Synthesis, barrier performance, and molecular simulation of a high-barrier polyimide that contains amide groups

Qian Wen1, Ao Tang, Chengliang Chen, Yiwu Liu2,*, Chenguang Xiao1, Jinghua Tan2 and Duxin Li1,∗*

1 State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, People’s Republic of China
2 National and Local Joint Engineering Center of Advanced Packaging Materials R & D Technology, Key Laboratory of Advanced Packaging Materials and Technology of Hunan Province, School of Packaging and Materials Engineering, Hunan University of Technology, Zhuzhou 412007, People’s Republic of China

* Authors to whom any correspondence should be addressed.

E-mail: liuyiwu@hut.edu.cn and liduxin6404@csu.edu.cn

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Abstract

4-Amino-4′-(4-aminobenzoyl)benzohydrazide (AAPDA), a diamine monomer that contains two amide groups, was synthesised by amidation and reduction, after which it was polymerised with pyromellitic dianhydride (PMDA) to prepare AAPPI, a novel polyimide. AAPPI exhibited excellent barrier performance, with oxygen- and water-vapor-transmission rates (OTR and WVTR, respectively) of only 1.7 cm² m⁻² d⁻¹ and 1.0 g m⁻² d⁻¹, respectively. This polyimide (PI) also exhibits outstanding thermal properties, with a glass transition temperature (Tg) of 423 °C, a 5% weight-loss temperature (T₅₀°) of 509 °C, and a coefficient of thermal expansion (CTE) of 2.58 ppm K⁻¹ under nitrogen. The barrier performance of AAPPI was also compared to that of DABPI, a structurally similar PI. Molecular simulations, wide-angle x-ray diffractometry (WAXD), and positron annihilation lifetime spectroscopy (PALS) revealed that AAPPI forms many more interchain hydrogen bonds than DABPI due to its additional amide groups. Consequently, AAPPI has very tightly packed polymer chains, a high degree of crystallinity, a small free volume, and poor chain mobility. These factors generally inhibit the permeation of small molecules, which explains why AAPPI has better barrier properties than DABPI. This novel PI has broad applications for the packaging of flexible electronics.

1. Introduction

Packaging materials are usually made of paper, metals, ceramics, or plastics, with plastics an especially popular choice due to their diversity and cost-effectiveness [1, 2]. Plastic films are often used in microelectronics as substrates for active-matrix organic light emitting diodes (AMOLED), due to their lightweightness, flexibilities, and strengths, which facilitate the manufacture of flexible, foldable, and wearable displays [3, 4]. Advances in display technologies require substrate materials to also possess outstanding high-temperature resistance characteristics (glass transition temperature (Tg) > 400 °C and coefficient of thermal expansion (CTE) ≤ 8 ppm K⁻¹) because high-performance thin-film transistors (TFTs) are critical for AMOLED displays, and high-performance low-temperature polycrystalline silicon (LTPS) TFTs are usually processed at temperatures around 400 °C [5, 6]. In addition, the substrate must be highly dimensionally stable to ensure substrate alignment with the TFT array during high-temperature processing [7]. Atmospheric water and oxygen can penetrate into the internals of such a device and corrode the organic-emitter layer, which damages the device. Therefore, the substrate must also exhibit excellent barrier performance against the intrusion of water and oxygen (water-vapor-transmission rate (WVTR) < 10⁻⁶ g m⁻² d⁻¹ and oxygen transmission rate (OTR) < 10⁻³ cm² m⁻² d⁻¹) [8, 9]. Many high-barrier materials (e.g., polyethylene terephthalate (PET), polyethylene naphthalate (PEN), and polyamide (PA) plastics) do not deliver the required barrier performance. They also do not have the required high-temperature stability, since their Tg's are generally lower than 200 °C [10, 11].

