

# Design, Synthesis, and Gas Permeation Properties of Polyimides Containing Pendent Imidazolium Groups

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Received 25 January 2018; accepted 22 April 2018; published online in Wiley Online Library DOI: 10.1002/pola.29053

ABSTRACT: Film-forming polymers containing ionic groups have attracted considerable attention as emerging materials for gas separation applications. The aim of this article was to synthesize new film-forming polyimides containing imidazolium groups (PI-IMs) and establish their structure-performance relationship. In this context, a new aromatic diamine, namely, N<sup>1</sup>-(4-aminophenyl)-N<sup>1</sup>-(4-(2-phenyl-1H-imidazol-1-yl)phenyl)benzene-1,4diamine (ImTPADA), was synthesized and polycondensed with three aromatic dianhydrides, namely, 4,4'-(hexafluoroisopropylidene)diphthalic anhydride, 4,4-(4,4-isopropylidenediphenoxy) bis(phthalic anhydride), and 4,4'-oxydiphthalic anhydride to form the corresponding polyimides containing pendent 2phenylimidazole groups (PI-IEs). Next, PI-IMs were prepared by N-quaternization of pendent 2-phenylimidazole groups present in PI-6FDA using methyl iodide followed by anion exchange with bis(trifluoromethane)sulfonimide lithium salt (LiTf<sub>2</sub>N). PI-IEs and PI-IMs exhibited reasonably high molecular weights, amorphous

nature, good solubility, and could be cast into self-standing films from their DMAc solutions. Thermogravimetric analysis showed that 10% weight loss temperature of PI-IEs and PI-IMs were in the range 545–475 °C and 303–306 °C, respectively. Gas permeability analysis of films of PI-IEs and PI-IMs was investigated by variable-volume method and it was observed that incorporation of ionic groups into PI-6FDA resulted in increased permeability while maintaining selectivity. In particular, polymer bearing Tf\_2N<sup>-</sup> anion exhibited high CO<sub>2</sub> permeability (33.3 Barr) and high selectivity for CO<sub>2</sub>/CH<sub>4</sub> (41.1) and CO<sub>2</sub>/N<sub>2</sub> (35.4). © 2018 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2018**, *56*, 1721–1729

**KEYWORDS**: gas permeation; ionic liquids; membrane; polyimides; polyimides-containing imidazolium groups; structureproperty relationship

INTRODUCTION Owing to their excellent thermal and mechanical stability, structural tunability, and film-forming ability, polymeric membranes have attracted considerable attention for various applications such as hydrogen recovery, O2 enrichment, purification of natural gas, and so forth.<sup>1-5</sup> The performance of membranes for gas separation applications is judged by permeability and selectivity.<sup>6</sup> The high permeability and selectivity leads to the lower capital area and higher product purity, respectively. For polymeric membranes, there exists a tradeoff relationship between gas permeability and selectivity, wherein increased permeability is accompanied by the decrease in selectivity or vice versa.<sup>2,7</sup> Therefore, the current research efforts in the field of membrane technology are directed toward overcoming the limit of Robeson upper bound by designing polymers with high permeability and good selectivity. It has been demonstrated that increasing polymer chain rigidity and incorporation of ionic groups into polymers used for gas

separation membranes enhances their gas separation performance.<sup>8,9</sup>

In the recent years, polymers containing ionic groups have gained significant attention for various applications in the fields such as gas separation, lithium ion batteries, protonexchange membrane fuel cells (PEMFC), supercapacitors, and so forth.<sup>10-20</sup> It has been demonstrated that polymers containing ionic groups exhibit excellent gas permeation properties and their gas permeation properties can be tuned by varying compositions of ionic groups.<sup>13</sup> For CO<sub>2</sub> separation, polymers containing ionic groups showed high selectivity and high permeability because of interaction of ionic counterpart with CO<sub>2</sub>.<sup>4,10</sup> To date, various examples of polymers containing ionic groups have been reported for gas separation applications including polybenzimidazoles, polyethers, polyimides, and so forth.<sup>8,21-26</sup> Taking into consideration the attractive performance offered by polymers containing ionic groups based on high-performance polymers, it is of further

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interest to synthesize new film-forming polymers containing ionic groups and investigate their gas permeation properties so as to improve the understanding of structure-property relationships.

Due to their highly rigid structure, high thermo-chemical stability and possibilities of structural variations via choice of appropriate monomers, polyimides are widely studied polymers for gas separation applications.<sup>27–29</sup> Generally, most of the polyimides exhibited low permeability and high selectivity of one gas over another. Various moieties have been incorporated into polyimides that include bulky groups, spiro-center, cardo groups, propeller, and ionic groups to improve gas separation performance.<sup>3,27,28,30-35</sup> The incorporation of ionic groups into polyimide was first reported by Li et al. in 2010 and it was demonstrated that there was an increase in CO2-based selectivity by the incorporation of ionic groups.<sup>36</sup> The postmodification of polyimides and evaluation of obtained polymers containing imidazolium groups as membrane materials for gas separation applications was firstly reported by Shaplov et al. They found an improvement in gas separation performance compared to parent polymer.<sup>37</sup> These results point out the favorable effect of incorporation of ionic groups into polymers for obtaining both high permeability and selectivity.

In this work, a new aromatic diamine, namely, N<sup>1</sup>-(4-aminophenyl)-N<sup>1</sup>-(4-(2-phenyl-1H-imidazol-1-yl) phenyl)benzene-1,4-diamine (ImTPADA), was synthesized. ImTPADA was polycondensed with commercially available aromatic dianhydrides, namely, 6FDA, BPADA, and ODPA, to obtain polyimides containing pendent 2-phenylimidazole groups (PI-IEs). Polyimides containing imidazolium groups (PI-IMs) were obtained by *N*-quaternization of 2-phenylimidazole groups present in PI-6FDA and its anion exchange reaction. PI-IEs and PI-IMs were characterized by IR and <sup>1</sup>H NMR spectroscopy, GPC, XRD, TGA, and DSC. The effects of imidazolium groups and anion variation on physical and gas permeation properties of polyimides were investigated.

