# Macromolecules

# Effect of Isomerism on Molecular Packing and Gas Transport Properties of Poly(benzoxazole-*co*-imide)s

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# **S** Supporting Information

**ABSTRACT:** A facile approach to synthesize poly-(benzoxazole-*co*-imide)s without thermal rearrangement at high temperature is proposed. Poly(benzoxazole-*co*-imide)s with improved mechanical and solution-processable properties were prepared through polycondensation of 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) with three synthesized novel benzoxazole-containing diamines and a commercial diamine. These poly(benzoxazole-*co*-imide)s had high tensile strengths of 110.3–122.0 MPa and good elongation at break of 11.9–26.3%, good thermal stability



and high glass transition temperatures ( $T_{g}$ s) of up 306 °C. The effect of chain isomerism on molecular packing and physical and gas transport properties of the poly(benzoxazole-*co*-imide)s was investigated. The *para*-connecting isomers exhibited higher molecular weights ( $M_w$ s), better mechanical properties, higher  $T_g$ s, higher chain packing order and better overall performance for CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> separations as compared to the corresponding *meta*-connecting ones. This study guides molecular architecture to improve particular membrane separation performance by introducing either *para*- or *meta*-connections into polymeric main chains.

# INTRODUCTION

Polyimides (PIs) are one of the most attractive polymers for membrane-based gas separations because they exhibit high gas selectivity for major gas pairs (e.g., O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub>) and desirable permeability. <sup>1-9</sup> They also have good thermal stability and chemical resistance, and excellent mechanical properties, which make them suitable for use in harsh conditions, such as high temperatures, high pressures, high stress, and aggressive chemical environments. More importantly, the specific design architecture within the diverse family of polyimides can be tailored to improve their processability and other performance parameters for particular applications by simply adjusting diamine and dianhydride monomer structures. However, for many polymeric membranes used for gas separation applications, a gain in permeability is usually countered by a decline of selectivity, which has been described by Robeson for several gas pairs.<sup>10,11</sup> In an effort to achieve optimum economic performance for membrane materials used as gas separation media, high permeability along with high selectivity are desirable. Commercial polyimides, such as Upilex and Kapton films usually exhibit low permeability (e.g., the permeability to  $CO_2$  is less than 10 Barrer). Therefore, much of the research work is being addressed to explore novel polyimides with improved permeability to

specific gases without significantly impairing their inherently good selectivity.

It is well-known that the gas permeability of a polymer can be effectively improved by introducing bulky groups or contorted moieties into backbones to prevent effective chain packing. For example, polyimides incorporating large  $-C(CF_3)_2$  – linkages in the backbones usually exhibited favorable permeability.<sup>12,13</sup> Also, the increase in polymer backbone rigidity improved gas separation performance, especially in terms of enhancing size sieving ability.<sup>14,15</sup> Polybenzoxazole (PBO)<sup>16,17</sup> is a representative example of highly rigid polymers that are thermally and chemically resistant. Fluorinated PBO membranes have been investigated as gas separation materials previously by Maruyama et al.<sup>18</sup> In recent years, high temperature conversion of  $\alpha$ hydroxy-polyimide precursors into PBOs has been widely utilized to construct high performance gas separation membranes (so-called thermal rearrangement (TR) membranes<sup>1,19-31</sup>). TR membranes exhibit extraordinary gas separation properties as compared to other polymer membranes, mainly due to the formation of microporosity and their particular

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## Scheme 1. Synthesis of Benzoxazole-Containing Diamine Monomers (p-BFO, m-BFO, and m-BOA)



Scheme 2. Synthesis of the Poly(benzoxazole-co-imide)s Based on the Benzoxazole-Containing Diamines



pore size distributions within membranes derived from thermally driven structural rearrangements in the solid state.<sup>20</sup> However, some of these TR membranes exhibit poor mechanical properties compared to conventional polyimide membranes, and they are also insoluble and cross-linked after  $\alpha$ -hydroxypolyimide precursors were treated at high temperatures (>400 °C). Moreover, there is a possibility of chain decomposition during high temperature treatment above 450 °C.

In view of the desirable properties of PIs and PBOs, nonthermally rearranged poly(benzoxazole-*co*-imide)s are expected to integrate the advantages of both PIs and PBOs. A series of nonthermally rearranged aromatic poly(benzoxazole-imide)s, such as fluorinated aromatic poly(ether imide benzoxazole)s (PEIBs), have been prepared previously for microelectronic applications by using commercially available dianhydrides and diamines containing preformed benzoxazole)<sup>32</sup> and 2,2'-bis[2-(4-aminophenoxy)benzoxazol-6-yl]hexafluoropropane.<sup>33,34</sup> Fluorinated PEIBs showed excellent solubility and processability using current commercial fabrication processes due to the introduction of flexible ether bonds into chain backbones. However, they were not suitable for membrane-based gas separation applications because of their low gas permeability and poor thermal-resistance properties, resulting from low chain rigidity.

The effects of structural symmetry and isomerism on the polymer properties are of interest because they provide a means to further understand how interchain packing and chain

flexibility affect the resulting properties of the corresponding polymers, e.g., gas permeability.<sup>3,9,36–38</sup> The effects of structural symmetry and isomeric chain orientation on the physical and gas separation properties of rigid polymers have been previously reported for polymer membranes to a certain de-gree.<sup>3,9,13,19,20,24,36,39,40</sup> In general, changing the connecting bond positions in polyimide backbones from para-connecting linkages to meta-connecting ones appears to reduce their permeability and diffusivity to gases, while correspondingly increasing selectivity. For example, the para-connecting polyimide PMDA-pp'ODA derived from pyromellitic dianhydride (PMDA) and 4,4'-oxidianiline exhibited about 2.7 times higher permeability to O2 and relatively lower selectivity of O2/ N<sub>2</sub>, in comparison with the one from the meta-connecting PMDA-mp'ODA polymerized from PMDA and 3,4'-oxidianiline.<sup>13</sup> To date, no related data was available on the gas transport properties for these nonthermally rearranged poly(benzoxazoleco-imide) membranes derived from the preformed benzoxazolecontaining diamines.

In this study, two fluorinated diamine monomers (*p*-BFO and *m*-BFO) and one nonfluorinated diamine monomer (*m*-BOA) containing benzoxazole moieties depicted in Scheme 1 were synthesized. The corresponding poly(benzoxazole-*co*-imide)s were prepared by using a dianhydride, 6FDA, having a bulky 6F  $(-C(CF_3)_2-)$  group, with the three novel synthesized diamine monomers along with a commercial diamine containing a benzoxazole moiety, 5-amino-2-(4-aminobenzene)benzoxazole

(*p*-BOA). Obviously, the *para*-connecting *p*-BFO and *p*-BOA are isomers of *meta*-connecting *m*-BFO and *m*-BOA, respectively. The molecular packing and properties including single gas permeability for the resulting four rigid poly(benzoxazole-*co*-imide)s shown in Scheme 2 were investigated. The influence of polymer structural isomerism on molecular packing and properties were identified. Systematic investigations and analyses provide a useful framework for designing modified polyimides to meet the requirements in commercial membrane-based gas separations such as desirable permeability, excellent mechanical and thermal stability etc.