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Polyimides (PIs) are among the best substrate materials for AMOLED displays, as they are some of the most heat-tolerant polymers known to mankind [12, 13]. However, the barrier performance of PIs is rather poor [14, 15]. Some researchers have used surface sputtering or chemical vapor deposition (CVD) to coat PI films with inorganic barriers, such as aluminium oxide or silicon dioxide, or to create alternating inorganic and organic layers [16–18]. However, these methods involve cumbersome processes and large specialised equipment, which inevitably leads to high production costs. Therefore, improving PI barrier performance by modifying the molecular structure will greatly reduce the complexity and cost associated with producing flexible displays [19–21].

The gas permeability of a polymer is well-known to be closely related to its chemical structure. In our previous work [22], we polymerised 4,4′-diaminobenzanilide (DABA), a diamine monomer bearing an amide group (figure 1) with commercial pyromellitic dianhydride (PMDA) to produce a high-barrier PI with excellent high-temperature resistance (DABPI, figure 1). DABPI exhibits strong interchain interactions, as its repeating unit contains an amide group that increases its packing density and improves its barrier properties.

In our previous study, we demonstrated that the barrier performance of a PI can be improved by the incorporation of an amide group. In this work, 4-amino-N′-(4-nitrobenzoyl)benzohydrazide (AAPDA, figure 1), a diamine monomer bearing two amide groups, was synthesised by amidation and reduction, after which it was polymerised with commercial PMDA to prepare AAPPI, a high-barrier PI film (figure 1). The incorporation of multiple amide groups in the PI improves its barrier performance and ensures outstanding thermal and mechanical properties. Molecular simulations, wide-angle x-ray diffractometry (WAXD), and positron annihilation lifetime spectroscopy (PALS) were used to understand the relationship between barrier performance and molecular structure by quantifying molecular packing, intermolecular hydrogen bonding, free volume, chain mobility, permeation trajectories, diffusion coefficients, and solubility coefficients. In summary, we developed a high-barrier polymer film and elucidated its barrier mechanism.

2. Experimental section

2.1. Materials

All raw materials were presented in supporting information (available online at stacks.iop.org/MRX/8/045305/mmedia).

2.2. Instrumentation

All characterization methods were shown in supporting information.

2.3. Synthesis of 4-nitro-N′-(4-nitrobenzoyl)benzohydrazide (AAPDN)

Triethylamine (Et3N, 16 ml) and hydrazine monohydrate (1.455 ml) in dry tetrahydrofuran (THF, 200 ml) were added to a three-neck round-bottom flask cooled in an ice bath, with stirring for 10 min. p-Nitrobenzoyl chloride (12.8 g) was dissolved in dry THF (200 ml) and the resulting solution was added dropwise to the abovementioned solution, which produced a large amount of precipitate. After stirring for 6 h at 0 °C, the solution was refluxed for 6 h by raising the bath temperature to 75 °C. The reaction was terminated after this point. The precipitate was collected and washed with water (50 ml) followed by ethyl acetate (200 ml). The light-yellow product was collected and dried under vacuum for 24 h at 80 °C to afford the title product in 85% yield (8.42 g). IR (KBr, ν, cm⁻¹): 1582 (−NO2 stretching), 1613 (C==O stretching), 1347 (C−N stretching), 3194 (N−H stretching), 1100−700 (Ar−H stretching).1H NMR (400 MHz, DMSO-d6, δ, ppm): 11.05 (s, 2H), 8.58–8.33 (m, 4H), 8.30–8.10 (m, 4H). 13C NMR (100 MHz, DMSO-d6, δ, ppm): 164.74, 149.95, 138.37, 129.50, 124.27. MS (EI, m/z): 331(100) ([M+ + H]+, calcd for C14H10N2O6, 330.06). Anal. Calcd for C14H10N2O6: C, 50.92; H, 3.05 and N, 16.97; found: C, 50.83; H, 3.11 and N, 17.03.