# EXPERIMENTAL

# Materials

2-Phenylimidazole (Alfa Aesar), sodium hydride (Alfa Aesar), 10 wt % Pd/C (Aldrich), isoquinoline (Aldrich), 1-fluoro 4nitrobenzene (Aldrich), iodomethane (Aldrich), bis(trifluoromethane) sulfonimidelithium salt (LiTf<sub>2</sub>N, Aldrich), and hydrazine hydrate (Alfa Aesar) were used as received. *N*,*N*-Dimethylformamide (DMF) and *m*-cresol (Alfa Aesar) were distilled before use. 4,4'-(Hexafluoroisopropylidene) diphthalic anhydride (6-FDA), 4,4-(4,4-isopropylidenediphenoxy)bis (phthalic anhydride) (BPADA), and 4,4'-oxydiphthalic anhydride (ODPA) were procured from Aldrich and were sublimed prior to use.

# Characterizations

IR spectra were recorded using Perkin Elmer spectrum GX spectrophotometer in the range 4000–400  $\rm cm^{-1}.~NMR~(^{1}H$  and  $^{13}C)$  spectra were recorded using a Bruker-AV

spectrometer at the frequency of 200 MHz in  $\text{CDCl}_3$  or  $\text{DMSO-}d_6$ . High-resolution mass spectrometry (HR-MS) analysis of monomers was performed on Thermo Scientific Q-exacative with Accela 1250 Pump. Molecular weights of polymers were measured using GPC analyses in DMF containing LiBr (0.25 M) with polystyrene as a standard. TGA of PI-IEs and PI-IMs were performed in N<sub>2</sub> on Perkin Elmer TGA-7 system. Polymer samples were heated from 30 to 900 °C at a heating rate of 10 °C/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) analysis was performed with DSC Q10 at a heating rate of 10 °C/min from 30 to 380 °C under nitrogen. X-Ray diffractograms of PI-IEs and PI-IMs were obtained on Rigaku Dmax 2500 with a scanning rate of 2°/min and *d*-spacing values of polymers were calculated using Bragg's equation.

# Synthesis of 1-(4-Nitrophenyl)-2-Phenyl-1H-Imidazole (ImN)

Into a 500 mL two-necked round-bottom flask equipped with a magnetic stirring bar, a reflux condenser and a nitrogen inlet were charged dry dimethyl sulfoxide (250 mL), sodium hydride (5 g, 208 mmol) and 2-phenylimidazole (20 g, 138.7 mmol). The reaction mixture was stirred under nitrogen at room temperature for 1 h and then 1-fluoro-4nitrobenzene (17.67 mL, 166.4 mmol) in dimethyl sulfoxide (30 mL) was added dropwise over a period of 30 min. The reaction mixture was heated at 140 °C for 48 h under nitrogen, cooled to room temperature and precipitated into icecold water (1000 mL). The crude product was collected by filtration, washed several times with water and dried under vacuum at 70 °C. ImN was purified by recrystallization from methanol.

Yield: (28 g, 76%); melting point: 110 °C; IR (CHCl<sub>3</sub>, cm<sup>-1</sup>): 1597 (-NO<sub>2</sub> asymmetric stretching) and 1345 (-NO<sub>2</sub> symmetric stretching); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm): 8.23 (d, 2H), 7.42–7.33 (m, 8H), 77.26 (d, 1H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm): 146.8, 146.6, 143.4, 129.8, 129.4, 129.0, 128.7, 128.4, 126.0, 124.8, 122.0.; HRMS (ESI): calcd. for C<sub>15</sub>H<sub>12</sub>N<sub>3</sub>O<sub>2</sub> ([M + H]<sup>+</sup>): 266.0924; found 266.0922.

#### Synthesis of 4-(2-Phenyl-1H-Imidazol-1-Yl) Aniline (ImA)

Into a 500 mL three-necked round-bottom flask equipped with a magnetic stirring bar, a nitrogen inlet and a reflux condenser were charged ImN (26 g, 98 mmol), 10 wt % Pd/C (1 g) and ethanol (200 mL). To the reaction mixture, hydrazine hydrate (10 mL) was added dropwise over a period of 30 min at room temperature under nitrogen atmosphere and then refluxed overnight. After completion of reaction (monitored by TLC), the reaction mixture was filtered, cooled, and precipitated into ice-cold water (1000 mL). The crude product was collected by filtration and dried under vacuum at 70 °C. The product was recrystallized from ethanol to afford ImA as colorless crystals.

Yield: (18 g, 78%); melting point: 170 °C; IR (CHCl<sub>3</sub>, cm<sup>-1</sup>): 3463 (N—H asymmetric stretching) and 3387 (N—H symmetric stretching); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm): 7.46 (d, 2H), 7.28–7.24 (m, 4H), 7.11 (s, 1H) (d, 2H), 6.67 (d, 2H).

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3.71 (s, 2H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm): 146.5, 146.4, 129.9, 129.0, 128.4, 128.3, 128.1, 127.8, 126.9, 123.3, 115.2.; HRMS (ESI): calcd. for C<sub>15</sub>H<sub>14</sub>N<sub>3</sub> ([M + H]<sup>+</sup>): 236.1182; found 236.1181.

