Mechanically and Thermally Enhanced Intrinsically Dopeable Polyimide Membrane with Advanced Gas Separation Capabilities

Chang-Jian Weng,† Yu-Sian Jhuo,† Kuan-Yeh Huang,† Chun-Fang Feng,† Jui-Ming Yeh,†,* Yen Wei,§† and Mei-Hui Tsai‡

†Department of Chemistry and Center for Nanotechnology, Chung-Yuan Christian University, Chung Li 32023, Taiwan, R.O.C
‡Material and Chemical Research Laboratories, Industrial Technology Research Institute, Hsin Chu 310, Taiwan, R.O.C
§Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104, United States

ABSTRACT: In this paper, we present the first preparation of an intrinsically dopeable polyimide (DPI) membrane containing an amine-capped aniline trimer (ACAT) that reveals advanced gas separation capabilities as well as mechanically and thermally enhanced properties. The as-prepared DPI membrane was synthesized by reacting ACAT and 4,4’-(4,4’-isopropylidenediphenoxy)bis(phthalic anhydride) (BSAA) through a conventional thermal imidization reaction. Polyaniline (PANI) and conventional nondopeable polyimide (NDPI) membranes were also prepared as controls. The DPI membranes were found to reveal permselectivities of about 13.54, which is about 1.96- and 1.54-fold higher than that of NDPI and PANI, respectively, based on the investigation of gas permeability analysis (GPA). Upon doping with 1.0 M HCl (aq), the permselectivities of DPI for O2/N2 were found to be further increased to about 16.63. Moreover, significantly enhanced mechanical and thermal properties of the as-prepared DPI membrane were also found as compared to those of NDPI and PANI membranes, based on the studies of dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA), respectively.

INTRODUCTION
Membrane science and technology are recognized today as powerful tools in solving some important global problems, such as developing new processes needed for sustainable industrial growth. The key for new applications of membranes in challenging and harsh environments (e.g., petrochemistry) lies in the development of new, tough, high performance materials. To develop good gas separation membrane materials, it is important to investigate the factors influencing gas permeation, permselectivity, thermal stability, and mechanical properties of polymers.

A number of reviews examining the various materials for gas separation membranes have been published over the last two decades.1–10 Among the studied materials, it was noted that polyimides (PI), which exhibit high permselectivity for various gas pairs (e.g., CO2/CH4 and O2/N2), high chemical resistance, thermal stability, and mechanical strength, have attracted much attention. To the best of our knowledge, there are about 450 publications related to gas separation studies of polyimide membranes in the ISI web database.

Gas separation studies associated with polyaniline (PANI) membranes were first initiated by Anderson et al. in early 1990.11,12 Research interest in using PANI also lies in the fact that film morphology can be modified after synthesis by a convenient doping process, which enables the optimization of a particular separation. In contrast, controlling the morphology of a polymer after its synthesis is difficult to accomplish with conventional polymers such as polyimide since they cannot readily be intrinsically doped. Therefore, some research groups have attempted to control the morphology of a polyimide membrane in order to fine-tune the gas separation by blending different feeding ratios of PANI.13–15

Recently, research activities in terms of oligoanilines with well-defined structures for modeling the electronic, magnetic, and optical properties of PANI have been evoked.16,17 Moreover, electroactive polymers derived from oligoaniline, such as electroactive polyamide,18–20 electroactive polyimide,20–23 and electroactive epoxy,24,25 have also attained considerable research interest. However, to the best of our knowledge, reports on gas separation studies using electroactive polyimide membranes are limited. In this paper, therefore, we present the first preparation of an intrinsically dopeable polyimide (DPI) membrane and investigate its advanced gas separation capabilities using gas permeability analysis (GPA), followed by an evaluation of the mechanical strength and thermal stability of the corresponding membrane by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA), respectively.

Received: May 17, 2011
Revised: June 26, 2011
Published: July 11, 2011
EXPERIMENTAL SECTION

Chemicals and Instrumentation. Aniline (Sigma-Aldrich) was distilled prior to use. The compounds 4,4'-oxidianiline (ODA; Fluka, Buchs, Switzerland), 1,4-phenylenediamine (Sigma-Aldrich), N,N-dimethylacetamide (DMAc; Mallinckrodt/Baker, Paris, KY), 4,4'-(4,4'-isopropylidenediphenoxy)bis(phthalic anhydride) (BSAA, Sigma-Aldrich, 97%) and sodium chloride (NaCl, Sigma-Aldrich) were used as received without further purification. All the reagents were reagent grade unless otherwise stated.

