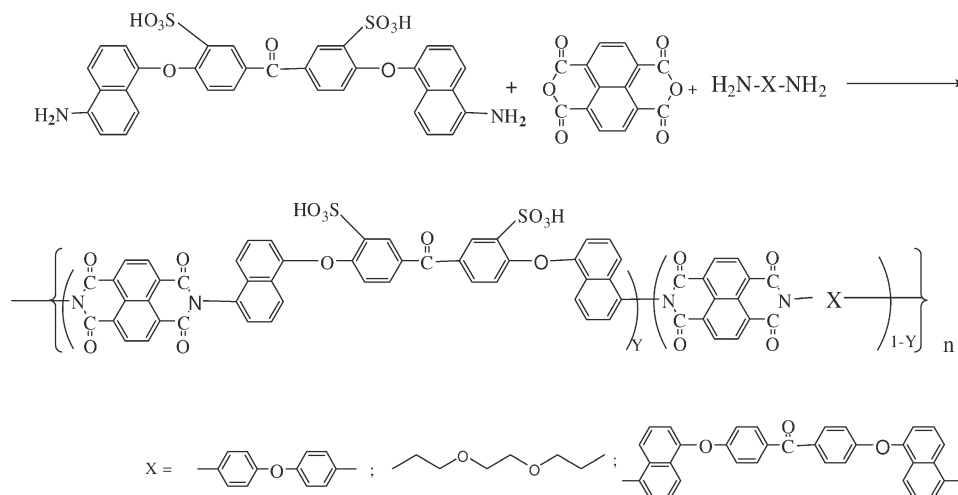
Normally, due to the high melting or glass transition temperatures and limited solubility of the polyimides in organic solvents, the processability of them is restricted. It has been known that parts of these problems originated from strong intermolecular donor/acceptor interaction of the imide functions that causes chain stiffness. Also, it has been found that introduction of flexible bond into the rigid polymer backbone is an effective method to enhance the solubility of these polymers while minimizing the deterioration of their physical properties.



**Figure 3** FT-IR spectrum of BANBP.



**Figure 4**  $^1\text{H}$  NMR spectrum of BANBP.



**Scheme 4** Preparation of sulfonated copolyimides.

However, the acidic form of the prepared copolyimides showed good solubility at ambient temperature in common dipolar solvents including NMP, DMAc, DMF, DMSO, and *m*-cresol. They were also partially soluble in THF and pyridine by heating. Presence of polar sulfonated units and flexible ether groups and oligo ethylene sequences were main important factors for improving the solubility of the prepared copolymers. Additionally, the presence of bulky naphthyl group in the backbones of copolymers due to disruption of symmetry and consequently close packing and chain-chain interaction improved the solubility of the copolymers. Also, solubility was increased by increasing the sulfonation content of the prepared copolyimides. Under similar conditions, DADO-based polyimides showed highest solubility among the prepared polyimides that was related to the presence of flexible ether groups and oligo ethylene units. Also, BANBPDS-based

polyimides were more soluble than ODA ones due to the existence of more flexible groups as well as bulky naphthyl group.

It should be mention that solubility of the polyimides prepared via IL method was slightly lower than the same polyimides prepared using common organic solvent method. This was related to the fact that interchain interaction by higher-molecular-weight polyimides increased and penetration of solvent decreased.

### Thermal properties

Thermal behavior of the polymers was studied using DSC and DMTA methods. The glass transition temperatures ( $T_g$ ) of copolymers were about 203–256°C derived from DSC (the midpoint of the change in slope of baseline) and also DMTA (decrease in storage modulus with increase in  $\tan \delta$ ) techniques.