# Synthesis of 4-Nitro-N-(4-Nitrophenyl)-N-(4-(2-Phenyl-1H-Imidazol-1-Yl)Phenyl) Aniline (ImTPADN)

Into a 500 mL two-necked round-bottom flask equipped with a magnetic stirring bar, a reflux condenser and a nitrogen inlet were charged ImA (16 g, 68 mmol), sodium hydride (4.9 g, 204 mmol), and dry dimethyl sulfoxide (150 mL). The reaction mixture was stirred under nitrogen atmosphere at room temperature for 1 h and then 1-fluoro-4-nitrobenzene (17.34 mL, 163.2 mmol) in dimethyl sulfoxide (30 mL) was added dropwise. The reaction mixture was heated at 140 °C for 72 h, cooled to room temperature and precipitated into ice-cold water (1000 mL). The solids were collected by filtration, washed several times with water and dried under vacuum at 70 °C. The product was dissolved in ethyl acetate. The ethyl acetate solution was washed with brine and water, dried over sodium sulfate, and filtered. Ethyl acetate was evaporated on a rotary evaporator. The crude product was purified by silica gel column chromatography using pet ether: ethyl acetate (50:50, v/v) as an eluent to afford ImTPADN as a faint yellow solid.

Yield: (15 g, 46%); Melting point: above 300 °C; IR (CHCl<sub>3</sub>, cm<sup>-1</sup>): 1580 ( $-NO_2$  asymmetric stretching) and 1312 ( $-NO_2$  symmetric stretching); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>,  $\delta$ / ppm): 8.21 (d, 4H), 7.40 (d, 2H), 7.31-7.27 (m, 7H), 7.24-7.19 (m. 6H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm): 151.2, 146.0, 145.4, 143.4, 135.1, 129.9, 129.0, 128.6, 127.8, 127.2, 126.7, 125.7, 123.1, 122.7.; HRMS (ESI): calcd. for C<sub>27</sub>H<sub>20</sub> N<sub>5</sub>O<sub>4</sub> ( $[M + H]^+$ ): 478.1510; found 478.1511.

# Synthesis of $N^1$ -(4-Aminophenyl)- $N^1$ -(4-(2-Phenyl-1H-Imidazol-1-Yl)Phenyl)Benzene-1,4-Diamine (ImTPADA)

Into a 500 mL three-necked round-bottom flask equipped with a magnetic stirring bar, a nitrogen inlet and a reflux condenser were charged ImTPADN (14 g, 29.3 mmol), 10 wt % Pd/C (1 g) and ethanol (150 mL). To the reaction mixture, hydrazine hydrate (30 mL) was added dropwise over a period of 1 h at room temperature under nitrogen atmosphere and then refluxed overnight. After completion of reaction (monitored by TLC), the reaction mixture was filtered while hot, cooled, and precipitated into ice-cold water (800 mL). The crude product was collected by filtration, washed with water and dried under vacuum at 70 °C. The product was purified by recrystallization from ethanol to afford ImTPADA as colorless crystals.

Yield: (9 g, 74%); melting point: 204 °C; IR (CHCl<sub>3</sub>, cm<sup>-1</sup>): 3463–3400 (N—H stretching); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>,  $\delta$ / ppm): 7.52 (d, 2H), 7.32–7.27 (m, 4H), 7.11 (d, 1H), 6.99–6.93 (m, 6H), 6.83 (d, 2H), 6.65 (d, 4H), 3.38 (s, 4H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm): 149.4, 146.1, 143.1, 138.1, 128.9, 128.8, 128.6, 128.5, 128.2, 127.4, 126.8, 126.4, 123.3, 118.2, 116.1.; HRMS (ESI): calcd. for C<sub>27</sub>H<sub>23</sub>N<sub>5</sub> ([M + H]<sup>+</sup>): 417.1948; found 417.1945.

# General Procedure for the Synthesis of Polyimides

Into a 100 mL three-necked round-bottom flask equipped with a magnetic stirring bar, a nitrogen inlet and a calcium chloride guard tube were charged ImTPADA (2.5 g, 6 mmol) and freshly distilled *m*-cresol (35 mL). After complete dissolution of ImTPADA, 6-FDA (2.66 g, 6 mmol) and isoquinoline (1 mL) were added. The reaction mixture was initially stirred at room temperature for 4 h followed by heating at 140 °C for 12 h. Finally, the reaction temperature was increased to 200 °C and held at that temperature for 8 h. The viscous polymer solution was poured into methanol (1000 mL), filtered, washed with methanol, and dried at 80 °C for 48 h under reduced pressure.

IR (Film, cm<sup>-1</sup>): 1784 (C=O asymmetric stretching) and 1722 (C=O symmetric stretching); <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm): 8.06 (d, 2H), 7.92 (d, 4H), 7.38–7.16 (m, 19H).

The other polyimides, namely, PI-BPADA and PI-ODPA were synthesized following the similar procedure by polycondesation of ImTPADA with aromatic dianhydrides, namely, BPADA and ODPA, respectively.

# Postmodification

# N-Quaternization of PI-6FDA

Into a 250 mL two-necked round-bottom flask equipped with a magnetic stirring bar and a nitrogen inlet were charged PI-6FDA (2.9 g, 3.5 mmol) and DMSO (30 mL). To the reaction mixture, methyl iodide (0.16 mL, 2.5 mmol) was added dropwise and stirred at room temperature for 48 h. The polymer solution was precipitated into methanol, filtered, washed with methanol (2  $\times$  500 mL), and dried at 100 °C for 4 days.

IR (Film, cm<sup>-1</sup>): 1784 (C=O asymmetric stretching) and 1722 (C=O symmetric stretching); <sup>1</sup>H-NMR (200 MHz, DMSO- $d_6$ ,  $\delta$ /ppm): 8.21–8.12 (m, 4H), 7.95 (s, 2H), 7.78 (s, 2H), 7.62–7.44 (m, 6H), 7.37–7.09 (m, 13H), 3.8 (s, 3H).