Attenuated total reflectance FTIR was obtained with an FTIR spectrometer (JASCO FTIR-4100) at room temperature. Electroactive experiments were performed using a VoltaLab 40 (PGZ 301) analytical voltameter with a conventional three-electrode system. A Yanagimoto Co., Ltd. gas permeability analyzer (model GTR31) was employed to perform the permeation experiment for oxygen/nitrogen and carbon dioxide/methane gases. Dynamic mechanical analysis (DMA) measurements were made using a TA Instruments DMA Q 800 at a heating rate of 3 °C/min from 30 to 350 °C and a frequency of 1 Hz. The thermal stabilities of all the samples were characterized by thermal gravimetric analysis (TGA). TGA scans were performed under air flow using a TA Q50 at a heating rate of 10 °C/min.

Figure 1. (a) Schematic representation of the synthesis of ACAT and dopable polyimide (DPI) and (b) photographs of DPI.

Figure 2. FTIR spectra of the obtained (a) DPAA and (b) DPI without additional dopant.

Figure 3. Cyclic voltammetry of the DPI membranes measured in aqueous H$_2$SO$_4$ (1.0 M) at a scan rate of 50 mV s$^{-1}$. 
The resulting precipitate was collected by filtration and washed with 1 M NH₄OH (aq) and magnetically stirred for 30 min, both solutions were mixed together. The as-prepared DPI membrane with membrane thickness of 50 μm and exhibiting a shiny surface was found to exhibit toughness and flexibility simultaneously, as shown in Figure 1b.

Figure 2 shows the FTIR spectra of obtained intrinsically (a) and nondopable polyimide (NDPI) membranes and (b) DPI membranes without dopant. For example, the characteristic absorption bands appearing at 3300 and 3200 cm⁻¹ were assigned to the terminal –NH₂ groups of ACAT. The characteristic absorption peaks found at 1600 and 1500 cm⁻¹ were attributed to the characteristic vibration bands of the quinoid and benzoid rings of ACAT, respectively. The absorption peak located at 830 cm⁻¹ was determined to be a characteristic of the para-substitution of the 1,4-disubstituted benzene ring. An obvious peak found at 3405 cm⁻¹ was attributed to the vibration band of N–H stretching. Moreover, the vibration bands appearing at around 1778 and 1720 cm⁻¹ resulted from the asymmetric and symmetric carbonyl stretching of imide groups. The characteristic peak occurred at 1346 cm⁻¹ was attributed to the vibration of the terminal –NH₂ groups of ACAT. The characteristic peak of 2365 cm⁻¹ was attributed to the characteristic vibration bands of the quinoid and benzoid rings of ACAT, respectively.

RESULTS AND DISCUSSION

Intrinsically dopeable polyaniline (DDPA) membranes and (b) DPI membranes without dopant. For example, the characteristic absorption bands appearing at 3300 and 3200 cm⁻¹ were assigned to be the terminal –NH₂ groups of ACAT. The characteristic absorption peaks found at 1600 and 1500 cm⁻¹ were attributed to the characteristic vibration bands of the quinoid and benzoid rings of ACAT, respectively. The absorption peak located at 830 cm⁻¹ was determined to be a characteristic of the para-substitution of the 1,4-disubstituted benzene ring. An obvious peak found at 3405 cm⁻¹ was attributed to the vibration band of N–H stretching. Moreover, the vibration bands appearing at around 1778 and 1720 cm⁻¹ resulted from the asymmetric and symmetric carbonyl stretching of imide groups. The characteristic peak occurred at 1346 cm⁻¹ was attributed to the vibration of the terminal –NH₂ groups of ACAT. The characteristic peak of 2365 cm⁻¹ was attributed to the characteristic vibration bands of the quinoid and benzoid rings of ACAT, respectively.
A characteristic peak associated with the out-of-plane C—H bending existing in the 1,4-disubstituted benzene ring was reflected at 830 cm$^{-1}$. A characteristic peak near 740 cm$^{-1}$ due to the imide ring deformation$^{26}$ of DPI was also found in the FTIR spectra.
According to the proposed mechanism for electrochemical redox reaction of aniline oligomers, the electrochemical behavior of the obtained DPI membranes was examined in a strongly acidic electrolyte composed of 1.0 M H2SO4 aqueous solution. DPI was formed by coating DPAA on the surface of a Pt working electrode, followed by thermal imidization into DPI. Figure 3 shows the cyclic voltammetry (CV) of the DPI obtained using a saturated calomel electrode (SCE) as the reference electrode with a scan rate of 50 mV s⁻¹. Under these conditions, CV studies of the DPI membrane showed a pair of reversible redox peaks, which was similar to many longer oligomers that undergo a two-electron-transfer process. For the studies of DPI, a single oxidation peak was found to occur at a lower potential of 582 mV as compared to that of PANI at a potential of 800 mV. We envisioned that the oxidation peak shift of DPI as compared to that of PANI could be attributed to the transition of DPI from a reduced state to an oxidized state.