**TABLE I**  
Polymer Characterization Data

Compound	IR (KBr) $\text{cm}^{-1}$	NMR(DMSO- $d_6$ ) $\delta$
BANBPDS-ODA(40)	3427(N-H, Str); 1786(C=O, Symm);	8.75 (SO <sub>3</sub> NH), 8.69 (NTDA);
BANBPDS-ODA(50)	1713(C=O, Symm); 1673(C=O, Asymm);	8.43 (Ph), 8.29 (Ph), 7.82 (Naph),
BANBPDS-ODA(60)	1344(C-N, Symm);	7.78 (ODA), 7.67 (Naph), 7.53 (ODA),
BANBPDS-ODA(70)	1082(S=O, Asymm); 1026(S=O, Symm)	7.28 (Ph, Naph), 6.81 (Naph),
BANBPDS-ODA(80)		6.55 (Naph), 3.06(CH <sub>2</sub> ), 1.17 (CH <sub>3</sub> )
BANBPDS-DADO(40)	3426(N-H, Str); 1767(C=O, Symm);	8.78 (SO <sub>3</sub> NH), 8.68 (NTDA), 8.43 (Ph),
BANBPDS-DADO(50)	1707(C=O, Symm);	8.30 (Ph), 7.82 (Naph), 7.77 (Naph), 7.67 (Naph),
BANBPDS-DADO(60)	1665(C=O, Asymm); 1341(C-N, Symm);	7.46 (Naph), 7.27 (Naph), 6.82 (Naph), 6.55 (Naph),
BANBPDS-DADO(70)	1084(S=O, Asymm); 1027(S=O, Symm)	3.97. (-CH <sub>2</sub> -O), 3.76 (-CH <sub>2</sub> -CH <sub>2</sub> -),
BANBPDS-DADO(80)		3.54, (CH <sub>2</sub> -NH-), 3.04 (CH <sub>2</sub> ), 1.17 (CH <sub>3</sub> )
BANBPDS-BANBP(40)	3418(N-H, Str); 1784(C=O, Symm);	8.78 (SO <sub>3</sub> NH), 8.73 (NTDA), 8.63 (Ph),
BANBPDS-BANBP(50)	1714(C=O, Symm);	8.56 (Ph), 8.30 (BANBP), 8.26 (Naph),
BANBPDS-BANBP(60)	1672(C=O, Asymm); 1345(C-N, Symm);	8.18 (BANBP), 7.88 (Naph), 7.83 (BANBP),
BANBPDS-BANBP(70)	1082(S=O, Asymm); 1024(S=O, Symm)	7.77 (Ph), 7.75 (BANBP), 7.73 (Naph),
BANBPDS-BANBP(80)		7.64 (BANBP), 7.52 (Naph), 7.50 (BANBP),
		7.35 (Naph), 7.30 (BANBP),
		7.20 (Naph), 6.80 (BANBP), 3.08 (CH <sub>2</sub> ), 1.17 (CH <sub>3</sub> )



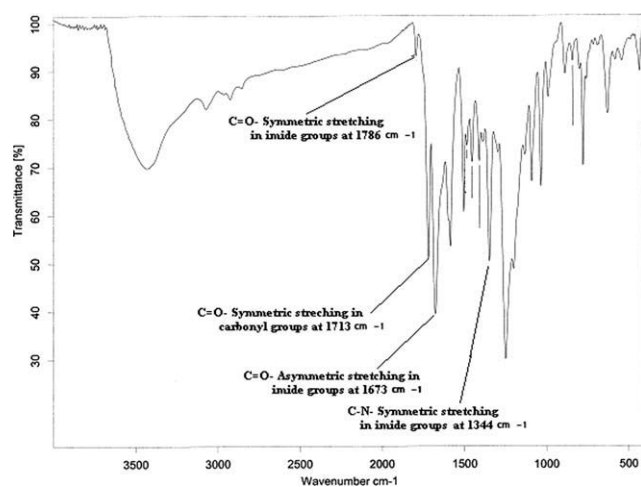


Figure 5 FT-IR spectrum of BANBPDS-ODA copolyimide.

A representative DSC and DMTA curve was shown in Figures 6 and 7, respectively. The presence of flexible ether units lowered the  $T_g$  of these polymers due to the reduced crystallinity that signifies better processability in respect to common polyimides.<sup>45</sup> ODA-based copolyimides showed highest and DADO-based copolyimides revealed lowest  $T_g$  among the prepared copolyimides which were related to flexible character of monomers. Also,  $T_g$  decreased by increasing the sulfonation content of polymers.