Figure 1. The chemical structure of PMDA, DABA, AAPDA, DABPI and AAPPI.
2.4. Synthesis of 4-amino-N′-(4-aminobenzoyl)benzohydrazide (AAPDA)

AAPDN (3.303 g) was added to a three-neck round-bottom flask, followed by absolute ethanol (100 ml). The reaction solution was thoroughly deoxygenated by bubbling with argon. The temperature of the reaction solution was raised to 80 °C, after which palladium on carbon (Pd/C, 0.02 g) was added to the solution, and then hydrazine hydrate was added dropwise over 2 h. The reaction mixture was then allowed to react under argon for 6 h at 80 °C before the reaction was terminated. The reaction solution was cooled to room temperature and vacuum filtered to remove the Pd/C. The filtrate was evaporated close to dryness on a rotary evaporator and the residue crystallized at low temperature. The product was collected and dried under vacuum for 24 h at 80 °C to afford the title diamine monomer as white crystals in 88% yield (2.379 g). IR (KBr, v, cm⁻¹): 3416 (N-H stretching), 3294 (-NH₂ stretching), 1597 (δ N-H)1630 (C=O stretching), 1276 (C-N stretching), 1100 ~ 700 (Ar–H stretching).¹H NMR (400 MHz, DMSO-d₆, δ, ppm): 10.12 – 9.54 (m, 2H), 7.84 – 7.37 (m, 4H), 6.56 (d, J = 8.6 Hz, 4H), 5.69 (s, 4H).¹³C NMR (100 MHz, DMSO-d₆, δ, ppm): 166.44, 152.52, 129.53, 119.80, 113.04. MS (EI, m/z): 293(100) [(M⁺ + Na)+], calcd for C₁₄H₁₂N₄O₂, 270.11. Anal. Calcd for C₁₄H₁₂N₄O₂: C, 62.21; H, 5.22 and N, 20.73; found: C, 62.16; H, 5.27 and N, 20.76.
2.5. Polyimide synthesis

The PI was synthesised in a clean room. AAPDA (0.5946 g, 2.2 mmol) and dry N,N'-dimethylformamide (DMF, 15 ml) were added to a round-bottom flask. Commercial PMDA (0.4799 g, 2.2 mmol) was then added, which resulted in a suspension with a solid content of approximately 9 wt%. Argon gas was bubbled through the reaction mixture, which was then allowed to react for 8 h at 0 °C to produce a viscous polyamic acid (AAPPAA) solution. The gel was thoroughly defoamed, and then scraped onto a clean glass plate. The height of the AAPPAA solution (and consequently, the thickness of the PI film) was manipulated by adjusting the effective height of the scraper. The AAPPAA solution was then thermally imidised in a high-temperature vacuum oven, with the following temperature program: room temperature to 100 °C (1 h) / 100 °C–200 °C (1 h) / 200 °C–300 °C (1 h) / 300 °C–420 °C (1.5 h). The AAPPI film was removed from the glass plate after cooling to room temperature.

IR (KBr, v cm⁻¹): 1777 and 1719 (C=O stretching), 1360 (C-N stretching), 1100–700 (Ar-H stretching). Anal. Calcd for C₂₄H₁₂N₄O₆: C, 63.72; H, 2.67 and N, 12.39; found: C, 63.77; H, 2.71 and N, 12.38.

2.6. Molecular simulation

Firstly, a polymer chain consisting of 25 repeating units was constructed, and five polymer chains were then used to construct the PI model. The structure of the model and the values of the molecular-simulation parameters are detailed in the Supporting Information. These simulations were used to calculate the following PI parameters: free volume, number of hydrogen bonds, radius of gyration, radial distribution function, local polymer-chain mobility, and the gas diffusion and solubility coefficients. Full information is provided in the Supporting Information.