Upon doping with HCl, the corresponding electrical conductivity of DPI membranes was also found to change, as demonstrated by the diffuse reflectance UV–visible spectrum by using an integrating sphere and BaSO4 as a white standard. Diffuse reflectance spectrum were recorded as Rstand/Rsample versus wavelength, where R is the absolute reflection intensity (Figure 4). Similar to PANI, the quinoid (Q) absorption peak appearing at 509 nm and the benzenoid (B) peak located at 312 nm were assigned to two characteristic peaks existing in the emeraldine base (EB) form of DPI. These peaks were associated with the transition of π→π* from a benzene unit to a quinone unit and from the π−→π transition in the benzene unit, respectively. Moreover, the emeraldine salt (ES) form of DPI could be generated upon doping with HCl. It should be noted that the two electronic transitions found at 312 and 509 nm gradually disappeared upon doping with HCl; instead, new bands were observed at around 415 and 800 nm. The peak appearing at 415 nm was probably due to the formation of polarons (radical cations) caused by the electron transition of quinoid to benzenoid units. The peak found at 800 nm with a long tail was assigned to the polaron transition, which typically characterizes protonation and is identical to that of the emeraldine salt (ES) form of the DPI membrane.

The effectiveness of the doping process in the DPI polymer matrix was also studied using an SEM mapping technique. Figure 5 shows SEM mapping and energy dispersive X-ray (EDX) spectra of the surfaces of the DPI and DPI doped with 1 M HCl (aq).

Table 1. Physical Properties of NDPI, DPI, DPI-Doped, PANI, and PANI-Doped Membranes

<table>
<thead>
<tr>
<th>compound code</th>
<th>θ (deg)</th>
<th>d-spacing (Å)</th>
<th>ρ (g/cm³)</th>
<th>FFV</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDPI</td>
<td>14.44</td>
<td>6.13</td>
<td>1.268</td>
<td>0.152</td>
</tr>
<tr>
<td>DPI</td>
<td>15.56</td>
<td>5.69</td>
<td>1.283</td>
<td>0.133</td>
</tr>
<tr>
<td>DPI-doped</td>
<td>17.65</td>
<td>5.02</td>
<td>1.313</td>
<td>0.112</td>
</tr>
<tr>
<td>PANI</td>
<td>18.73</td>
<td>4.73</td>
<td>1.258</td>
<td>0.090</td>
</tr>
<tr>
<td>PANI-doped</td>
<td>23.68</td>
<td>3.75</td>
<td>1.320</td>
<td>0.056</td>
</tr>
</tbody>
</table>

Figure 7. Variation of permeability coefficient for the studied membranes with temperature—mixed air gases: (a) O₂, (b) N₂ and pure gases, and (c) CO₂ at 1 barrer. (d) Variation of permeability coefficient for membranes at 303 K.
Figure 5b shows the SEM chloride mapping image on the DPI-doped membrane, in which we see many white spots (i.e., the chloride element) dispersed uniformly in a black background (i.e., the polymer matrix), but the white spots essentially disappear in the DPI matrix (Figure 5a). Compared with the DPI membrane, a new element (Cl) appears in the DPI-doped membrane in the EDX spectra, as shown in Figure 5, parts c and d. These results indicate the DPI can be easily doped with HCl and the chloride dopant counterions can be well dispersed in the DPI-doped matrix.