Thermal stability of the sulfonated polyimides was investigated by thermogravimetric analysis (TGA) in air at a heating rate of  $10^\circ\text{C min}^{-1}$ . All the sulfonated copolyimide exhibited a two-step degradation pattern. The first step of degradation that was observed around  $300^\circ\text{C}$  was corresponded to the

TABLE II  
Inherent Viscosity, IEC, and Water Uptake of Copolyimides

Compound	$\eta_{\text{inh}}^a$ (dL g <sup>-1</sup> )	$\eta_{\text{inh}}^b$ (dL g <sup>-1</sup> )	IEC (mequiv g <sup>-1</sup> )	Water uptake (%)
BANBPDS-ODA(40)	0.47	0.82	1.52	16
BANBPDS-ODA(50)	0.48	0.84	1.65	29
BANBPDS-ODA(60)	0.49	0.89	1.78	36
BANBPDS-ODA(70)	0.48	0.80	1.93	45
BANBPDS-ODA(80)	0.50	0.90	2.12	50
BANBPDS-DADO(40)	0.49	0.82	1.56	28
BANBPDS-DADO(50)	0.48	0.85	1.68	35
BANBPDS-DADO(60)	0.47	0.80	1.81	42
BANBPDS-DADO(70)	0.46	0.83	1.95	57
BANBPDS-DADO(80)	0.49	0.88	2.15	70
BANBPDS-BANBP(40)	0.48	0.78	1.46	20
BANBPDS-BANBP(50)	0.47	0.83	1.52	31
BANBPDS-BANBP(60)	0.46	0.78	1.65	38
BANBPDS-BANBP(70)	0.48	0.79	1.83	48
BANBPDS-BANBP(80)	0.47	0.87	1.95	55

<sup>a</sup> Inherent viscosity of copolyimide synthesized in organic solvent.

<sup>b</sup> Inherent viscosity of copolyimide synthesized in ionic liquid.

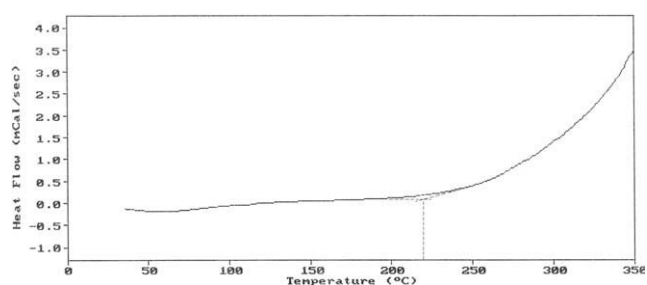


Figure 6 DSC curve of BANBPDS-DADO (70) copolyimide.

degradation of aromatic sulfonyl groups and also aliphatic units in DADO-based polyimides. As the sulfonated parts of the copolyimides are the weak units from the thermal stability point of view in these polymers, by increasing the sulfonation content of the copolymers, the mass loss at the first step was increased and also the degradation temperature decreased. The second weight loss was attributed to the decomposition of the polyimide main chain which showed thermal stability of the polyimide units up to  $430^\circ\text{C}$ .<sup>46,47</sup> The results were collected in Table III and a representative curve was shown in Figure 8.

The trend of thermal stability for similar polymers was: ODA-based > BANBP-based > DADO-based polyimides that were attributed to the rigidity of their structures.

In comparison, the thermal stability of the identical polyimides prepared via common solvent method showed decreasing of  $15\text{--}25^\circ\text{C}$  for  $T_0$  and  $3\text{--}7\%$  for char yield (Table III), that was another indication for diminishing of chain interactions due to decreasing of molecular weights.

The first step thermal degradation was adequately higher than required operation temperature for conventional fuel cells. Generally, sulfonated copolyimides were suitable choices to improve fuel cell performance to operate them at higher temperatures.

### Crystallinity

According to XRD analysis, all of the sulfonated polyimides (prepared from two different methods) were almost amorphous, however DADO- and BANBP-based polyimides were more amorphous than ODA-based ones (Fig. 9). The amorphous structure was mainly attributed to the presence of bulky naphthyl groups and flexible ether units which affected the crystallinity as well as packing order of the polymers. Also presence of oligo ethylene sequence was intensified this behavior in the related polymers. Generally, the amorphous nature of sulfonated copolyimides was favorable for high water absorption due to the fact that the water molecules can easily diffuse into the amorphous region with looser molecular packing.<sup>48,49</sup>



