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Short Communication

Fuel cell: Synthesis and Properties of Polyimide for PEMFC at High Temperature

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Polyimides (PIs) with pendant benzimidazole groups have been synthesized via different ratio of 5-(1*H*-benzoimidazol-2-yl)-benzene-1-3-diamine (DABI) and dianhydride monomers (6FDA) and utilized as efficient proton conducting membranes for fuel cell applications. The synthesized polyimides showed an excellent performance in terms of proton conductivity, studied by impedance analyzer and polyimide with high DABI content exhibit highest conductivity (0.097 S/cm) at high temperature (150 °C). Additionally, synthesized polyimides are thermally stable and exhibit high dielectric constants which were investigated by thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC) and capacitance method, respectively. Thus the synthesized polyimides open a new gate way to utilize them as an efficient proton conductor to fabricate proficient fuel cell.

Keywords: Polyimides, Chemical structure, Thermal stability, Dielectric constants, Proton conductivity

1. INTRODUCTION

Fuel cell is getting more importance due to high energy demand because it produces electrical energy by electrochemical reactions which is cheap and simple conversion device [1-3]. As a matter of conversion devices, it has better efficiency than power generation because it does not need thermodynamic limitation what heat engines have in principle [4-6]. Fuel cell has wide choice of fuel demand and supply on account of its variety of fuels (natural gas, coal gas, oil and alcohol).

Membrane materials with proton conductivity are the best candidates for polymer electrolyte membrane fuel cells (PEMFCs) which operate without creating pollution, a lesser amount of corrosion and elevated power density [7-9]. PEMFCs need a membrane to split the chemical reactions at the anode from the cathode both chemically and electronically. A flourishing fuel cell membrane should allow protons to be in motion freely [10-15]. This prerequisite has led a lot of researchers to concentrate on cation exchange membranes. At present the most extensively utilized polymer electrolyte membrane is Nafion. Nafion has many advantages such as high oxygen solubility, high ionic conductivity, low density, chemical stability, high mechanical strength and is qualified polymer [16-20]. In addition, it has another strength that it does not influenced by strong acid and oxidants. However, it has difficult manufacturing process and cause degradation of performance at more than 80 degrees celsius. Because of these reasons, development of new membranes to replace Nafion is being carried globally [1-3]. Recently Polyimide is one of the most studied polymers. Polyimide is the center of attention due to its ability as the most suitable electrolyte membrane for high temperature PEMFC. Polyimide possess outstanding properties such as thermal stability, impact resistance, and chemical resistance [4-7], but is has very low hydrolytic stability, so many researches are being studied to overcome this problem.

In this study, polyimides with pendant benzimidazole group were prepared and structurally characterized by FTIR in terms of their structural properties. Thermal properties of the synthesized polyimides were evaluated by TGA and DSC. All the synthesized polyimides performed well in terms of conductivity when studied as polymer electrolyte membrane fuel cells.

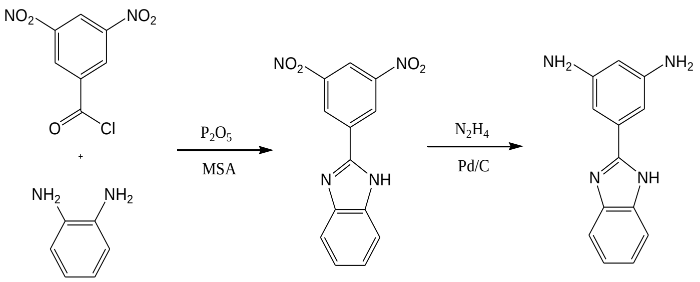
2. EXPERIMENTAL

2.1.Materials.