If the material is crystalline in nature, the peak from the X-ray diffraction (XRD) is sharp and the intensity is strong. However, when the material is amorphous, the peak is rather broad. In this study, the present NDPI, DPI, DPI-doped, PANI, and PANI-doped membranes, were all regarded as rather amorphous materials, as can be seen in the XRD patterns in Figure 6A. However, the XRD pattern of an amorphous polymer is typically dominated by one broad peak associated with the center-to-center chain distance or d-spacing. The d-spacing values were calculated from Bragg’s equation, \( n\lambda = 2d \sin \theta \), where \( \theta \) is the angle for a peak in the patterns. Here, \( 2\theta \) at the maximum intensity appearing at around 14°–24° was used to calculate the d-spacing, which was representative of the average degree of openness within the material. The \( 2\theta \) of the NDPI was around 14.44 Å and the d-spacing was about 6.13 Å. After the doping treatment, the \( 2\theta \) and d-spacing values were unchanged because the NDPI could not be doped. Interestingly, upon doping with 1 M HCl (aq), the d-spacing of the DPI and PANI membranes decreased from 5.69 to 5.02 Å and 4.73 Å to 3.75 Å, respectively. The results indicated that the HCl dopant causes a decrease of d-spacing between the center-to-center chain distances. It is believed that polymers with smaller d-spacing generally tend to have a smaller fractional free volume (FFV).32

The FFV can be calculated by the following equation33

\[
\text{FFV} = \frac{V - V_0}{V}
\]

Figure 8. Variation of permeability selectivity for the studied membranes at 303 K (a) O\(_2\)/N\(_2\) and (b) CO\(_2\)/N\(_2\).

<table>
<thead>
<tr>
<th>kind of materials</th>
<th>membranes</th>
<th>researcher</th>
<th>( P(\text{O}_2) )</th>
<th>( \text{O}_2/\text{N}_2 )</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>polyaniline (PANI)</td>
<td>PANI</td>
<td>Anderson et al. (1991)</td>
<td>0.1</td>
<td>6.66</td>
<td>11, 37</td>
</tr>
<tr>
<td></td>
<td>PANI</td>
<td>Wang et al. (1999)*</td>
<td>0.151</td>
<td>9.15</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>PANI</td>
<td>Young Moo Lee (1999)</td>
<td>0.49</td>
<td>7.2</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>PANI-doped</td>
<td>Young Moo Lee (1999)</td>
<td>0</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PANI</td>
<td>Min-Jong Chang (1996)</td>
<td>0.12</td>
<td>7.06</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>PANI-doped</td>
<td>Min-Jong Chang (1996)</td>
<td>0.016</td>
<td>–</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>PANI</td>
<td>Rebattet et al. (1995)*</td>
<td>0.121</td>
<td>6.36</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>PANI-doped</td>
<td>Rebattet et al. (1995)*</td>
<td>0.01</td>
<td>2.5</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>PANI</td>
<td>Martin et al. (1994)</td>
<td>0.164</td>
<td>14.8</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>PANI</td>
<td>Richard B. Kaner (1997)</td>
<td>0.174</td>
<td>9.1</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>PANI/Polyimide</td>
<td>Richard B. Kaner (1997)</td>
<td>0.282</td>
<td>10</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>BTDA/ODA</td>
<td>Richard B. Kaner (1997)</td>
<td>0.174</td>
<td>6.2</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>6FDA – TAPOB</td>
<td>Yasuhatu Yamada (2002)</td>
<td>2.25</td>
<td>6.21</td>
<td>45</td>
</tr>
<tr>
<td>nondopable polyimide (NDPI)</td>
<td>(BADBSBF–BTDA)</td>
<td>Soon-Ki Kwon (2005)</td>
<td>18</td>
<td>9</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>6FDA – NDA</td>
<td>Tai Shung Chung (2009)</td>
<td>8.99</td>
<td>5.18</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>6FDA – MDMA</td>
<td>L. M. Robeson (1999)</td>
<td>122</td>
<td>3.43</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>6FDA – MDA</td>
<td>Maria Coleman (2010)</td>
<td>0.86</td>
<td>5.3</td>
<td>49</td>
</tr>
<tr>
<td>dopable polyimide (DPI)</td>
<td>DPI</td>
<td>this work</td>
<td>1.06</td>
<td>13.54</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>DPI-doped</td>
<td>this work</td>
<td>0.93</td>
<td>16.63</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 2. Comparison of Permeability of O\(_2\) and Selectivity Factor of O\(_2\)/N\(_2\) Data Appearing in the Literature
where \( V \) is the specific volume and \( V_0 \) is the occupied volume of the polymer. The occupied volume was calculated by