#### EXPERIMENTAL SECTION

**Materials.** 2,4-Diaminophenol dihydrochloride (98.0%), 4-aminobenzoic acid (>98.0%), 3-aminobenzoic acid (>98.0%), polyphosphoric acid (PPA, 115%), tin(II) chloride dihydrate (98.0%), toluene (99.8%), and N-methyl-2-pyrrolidinone (NMP, >99.0%) were purchased from Sigma-Aldrich Chemical Co. (Milwaukee, WI) and used as received. 4,4'-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA) was obtained from Sigma-Aldrich Chemical Co. and purified by sublimation before use. 2,2'-Bis(3-amine-4-hydroxyphenyl)hexafluoropropane (APAF) was purchased from Central Glass Co. Ltd. (Tokyo, Japan) and was purified by sublimation before use. Sodium carbonate (>99.0%) was purchased from Tokyo Chemical Industry (Tokyo, Japan). 5-Amino-2-(4-aminobenzene)benzoxazole (*p*-BOA) was obtained from Changzhou Sunlight Medical Raw Material Co. Ltd. (Jiangsu, China) and was used as received.

Synthesis of 2,2'-Bis[2-(4-aminophenyl)benzoxazol-6-yl]hexafluoropropane (p-BFO). Under a nitrogen atmosphere, PPA (70.00 g) was added to a three-necked flask, and 4-aminobenzoic acid (5.80 g, 42.3 mmol), APAF (7.33 g, 20.0 mmol), and tin(II) chloride dihydrate (0.40 g, 1.8 mmol) were added. The mixture was heated to 110 °C with stirring overnight, and then the resulting solution was heated to 195 °C and maintained at that temperature for more than 7 h. After cooling to room temperature, the resulting reaction mixture was neutralized with 10% sodium carbonate solution. The precipitate was filtered off, rinsed with distilled water many times, recrystallized in an ethanol-water mixture, and dried in vacuum at 80 °C to give 9.30 g (yield: 81.9%) of white needle crystals. Melting point  $(M_p)$ : 256 °C. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ 6.10 (H-1, s, 4H), 6.69–6.70 (H-2, d, J = 4.5 Hz, 4H), 7.24–7.25 (H-5, d, J = 4.5 Hz, 2H), 7.62 (H-4, s, 2H), 7.74–7.75 (H-6, d, J = 4.5 Hz, 2H), 7.85–7.87 (H-3, d, J = 4.5, 4H). <sup>13</sup>C NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ 64.1, 110.1, 112.1, 113.5, 120.1, 121.3, 123.2, 125.0, 125.5, 128.7, 129.3, 142.2, 149.9, 152.8, 165.1. FTIR (powder, v, cm<sup>-1</sup>): 3475, 3337, 3216 (N-H stretching), 1630, 1606 (cyclic C=N/C=C stretching), 1497, 1483 (skeletal vibrations in conjugated phenyl/benzoxazole ring), 1251 (Ar-C-O asymmetric stretching). Anal. Calcd for C<sub>29</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub>F<sub>6</sub>: C, 61.27; H, 3.19; N, 9.86. Found: C, 60.98; H, 3.37; N, 10.07.

**Synthesis of 2,2'-Bis[2-(3-aminophenyl)benzoxazol-6-yl]-hexafluoropropane** (*m*-BFO). The synthetic procedure was similar to that used for diamine *p*-BFO except that 3-aminobenzoic acid was used as raw material. White needle-like crystals with a yield of 86.5% were obtained. M<sub>p</sub>: 112 °C. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  5.54 (H-1, s, 4H),  $\delta$ .81–6.83 (H-3, d, *J* = 5.4 Hz, 2H), 7.23–7.26 (t, H-4, *J* = 3.9 Hz, 2H), 7.33–7.36 (H-7, H-8, t, *J* = 4.5 Hz, 4H), 7.43 (H-6, s, 2H), 7.77 (H-2, s, 2H), 7.86–7.88 (H-5, d, *J* = 4.5 Hz, 2H). <sup>13</sup>C NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  64.3, 111.0, 112.2, 114.8, 117.7, 121.2, 123.1, 125.0, 126.4, 126.7, 129.1, 129.8, 141.7, 149.5, 150.1, 164.5. FTIR (powder,  $\nu$ , cm<sup>-1</sup>): 3452, 3354, 3226 (N–H stretching), 1623, 1593 (cyclic C=N/C=C stretching), 1493, 1480 (skeletal vibrations in conjugated phenyl/benzoxazole ring), 1252 (Ar–C–O asymmetric stretching). Anal. Calcd for C<sub>29</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub>F<sub>6</sub>: C, 61.27; H, 3.19; N, 9.86. Found: C, 60.87; H, 3.36; N, 10.02.

**Synthesis of 5-Amino-2-(3-aminobenzene)benzoxazole (m-BOA).** The synthetic procedure was similar to that used for diamine *p*-BFO except that 3-aminobenzoic acid and 2,4-diaminophenol dihydrochloride were used as raw materials, respectively. The precipitate was filtered off, rinsed with distilled water many times, recrystallized in

an ethanol–water mixture, dried in vacuum at 80 °C, and further purified by sublimation to give 6.94 g (yield: 76.9%) of yellow crystals. M<sub>p</sub>: 253 °C. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  5.10 (H-9, s, 6H), 5.44 (H-1, s, 2H), 6.63–6.65 (H-3, d, *J* = 4.2 Hz, 2H), 6.73–6.75 (H-8, d, *J* = 3.9 Hz, 2H), 6.84 (H-6, s, 2H), 7.18–7.20 (H-4, t, *J* = 3.9 Hz, 2H), 7.25–7.26 (H-7, d, *J* = 3.9 Hz, 2H), 7.36–7.38 (H-2, H-5, m, 4H). <sup>13</sup>C NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  64.3, 111.0, 112.2, 114.8, 117.6, 121.2, 123.1, 125.0, 126.4, 126.7, 129.1, 129.8, 141.6, 149.4, 164.6. FTIR (powder,  $\nu$ , cm<sup>-1</sup>): 3426, 3395, 3316, 3211 (N–H stretching), 1630, 1593 (cyclic C=N/C=C stretching), 1480, 1464 (skeletal vibrations in conjugated phenyl/benzoxazole ring), 1255 (Ar–C–O asymmetric stretching). Anal. Calcd for C<sub>13</sub>H<sub>11</sub>N<sub>3</sub>O: C, 69.32; H, 4.92; N, 18.66. Found: C, 67.82; H, 4.96; N, 18.59.

Synthesis of Poly(benzoxazole-co-imide)s. Poly(benzoxazoleco-imide)s were prepared by using dianhydride with four benzoxazolecontaining diamines, p-BFO, m-BFO, p-BOA, and m-BOA as raw materials via a two-step azeotropic imidization process, as shown in Scheme 2. Using the preparation of 6FDA-p-BFO (PIa) as an example, in a four-necked flask, p-BFO (1.7054 g, 30.0 mmol) was dissolved in NMP (28 mL), and then 6FDA (1.3327 g, 30.0 mmol) was added. After the mixture was stirred at room temperature for more than 12 h, 6 mL of toluene as an azeotropic agent was added to the reaction solution, and the solution mixture was then heated under reflux for at least 12 h under a N<sub>2</sub> atmosphere. While the toluene was refluxing, water was removed using a Dean-Stark trap. The resulting brownish solution was poured into a mixture of water and methanol (1 L, v/v = 1:1) under vigorous stirring. The resulting fibrous precipitate was filtered off, washed with cold water, methanol, and dried at 120 °C in a vacuum oven to yield the 6FDA-p-BFO (PIa) white fibrous powder.