3. Results and discussion

3.1. Synthesis and characterization of monomers and polyimides

The synthetic pathway for the preparation of AAPDA is shown in scheme 1. The AAPDN intermediate was prepared by the amidation of p-nitrobenzoyl chloride with hydrazine hydrate in THF; high-purity AAPDA (the diamine monomer) was then obtained by the reduction of AAPDN. Nuclear magnetic resonance (NMR) and Fourier-transform infrared (FTIR) spectroscopy, elemental analysis, and mass spectrometry (MS) were used to characterise both AAPDA and AAPDN. The spectroscopic results are consistent with their structures, which verified that these products had been successfully synthesised. The NMR and mass spectra of AAPDN and the mass spectrum of AAPDA are shown in figures S3 and S4, respectively, of the Supporting Information, with the FTIR spectra shown in figure S5. The NMR spectra of AAPDA are shown in figure 2 and elemental analysis data are provided in the previous section.

The pathway for the synthesis of AAPPI is shown in scheme 2. An equimolar mixture of AAPDA and PMDA was polymerised at low temperature to produce the highly viscous AAPPAA precursor, which was then imidised using a temperature program to form AAPPI. Since PIs are insoluble, gel permeation chromatography (GPC) was used to determine the molecular weight and weight-molecular distribution of AAPPAA, from which the molecular weight and molecular-weight distribution of the PI was inferred. The precursor was determined to have a weight-average molecular weight ($M_w$) of 2.21 × 10⁵ and a polydispersity ($M_w/M_n$) of 1.95. AAPPI has high $M_w$ and low polycondensation. The FTIR spectrum of AAPDA (figure S5) shows a C-N stretching band at 1360 cm⁻¹ and carbonyl stretching bands at 1777 cm⁻¹ and 1719 cm⁻¹, which are characteristic of imide rings [23–25]. Therefore, we conclude that AAPPI had successfully reacted with PMDA and that the resultant polyamic acid was fully imidised.
3.2. Thermal and mechanical properties

Thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC) and thermomechanical analysis (TMA) were used to probe the thermal performance of AAPPI, the results of which are summarised in Table 1. The TGA curve in Figure S6(a) shows that the 5% and 10% weight loss temperatures ($T_{d5\%}$ and $T_{d10\%}$) of AAPPI are 509 °C and 524 °C, respectively. According to the DMA data in Figure S6(b), AAPPI has a $T_g$ of 423 °C, while the TMA data in Figure S6(c) indicate that AAPPI is very dimensionally stable, as its CTE was only 2.58 ppm K$^{-1}$ in the 50 °C–300 °C range. Mechanical testing revealed that the tensile strength and tensile modulus of AAPPI are 143 MPa and 4.2 GPa, respectively. The film can be folded into a cylindrical shape, thereby confirming its flexibility. (Figure S7).

In comparison with DABPI, the introduction of amide structure ensured the excellent thermal and mechanical properties of the two PIS; however, the thermal decomposition temperatures of AAPPI ($T_{d5\%}$ and $T_{d10\%}$) decreased to a certain extent, which may be attributed to the fact that more amide structures of AAPPI cracked first. The outstanding thermal and mechanical properties of AAPPI are attributable to the incorporation of amide groups, which facilitate the formation of strong interchain interactions.

3.3. Barrier properties

The barrier performance of AAPPI with respect to H$_2$O and O$_2$ intrusion were quantified by its WVTR and OTR values, the results of which are listed in Table 2, with the barrier performance of DABPI, a PI that our group developed in a previous study, included for comparison. Both PIs were prepared by similar processes, and their dianhydrides were both derived from commercial PMDA. The difference between the diamine monomers lies in

| Table 1. Thermal and mechanical properties of the DABPI and AAPPI film. |
|---------------------------------------------------------------|
| **Polyimide** | $T_g$ (°C) | $T_{d5\%}$ (°C) | $T_{d10\%}$ (°C) | CTE (ppm K$^{-1}$) | Tensile strength (MPa) | Tensile modulus (GPa) |
|----------------|-----------|-----------------|-----------------|-----------------|-----------------------|----------------------|
| DABPI[22]     | 435       | 417             | 542             | 569             | −3.2                  | 156 ± 3.0            | 5.1 ± 0.1            |
| AAPPI          | 423       | —               | 509             | 524             | 2.58                  | 143 ± 3.0            | 4.2 ± 0.2            |