# Anion Exchange of [PI-6FDA] [1]

Into a 250 mL two-necked round-bottom flask equipped with a magnetic stirring bar and a nitrogen inlet were charged [PI-6FDA] [I] (1.5 g) and DMF (20 mL). To the reaction mixture, LiTFSI (0.89 g, 3.1 mmol) in DMF (5 mL) was added and stirred at room temperature for 48 h. The polymer solution was precipitated into water, washed thoroughly with methanol, and dried at 100  $^{\circ}$ C for 4 days.

IR (Film, cm<sup>-1</sup>): 1784 (C=O asymmetric stretching) and 1722 (C=O symmetric stretching); <sup>1</sup>H-NMR (200 MHz, DMSO- $d_6$ ,  $\delta$ /ppm): 8.20–8.09 (m, 4H), 7.76 (s, 2H), 7.60 (s, 2H), 7.47–7.08 (m, 19H), 3.79 (s, 3H).

The degree of *N*-quaternization was determined by <sup>1</sup>H NMR spectroscopy. Volhard's method was used to determine the percentage of the iodide exchanged with  $Tf_2N^-$  anion.<sup>23</sup> PI-IM (0.1 g) was added into 0.01 M AgNO<sub>3</sub> solution (10 mL) and stirred at room temperature for 30 h. An excess of





**SCHEME 1** Synthesis of  $N^1$ -(4-aminophenyl)- $N^1$ -(4-(2-phenyl-1H-imidazol-1-yl)phenyl)benzene-1,4-diamine (ImTPADA).

 $AgNO_3$  was titrated with 0.01 M KSCN, from which the iodide exchange in the polyimide containing imidazolium groups was estimated.

# **Preparation of Dense Membranes**

The dense membranes were prepared *via* solution casting method. The polymer was dissolved in DMAc, the solution was filtered, and poured onto a leveled glass surface, which was then kept in a vacuum oven at 90 °C for 20 h. Further, these films were dried at 100 °C in a vacuum oven for one week. The average membrane thickness was in the range 60–70 microns as measured by digital micrometer.

# **Gas Permeability Measurements**

The pure gas permeability measurements on films of PI-IEs and PI-IMs were carried out by the variable-volume method at pressure of 6–7 bar and at room temperature (28 °C) for He, H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub>.<sup>19,38</sup> The active area of membrane was 12.4 cm<sup>2</sup>. Gas permeability coefficient was determined using the following equation:

$$P = \frac{J.l}{p_1 - p_2}$$

where *P* is the permeability coefficient expressed in Barr (1 Barr =  $10^{-10}$  cm<sup>3</sup> (STP) cm cm<sup>-2</sup> s<sup>-1</sup> cmHg<sup>-1</sup>), *J* is the steady-state penetrant flux (cm<sup>3</sup>.cm<sup>-2</sup>·s), *l* is the membrane thickness (cm), while  $p_1$  and  $p_2$  are the feed and permeate side pressures (cmHg). Three membrane samples of each polymer were taken for gas permeability analysis prepared under similar conditions and the data were averaged. Depending on the gas, the variation in permeability measurement from average value was in the range 1–14% (2–6% for He, 1–5% for H<sub>2</sub>, 3–6% for N<sub>2</sub>, 4–8% for O<sub>2</sub>, 6–14% for CH<sub>4</sub>, and 3–10% for CO<sub>2</sub>).

#### **RESULTS AND DISCUSSION**

## **Monomer Synthesis and Characterization**

The route for synthesis of N<sup>1</sup>-(4-aminophenyl)-N<sup>1</sup>-(4-(2-phenyl-1H-imidazol-1-yl)phenyl)benzene-1,4-diamine (ImTPADA) comprised four steps as depicted in Scheme 1. These four steps involved *N*-arylation of 2-phenylimidazole with 4-nitro-1-fluorobenzene, reduction of nitro groups of 1-(4-nitrophenyl)-2-phenyl-1H-imidazole (ImN), aromatic nucleophilic substitution reaction ( $S_NAr$ ) of ImA with 4-nitro-1fluorobenzene, and reduction of nitro groups of ImTPADN to finally afford  $N^1$ -(4-aminophenyl)- $N^1$ -(4-(2-phenyl-1H-imidazol-1-yl)phenyl)benzene-1,4-diamine (ImTPADA).

The structural characterization of ImTPADA and other intermediates was carried out by IR, <sup>1</sup>H and 13C NMR spectroscopy and HR-MS. IR spectrum of ImTPADA (Supporting Information, Fig. S7) showed absorption bands of N—H stretching of amino group in the range 3463–3400 cm<sup>-1</sup>. In <sup>1</sup>H NMR spectrum of ImTPADA (Fig. 1), the broad peak appeared at  $\delta = 3.58$  ppm corresponding to four protons of amino group. The peaks due to aromatic protons of ImTPADA appeared in the range  $\delta = 6.64$ –7.53 ppm. The structure of ImTPADA was further supported by <sup>13</sup>C NMR (Supporting Information, Fig. S8) and HR-MS analysis (Supporting Information, Fig. S9).

## Synthesis and Properties of PI-IEs and PI-IMs

Three PI-IEs were synthesized by polycondensation of ImTPADA with three commercially available aromatic dianhydrides namely, 4,4'-(hexafluoro isopropylidene)diphthalic anhydride (6-FDA), 4,4-(4,4-isopropylidenediphenoxy)bis (phthalic anhydride) (BPADA), and 4,4'-oxydiphthalic anhydride (ODPA). Polycondensation was performed using onestep high-temperature method in *m*-cresol containing catalytic amount of isoquinoline (Scheme 2).