6FDA-p-BFO (Pla). ATR-FTIR (membrane,  $\nu$ , cm<sup>-1</sup>): 1787 (imide C=O symmetric stretching), 1724 (imide C=O asymmetric stretching), 1623, 1608 (cyclic C=N/C=C stretching), 1503, 1479 (skeletal vibrations in conjugated phenyl/benzoxazole ring), 1362 (imide -C-N), 1249 (Ar-C-O asymmetric stretching). Molecular weight:  $M_w = 64 \times 10^3$  with a polydispersity of 2.2. Anal. Calcd for C<sub>48</sub>H<sub>20</sub>F<sub>12</sub>N<sub>4</sub>O<sub>6</sub>: C, 59.03; H, 2.06; N, 5.74. Found: C, 58.19; H, 2.18; N, 5.70.

*6FDA-m-BFO* (*Plb*). ATR-FTIR (membrane,  $\nu$ , cm<sup>-1</sup>): 1786 (imide C=O symmetric stretching), 1723 (imide C=O asymmetric stretching), 1625, 1608 (cyclic C=N/C=C stretching), 1492, 1477 (skeletal vibrations in conjugated phenyl/benzoxazole ring), 1367 (imide -C-N), 1249 cm<sup>-1</sup> (Ar-C-O asymmetric stretching). Molecular weight:  $M_w = 114 \times 10^3$  with a polydispersity of 2.5. Anal. Calcd for C<sub>48</sub>H<sub>20</sub>F<sub>12</sub>N<sub>4</sub>O<sub>6</sub>: C, 59.03; H, 2.06; N, 5.74. Found: C, 58.54; H, 2.04; N, 5.71.

6FDA-p-BOA (Plc). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ 7.54 (br, s, 1H), 7.74 (br, s, 2H), 7.78 (br, s, 2H), 7.944 (s, 1H), 7.99 (m, 3H), 8.23 (br, s, 2H), 8.389 (br, s, 2H). ATR-FTIR (membrane, ν, cm<sup>-1</sup>): 1785 (imide C=O symmetric stretching), 1719 (imide C=O asymmetric stretching), 1622, 1608 (cyclic C=N/C=C stretching), 1502, 1478 (skeletal vibrations in conjugated phenyl/benzoxazole ring), 1361 (imide -C-N), 1252 cm<sup>-1</sup> (Ar-C-O asymmetric stretching). Molecular weight:  $M_w = 115 \times 10^3$  with a polydispersity of 3.3. Anal. Calcd for  $C_{32}H_{13}F_6N_3O_5$ : C, 60.67; H, 2.07; N, 6.63. Found: C, 59.63; H, 1.90; N, 6.45.

6FDA-m-BOA (**Pld**). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ 7.53 (br, s, 1H), 7.74–7.80 (m, 4H), 7.93–8.00 (m, 4H), 8.22–8.40 (m, 4H). ATR-FTIR (membrane,  $\nu$ , cm<sup>-1</sup>): 1785 (imide C=O symmetric stretching), 1720 (imide C=O asymmetric stretching), 1625, 1610 (cyclic C=N/C=C stretching), 1492, 1477 (skeletal vibrations in conjugated phenyl/benzoxazole ring), 1367 (imide –C–N), 1252 cm<sup>-1</sup> (Ar–C–O asymmetric stretching). Molecular weight:  $M_w = 188 \times 10^3$  with a polydispersity of 2.9. Anal. Calcd for C<sub>32</sub>H<sub>13</sub>F<sub>6</sub>N<sub>3</sub>O<sub>5</sub>: C, 60.67; H, 2.07; N, 6.63. Found: C, 59.07; H, 1.72; N, 6.56.

**Membrane Preparation.** The poly(benzoxazole-*co*-imide) fibrous powders were dissolved in NMP to form a 20 wt % polymer solution and were cast onto clean glass plates after filtering with 1.0  $\mu$ m Nylon (NY) filter cartridges. The glass plates were placed in a vacuum oven and slowly heated from 60 to 250 °C to evaporate solvent by successive heating at 60, 100, 150, 200, and 250 °C for 1 h at each temperature. The

resulting membranes were removed from the glass plates by immersion in hot water, washed with deionized water, and dried overnight in a vacuum oven at 120 °C. The dry membranes were further heated up to 300 °C in a muffle furnace at a rate of 5 °C/min with a Eurotherm controller, and were maintained at 300 °C for 1 h to obtain the fully imidized poly(benzoxazole-*co*-imide) membranes. The thickness of all films after treatment was approximately 42–62  $\mu$ m.

Characterization. An infrared microspectrometer (IlluminatIR, SensIR Technologies, Danbury, CT) was used to characterize the diamine monomers and polymer membranes. Nuclear magnetic resonance (NMR) spectra were obtained with a Mercury Plus 300 MHz spectrometer (Varian, Inc., Palo Alto, CA). Molecular weight was measured by gel permeation chromatography (Waters GPC Systems, Milford, MA) with polystyrene as an external standard and NMP as the eluent. Elemental analyses for the monomers and polymers were performed with a Thermofinnigan EA1108 (Fisions Instrument Co., Milan, Italy) elemental analyzer. Mechanical properties were obtained using a Universal Testing Machine, UTM (AGS-J, Shimadzu, Kyoto, Japan) with specimens prepared according to ASTM D638-Type 5 recommendations, and the result of each sample was averaged with at least five specimens. Differential scanning calorimetry (DSC) analysis and thermogravimetric analysis (TGA) were recorded on a TA Instruments Q-20 calorimeter and TGAQ50 instrument (TA Instrument, New Castle, DE), respectively, at a heating rate of 10 °C/min under a nitrogen atmosphere. The glass transition temperatures  $(T_{o}s)$  of the polyimide membranes were determined by second scan. Wide angle X-ray diffractometry (WAXD) spectra were recorded in the reflection mode at room temperature by using a Rigaku Denki D/MAX-2500 (Rigaku, Tokyo, Japan) diffractometer with Cu K $\alpha$  (wavelength  $\lambda = 1.54$ Å) radiation. The net charges by the Hirshfeld method were calculated by using the GGA-BLYP/DND method within Dmol3 module embedded in Materials Studio 5.0 program (Accelrys, San Diego, CA).<sup>41</sup> The geometry of a repeat unit was optimized by using the COMPASS force-field. The conformation rotation of single bonds was conducted using the conformer modulus.

Densities of the membranes were measured using a density measurement kit (Sartorius LA 120S, Sartorius AG, Goettingen, Germany) by the buoyancy method. The liquid used for measurement was 2,2,4-trimethylpentane (Sigma-Aldrich). Fractional free volume (FFV,  $V_f$ ) was calculated as follows:

$$V_{\rm sp} = \frac{M_0}{\rho} \tag{1}$$

$$V_{\rm f} = \frac{V_{\rm sp} - 1.3 \times V_{\rm w}}{V_{\rm sp}} \tag{2}$$

where  $V_{\rm sp}$  is the molar volume of polymers determined by the measured density and  $V_{\rm w}$  is the van der Waals molar volume based on Bondi's group contribution theory.