$^a$ Measured by DMA  
$^b$ Measured by DSC  
$^c$ CTE within the range of 50 °C–300 °C.

| Table 2. Barrier properties of DABPI and AAPPI films. |
|---------------------------------------------------------------|
| **PIs** | WVP (g·mil·m$^{-2}$·day$^{-1}$) | OP (cm$^3$·mil·m$^{-2}$·day$^{-1}$) | WVTR (g·m$^{-2}$·day$^{-1}$) | OTR (cm$^3$·m$^{-2}$·day$^{-1}$) |
|---------|---------------------------------|-------------------------------|-----------------|-----------------|
| DABPI$^a$ | 3.6 ± 0.2                       | 5.6 ± 0.2                     | 5.1 ± 0.3       | 7.9 ± 0.3       |
| AAPPI   | 0.7 ± 0.1                       | 1.2 ± 0.1                     | 1.0 ± 0.1       | 1.7 ± 0.1       |

$^a$ The barrier properties values are obtained from [22].
the number of amine groups between benzene rings. The WVTR and OTR of AAPPI were determined to be only 1.0 g m$^{-2}$ d$^{-1}$ and 1.7 cm$^3$ m$^{-2}$ d$^{-1}$, which are 80.4% and 78.5% lower than those of DABPI, respectively, and shows that the barrier performance of a PI film improves as the number of amide groups in the monomer increases. The underlying mechanisms responsible for the barrier properties of AAPPI are discussed below.

### 3.4. Aggregation structures analysis

To elucidate the barrier mechanisms of the abovementioned PIs, the aggregation structures of DABPI and AAPPI were probed by WAXD, with the corresponding WAXD spectra shown in figure 3. Interchain spacings were calculated using the Bragg equation and are listed in table 3 [26]; the interchain spacing of DABPI ($2\theta = 20.5^\circ$) was determined to be 4.33 Å, while that of AAPPI ($2\theta = 23.8^\circ$), which has an additional amide group in its monomeric unit, is only 3.74 Å. Furthermore, AAPPI exhibits a sharper and more-intense WAXD peak than DABPI, which implies that AAPPI is more crystalline. Small molecules are reportedly unable to diffuse through the crystalline regions of polymers [27]; therefore, the high crystallinity of AAPPI enhances its barrier properties. The densities of DABPI and AAPPI were also measured; AAPPI (1.60 g cm$^{-3}$) was found to be 6% more dense than DABPI (table 3). Given the shorter interchain distance, higher crystallinity, and higher density

| PIs     | Density (g cm$^{-3}$) | $2\theta$ ($^\circ$) | $d$-spacing (Å) | CED (J cm$^{-3}$) | N$^a$ (H-bonds) |
|---------|-----------------------|---------------------|-----------------|-------------------|-----------------|
| DABPI   | 1.51                  | 20.5                | 4.33            | 557               | 58              |
| AAPPI   | 1.60                  | 23.8                | 3.74            | 623               | 194             |

* The number of hydrogen bonds in the simulation cells.

Figure 4. The RDFs of the hydrogen atoms of –HN– and oxygen atoms of O=C– for DABPI(a) and AAPPI(b).
of AAPPI, we conclude that increasing the number of amide groups in the repeating unit of a PI helps to tighten its polymer-chain packing.

### 3.5. Hydrogen bonds analysis

Interchain interactions are very important for PI-chain stacking. These interactions are primarily determined by interchain hydrogen bonding in DABPI and AAPPI, which typically occurs between –NH– and O=–C– groups. DABPI and AAPPI were simulated to calculate the radial distribution functions (RDFs) of these PIs and to determine the number of hydrogen bonds in each PI.