\[
V_0 = \frac{1}{3} V_W
\]

where \( V_W \) is the van der Waals volume which was estimated by the group contribution method by Bondi\(^{34}\) for the copolymers, the \( V_W \) is calculated by \( V_W = m_1 V_{W1} + m_2 V_{W2} \), where \( m_1 \) and \( m_2 \) are the molar fractions and \( V_{W1} \) and \( V_{W2} \) refer to the Van der Waals volumes of the homopolyaniline.\(^{34}\) The specific free volume \( V_{\text{mix}} \) is calculated by using the addition method (\( V_{\text{mix}} = w_1 V_{f1} + w_2 V_{f2} \), where \( w_1 \) and \( w_2 \) are the weight fractions, and \( V_{f1} \) is the specific free volume of homopolymers). The obtained \( \rho \) and FFV of the specimens are listed in Table 1. The FFV of polymer membranes in this study was calculated to be in the range of 0.056–0.152 and the ordering of DPI-doped > PANI-doped > DPI > NDPI > PANI agreed with the density value. It is worth noticing that the FFV values of DPI decreased from 0.133 to 0.112 while the DPI was doped with 1 M HCl(aq).\(^{11}\)

This phenomenon was similar to PANI results listed in the literature.\(^{11}\) The decreased FFV can be attributed to the presence of chloride dopant counterions, which fill much of the free volume in the DPI structure.

Figure 9. Effect of temperature on the performance of as-prepared membranes: Arrhenius plot of the permeation of (a) \( O_2 \), (b) \( N_2 \), and (c) \( CO_2 \). (d) Activation energy values for the studied membranes.

Table 3. Thermal Properties and Mechanical Strength of NDPI, DPI, and PANI

<table>
<thead>
<tr>
<th>sample code</th>
<th>( T_d^a )(°C)</th>
<th>storage modulus (MPa)</th>
<th>( tan\delta^b )(°C)</th>
<th>thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDPI</td>
<td>547</td>
<td>2008</td>
<td>281</td>
<td>50</td>
</tr>
<tr>
<td>DPI</td>
<td>593</td>
<td>2800</td>
<td>299</td>
<td>49</td>
</tr>
<tr>
<td>PANI</td>
<td>462</td>
<td>1800</td>
<td>228</td>
<td>51</td>
</tr>
</tbody>
</table>

\(^a\) As measured by TGA (onset point). \(^b\) As measured by DMA at 30 °C.

In general, the performance of membrane units in the separation of a gaseous mixture is highly dependent on the intrinsic physicochemical characteristics of the polymeric materials utilized. The most important properties that need to be taken into account when selecting a polymeric membrane material are (i) its gas permeability and selectivity coefficients, (ii) its mechanical properties, and (iii) its thermal properties.