PI-IMs were synthesized from PI-6FDA (Scheme 3). The *N*-quaternization of PI-FDA containing pendent 2-phenylimidazole units was carried out with methyl iodide at room temperature to obtain [PI-6FDA] [I].

To synthesize film-forming PI-IMs with the optimum content of ionic character, PI-6FDA was reacted with various equivalent quantities (0.5, 0.7, and 1) of methyl iodide. PI-IMs prepared using 0.5 and 0.7 equivalents of methyl iodide formed strong and flexible films while the film was brittle in case of PI-IMs prepared using 1 equivalent of methyl iodide. The exchange of iodide anion in [PI-6FDA] [I] was performed using bis(trifluoromethane) sulfonimidelithium salt (LiNTf<sub>2</sub>) in DMF to form [PI-6FDA] [Tf<sub>2</sub>N]. The degree of *N*-quaternization and anion exchange was measured by <sup>1</sup>H NMR spectroscopy and Volhard's method and the results of both these methods were in good agreement.

The solubility tests of PI-IEs and PI-IMs were carried out at 3 wt % concentration in various organic solvents at room temperature and the results are summarized in Supporting Information, Table S1. PI-6FDA and PI-BPADA were soluble



FIGURE 1 1H NMR spectrum (in CDCl<sub>3</sub>) of ImTPADA. [Color figure can be viewed at wileyonlinelibrary.com]

in various organic solvents such as chloroform (CHCl<sub>3</sub>), dichloromethane (DCM), *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), and dimethyl sulfoxide (DMSO). PI-ODPA was insoluble in these organic solvents, thus the solution-based characterization of PI-ODPA by GPC and NMR was not possible. PI-IMs were found to be soluble in DMAc, NMP, DMSO, and DMF. The good solubility of PI-IMs could be attributed to the presence of propeller-shaped triphenylamine, bulky —CF<sub>3</sub> groups and ionic character. Except for PI-ODPA, films of PI-IEs and PI-IMs could be cast from their DMAc solution (Supporting Information, Fig. S15).

IR spectra (Supporting Information, Fig. S10) of PI-IEs and PI-IMs exhibited characteristics bands of C=O stretching at 1784 and 1722 cm<sup>-1</sup>. In addition, bands of C—N and imide ring deformation were observed at 1364 and 820 cm<sup>-1</sup>, respectively. <sup>1</sup>H NMR spectra of PI-IEs and PI-IMs along with assignments are presented in Supporting Information, Figures S11–S14. In <sup>1</sup>H NMR spectra of [PI-6FDA][I]

(Supporting Information, Fig. S13) and [PI-6FDA][Tf<sub>2</sub>N] (Supporting Information, Fig. S14), the peak observed at  $\delta$  = 3.8 ppm is attributed to methyl group of *N*-quaternized polymer, indicating *N*-quaternization reaction was successful.

Inherent viscosity of PI-IEs and PI-IMs were in the range 0.62–0.72 dL/g (Table 1). Molecular weights of PI-IEs and PI-IMs were measured by GPC in DMF using polystyrene as a standard. PI-IEs and PI-IMs showed number average molecular weight and dispersity values in the range 79,200–35,000 g/mol and 2.1–1.6, respectively (Table 1). The measured GPC molecular weights of PI-IMs were lower than that of corresponding parent polyimide which could be attributed to the differences in solubility parameters and hydrodynamic volume due to variation in their chemical structures. Similar observations have been reported in the literature for polymers containing ionic groups.<sup>37</sup>

The broad halo in wide-angle X-ray diffraction patterns (Fig. 2) confirmed that PI-IEs and PI-IMs were amorphous in



SCHEME 2 Synthesis of polyimides containing pendent 2-phenylimidazole groups (PI-IEs).





SCHEME 3 Synthesis of polyimides containing imidazolium groups (PI-IMs).

nature. The amorphous nature could be attributed to the loosening of polymer chain packing due to the presence of bulky triphenylamine and 2-phenylimidazole in the polymer.

The interchain spacing (d-spacing) was calculated using Bragg's equation from peak maxima of X-ray diffractogram. The *d*-spacing values of PI-IEs and PI-IMs were in the range 5.43–5.67 Å (Table 1). The order of *d*-spacing is as follows: PI-ODPA < PI-BPADA < PI-6FDA < [PI-6FDA] [I] < [PI-6FDA] [Tf<sub>2</sub>N]. In the series of PI-IEs, PI-6FDA showed higher dspacing compared PI-ODPA and PI-BPADA. This could be attributed to the bulky hexafluoroisopropylidene linkages which disturbed polymer chain packing more effectively as compared to PI-ODPA and PI-BPADA which contain isopropylidene and ether linkages, respectively.<sup>39,40</sup> PI-IMs exhibited higher *d*-spacing as compared to parent polyimide which could be due to the presence of bulky ionic groups. In the case of PI-IMs, the *d*-spacing of PI-6FDA [TF<sub>2</sub>N] is higher compared to [PI-6FDA] [I], which indicated more disordered chain packing due to the bulkier nature of anion in the former. These results implied that both bulk of hinge groups present in the dianhydride and bulk of anion play an important role in governing the polymer chain packing.