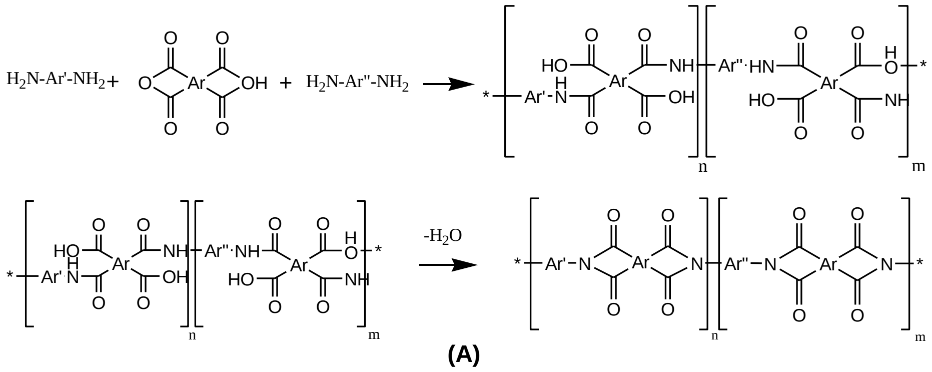
1,2-Phenylenediamine (PDA), 3,5-dinitrobenzoyl chloride (DNBC) and hydrazine monohydrate were purchased from Sigma-Aldrich Inc. *4,4'*-Oxydianiline (ODA), and 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) were purchased from Tokyo Chemical Industry *Co. Ltd. N,N*-Dimethylformamide *(*DMF*)* were purchased from Duksan *Co. Ltd.*

2.2. Synthesis of 2-(3,5-dinitro-phenyl)-1H-benzoimidazole (DNBI)

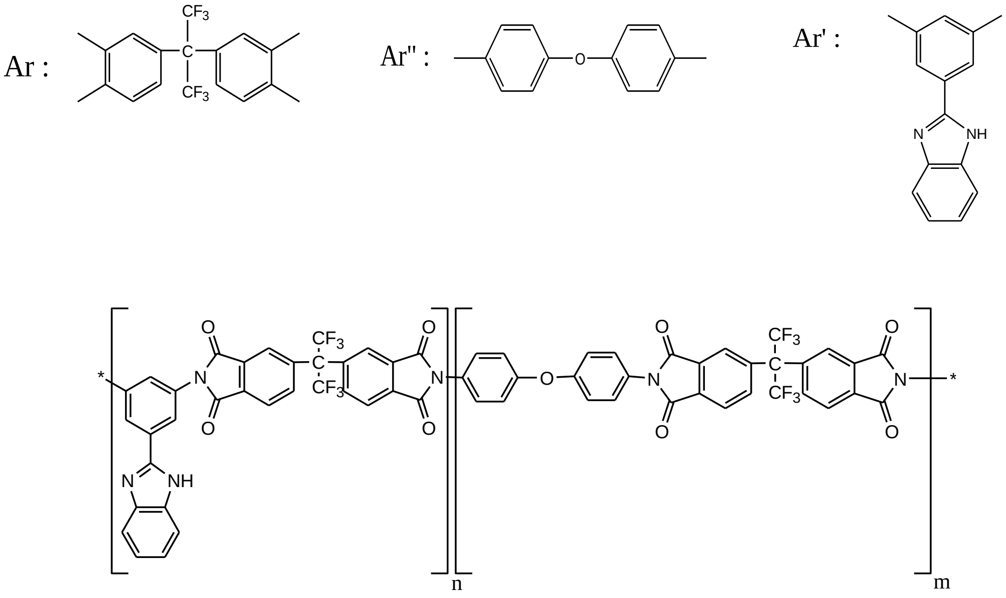
Phosphorus pentoxide (P_2O_5) was dissolved in methane sulfonic acid (MSA) followed by addition of 1,2-phenylenediamine (PDA) and 3,5-dinitrobenzoyl chloride (DNBC) and the mixture was stirred for 10 min in a three necked round bottom flask fitted with a reflux condenser under a nitrogen atmosphere. After stirring the mixture, the reaction was continued at 120 °C and after 12 hrs the mixture was cooled to room temperature and poured into water. The precipitate was filtered and dried in vacuum oven at 80 °C for 24 h. The product was obtained with 46% yield (Scheme 1).