The permeability coefficients of \( O_2 \), \( N_2 \), and \( CO_2 \) for DPI, NDPI, and PANI membranes were investigated by performing permeation tests at different operational temperatures, as shown in Figure 7 and listed in S-Table 1 (see Supporting Information). The permeability coefficients of corresponding samples for three gases decreased at each temperature, in the order \( P(CO_2) > P(O_2) > P(N_2) \). This was also the order of increasing kinetic molecular diameters (\( CO_2 \), 3.30 Å; \( O_2 \), 3.46 Å; and \( N_2 \), 3.64 Å) of the penetrant gases. It was observed that the permeability of NDPI and DPI was higher than that of PANI. Generally speaking, chemical structures coupled with subtle physical properties of the membrane material could influence the permeability and selectivity of a gas. The responses of a polymeric material to permeation are strongly influenced by the polarity and steric
characteristics of both the polymer and the permeate. The size and shape of bulky groups in both polymer backbones and side chains determine certain fundamental properties like packing density and rigidity, which in turn influence permeability. These parameters, along with the diffusion coefficient, govern the separating capabilities of polymers for O₂, N₂, and CO₂ gas pairs. As polymer molecular spacing becomes tighter the permeability decreases due to decreasing diffusion coefficients but the separation characteristics are enhanced. In this work, polyimide systems contained either rigid (ODA or ACAT) or flexible blocks (BSAA). Rigid block segments provided the main structural framework and better thermal resistance, while the flexible block governed the transportation of gas molecules. On the other hand, PANI consisting of a fully rigid aromatic structure has a higher packing density than polyimide systems. After doping protonic dopants (e.g., 1.0 M HCl) to imide nitrogen on either PANI or DPI backbones, the permeability decreased for all the gases. This effect was due to doping DPI or PANI, in which the dopant reduced the free volume in the polymer (morphological changes) and led to an obvious decrease in gas permeability.⁴⁸,⁴⁹

Permselectivity of the as-prepared membranes was calculated as the ratio of permeability coefficients of each gas pair, as shown in Figure 8. The temperature dependence of permeability was evaluated and the effect of temperature on the permeability coefficient is listed in S-Table 2 (see Supporting Information). The permselectivity decreased as the temperature increased. With an increase in temperature, the chain mobility and the frequency of intersegmental jumps of gas molecules increased, increasing the diffusion rate as the permeation rate also increased. At the same time, the chain segment motions may have widened, resulting in low selectivity for a gas pair.

We observed that the permselectivity of DPI was greater than it was in the PANI and NDPI membranes, especially in selectivity of O₂/N₂. For example, the permselectivity measured at an operational temperature of 303 K for DPI, NDPI, and PANI was found to be 13.54, 6.89, and 8.76, respectively. It is worth noting that the permselectivity of DPI was on the order of 1.96- and 1.54-fold higher than that of NDPI and PANI, respectively. Upon doping with 1.0 M HCl aqueous for 15 h, the permselectivity of the DPI obviously increased from 13.54 to 16.63, making it almost 2.4-fold higher than that of NDPI and PANI, respectively. Figure 9 and S-Table 3 (see Supporting Information) present an Arrhenius plot of permeation of O₂, N₂, and CO₂ for all as-prepared samples at an operational pressure of 294 kPa upstream pressure. In general, the temperature dependencies of P can be described by the Arrhenius equation³⁵

\[ P = P_0 \exp \left( \frac{-E_p}{RT} \right) \]

where \( P_0 \) represents pre-exponential factors, \( E_p \) is the apparent activation energy for gas permeation, \( R \) is the gas constant, and \( T \) is temperature. Figure 9d shows the calculated apparent activation energies of O₂, N₂, and CO₂ for permeation and the corresponding pre-exponential factors based on the Arrhenius plots. It can be seen that the activation energy of permeability, \( E_p \), increased with an increase in the kinetic diameter of a penetrant gas and was in the order of CO₂ (3.30 Å), O₂ (3.46 Å), and N₂ (3.64 Å). Although, permeability coefficients increased with temperature, permselectivity for gas pairs of O₂/N₂ and CO₂/N₂ decreased due to differences in permeation activation energies for various gas pairs. Dependence of permselectivity for a gas pair can be evaluated by the difference in activation energy.³⁶ The DPI exhibited much higher permselectivity than PANI and NDPI, ascribed to the fact that DPI has a much greater difference between N₂ and O₂ in activation energies of permeability, \( \Delta E_p \), than PANI and NDPI.
Permselectivity of O$_2$/N$_2$ of the as-prepared DPI presented in this study is compared and summarized in Table 2, which includes data proposed by other investigators for free-standing films of PANI and conventional PI. In this study, permselectivity of O$_2$/N$_2$, which was about 13.54 for the undoped DPI membrane, was quite comparable to that of PANI and conventional PI film as reported by other investigators$^{11,37-49}$ who reported O$_2$/N$_2$ permeability selectivity in the range of 2–10. However, upon doping with 1.0 M HCl (aq), the permselectivity of O$_2$/N$_2$ of the DPI membrane increased from 13.54 to 16.63.