The RDFs for DABPI and AAPPI are shown in figure 4. Hydrogen bond lengths have been reported to range between 0 and 3.1 Å [28]. DABPI and AAPPI exhibit significant peaks at 1.9 Å and 2.0 Å, respectively, in their RDFs, which shows that both PIs are likely to have formed interchain hydrogen bonds. The number of hydrogen bonds in DABPI and AAPPI were counted (table 3) and are shown in figure 5. AAPPI has 194 hydrogen bonds while DABPI has only 58 hydrogen bonds, which is ascribable to the additional amide groups in AAPPI. The

#### Figure 5. H–bonds in the simulation cell of DABPI (a1, a2) and AAPPI (b1, b2). H–bonds between –HN– and O=–C– in amide groups (a1, b1) and between –HN– and O=–C– in imide rings (a2, b2).

#### Table 4. The analyzed data for the positron lifetime and simulated FFV values in the DABPI and AAPPI films.

| PIs    | τ1(ns) | I1(%) | τ2(ns) | I2(%) | R(Å) | Vf2(Å³) | FFV | FFV(O2) | FFV(H2O) |
|--------|--------|-------|--------|-------|-------|---------|-----|---------|----------|
| DABPI  | 0.18   | 2.5   | 0.370  | 97.2  | 2.15  | 41.63   | 7.28| 4.52    | 9.60     |
| AAPPI  | 0.18   | 2.7   | 0.366  | 96.8  | 2.05  | 36.08   | 6.29| 3.07    | 8.03     |

* FFV determined by PALS.

Free volume parameters calculated by simulations; FFV(O2) and FFV(H2O) and based on probe radii of 1.73 Å and 1.325 Å, respectively.
simulations also show that AAPPI has a higher cohesive energy density (CED) than DABPI (table 3). Taken together, these results reveal that AAPPI has stronger interchain interactions than DABPI that are ascribable to its additional amide groups, which allows AAPPI to form more hydrogen bonds than DABPI; these hydrogen bonds strengthen interchain interactions in the former, resulting in more tightly packed polymer chains.

Figure 6. Positron lifetime spectra measured for DABPI and AAPPI film.

Figure 7. Distributions of void radius (a) and fractional free volume (b) as a function of probe radius in DABPI and AAPPI. The kinetic radii of O$_2$ and H$_2$O are indicated by vertical lines.
3.6. Free volume and cavity size distribution analysis

Free volume is closely related to the barrier performance of a polymer, and the size and distribution of the free volume in a polymer are determined by the stacking of its polymer chains. DABPI and AAPPI were subjected to PALS to quantify their free volumes. The PALS-derived data for these PIs are listed in Table 4, with their PALS spectra shown in Figure 6. Free volume radius is known to be closely related to positron lifetime; this relationship was used to calculate the free-volume radius \( R \), free-volume dimension \( V_{f2} \), and fractional free-volume \( FFV \) of each PI \([22, 29]\). The \( R \) value \( 2.05 \) Å of AAPPI is 4.7% lower than that of DABPI, while the \( FFV \) \( 6.28\% \) is 13.6% lower. The lower \( FFV \) and \( R \) for AAPPI are the result of tighter molecular-chain packing that, in turn, is due to the presence of additional amide groups. These qualities generally inhibit the diffusion of small molecules inside a film.

Molecular simulations can be used to determine the distribution of pores that are responsible for the free volume of a polymer; this information is very useful when developing an understanding of the barrier performance of a PI film. Therefore, molecular simulations were used to determine the numbers of cavities in these films and to analyse their size distributions. Figure 7(a) displays the size distributions of cavities with radii between 0 and 3 Å, which shows that the fraction of cavities with a given radius initially increases and then decreases with increasing \( R \). The cavities that are most significant for molecular diffusion are those with radii greater than the kinetic radius of the molecule in question (1.325 Å for \( H_2O \) and 1.73 Å for \( O_2 \)). Both PIs have very few cavities with radii greater than 1.2 Å. Nonetheless, the cavity size distribution of AAPPI is shifted to...
lower values compared to that of DABPI; therefore, AAPPI strongly inhibits molecular diffusion and, consequently, exhibits better barrier performance than DABPI.