The constant volume method, so-called time-lag method, was used to measure the gas permeability of the membranes as described in our previous study.<sup>42</sup> The permeability of all gases was measured at 1 atm at 35 °C and was calculated by using the following equation:

$$P = \left(\frac{273.15Vl}{76T\Delta pA}\right)\frac{\mathrm{d}p}{\mathrm{d}t} \tag{3}$$

where *P* (Barrer) is the gas permeability, *l* (cm) is membrane thickness,  $V(\text{cm}^3)$  is the downstream chamber volume, T(K) is the measurement temperature,  $\Delta p$  (cmHg) is the pressure difference between upstream and downstream,  $A(\text{cm}^2)$  is the effective membrane area, and dp/dt is the rate of the pressure rise in the downstream chamber at steady state. The ideal selectivity ( $\alpha_{x/y}$ ) for components *x* and *y* was defined as the ratio of gas permeability of the two components. The diffusion coefficient (*D*), could be calculated from the time-lag apparatus by using the following equation:

$$D = \frac{l^2}{6\theta} \tag{4}$$

where  $\theta$  is "time-lag" and *l* is the membrane thickness. Solubility coefficient (*S*) was obtained indirectly via the equation:

$$= P/D \tag{5}$$

#### RESULTS AND DISCUSSION

S

**Monomer Syntheses and Electronic Effect.** Three new benzoxazole-containing diamine monomers, *p*-BFO, *m*-BFO, and *m*-BOA, were synthesized in PPA at elevated temperatures using 4-aminobenzoic acid/3-aminobenzoic acid with 2,2'-bis(3-amine-4-hydroxyphenyl)hexafluoropropane (APAF)/2,4-diaminophenol dihydrochloride following literature procedures, <sup>33,34</sup> as shown in Scheme 1. The structures of diamine monomers were confirmed by FTIR spectroscopy, elemental analyses, <sup>1</sup>H NMR (Figure 1) and <sup>13</sup>C NMR recorded in DMSO-*d*<sub>6</sub>. In <sup>1</sup>H NMR, the



Figure 1. <sup>1</sup>H NMR spectra (300 MHz, in DMSO- $d_6$ ) of synthesized benzoxazole-containing diamines (*p*-BFO, *m*-BFO, and *m*-BOA) and the commercial *p*-BOA for comparison.

proton signals of the amine groups appeared obviously at 5.10-6.10 ppm depending on the diamine structures, as shown in Figure 1. As expected, *m*-BOA has two obvious amine proton signals located at 5.10 (H-9) and 5.44 ppm (H-1) corresponding to the amine protons linked to benzoxazole ring and phenyl ring, respectively, indicating the asymmetric nature of the *m*-BOA. Only one amine proton signal was observed for both the *p*-BFO and *m*-BFO monomers near 6.10 (H-1) and 5.54 ppm (H-1),



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**Figure 2.** Net charges of nitrogen atoms in amine groups of benzoxazole-containing diamines by the Hirshfeld method, calculated using the Dmol3 program embedded in the Materials Studio package.<sup>41</sup>

polymer	code	inherent viscosity <sup><math>a</math></sup> (dL/g)	$M_{\rm n}  (\times 10^{-3})^b$	$M_{\rm w}  (\times 10^{-3})^b$	PDI $(M_{\rm w}/M_{\rm n})$	ho (g/cm <sup>3</sup> )	FFV		
6FDA-p-BFO	PIa	0.31	28.6	64	2.2	1.4388	0.170		
6FDA-m-BFO	PIb	0.35	45.6	114	2.5	1.4484	0.165		
6FDA-p-BOA	PIc	0.72	34.7	115	3.3	1.4528	0.153		
6FDA-m-BOA	PId	1.14	64.0	188	2.9	1.4349	0.164		
<sup>a</sup> Inherent viscosity measured at a concentration of 0.5 g/dL in NMP at 25 °C <sup>b</sup> Relative to polystyrene standards									

Table 2. Solubility of Poly(benzoxazole-co-imide) F	ibrous Powders
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	solvent									
code	acetone	THF	DMSO	NMP	DMAc	methanol	ethanol	chloroform		
PIa	-	-	-	+	+	-	-	+		
PIb	-	-	-	+	+	-	-	+		
PIc	-	+	+	+	+	-	-	+		
PId	-	+	+	+	+	-	-	+		
$^{3}$ Kev: +, soluble at room temperature: —, insoluble at room temperature.										

respectively, indicative of their symmetric structures. In addition, the chemical shifts of the amine protons are significantly affected by the amine substitution positions in the phenyl rings and are also affected by the introduction of  $-C(CF_3)_2$ - in the backbones. As shown in Figure 1, a downfield shift of 0.36 ppm occurs for the H-1 amine protons in para-BOA (5.80 ppm) versus meta-BOA (5.44 ppm), and a downfield shift of 0.56 ppm occurs for the para-BFO (6.10 ppm) versus the meta-BFO (5.54 ppm), highlighting the strong resonance induced electron-withdrawing effect on the substituted aniline.<sup>43</sup> This effect is greater in the case of the para-substituted amine groups than that of the metasubstituted ones, resulting in a downfield chemical shift of the para-substituted amine proton. Also, the electron-withdrawing effect of  $-C(CF_3)_2$ - on amine H-1 induced a small 0.30 ppm downfield shift to 6.10 ppm in *p*-BFO in comparison with a 5.80 ppm in *p*-BOA.

The net charges in the amine N atoms were also calculated by the Hirshfeld method using the Dmol3 program<sup>41</sup> embedded in the Materials Studio 5.0 package as shown in Figure 2. Obviously, the net charges of the amine N atoms in *para*-substituted anilines are significantly lower than those from the corresponding *meta*substituted ones, and the net charges of the amine N atoms in 6Fcontaining diamines are significantly lower than the corresponding ones in non-6F diamines, because of the electronwithdrawing effect of the  $-C(CF_3)_2-$  groups. Since the nucleophilicity of diamines decreases by introducing strong electron-withdrawing  $-C(CF_3)_2-$  and oxazole substituents into the polymer backbones, it can be inferred that for polymerization with the same dianhydride, the *para*-substituted diamines and the 6F-containing diamines would possess lower nucleophilicity than the corresponding *meta*-substituted and non-6F ones, respectively. Therefore, the nucleophilicity of the diamines would increase in the order *p*-BFO (least nucleophilic) < m-BFO/p-BOA < m-BOA (most nucleophilic).

**Polymerization.** The novel poly(benzoxazole-co-imide)s were synthesized directly from 6FDA and benzoxazolecontaining diamines by a two-step procedure via poly-(benzoxazole-co-amic acid) intermediates, as shown in Scheme 2. The results of the polymerization are summarized in Table 1. The inherent viscosities and  $M_w$ s of poly(benzoxazole-*co*-imide)s were in the range of 0.31-1.14 dL/g and 64-188  $\times$  10<sup>3</sup> depending on the diamine residues. The  $M_{\rm w}$ s of these polyimides follows the sequence: PIa < PIc/PIb < PId, which is exactly the same as the nucleophilicity order of the diamines from the results of <sup>1</sup>H NMR and molecular modeling. The higher nucleophilicity of the N atom will induce higher reactivity for the polycondensation reaction, implying that the  $M_{w}$ s of the resulting poly(benzoxazole-co-imide)s depend significantly on the reactivity of the corresponding diamine monomers when the polymerizations were performed with the same dianhydride, 6FDA. The solubility of these poly(benzoxazole-*co*-imide) fibrous powders was tested in various common solvents, as shown in Table 2. All the polyimides were soluble in NMP, N,Ndimethylacetamide (DMAc) and chloroform, indicating that they have good solution processability.