Scheme 1. Synthesis of 5-(1H-benzoimidazol-2-yl)-benzene-1-3-diamine (DABI).



Scheme 2. Synthetic route of the polyimides.



6FDA-DABI-ODA

Scheme 3. Chemical structure of polyimides.

2.3. Synthesis of 5-(1H-benzoimidazol-2-yl)-benzene-1-3-diamine (DABI)

DNBI was dissolved in ethanol in a three-necked flask, with the addition of Pd/C (10%) into the flask. In the next step hydrazine monohydrate was added drop-wise. The solution was disturbed at

75 °C for 12 h in the presence of nitrogen atmosphere. The prepared solution was cooled to room temperature. The catalyst, Pd/C, was eliminated by filtration and the filtrate was concentrated. This concentrated filtrate was decanted into three fold excess of water (several times) and the resulting precipitate was filtered, dried and recrystallized from water to give product with 31% yield (Scheme 1).

2.4. Polymerization.

All polymerizations were performed by equimolar amounts of diamine and dianhydride monomers in the presence of nitrogen flow. Nonetheless two different diamine ratio i.e. (DABI/ODA), 40/60 and 35/65 were utilized. A representative polymerization process is as follows: A three-necked flask provided with a nitrogen inlet and a mechanical stirrer was charged with the suitable amount of DABI and ODA. 20 wt% of DMF was added and the mixture was swirled at room temperature. In the next step equimolar amount of dianhydride (6FDA) was added and additionally mixed for 24h at ice bath (Scheme 2 and 3). The films of all polyimides were prepared in a similar way reported elsewhere [21].

2.6. Characterization

FT-IR (Fourier transform infrared spectrometer) spectra were recorded on Excalibur Series FT-IR (DIGLAB Co.) instrument. Thermogravimetric analysis (TGA) was conducted using thermogravimetry analyzer (Q 50, TA Instrument), at a heating rate of 10 ℃/min in nitrogen atmosphere. The glass transition temperature (Tg) of nanocomposites was analyzed by a differential scanning calorimeter (Q 10, TA Instrument), in a N_2 environment. The dielectric properties of polyimides were measured by the capacitance method. The dielectric measurements of polyimide thin films were monitored at room temperature and 1 kHz with a Fluke PM6304 thin film dielectric analyzer. A sample was placed inside a chamber that isolated the sample from the outside ambient relative humidity and temperature. The capacitance was recorded at room temperature. The dielectric constant (ε′) by the capacitance method was calculated from the measured capacitance data as follows.

$$\varepsilon' = \frac{CL}{\varepsilon_o A}$$

where C is the capacitance, ε′ is dielectric constant, ε_o is the permittivity of free space (8.854×10^{-12} F/m), L is the film thickness, and A is the electrode area.

Proton conductivity (σ) was measured using electrochemical impedance spectroscopy technique over the frequency range of 100 kHz-10 kHz up to 150 °C and was calculated by the following equation:

$$\sigma = \frac{d}{L_S W_S R}$$

Where d, L_S W_S and R are the distance of the electrodes, film thickness, film width and the resistance of the polyimide membrane respectively [1].

3. RESULTS AND DISCUSSION

3.1. FT-IR

Chemical structure of the synthesized DABI and polyimides were confirmed by FT-IR spectra which are shown in Figure 1. FTIR spectrum of DABI exhibits an absorption band at 3400 cm^{-1} which is responsible for the N-H group of imidazole ring. Appearance of this band confirms the formation of benzimidazole ring. Further an absorption band appeared at 1605 cm^{-1} which represent the formation of amine group by reduction of nitro group. The characteristic absorption bands of the imide ring were observed near 1785 cm^{-1}, 1719 cm^{-1} (asymmetrical and symmetrical C=O stretching vibration), 1375 cm^{-1} (C-N stretching vibration), 1671 cm^{-1} (Ar_2-C=O stretching) and 1080–1250 cm^{-1} showed some stronger peaks (C-O and C-F stretching). The data is in good agreement with our previous results [21].