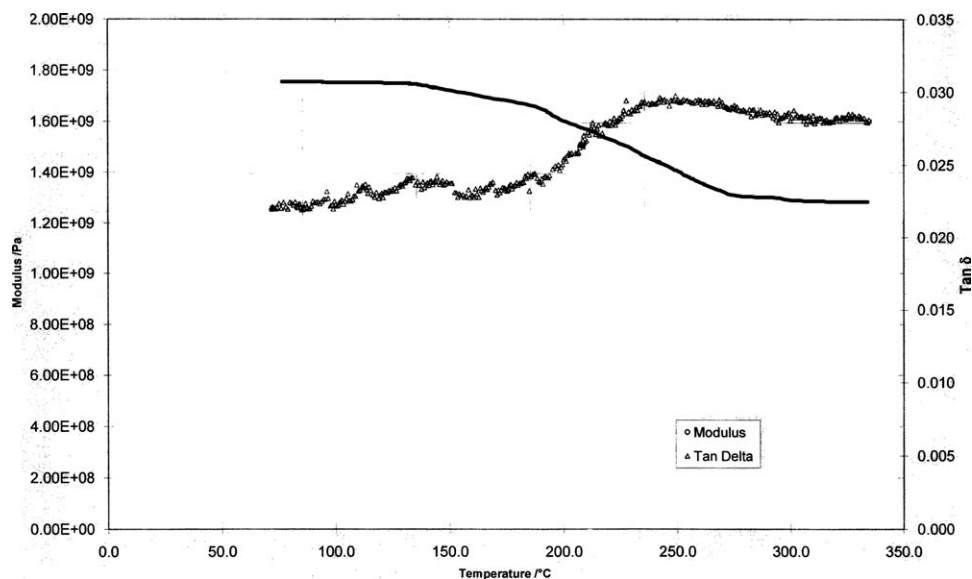


Figure 7 DMTA curve of BANBPDS-DADO (70) copolyimide.

### Water uptake

The water uptake of polyimide membranes was directly proportional to IEC of the polymer. Generally, the water sorption would increase by increasing the sulfonation content, however it does not necessarily mean that there is a constant increase between water uptake and sulfonation content. The sulfonic acid groups were responsible for water sorption and conductivity of membranes owing to ionic character of  $-\text{SO}_3\text{H}$  groups. Other factor affecting the water uptake is the structural feature of unsulfonated segment. Incorporation of flexible and bulky groups that reduce close packing as well as presence of hydrophilic group that increase water absorption, increase the water uptake of system. According to

the structure, DADO- and BANBP-based polyimides disclosed higher degree of water uptake than ODA-based polyimides under identical conditions.

Some properties of membranes including proton conductivity and mechanical properties strongly affect by water sorption of sulfonated polymer.<sup>50</sup> It has been revealed that membranes with more water uptake have high proton conductivity and lower mechanical properties. The water molecules diffuse into the polymer chains and cause the imide functions to hydrolyze leading to reduction of mechanical properties. Therefore, based on the structural design, the optimized amount of water uptake should also be considered for the membranes. The water sorption of prepared copolymers concerning the sulfonic acid content, were from 16 up to 70% (Table II) which showed reasonable water sorption in comparison with Nafion-117 (19% at 30°C).

The increased molecular weight of the similar polyimides resulted from preparation methods (via IL instead of common solvent method) had not profound effect on the water uptake behavior.<sup>51</sup>

TABLE III  
Thermal Properties of Copolyimides

Polymer	$T_g$ (°C)	$T_0$ (°C)	$T_{10}$ (°C)	$T_{max}$ (°C)	Char yield at 600°C (%)
BANBPDS-ODA(40)	256	340	495	540	63
BANBPDS-ODA(50)	250	320	479	531	61
BANBPDS-ODA(60)	242	315	467	522	60
BANBPDS-ODA(70)	230	300	456	514	58
BANBPDS-ODA(80)	223	295	442	505	55
BANBPDS-DADO (40)	234	312	460	502	55
BANBPDS-DADO (50)	229	301	445	498	53
BANBPDS-DADO (60)	220	294	432	488	50
BANBPDS-DADO (70)	213	283	419	475	48
BANBPDS-DADO (80)	203	277	410	465	46
BANBPDS-BANBP(40)	252	334	481	525	60
BANBPDS-BANBP(50)	246	313	463	517	59
BANBPDS-BANBP(60)	239	304	451	509	57
BANBPDS-BANBP(70)	224	298	440	496	56
BANBPDS-BANBP(80)	212	290	427	489	54

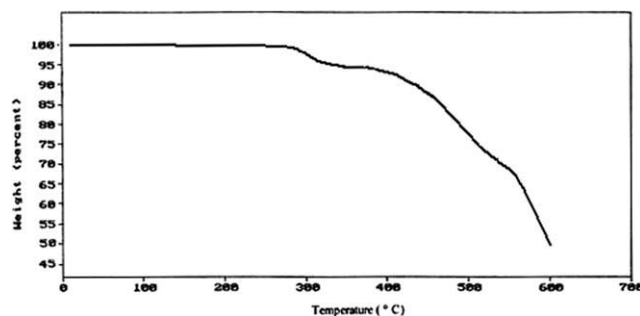


Figure 8 TGA curve of BANBPDS-DADO (70) copolyimide.