The anticipated chemical structures of the poly(benzoxazole*co*-imide) membranes resulting from the fabrication process are supported by ATR-FTIR (Figure 3) and elemental analyses. All



**Figure 3.** ATR-FTIR spectra of the poly(benzoxazole-*co*-imide) membranes. Gray band refers to the characteristic C=O stretching domain from –CONH of the unimidized intermediate poly(amic acid)s (PAAs).

membranes exhibited typical characteristic imide absorption bands at around 1785 cm<sup>-1</sup> (imide carbonyl symmetric stretching), 1720 cm<sup>-1</sup> (imide carbonyl asymmetric stretching) and 1367 cm<sup>-1</sup> (–C–N stretching), respectively, but bands at about 1660 cm<sup>-1</sup> (C=O stretching from the intermediate –CONH, gray band domain in Figure 3) were not detected, indicating that imidization was complete. Additionally, characteristic absorptions at about 1252 cm<sup>-1</sup> (Ar–C–O asymmetric stretching) and 1053 cm<sup>-1</sup> (Ar–C–O symmetric stretching), were indicative of the incorporation of benzoxazole. Moreover, the experimental elemental analyses of the poly(benzoxazole-*co*imide)s agree well with the calculated values of carbon, hydrogen and nitrogen.

Molecular Packing and FFV. The chain packing density of poly(benzoxazole-co-imide)s was evaluated by their FFV, which was determined by density measurements of membranes. The FFV values (Table 1) were in the range of 0.153–0.170, which are close to those of conventional polyimide membranes, such as 6FDA-*p*PD (FFV =  $0.161^{12}$ ) and 6FDA-*m*PD (FFV =  $0.160^{12}$ ) derived from 6FDA and phenylenediamine, and also the TRPBO-*co*-PI (5:5) (FFV =  $0.156^{-1}$ ). However, they are significantly less than those of typical TR membranes, such as TR-cPBO (FFV =  $0.35^{25}$ ) and TR-aPBO (FFV =  $0.22^{25}$ ), which exhibited better microporosity and particular pore size distributions due to the thermally driven structural rearrangements.<sup>20</sup> This indicated that the microporosity within the membranes played a key role in improving the FFV of the corresponding membranes. Additionally, the para-connecting PIa exhibited slightly higher FFV than the corresponding metaconnecting PIb, which is similar to previous findings.<sup>12,13</sup> However, a comparison of para-connecting PIc and metaconnecting PId shows opposite behavior, i.e. the FFV of PIc is less than that of PId.

In order to probe the cause for the abnormal FFV behavior of **PIc** and **PId**, out-of-plane wide-angle X-ray diffraction (WAXD) measurements were conducted to examine the polymer chain packing, as shown in Figure 4. All poly(benzoxazole-*co*-imide) membranes exhibited at least two diffraction peaks, A and B, located at about  $2\theta = 15.0^{\circ}$  and  $24.5^{\circ}$ , respectively, although they are relatively broad in comparison with those from typical crystalline polymers. This indicates the existence of some ordered packing domains combined with primarily amorphous morphology domains in the membranes, which is similar to other reported polyimides containing benzoxazole rings in the



Figure 4. WAXD curves of poly(benzoxazole-co-imide) membranes.

backbones.<sup>35,44</sup> In addition, the XRD pattern of the **PIa** membrane shows an additional low angle peak at about  $2\theta = 9.0^{\circ}$  (peak C), which may correspond to a (00*l*) diffraction peak derived from the order along the molecular chain axis.<sup>5,7</sup>

Since the calculated *d*-spacing values of peak A at about  $2\theta=15^{\circ}$  (~5.9 Å) and B at 24.5° (~3.6 Å) were close to the interchain distance and typical  $\pi-\pi$  stacking distances of aromatic polyimides,<sup>45</sup> respectively, peak A (near  $2\theta = 15^{\circ}$ ) likely corresponds to the average interchain packing in the ordered domains, whereas peak B ( $2\theta = 24.5^{\circ}$ ) could be assigned to the  $\pi - \pi$  stacking order. The presence of the ordered  $\pi - \pi$ stacking implies that some planar and rigid aromatic heterocyclic rings in the polymer backbones are arranged parallel to each other. From peak A, the order of the interchain distances (dspacing values) in the ordered domains is PIa (5.98 Å) > PIc(5.86 Å) > **PIb** (5.81 Å) > **PId** (5.80 Å). This indicates that the meta-substituted isomers showed closer chain packing as compared to the corresponding para-substituted ones in the ordered domains. It also implies that the introduction of paraconnections in the polymer chain is more effective than *meta*connections for increasing interchain distance.<sup>3,9,36</sup> However, the overall mean interchain distances should be estimated by considering the contributions of chain packing *d*-spacing from both the ordered and the amorphous domains. The overall mean *d*-spacing value in the whole membrane can be estimated by<sup>42</sup>

$$d_{mean} = \frac{A_a}{A_a + A_b} d_a + \frac{A_b}{A_a + A_b} d_b \tag{6}$$

where  $A_a$  and  $A_b$  are the diffraction peak areas from the amorphous diffraction peak and ordered diffraction peak, respectively, and  $d_a$  and  $d_b$  are the *d*-spacing values of macromolecules from the amorphous domains and the ordered domains, respectively. When  $H_b = (A_b/(A_a + A_b))$ , eq 6 can be rewritten in the following form:

$$d_{mean} = d_a - (d_a - d_b)H_b \tag{7}$$

Obviously, the mean interchain distance in the whole membrane is affected by  $H_b$  in addition to  $d_a$  and  $d_b$  according to eq 7. It is well-known that the chain packing in completely amorphous domains is looser than that in ordered domains,<sup>46</sup> implying that  $d_a > d_b$  (that is  $d_a - d_b > 0$ ). If  $\Delta k = d_a - d_b$ , eq 7 can be further converted to

$$d_{mean} = (d_b + \Delta k) - \Delta k H_b (\Delta k > 0)$$
(8)

From eq 8, a smaller overall mean interchain distance  $(d_{\text{mean}})$  may be obtained by increasing the  $H_{\text{b}}$  or decreasing the  $d_{\text{b}}$  (the *d*-

spacing value of macromolecules from the ordered domains within the membranes). To estimate the difference of the overall mean interchain distances within the combined membrane domains between the *para*-connecting poly(benzoxazole-*co*-imide) membranes and the corresponding *meta*-connecting ones, eq 9 can be used as

$$\Delta d = d_{mean-para} - d_{mean-meta} = (d_{bp} - d_{bm}) + (\Delta k_p - \Delta k_m) + (\Delta k_m H_{bm} - \Delta k_p H_{bp})$$
(9)

where subscripts *p* and *m* correspond to the related parameters from the *para*-connecting poly(benzoxazole-*co*-imide) membranes and the corresponding *meta*-connecting ones, respectively. The relative value of the overall mean interchain distances between two membranes is either positive or negative, which is determined by a combined contribution from various chain packing parameters, including the shift of the interchain distances in the ordered packing domains, " $d_{bp} - d_{bm}$ " value (represented by the first term of eq 9), but also the other two terms in eq 9, " $\Delta k_p - \Delta k_m$ " and " $\Delta k_m H_{bm} - \Delta k_p H_{bp}$ ".