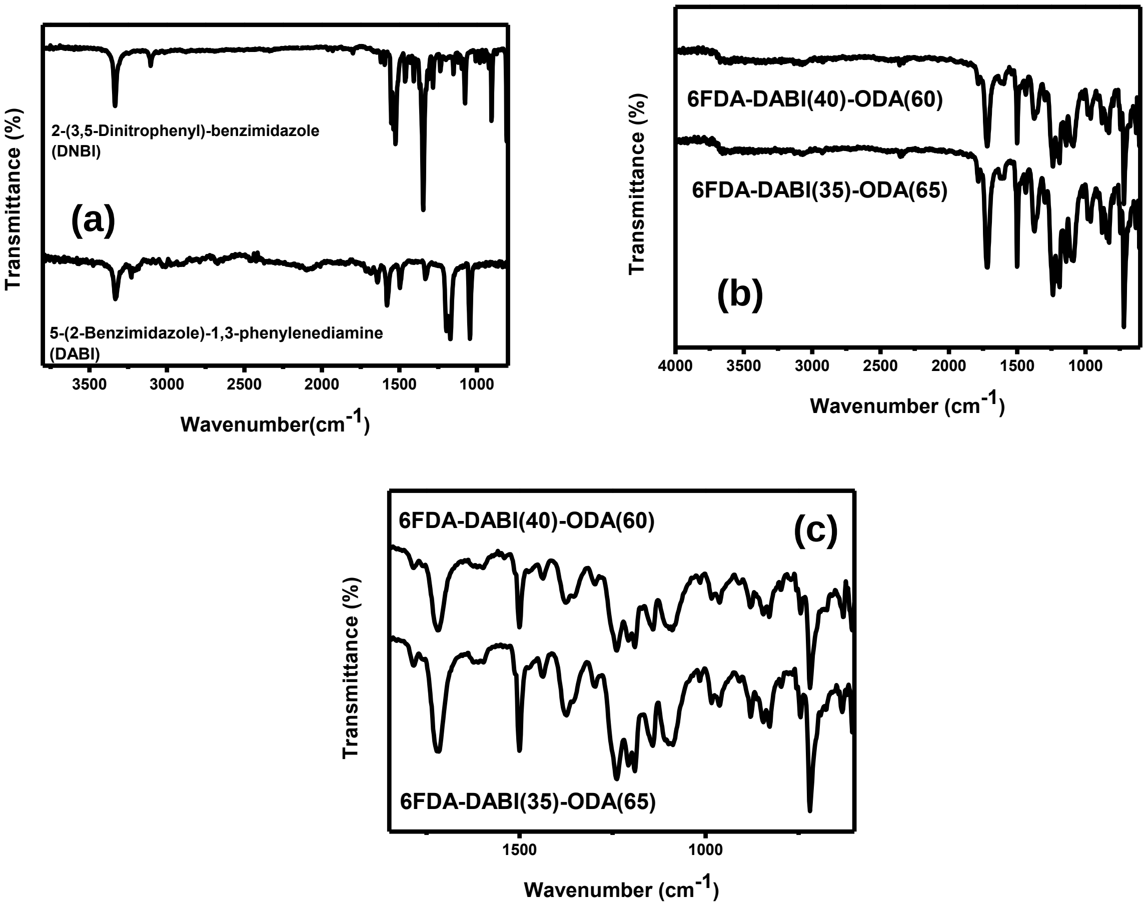


Figure 1. Typical FT-IR spectra of (a) 5-(1H-benzoimidazol-2-yl)-benzene-1-3-diamine (DABI) and (b,c) polyimides.