The thermal properties of PI-IEs and PI-IMs were determined by TGA and DSC (Table 1 and Fig. 3). PI-IEs

TABLE 1 Synthesis and Properties of PI-IEs and PI-IMs

demonstrated excellent thermal stability with 10% weight loss and % char yield in the range 475–545 °C and 55–60, respectively. The 10% weight loss of PI-IMs was in the range 303–306 °C. PI-IMs exhibited lower  $T_{10}$  values compared to corresponding polyimide due to the decreased rigidity of polymer chains and the higher propensity of ionic moieties to degrade at a lower temperature compared to the parent heterocyclic moiety.<sup>33</sup> Glass transition temperature ( $T_g$ ) of PI-IEs were in the range 248–303 °C, as measured by DSC (Table 1). In case of PI-IEs with varying dianhydrides,  $T_g$  was in accordance with the order of rigidity of dianhydrides: 6FDA > ODPA > BPADA. No  $T_g$  was detected in DSC analysis of PI-IMs. Similar observations have been reported for polymers containing ionic groups in the literature.<sup>37</sup>

For gas separation applications, membranes should exhibit acceptable mechanical properties and sustain pressure during measurements. The films of PI-IEs and PI-IMs withstood pressure of 5–6 bar during gas permeability measurement experiments.

PI-IEs and PI-IMs exhibited tensile strength, Young's modulus, and elongation at break in the range 43.5–49.3 MPa, 0.91–1.38 GPa, and 7.9–31.5%, respectively. It was observed that the mechanical properties of PI-IMs were inferior to that of parent polyimide. This could be attributed to the

Sr. No.	Polymer	η <sub>inh</sub> (dL/ g) <sup>a</sup>	<i>M</i> <sub>n</sub> <sup>b</sup>	<i>M</i> <sub>w</sub> <sup>b</sup>	Dispersity <sup>c</sup>	<i>d</i> -Spacing (Å) <sup>d</sup>	T <sub>10</sub> <sup>e</sup> (°C)	τ <sub>g</sub> <sup>f</sup> (°C)	Char Yield <sup>g</sup> (%)	Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation at Break (%)
1	PI-6FDA	0.72	79200	128000	1.6	5.49	545	303	55	47.1	1.34	31.5
2	[PI-6FDA] [I]	0.65	40200	85000	2.1	5.63	303	ND	38	43.5	0.91	9.2
3	[PI-6FDA] [Tf <sub>2</sub> N]	0.62	35000	60000	1.7	5.67	306	ND	49	44.6	1.0	7.9
4	PI-BPADA	0.70	73000	117000	1.6	5.46	475	248	56	49.3	1.38	22.7
5	PI-ODPA	ns	ns	ns	ns	5.43	508	298	60	-	-	-

 $^a$  Measured at a concentration of 0.5 g/dL in DMAc at 35  $\pm$  °C.

<sup>b</sup> Molecular weights were obtained from GPC in DMF (Polystyrene standard).

<sup>c</sup> Dispersity =  $M_{\rm w}/M_{\rm n}$ .

<sup>d</sup> *d*-Spacing was calculated from X-ray diffractograms.

 $^{\rm e}$  Temperature at which 10% weight loss recorded by TGA at a heating rate of 10  $^{\circ}\text{C/min}.$ 

<sup>f</sup> Glass transition temperature ( $T_g$ ) recorded by DSC.

<sup>g</sup> Char yield at 900 °C.

Abbreviations: ND, not detected; ns, inherent viscosity and GPC measurements could not be carried out due to insolubility of polyimide in chloroform, tetrahydrofuran, and DMF.



FIGURE 2 X-ray diffractrograms of PI-IEs and PI-IMs. [Color figure can be viewed at wileyonlinelibrary.com]

weaker interchain interactions between polymer chains in PI-IMs as compared to parent polyimide. Similar observation has been reported in the literature for polybenzimidazole.<sup>23</sup>

# **Gas Permeability**

The gas permeability measurements of films of PI-6FDA, PI-BPADA, [PI-6FDA] [I], and [PI-6FDA] [Tf<sub>2</sub>N] were carried out by variable-volume method<sup>19,38</sup> and the data are summarized in Table 2. The sequence of gases studied is as follows: He,  $H_2$ ,  $N_2$ ,  $O_2$ ,  $CH_4$ , and  $CO_2$ . For easy comparison, the gas permeability data of commercially available polymers such as Matrimid<sup>9</sup> and polysulfone,<sup>41</sup> which are widely studied for gas separation applications is included in Table 2 (entries 5 and 6). Also included in Table 2 is the reported gas permeability data of polyamide<sup>42</sup> and polyimide<sup>32</sup> containing triphenylamine units (entries 7 and 8). The present polymers exhibited higher permeability than Matrimid and polysulfone. The selectivity data of PI-IEs and PI-IMs are comparable with the reported polyimide<sup>32</sup> and polyamide<sup>42</sup> containing triphenylamine units. The gas permeability order in this series is as PI-BPADA < PI-6FDA < [PI-6FDA] [I] < [PI-6FDA] [Tf<sub>2</sub>N]. PI-IEs exhibited CO<sub>2</sub> permeability in the range 11.9-19.7 Barr and selectivity for  $CO_2/CH_4$  and  $CO_2/N_2$  gas pairs was in the range 35.2-42.5 and 27.0-34.0, respectively. The relatively higher permeability of PI-6FDA could be due to presence of bulky hexafluoroisopropylidene linkages which



FIGURE 3 (a) TG curves of PI-IEs and PI-IMs and (b) DSC curves of PI-IEs. [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Gas Permeability and Selectivity Data of PI-IEs and PI-IMs<sup>a</sup>