As reported previously, the average interchain distance in completely amorphous domains may be obtained by deconvoluting and fitting the WAXD patterns with Gaussian broadening functions on a single baseline and estimating the central position of broad amorphous diffraction halo.<sup>42,45,47</sup> However, this not easy to do in this study due to the monotonicity of these WAXD patterns (Figure 4). Then, it is difficult to obtain the exact values of " $\Delta k_p$ ", " $\Delta k_m$ " and also " $\Delta k_p - \Delta k_m$ " in eq 9 in this study. Similar to the *d*-spacing value in amorphous domains, the  $H_{bp}$ and  $H_{\rm hm}$  are also very difficult to estimate directly in this study because contributions due to the ordered packing domains and completely amorphous domains are not easily identified in the WAXD patterns. However, in order to estimate the differences in the ordered degrees in these poly(benzoxazole-co-imide) membranes, we calculated the ordered degree of macromolecules (X) according to eq 10<sup>48</sup> based on the characteristic peak A at around  $2\theta = 15^{\circ}$  as follows:

$$X = \frac{I_X}{U_X} \times \frac{U_0}{I_0} \times 100\%$$
<sup>(10)</sup>

where  $U_0$  and  $U_x$  represent the backgrounds of the reference and experimental samples, whereas  $I_0$  and  $I_x$  are the integral intensities of the diffraction lines of the reference and experimental samples, respectively. The ordered degree values of these poly(benzoxazole-*co*-imide) membranes gradually decreased in the order of **PIa** (11.22  $U_0/I_0$ ) > **PIc** (9.91  $U_0/I_0$ ) > **PIb** (6.73  $U_0/I_0$ ) > **PId** (6.60  $U_0/I_0$ ), indicating the *para*connecting linkages significantly improve the packing ordered degrees of the macromolecules. This also implies that changing the *para*-connecting linkages into *meta*-connecting ones induce a significant decrease in  $H_b$  values for the corresponding membranes, that is  $H_{bp} \gg H_{bm}$ .

According to the results from wide-angle X-ray diffraction spectra (Figure 4), the interchain distance  $(d_{bp} = 5.96 \text{ Å})$  of the **PIa** membrane in the ordered domains is much larger than that  $(d_{bm} = 5.81 \text{ Å})$  of the **PIb** membrane. From eq 9, a very large positive " $d_{bp} - d_{bm}$ " value can significantly benefit a positive  $\Delta d$  value,  $d_{mean-para}$  (PIa) >  $d_{mean-meta}$  (PIb), which was confirmed by the order of their FFV values: PIa (0.170) > PIb (0.165). In the case of the comparison of **PIc** with **PId**, the interchain distance  $(d_{bp} = 5.86 \text{ Å})$  in the ordered domains of the **PIc** membrane is very similar to that  $(d_{bm} = 5.80 \text{ Å})$  of the **PId** membrane. This

corresponds to a very small positive " $d_{\rm bp} - d_{\rm bm}$ " value in eq 9. However, the degree of order of **PIc** ( $X = 9.91 U_0/I_0$ ) is about 1.5 times higher than that in **PId** ( $X = 6.60 U_0/I_0$ ), implying  $H_{\rm bm} \ll H_{\rm bp}$ . Since  $H_{\rm bm}$  is much smaller than  $H_{\rm bp}$ , as the  $\Delta k_{\rm p}$  is similar to  $\Delta k_{\rm m}$ , it will result in a large negative " $\Delta k_{\rm m} H_{\rm bm} - \Delta k_{\rm p} H_{\rm bp}$ " value in eq 9. Therefore, the combined result due to the large negative contribution from " $\Delta k_{\rm m} H_{\rm bm} - \Delta k_{\rm p} H_{\rm bp}$ " value and small positive contribution from " $\Delta k_{\rm m} H_{\rm bm} - \Delta k_{\rm p} H_{\rm bp}$ " value and small positive in eq 9,  $d_{\rm mean-para}$  (**PIc**) <  $d_{\rm mean-meta}$  (**PId**), and then a lower FFV value of the *para*-connecting **PIc** relative to that of *meta*-connecting **PId**.

**Mechanical and Thermal Properties.** Good thermal and mechanical properties are key factors for gas separation membrane applications, especially under harsh environments such as elevated temperature and high stress. Thermal analyses were performed by TGA (Figure 5) and DSC (Figure 6) and the



Figure 5. TGA curves of poly(benzoxazole-co-imide) membranes.



Figure 6. DSC curves of poly(benzoxazole-co-imide) membranes.

data are summarized in Table 3. The observed 5% and 10% weight losses of the poly(benzoxazole-*co*-imide)s were in the ranges of 528–559 °C and 548–586 °C, which confirms their high thermal stability characteristics. The  $T_{\rm g}$ s were in the range of 306 to 366 °C depending on the polymer structure and isomerism. The *para*-connecting polyimide isomers exhibited relatively higher  $T_{\rm g}$ s than those from the *meta*-connecting ones. It is well-known that the  $T_{\rm g}$  values of polymers are closely related to the chain rigidity and interchain interactions. In order to understand the reason for the differences in  $T_{\rm g}$ s between the *para*-connecting and *meta*-connecting isomers, geometric optimization conformations were performed by using Materials Studio software. There is some conformational flexibility about the single bonds in each repeat unit shown in Figure 7, in which

char yield<sup>d</sup> (%)

Table 3. Mechanical and Thermal Properties of the Poly(benzoxazole-co-imide) Membranes										
polymer code	tensile strength (MPa)	tensile modulus (GPa)	elongation at break (%)	$T_{g}^{a}(^{\circ}C)$	$T_5^{b}(^{\circ}\mathrm{C})$	$T_{10}^{c}$ (°C)				
PIa	$110.3 \pm 4.5$	$1.90\pm0.06$	$22.3 \pm 2.4$	366	528	548				

				1			
PId	$115.1 \pm 7.8$	$1.90 \pm 0.08$	14.9 ± 1.7	317	559	586	54.1
PIc	$120.0 \pm 7.4$	$2.10 \pm 0.04$	$26.3 \pm 6.5$	357	531	556	50.7
PIb	$122.0 \pm 4.9$	$1.80\pm0.10$	11.9 ± 0.6	306	553	576	46.6
Pla	$110.3 \pm 4.5$	$1.90 \pm 0.06$	$22.3 \pm 2.4$	366	528	548	47.5

"Midpoint temperature of baseline shift on the second DSC heating trace of the sample after quenching. <sup>b</sup>Temperature at which 5% weight loss was recorded by TGA. <sup>c</sup>Temperature at which 10% weight loss was recorded by TGA. <sup>d</sup>Residual weight retention when heated to 800 °C in nitrogen.



**Figure 7.** Energy variation of the poly(benzoxazole-*co*-imide)s with the rotation angles  $\Phi$  and  $\delta$  in backbones (Scheme 2), calculated using the conformers package in Materials Studio.

typical dihedral angles,  $\delta$  and  $\Phi$  are illustrated in the chain segment. The energy variation of the poly(benzoxazole-coimide)s as a function of the dihedral angles,  $\delta$  and  $\Phi$ , is presented in Figure 7. Obviously, both of the dihedral angles,  $\delta$  and  $\Phi$ , with the lowest energy conformation in the para-connecting polyimides are closer to 0°, indicative of more coplanar chain conformations, in comparison with the corresponding metaconnecting ones with conformations significantly deviating from coplanarity. It is well-known that strong interchain interactions in polyimides originate mainly from interchain charge transfer complex (CTC) formation. The large amount of coplanar/ conjugated segments in the para-connecting polyimide backbones significantly limit the rotational freedom around single bonds and also favor interchain interactions, resulting in stronger CTC interactions and higher rigidity of macromolecules, which are responsible for the higher  $T_{g}s$  of para-connecting isomers (see Table 3 and Figure 6) as compared to the corresponding ones from *meta*-substituted isomers. In addition, the  $T_{\sigma}$  values of the PIc  $(357 \,^{\circ}\text{C})$  and PId  $(317 \,^{\circ}\text{C})$  are slightly higher than the reported 6FDA-*p*PD derived from 4,4'-phenylenediamine and 6FDA ( $T_g = 351 \ ^{\circ}C^{12}$ ) and the 6FDA-*m*PD derived from 3,3'-phenylenediamine and 6FDA, ( $T_g = 298 \ ^{\circ}C^{12}$ ), respectively, showing that benzoxazole units increase  $T_{g}$ .