3.2. Thermal Properties

Thermal properties of polyimides were evaluated by TGA and DSC and the results are shown in Table 1 and Fig. 2. In TGA, the thermal degradation values at 5% ($T_{d5\%}$) and 10% ($T_{d10\%}$) weight loss are given in Table 1 and Figure 2. Both the polyimides have good thermal stability and the thermal degradation temperatures which exceeded 490 ^oC at 5% ($T_{d5\%}$) weight loss [22-24]. This thermal stability of polyimides may be due to the rigidity of the polyimide. The glass transition temperatures (Tg) of polyimides were evaluated by DSC and the results are given in Table 1 and Fig. 2. The synthesized polyimides showed a higher Tg value which may be due to increasing order of rigidity and polarity of the polyimides chains. These results prove that these polymers can be applied for high temperature applications [25-27].

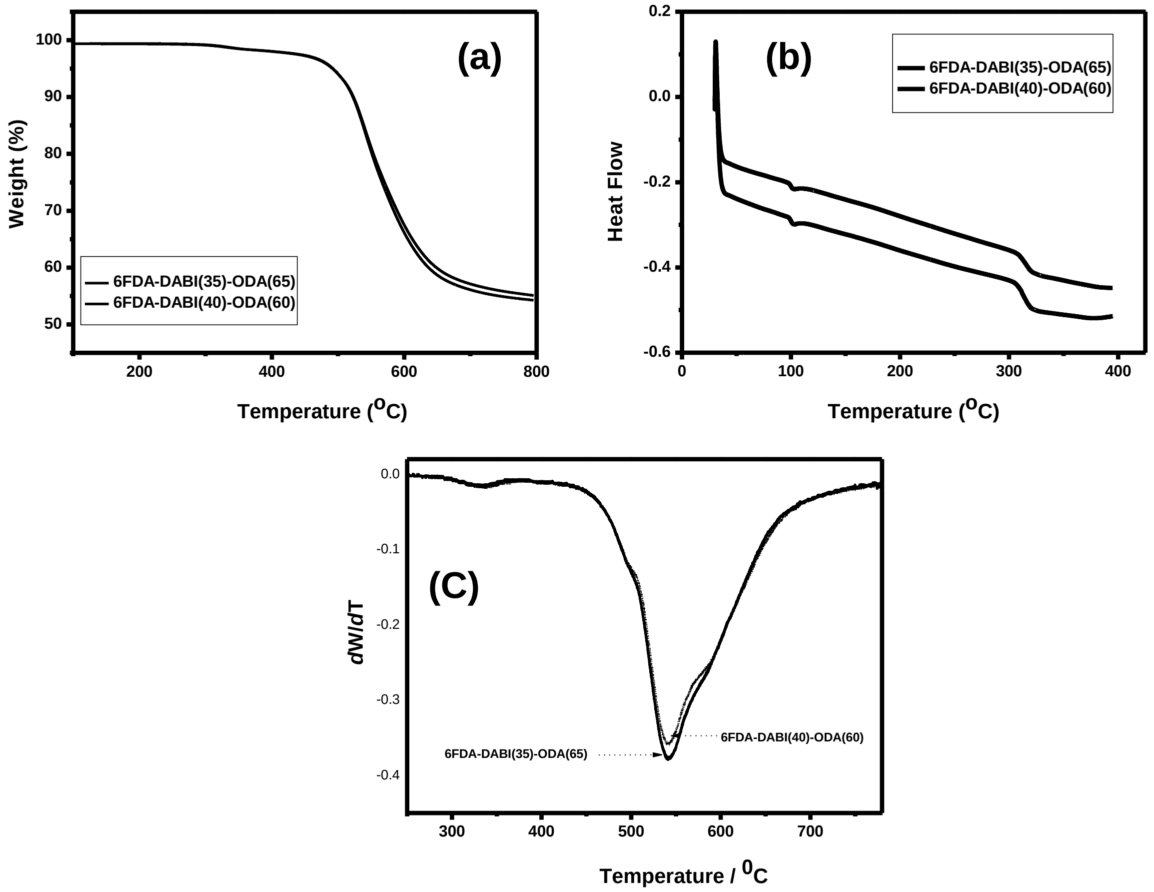


Figure 2. TGA (a), DSC (b) and DTG (c) curves of polyimides.