		Permeability <sup>b</sup>						Selectivity <sup>c</sup>				
Sr.	Polymor	Цо	ц	N	0	сц	<u> </u>		0 /N			
INO.	rolymei	ne	112	112	02	CH <sub>4</sub>	$CO_2$	112/112	$O_2/N_2$	CO <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>	
1	PI-6FDA	31.1	23.0	0.73	3.5	0.56	19.7	31.5	4.8	27.0	35.2	
2	PI-BPADA	14.5	9.9	0.35	1.8	0.28	11.9	28.3	5.1	34.0	42.5	
3	[PI-6FDA] [I]	33.1	24.8	0.78	3.9	0.65	26.2	31.8	5.0	33.6	40.3	
4	[PI-6FDA] [Tf <sub>2</sub> N]	44.3	29.6	0.94	4.6	0.81	33.3	31.5	4.9	35.4	41.1	
5	Matrimid <sup>9</sup>	-	18.0	0.32	2.1	0.28	10.0	56.0	6.6	31.2	36.0	
6	Polysulfone <sup>41</sup>	-	14.0	0.25	1.40	0.25	5.6	56.0	5.6	22.4	22.0	
7	PA-A <sup>42</sup>	-	-	3.94	33.4	3.18	141	-	8.47	35.78	44.33	
8	PI-IIb <sup>32</sup>	-	-	0.89	4.28	0.50	16.8	-	4.81	18.9	33.43	

 $^{\rm a}$  Gas permeability measurements were carried out at room temperature (28 °C) and 5–7 bar.

 $^{\rm b}$  Units of permeability (P): 1 Barr = 10<sup>-10</sup> cm<sup>3</sup> (STP) cm/cm<sup>2</sup> s cmHg.  $^{\rm c}$  Selectivity ( $\alpha)=P_1/P_2.$ 





**FIGURE 4** Robeson plots of (1) PI-6FDA, (2) [PI-6FDA] [I], (3) [PI-6FDA] [Tf<sub>2</sub>N], and (4) 6.5 mol % mRTIL [36], (5) 14.8 mol % mRTIL [36], (6) 25.8 mol % mRTIL [36], (7) 8 mol % diRTIL [36], (8) PI-1–50 IL [37], (9) PI-1.TFSI [37], (10) PI-1.TFSI-50 IL [37] for (a)  $CO_2/CH_4$  and (b)  $CO_2/N_2$  gas pairs. [Color figure can be viewed at wileyonlinelibrary.com]

disturbed polymer chain packing more effectively compared to PI-BPADA which contains isopropylidene linkages.

PI-6FDA was chosen for the synthesis of PI-IMs due to its higher permeability than PI-BPADA. It was observed that incorporation of ionic groups into polyimide resulted in increased permeability while selectivity was maintained. PI-6FDA] [Tf<sub>2</sub>N] showed higher permeability compared to [PI-6FDA] [I]. For instance, [PI-6FDA] [Tf<sub>2</sub>N] exhibited CO<sub>2</sub> permeability of 33.3 Barr and selectivity for CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/ CH<sub>4</sub> was 35.4 and 41.1, respectively. The increment of gas permeation properties of PI-IMs could be attributed to the presence of ionic moieties which are known to interact with carbon dioxide and loosening of packing of polymer chains. This trend was also in good agreement with the *d*-spacing values. Overall, these results indicated that permeability of PI-IEs and PI-IMs increased with the bulkiness of hinge groups, ionic character, and bulk of anion.

The gas permeability and selectivity data of PI-6FDA, [PI-6FDA] [I], and [PI-6FDA] [Tf<sub>2</sub>N] were plotted against Robeson upper bound for  $CO_2/CH_4$  and  $CO_2/N_2$  gas pairs (Fig. 4) and compared with reported polyimides containing ionic groups.<sup>36,37</sup> It can be seen from Figure 4 that the present PI-IMs were placed above reported polymers containing imidazolium groups and specifically for the  $CO_2/CH_4$  gas pair, the present PI-IMs were located near Robeson upper bound.

# CONCLUSIONS

In this work, a new aromatic diamine, namely,  $N^{1}$ -(4-aminophenyl)- $N^{1}$ -(4-(2-phenyl-1H-imidazol-1-yl)phenyl)benzene-

1,4-diamine (ImTPADA), was successfully synthesized. ImTPADA was polycondensed with commercially available aromatic dianhydrides to obtain PI-IEs. PI-IMs were synthesized by *N*-quaternization of 2-phenylimidazole groups in [PI-6FDA] with methyl iodide followed by anion exchange with bis(trifluoromethane)sulfonimide lithium salt (LiTf<sub>2</sub>N). PI-IEs and PI-IMs were of reasonably high molecular weights, exhibited good solubility in organic solvents, and film-forming ability. The gas permeability increased by incorporation of ionic moieties into PI-6FDA and with the increase in the bulkiness of anion. Overall, the gas permeability data demonstrated that the present PI-IMs are attractive candidates for gas separation applications, particularly for  $CO_2$  separation.

#### ACKNOWLEDGMENT

Bharat Shrimant would like to thank University of Grant Commission (UGC), New Delhi, India for fellowship.

#### REFERENCES

- 1 D. R. Paul, Y. P. Yampolskii, Macromolecules 2012, 45, 3298.
- 2 L. M. Robeson, J. Membr. Sci. 1991, 62, 165.
- 3 N. Du, H. B. Park, M. M. Dal-Cin, M. D. Guiver, *Energy Environ. Sci.* 2012, *5*, 7306.
- **4** J. Liu, X. Hou, H. B. Park, H. Lin, *Chem. Eur. J.* **2016**, *22*, 15980.
- **5** Y. Alqaheem, A. Alomair, M. Vinoba, A. Pérez, *Int. J. Polym. Sci.* **2017**, *2017*, 1.
- 6 K. E. Hart, C. M. Colina, J. Membr. Sci. 2014, 468, 259.
- 7 L. M. Robeson, J. Membr. Sci. 2008, 320, 390.

8 S. Zulfiqar, M. I. Sarwar, D. Mecerreyes, *Polym. Chem.* 2015, *6*, 6435.

**9** D. F. Sanders, Z. P. Smith, R. Guo, L. M. Robeson, J. E. McGrath, D. R. Paul, B. D. Freeman, *Polymer* **2013**, *54*, 4729.