The poly(benzoxazole-*co*-imide) membranes exhibited excellent mechanical properties with tensile strengths of 110.3–122.0 MPa, elongation at break of 11.9–26.3% and initial modulus values of 1.8–2.1 GPa. The *para*-connecting isomers revealed slightly higher modulus and significantly larger elongation at break than the corresponding *meta*-connecting ones. Higher chain rigidity usually induces higher molecular inplane orientation, as found in the *para*-connecting polyimide isomer, resulting in higher in-plane modulus.<sup>49</sup> A much higher level of molecular ordering and more limited chain flexibility in the *para*-connecting isomers results in significantly improved

Table 4. Single Gas Permeabilities (P) and Ideal Selectivities ( $\alpha$ ) for the Poly(benzoxazole-co-imide) Membranes

								ideal selectivity $(\alpha)^b$					
code	variable	He	$H_2$	$N_2$	O <sub>2</sub>	$CH_4$	$CO_2$	$H_2/N_2$	$O_2/N_2$	$\rm CO_2/CH_4$	$CO_2/N_2$	$H_2/CO_2$	$H_2/CH_4$
PIa <sup>a</sup>	Р	99	95	1.98	10	1.06	47	48	5.11	44	24	2.04	90
	D	1939	1692	16	54	1.54	19	108	3.47	12	1.21	90	1098
	S	0.39	0.43	0.96	1.42	5.21	19	0.44	1.47	3.60	20	0.02	0.08
PIb <sup>a</sup>	Р	89	68	0.79	4.75	0.41	18	86	6.02	44	23	3.82	166
	D	4055	956	6.39	33	0.74	8.8	150	5.14	12	1.37	109	1294
	S	0.17	0.54	0.94	1.10	4.26	16	0.58	1.17	3.65	17	0.04	0.13
PIc <sup>a</sup>	Р	76	69	0.98	5.61	0.54	25	70	5.71	46	25	2.76	127
	D	673	551	4.83	16	0.78	5.10	114	3.33	6.57	1.06	107	706
	S	0.86	0.95	1.54	2.65	5.26	37	0.61	1.72	7.04	24	0.03	0.18
PId <sup>a</sup>	Р	98	80	0.89	5.59	0.43	19	90	6.31	44	21	4.31	186
	D	3733	945	9.01	33	0.78	8	105	3.69	10	0.89	118	1215
	S	0.20	0.64	0.75	1.28	4.22	18	0.86	1.71	4.18	24	0.04	0.15

<sup>*a*</sup>Units: *P* (Barrer),  $10^{-10}$  cm<sup>3</sup>(STP)/cm s cmHg; *D*,  $10^{-9}$ cm<sup>2</sup>/s, and *S*, cm<sup>3</sup>(STP)/cm<sup>3</sup> atm, measured at 1 atm, 35 °C. <sup>*b*</sup>Ideal selectivity  $\alpha = P_1/P_2$ .



**Figure 8.** Robeson plots relevant to **PIa** (red  $\blacksquare$ ), **PIb** (red  $\blacktriangle$ ), **PIc** (blue  $\blacklozenge$ ), **PId** (blue  $\bigstar$ ) for (a) H<sub>2</sub>/CH<sub>4</sub>, (b) H<sub>2</sub>/N<sub>2</sub>, (c) H<sub>2</sub>/CO<sub>2</sub>, (d) CO<sub>2</sub>/CH<sub>4</sub>, (e) CO<sub>2</sub>/N<sub>2</sub>, and (f) O<sub>2</sub>/N<sub>2</sub> gas pairs (solid lines represent the 2008 upper bound). Data points are from reported 6FDA-*p*PD<sup>12</sup> (1), 6FDA-*m*PD<sup>12</sup> (2), 6FDA-*pp'*ODA<sup>13</sup> (3), 6FDA-*mp'*ODA<sup>13</sup> (4), and Matrimid<sup>51</sup> (5) along with TR-*α*PBO<sup>25</sup> (6), TR-PBO-*co*-PI (5:5)<sup>1</sup> (7), and AD-*c*PBO–PI (5:5)<sup>30</sup> (8) membranes for comparison.

elongation at break in comparison with the corresponding metaconnecting ones.<sup>49</sup> Additionally, significantly greater tensile and much higher elongation at break are observed for these 6FDAbased poly(benzoxazole-co-imide) membranes relative to the conventional TR membranes such as TR-1-450<sup>20</sup> (tensile strength: 98 MPa, elongation at break: 3.9%) and even TR poly(ether-imide)<sup>28</sup> (sample 450-1, tensile strength: 54 MPa, elongation at break: 4.0%). Moreover, the incorporation of benzoxazole rings also significantly improved the tensile properties as compared with the conventional polyimides, as shown by comparing PIc with the reference 6FDA-pPD membrane reported previously.<sup>49</sup> The pPD is believed to assume a conjugated planar conformation and thus the corresponding 6FDA-pPD polymer necessarily possesses high chain rigidity. Both the tensile strength (120 MPa) and elongation at break (26.3%) of the **PIc** are higher than the corresponding values of 6FDA-pPD (tensile strength of 108 MPa and elongation at break of 6%<sup>49</sup>). Especially, the elongation of the PIc was about 4.4 times higher than that of 6FDA-pPD. This indicated that incorporation of benzoxazole rings in polyimide significantly improved the tensile properties of the resulting copolymer membrane. Furthermore, all *para*-connecting poly(benzoxazole-*co*-imide) membranes exhibited much higher tensile strength, modulus, and also slightly higher elongation at break in comparison with Matrimid,<sup>51</sup> which has a tensile strength of 72.3 MPa, a modulus of 1.4 GPa and an elongation at break of 19.4%. The excellent tensile strength and thermal properties of the poly(benzoxazole-*co*-imide) class of membranes is of interest for commercial gas separation applications.

**Single Gas Permeability.** Six gases (He, H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub>) were used to determine the gas permeabilities, which are presented in Table 4. The sequence in permeability coefficients from highest to the lowest for all the poly-(benzoxazole-*co*-imide) membranes was He > H<sub>2</sub> > CO<sub>2</sub> > O<sub>2</sub> > N<sub>2</sub> > CH<sub>4</sub>, following the gas kinetic diameter order, i.e., He (2.60 Å) < H<sub>2</sub> (2.89 Å) < CO<sub>2</sub> (3.30 Å) < O<sub>2</sub> (3.46 Å) < N<sub>2</sub> (3.64 Å) < CH<sub>4</sub> (3.80 Å). The permeability coefficients of the membranes strongly depended on the chemical structures of the corresponding polymers. The *para*-connecting **PIa** exhibited higher permeability coefficients than *meta*-connecting **PIb** for all

gases (e.g., CO<sub>2</sub> permeability was about 2.6 times higher). For larger gases  $(N_2, O_2, CH_4, and CO_2)$  the para-connecting isomer membrane revealed much higher diffusivity coefficients than the corresponding meta-connecting ones. These results correlate well with the FFV values of the para- and meta-linked PIa isomers. A previous investigation of cavity size distributions and diffusion in para- and meta-linked isomers by molecular simulation studies confirmed that the average cavity size in para-linked isomers is larger than the corresponding ones in meta-linked isomers.<sup>36</sup> The solubility coefficients of the paraisomers had slightly higher values for the larger N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> gases than the corresponding meta-isomers, which is consistent with an interpretation previously reported by Nevertz et al.<sup>52</sup> In contrast, the PIc para-isomer had lower permeability coefficients for small size He and H<sub>2</sub> gases, due to a lower FFV than the *meta*-isomer. However, for large gases  $(N_2, O_2 CH_4 and$ CO<sub>2</sub>) the PIc para-isomer had higher permeabilities than the meta-isomer, even though the former had relatively smaller FFVs. This is due to higher solubility coefficients for these larger gases (see Table 4), which depend on both the polymeric chain structures and the interfaces formed between the polymer chains and permeating gases.<sup>52</sup>