3.3. Dielectric properties

Capacitance method was used for the calculation of dielectric constants of both polyimide films utilizing 40 to 60 μm thick films and the data is given in Table 1. The capacitance data clearly shows that dielectric constant of the polyimides decreases with increasing DABI contents and the polyimide with low DABI content showed the highest dielectric constant as compared to the polyimide with high

DABI content. The lower dielectric constants with high DABI contents might be due to low molecular packing order because lower molecular packing order direct to fewer polarizable groups per unit volume which subsequently gives polyimides with low dielectric constant. This clearly indicates that dielectric constant strongly depends on the rigidity, packing order and morphological structure of the polyimide films [28].

Table 1. Thermal properties and dielectric properties of polyimide membranes.

Polyimide	**Thermal properties**			**Dielectric constant**
	Tg (ºC)	T_5%(ºC)	T_{10}%(ºC)	(1kHz)
6FDA-DABI(40)-ODA(60)	316	492	523	3.18
6FDA-DABI(35)-ODA(65)	315	492	522	3.31

3.4. Conductivity

Proton conductivity for both polyimides were evaluated in the temperature range of 150 °C to 60 °C and studied the effect of temperature as well as DABI contents and the data is depicted in Figure 3. Both polyimides showed good proton conductivity and it gradually increased with increase in temperature.

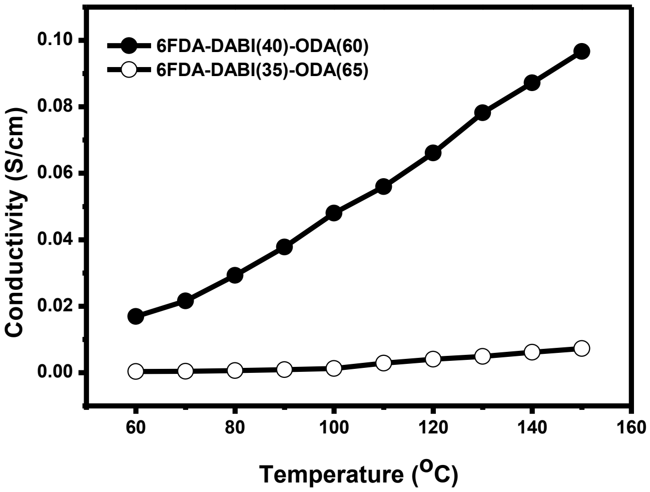


Figure 3. Proton conductivity of acid-doped membranes of polyimides.

Further we studied the effect of DABI contents on the proton conductivity and it was found that proton conductivity increased with increase in DABI contents. Polyimide with high mole ratio of DABI (40:60 ratio of DABI:ODA) have the highest conductivity of 0.097 (S/cm) at 150 °C while polyimide with lower mole ratio of DABI (35:65 ratio of DABI:ODA) exhibited lower proton conductivity of 0.0073 (S/cm) at 150 °C. This result noticeably illustrates that the proton conductivity of polyimide enhances as the DABI content in polyimide increase, this fact might be attributed to the more flexibility of DABI in the polyimide series which cause easier bonding with inorganic acid [1,2]. Accordingly quantity of phosphoric acid in the membranes enhanced with increase of DABI ratio in polyimide. The proton conductivity of acid doped polyimide increases with the raise in temperature. Proton transport in H_3PO_4 doped polyimide takes place chiefly because of two reasons. One is due to the rapid proton exchange between the phosphate and imidazole, and the other is as a result of the self-diffusion of the phosphate moieties. As a result, the proton conductivity of polyimide membranes rises constantly with increasing temperature, thus causing increase in activation energy of proton transport [21].

4. CONCLUSIONS

Polyimides having benzimidazole groups were effectively synthesized and its characterization was done by FTIR. All polyimides demonstrated high thermal stability and dielectric constant. Considering application, the proton conductivity of polyimide membranes was examined and the synthesized membranes doped with phosphoric acid displayed high proton conductivity. This specifies that the synthesized membranes have the ability to be a fine substitute for the PEMFC applications working at high temperature even in the fairly low humidification condition.

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