Polymeric membranes generally undergo a trade-off limitation between permeability and selectivity: as selectivity increases, permeability decreases, and vice versa. Robeson,$^{50}$ collecting a large number of permeation data for different polymeric membranes, showed that for small gaseous molecules (e.g., O$_2$, N$_2$, and CO$_2$) a superior limit (upper bound) exists in a selectivity/permeability diagram. In this work, DPI for gas pairs were also evaluated and compared to Robeson’s upper bound,$^{50}$ as shown in Figure 10. The upper bound demarcated the optimum performance of the polymeric membranes, which typically display a trade-off between permeability and permselectivity. As depicted in Figure 10, the N$_2$/O$_2$ separation performances of DPI, NDPI, and PANI displayed a typical trade-off relationship between permeability and permselectivity. The NDPI and PANI permselectivities were lower than those of the DPI and fell below Robeson’s old upper bound (1991). Surprisingly, the DPI with doping had a permselectivity that was much higher than Robeson’s new upper bound (2008).

An enhancement of the thermal stability behavior of the as-prepared membranes was determined by thermal gravimetric analysis (TGA) under air atmosphere, as shown in Figure 11 and summarized in Table 3. It should be noted that the decomposition temperature ($T_d$) of DPI was found to be $593^\circ$C, which was significantly higher than that of PANI ($462^\circ$C) and NDPI ($547^\circ$C). The dynamic mechanical properties of DPI, NDPI, and PANI films are presented in Figure 12A and are also summarized in Table 3. Specifically, the DPI membrane exhibited storage modulus at about 2800 MPa, which was found to be larger than that of NDPI (about 2008 MPa) and PANI (about 1800 MPa) at room temperature of about 30 $^\circ$C. At an elevated temperature of about 350 $^\circ$C, the DPI membrane had a remarkable increase of modulus compared to NDPI and PANI. For as-prepared membranes, the maximum tan $\delta$ (E’/E”) is defined as the glass transition temperature ($T_g$)$^{51}$ NDPI and PANI were found to show lower glass transition temperatures ($T_g$) compared with DPI, as shown in Figure 12B. Enhanced mechanical and thermal properties for as-prepared DPI membrane as compared to those of NDPI membrane prepared from similar thermal imidization reactions might be attributed to the incorporated aromatic rigid structure of ACAT into the PI membrane.

**CONCLUSIONS**

In conclusion, we present the first preparation of an intrinsically dopable polyimide (DPI) membrane containing an amine-capped aniline trimer (ACAT) that reveals advanced gas separation capabilities as well as mechanically and thermally enhanced properties. In regard to gas separation, the permeability and permselectivity of the DPI membrane can be tuned by doping with a dopant. This doping behavior is similar to PANI. Compared with a conventional nondopable PI (NDPI) and PANI, the DPI has good permselectivity about 1.5-fold higher than PANI and 2-fold higher than NDPI. Upon doping with 1.0 M HCl (aq), the permselectivity of DPI was about 2.4-fold higher than that of NDPI. In regard to physical properties, DPI has excellent thermal stability and mechanical properties similar to NDPI. Comparing the mechanical properties of the NDPI and PANI membranes, the DPI membrane showed a storage modulus of 2800 MPa at 30 $^\circ$C, which was an increase of about 39.4% and 55.5% higher than that of NDPI and PANI membranes, respectively. The decomposed temperature of DPI also increased substantially, to around 131 $^\circ$C as compared with PANI and to around 46 $^\circ$C as compared with NDPI. The DPI has good thermal stability, mechanical properties, and high permselectivity, characteristics which might be very useful in the gas separation field.

**ASSOCIATED CONTENT**

Supporting Information. $^1$H NMR and $^{13}$C NMR spectra of dopable polyimide model compound, $^1$H NMR spectra of dopable polyimide, gas permeability of NDPI, DPI, and PANI, ideal separation factors, and activation energies for DPI, NDPI, and PANI membranes. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Author

E-mail: juiming@cycu.edu.tw. Telephone: +886-3-2653340. Fax: +886-3-2653399.
REFERENCES

(4) Freeman, B. D.; Pinnau, I. Polymer membranes for gas and vapor separations; ACS Symposium Series 733; American Chemical Society: Washington DC, 1999; Chapter 1.