The incorporation of highly rigid benzoxazole rings into the polyimide backbones can significantly improve the permeability. as can be confirmed by comparing PIc and PId with reference membranes 6FDA-pPD and 6FDA-mPD, respectively, reported previously.<sup>12</sup> Obviously, the permeabilities to CO<sub>2</sub> of the PIc membrane (25 Barrer) and the PId membrane (19 Barrer) increased 63% and 107%, respectively, as compared to the corresponding reference membranes 6FDA-pPD (15.3 Barrer) and 6FDA-mPD (9.2 Barrer). Also, in comparison with membrane made from commercial Matrimid, the poly-(benzoxazole-co-imide) membranes exhibited significantly higher permeability, e.g., the CO<sub>2</sub> permeability of PIa was about 8.7 times higher than that of Matrimid (5.39 Barrer<sup>51</sup>). However, these nonthermally rearranged poly(benzoxazole-co-imide) membranes are much less permeable than the TR-PBO-co-PI membranes. Note that thermal rearrangement is conducted in the solid state and therefore creates change in chain angles, which would force open free volume spaces.<sup>20</sup> However, if the benzoxazole group is already formed, and then cast as a polymer solution, the same process would not occur. In this case, interchain packing would be closer, because it had more degrees of freedom to move and thus had more packing density.

The influence of structural isomerism of poly(benzoxazole-coimide)s on gas transport properties is readily visualized in the Robeson permeability/selectivity trade-off plots, as shown in Figure 8. The permeability/selectivity trade-off performance of the present membranes is clearly well below that of thermally rearranged (TR) membranes such as TR- $\alpha$ PBO, especially for the  $CO_2/CH_4$ ,  $CO_2/N_2$  and  $O_2/N_2$  gas pairs.<sup>25</sup> The poly-(benzoxazole-co-imide) meta-isomers had better overall trade-off performance relative to the para-isomers for separating smaller gases (e.g., H<sub>2</sub>) from larger gases (e.g., N<sub>2</sub> and CO<sub>2</sub>), as shown in Figure 8, parts b and c. In contrast, the para- isomers showed better overall performance for larger gas pairs such as CO<sub>2</sub>/CH<sub>4</sub> and  $CO_2/N_2$  (Figure 8, parts d and e). It is noteworthy that among these poly(benzoxazole-co-imide) membranes, the PId *meta*-isomer membrane had the best performance for the  $H_2/$  $CH_4$ ,  $H_2/N_2$  and  $H_2/CO_2$  gas pairs. In particular, the separation performance for  $H_2/CH_4$  is very close to the Robeson 2008 upper bound, exceeding conventional/commercial polyimide membranes, e.g., 6FDA-pPD,<sup>12</sup> 6FDA-mPD,<sup>12</sup> 6FDA-

*pp*′ODA,<sup>13</sup> 6FDA-*mp*′ODA,<sup>13</sup> Matrimid,<sup>51</sup> and even TR-PBO*co*-PI (5:5),<sup>1</sup> AD-cPBO–PI (5:5),<sup>30</sup> and TR-αPBO<sup>25</sup> for the H<sub>2</sub>/ CH<sub>4</sub> and H<sub>2</sub>/CO<sub>2</sub> gas pairs. However, the *para*-connecting **PIa** had the best performance for the CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> gas pairs among the poly(benzoxazole-*co*-imide) membranes, exceeding the above conventional/commercial polyimide membranes, but below the TR-PBO-*co*-PI (5:5),<sup>1</sup> AD-cPBO– PI (5:5),<sup>30</sup> and TR-αPBO<sup>25</sup> membranes.

The present nonthermally rearranged poly(benzoxazole-coimide) membranes also exhibited improved mixed gas transport and plasticization resistance properties as compared to conventional polyimides. As shown in the Supporting Information (Table S1), the nonthermally rearranged **PIa** exhibited retained  $CO_2/CH_4$  selectivity (42.2) as compared to the commercial Matrimid membrane (structure shown in Scheme S1 in the Supporting Information) with a  $CO_2/CH_4$  selectivity of 36.4, for the  $50/50 \text{ CO}_2/\text{CH}_4$  mixed gas at 600 psig and 50 °C. Also, the un-cross-linked PDMC membrane<sup>53</sup> (6FDA-DAM3:DABA2), a representative 6FDA-based polyimide membrane, exhibited increased CO<sub>2</sub> permeability as the increase of the CO<sub>2</sub> feed pressure (Figure S1 in the Supporting Information), indicative of CO<sub>2</sub>-induced plasticization phenomenon. However, similar to that of the cross-linked PDMC, the CO<sub>2</sub> permeability of the PIa membrane decreased from 5 to 25 bar and then remained almost constant in the range of 30-40 bar as increasing CO<sub>2</sub> feed pressure (Figure S1), implying it has good plasticization resistance. The enhanced CO<sub>2</sub> plasticization resistance of the PIa membrane is mainly attributed to an introduction of the highly rigid benzoxazole units into the polymer chain backbone. Further study will be conducted to demonstrate the effect of the introduction of rigid moieties on gas transport properties including mixed gas permeation as well as plasticization resistance.

## CONCLUSIONS

Three novel benzoxazole-containing diamine monomers, p-BFO, m-BFO, and m-BOA, were synthesized via a high-yield one-step route from commercially available starting materials. The resulting poly(benzoxazole-*co*-imide)s were prepared by using 6FDA with three synthetic diamine monomers and also a commercial diamine, p-BOA. Because of introduction of benzoxazole moieties into the polyimides, the resulting poly-(benzoxazole-co-imide)s exhibited an excellent combination of properties, such as good solubility, excellent thermal and mechanical properties, and moderate permeability. Structural isomerism in the linkages had a significant impact on molecular packing and properties of the resulting poly(benzoxazole-coimide) membranes. The para-connecting poly(benzoxazole-coimide) isomers exhibited higher molecular weights  $(M_w s)$ , higher modulus and significantly larger elongation at break, higher  $T_{\sigma}s_{r}$ higher ordering of macromolecules, along with better overall performance for CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> separations as compared to the corresponding meta-connecting ones. However, the changes in FFV values from para-connecting polymer isomers to meta-connecting ones greatly depended on a combined contribution from both the chain packing and interchain distances in ordered domains. Systematic investigations and analyses of the correlation between molecular packing and properties of these poly(benzoxazole-co-imide)s in this study provide useful insight for adjusting specific performance parameters to meet the requirements of membrane-based gas separations.

# ASSOCIATED CONTENT

#### **S** Supporting Information

Mixed gas permeation test, a scheme showing the chemical structure of commercial Matrimid 5218, a table of pure gas and mixed gas transport properties for PIa and Matrimid, and  $CO_2$  plasticization resistance of membranes, including a figure showing pure  $CO_2$  permeation isotherms. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest. <sup>||</sup>M.D.G. is a visiting professor at Hanyang University.

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