10 M. G. Cowan, D. L. Gin, R. D. Noble, *Acc. Chem. Res.* 2016, 49, 724.

11 L. C. Tome, I. M. Marrucho, *Chem. Soc. Rev.* 2016, *45*, 2785.
12 J. Qin, J. Guo, Q. Xu, Z. Zheng, H. Mao, F. Yan, *ACS Appl. Mater. Interfaces* 2017, *9*, 10504.

**13** J. Yuan, D. Mecerreyes, M. Antonietti, *Prog. Polym. Sci.* **2013**, *38*, 1009.

14 H. Chen, Y. A. Elabd, Macromolecules 2009, 42, 3368.

JOURNAL OF POLYMER SCIENCE Chemistry

**15** S. M. Morozova, A. S. Shaplov, E. I. Lozinskaya, D. Mecerreyes, H. Sardon, S. Zulfiqar, F. Suárez-García, Y. S. Vygodskii, *Macromolecules* **2017**, *50*, 2814.

**16** L. Porcarelli, A. S. Shaplov, M. Salsamendi, J. R. Nair, Y. S. Vygodskii, D. Mecerreyes, C. Gerbaldi, *ACS Appl. Mater. Inter-faces* **2016**, *8*, 10350.

**17** F. N. Ajjan, M. Ambrogi, G. A. Tiruye, D. Cordella, A. M. Fernandes, K. Grygiel, M. Isik, N. Patil, L. Porcarelli, G. Rocasalbas, G. Vendramientto, E. Zeglio, M. Antonietti, C. Detrembleur, O. Inganäs, C. Jérôme, R. Marcilla, D. Mecerreyes, M. Moreno, D. Taton, N. Solin, J. Yuan, *Polym. Int.* **2017**, *66*, 1119.

**18** L. C. Tomé, M. Isik, C. S. R. Freire, D. Mecerreyes, I. M. Marrucho, *J. Membr. Sci.* **2015**, *483*, 155.

**19** A. S. Rewar, S. V. Shaligram, U. K. Kharul, *J. Membr. Sci.* **2016**, *497*, 282.

**20** M. S. Mittenthal, B. S. Flowers, J. E. Bara, J. W. Whitley, S. K. Spear, J. D. Roveda, D. A. Wallace, M. S. Shannon, R. Holler, R. Martens, D. T. Daly, *Ind. Eng. Chem. Res.* **2017**, *56*, 5055.

**21** R. S. Bhavsar, S. C. Kumbharkar, U. K. Kharul, *J. Membr. Sci.* **2012**, *389*, 305.

22 R. S. Bhavsar, S. C. Kumbharkar, U. K. Kharul, *J. Membr. Sci.* 2014, *470*, 494.

**23** R. S. Bhavsar, S. C. Kumbharkar, A. S. Rewar, U. K. Kharul, *Polym. Chem.* **2014**, *5*, 4083.

24 S. C. Kumbharkar, R. S. Bhavsar, U. K. Kharul, *RSC Adv.* 2014, *4*, 4500.

25 P. Li, M. R. Coleman, Eur. Polym. J. 2013, 49, 482.

26 M. G. Cowan, M. Masuda, W. M. McDanel, Y. Kohno, D. L. Gin, R. D. Noble, *J. Membr. Sci.* 2016, *498*, 408.

**27** D. J. Liaw, K. L. Wang, Y. C. Huang, K. R. Lee, J. Y. Lai, C. S. Ha, *Prog. Polym. Sci.* **2012**, *37*, 907.

28 M. G. Dhara, S. Banerjee, Prog. Polym. Sci. 2010, 35, 1022.

29 L. S. White, T. A. Blinka, H. A. Kloczewski, I. f. Wang, J. Membr. Sci. 1995, 103, 73.

**30** S.-H. Park, K.-J. Kim, W.-W. So, S.-J. Moon, S.-B. Lee, *Macromol. Res.* **2003**, *11*, 157.

**31** H. Yen, S. Guo, J. Yeh, G. Liou, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 3637.

**32** C. W. Chang, H. J. Yen, K. Y. Huang, J. M. Yeh, G. S. Liou, *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *49*, 487.

**33** Y. Nagase, B. Suleimenova, C. Umeda, K. Taira, T. Oda, S. Suzuki, Y. Okamura, S. Koguchi, *Polymer* **2018**, *135*, 142.

34 X. Ma, O. Salinas, E. Litwiller, I. Pinnau, *Macromolecules* 2013, *46*, 9618.

**35** X. Ma, R. Swaidan, Y. Belmabkhout, Y. Zhu, E. Litwiller, M. Jouiad, I. Pinnau, Y. Han, *Macromolecules* **2012**, *45*, 3841.

**36** P. Li, Q. Zhao, J. L. Anderson, S. Varanasi, M. R. Coleman, *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 4036.

**37** A. S. Shaplov, S. M. Morozova, E. I. Lozinskaya, P. S. Vlasov, A. S. L. Gouveia, L. C. Tomé, I. M. Marrucho, Y. S. Vygodskii, *Polym. Chem.* **2016**, *7*, 580.

38 I. Sava, S. Chisca, A. Wolinska-Grabczyk, A. Jankowski, M. Sava, E. Grabiec, M. Bruma, *Polym. Int.* 2015, *64*, 154.

39 K. Matsumoto, P. Xu, J. Membr. Sci. 1993, 81, 23.

40 M. R. Coleman, W. J. Koros, *Macromolecules* 1997, 30, 6899.

**41** C. L. Aitken, W. J. Koros, D. R. Paul, *Macromolecules* **1992**, *25*, 3424.

**42** D. Bera, P. Bandyopadhyay, S. Ghosh, S. Banerjee, V. Padmanabhan, *J. Membr. Sci.* **2015**, *474*, 20.