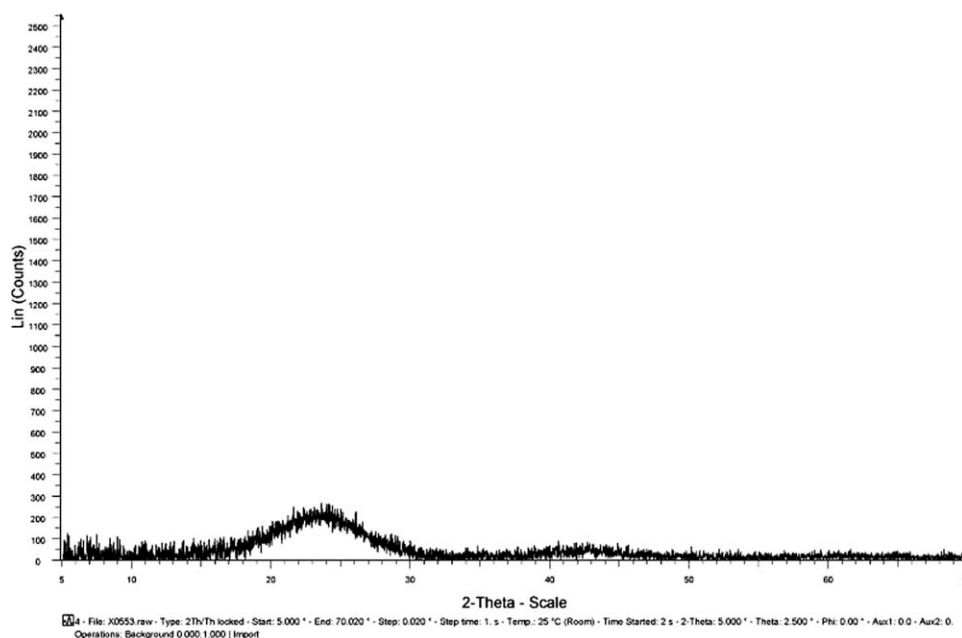


Figure 9 XRD of BANBPDS-BANBP (70) Copolyimide.

### Ion exchange capacity

Many important properties of the sulfonated polyimide membrane such as proton conductivity and water uptake depend on the IEC of the polymer. The IEC values directly depend on the content of the sulfonyl groups present in the polymer.<sup>52–54</sup> The IEC values for the sulfonated polyimides were given in Table II. No remarkable effect was observed for the IEC behavior of similar polyimides resulted from different preparation methods (IL and common solvent method).<sup>51</sup>

The IEC values decreased in the order of BANBPDS-DADO > BANBPDS-ODA > BANBPDS-BANBP. Here, the BANBPDS content was kept constant so that the amount of the sulfonyl substitution was the same in all the polymers. The decrease in the IEC values despite similar BANBPDS contents could be attributed to the molecular weight of the repeating unit. The increase in the molecular weight of the repeating unit effectively reduced the amount of SO<sub>3</sub>H groups in a unit weight of the polymer thus reducing the IEC values, due to the fact that the increase in the molecular weight of the unsulfonated comonomer increased the molecular weight of the repeating unit. Also, higher amorphous nature of BANBPDS-DADO copolyimides led to more water uptake and consequently higher IEC values.