Spherical probes of varying size were used to determine the free volumes of the PIs, thereby elucidating how the accessibility of the free volume in each PI varies with the size of the diffusing molecule. The relationship between probe size and FFV is shown in figure 7(b), which reveals that FFV generally decreases with increasing probe size. Furthermore, the FFV of AAPPI is lower than that of DABPI for each probe size. Vertical lines are drawn at the kinetic radii of H₂O and O₂ (1.325 Å and 1.73 Å) in figure 7(b) to determine their FFVs (FFV(H₂O) and FFV(O₂)), which are summarised in table 4. AAPPI exhibits lower FFV values for both of these gaseous molecules than DABPI. Hence, the free volume available for H₂O and O₂ diffusion is smaller in AAPPI than in DABPI. The accessible volumes of DABPI and AAPPI for the H₂O and O₂ probes are shown in figure 8, in which the areas in blue represent the free-volume cavities of each polymer. It is clear from this figure that AAPPI has fewer accessible cavities than DABPI, which is attributable to the tighter packing and smaller free volume of AAPPI.

3.7. Local mobility of polymer chains
Molecular simulations were used to calculate the mean square displacements (MSDs) of AAPPI and DABPI, in order to determine how the local mobilities of their polymer chains affect barrier performance. The time-dependence of the MSD of each PI is shown in figure 9. In a polymer, small molecules generally diffuse through channels formed by the transient motions of the polymer chains [30]. Therefore, greater local polymer-chain mobility leads to poorer barrier performance. A high MSD in figure 9 corresponds a high degree of polymer-chain mobility [31, 32]. Since AAPPI is generally observed to exhibit lower MSDs than DABPI, the polymer chains of the former are less mobile than those of the latter, which is un conducive for the diffusion of small molecules and one of the reasons why AAPPI exhibits excellent barrier performance.

Figure 10. The representative trajectories of O₂ and H₂O in (a) DABPI and (b) AAPPI.
3.8. Free volume and cavity size distribution analysis

Molecular simulations were used to study the gas transport behaviour of AAPPI by elucidating the gas-diffusion and solubility behaviour of AAPPI and DABPI.

3.8.1. Gas diffusion

Molecular simulations were used to study the gas transport behaviour of AAPPI by elucidating the gas-diffusion and solubility behaviour of AAPPI and DABPI. Molecular simulations can be used to determine the motional trajectories of H$_2$O and O$_2$ in a polymer, which reflect the diffusion behaviour of small molecules in the polymer film [33]. The motional trajectories of molecular O$_2$ and H$_2$O in AAPPI and DABPI that occur within 10 ns were simulated, the results of which are shown in figure 10, with the |r(t) - r(0)| curves that correspond to these trajectories shown in figure S6; the displacement curves for O$_2$ and H$_2$O in AAPPI are shifted upwards to facilitate comparison. Based on the trajectories shown in figure 10, it is clear that the O$_2$ and H$_2$O trajectories are shorter in AAPPI than in DABPI, which is supported by the data in figure S6 that show that O$_2$ and H$_2$O have low hopping frequencies and short displacement lengths in AAPPI.

Logarithmic MSD versus time curves for H$_2$O and O$_2$ in DABPI and AAPPI are plotted in figure 11. According to the Einstein relationship, the coefficient of diffusion of a gas in a matrix is the point at which the gradient of this log plot is equal to unity [34]. The diffusion coefficients of DABPI and AAPPI are summarized in table 5, which reveals that the values of these coefficients are generally lower in AAPPI than in DABPI, a result of

Figure 11. MSD of O$_2$ and H$_2$O in DABPI and AAPPI as a function of time.