### Stability in water

Polymer chain flexibility and sulfonation content are two main factors that control the stability of polyimide film in water.<sup>17</sup> It means that by the same sulfonation content, more flexible units in the structure

of backbone increases the stability in water. However, by increasing the sulfonation content, the hydrophilicity of the polymers will increase leading to increased polymer swelling and membrane instability. Considering same sulfonation content and according to the flexibility of monomers in the

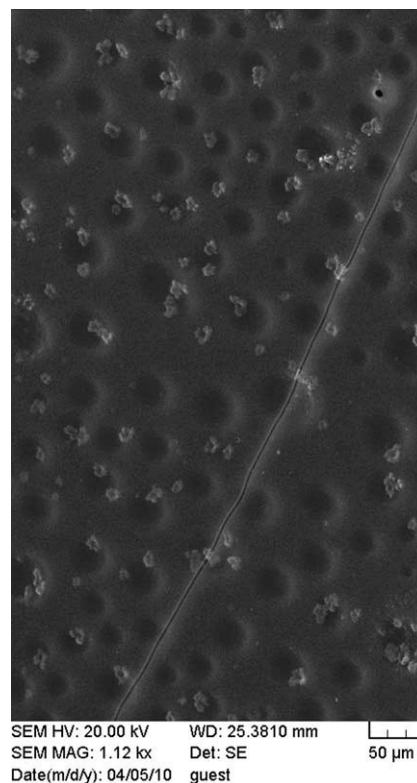
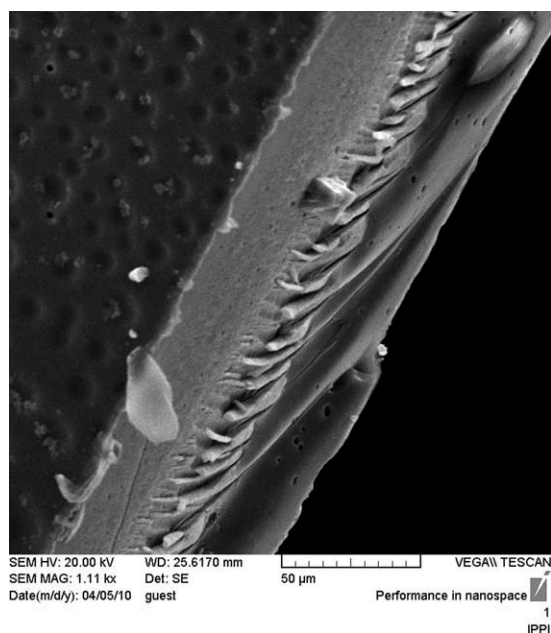


Figure 10 SEM micrograph of sulfonated copolyimide film BANBPDS-BANBP (70).



**Figure 11** Cross section SEM micrograph of sulfonated copolyimide film BANBPDS-BANBP (70).

prepared polymers, the stability of BANBPDS-DADO polyimide films in water was higher than other polymers. On the other hand, water stability of the polyimides prepared from IL method was higher than the same polyimides prepared via common solvent method. By increasing the molecular weight of the polymer, the interlayer interaction and therefore water stability increased due to the fact that more interactions occurred in the polymer chain.<sup>29</sup>

### Morphology

The hydrophilic–hydrophobic phase separation is an important factor for evaluation of membranes performance for application in fuel cell system. Formation of interconnected hydrophilic channels is an effective method for improving proton conductivity of membranes. Proton transfer through these interconnected channels could be possible even in the absence of water and therefore reduces the morphological barrier for proton transport. Many SPI membranes show anisotropic membrane swelling and anisotropic proton conductivity behavior which means different behaviors in membrane thickness direction than in plane direction mainly due to the polymer chain alignment in plane direction. Therefore, it is very important to study the cross-sectional morphology of membrane in addition to the proton conductivity and membrane swelling in both the thickness and plane directions for SPI membranes including sulfonated polyimides bearing pendant groups. The typical micrographs of the prepared polymers depicted in Figures 10 and 11 showed the

aforementioned explanation for the prepared sulfonated copolyimides.<sup>55–57</sup>

### CONCLUSIONS

A new sulfonated diamine was prepared and three different categories of SPIs were synthesized for PEMFC applications. Use of ILs for preparation of copolyimides was investigated. Results showed that ionic liquids seem to be suitable reaction and activating media for the synthesis of high-molecular-weight aromatic polyimides. By increasing the sulfonation content of the acidic form of the membranes, the solubility, water uptake, and ion exchange capacity increased, whereas their thermal stability decreased. The stability in water of sulfonated copolyimides was increased by increasing the flexibility and symmetry character of monomers. The copolymers revealed high thermal stability, which means higher working temperatures for fuel cells. According to the obtained results, these polymers contain prerequisite conditions for application in proton exchange membrane fuel cell. Complementary works in this field are in progress.

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