Figure 12. The adsorption isotherms of O$_2$ and H$_2$O in DABPI and AAPPI.
the smaller free volume and poorer connectivity of AAPPI that obstructs small-molecule diffusion. Furthermore, H2O is observed to have a lower coefficient of diffusion than O2 in both PIs, despite having the smaller kinetic radius, which is the result of polar interactions between H2O and the PI matrix that inhibit H2O diffusion.

3.8.2. Gas solubility
To elucidate the solubilities of O2 and H2O in these PIs, we used grand canonical Monte Carlo simulations to probe the adsorption of O2 and H2O by DABPI and AAPPI at various levels of pressure; the corresponding adsorption isotherms are shown in figure 12. The gases are rapidly adsorbed by the PIs in the low-pressure region, with micropores primarily adsorbing these molecules; this adsorption behaviour is consistent with the Langmuir adsorption model. These gaseous molecules were adsorbed more slowly in the high-pressure region, with polymer-chain free volume primarily responsible for adsorption; this behaviour is consistent with the Henry adsorption model. Therefore, the adsorption data for O2 and H2O can be fitted to two adsorption models, and their solubility coefficients can be obtained from their adsorption isotherms [35]. The solubility coefficients of H2O and O2 are generally lower in AAPPI than in DABPI. Since the cavities in AAPPI are smaller and fewer than those in DABPI, it follows that AAPPI also has fewer accessible adsorption sites, which explains its lower solubility coefficients. The solubility coefficient of H2O is observed to generally be larger than that of O2, in stark contrast to their diffusion coefficients. This is primarily due to the stronger affinity between the polar H2O molecule and the PI. H2O is also able to access a greater number of adsorption sites due to its smaller kinetic radius.

3.8.3. Gas Permeability
According to the solution-diffusion model, the permeability coefficient \( P \) depends on the diffusion \( D \) and solubility \( S \) coefficients; i.e., \( P = D \times S \) [36]. Values of \( P \), \( D \), and \( S \) calculated for O2 and H2O in DABPI and AAPPI are listed in table 5. The \( P \) values for AAPPI, which has additional amide groups, are lower than those of DABPI, which is consistent with previous experimental data that show that AAPPI has a lower \( P \) than DABPI; therefore, the simulation results are reliable. In summary, the barrier performance of AAPPI is superior to that of DABPI, and is the result of the former having additional amide groups. The enhanced barrier performance of AAPPI is due to its tighter polymer-chain stacking, higher crystallinity, smaller free volume, and lower chain mobility than those of DABPI.

### 4. Conclusion

Based on our previous work on DABA, a diamine monomer bearing one amide group, we designed and synthesised AAPDA, a new diamine monomer with two amide groups. AAPDA was polymerised with PMDA to prepare AAPPI, a polyimide. AAPPI exhibited excellent barrier performance, as its OTR and WVTR are only 1.7 \( \text{cm}^3 \text{m}^{-2} \text{d}^{-1} \) and 1.0 \( \text{g} \text{m}^{-2} \text{d}^{-1} \), respectively. Furthermore, AAPPI is outstandingly thermally and dimensionally stable.

Molecular simulations, WAXD, and PALS were used to determine the underlying reasons for the superior barrier performance of AAPPI. Aggregation structure analysis revealed that AAPPI is highly crystalline with small interchain spacings, indicative of tight polymer-chain packing. Molecular simulations show that the additional amide group in the repeating structure of AAPPI substantially increases the number of interchain hydrogen bonds in this PI (compared to DABPI), which is conducive for tight polymer-chain packing. Free-volume analysis revealed that AAPPI contains only small and discontinuous free-volume cavities; hence, it is difficult for O2 and H2O to diffuse and dissolve in the film. According to the MSD values for the PI chains, the AAPPI chains are very immobile, which inhibits the diffusion of small molecules. Since the diffusion and

| PIs  | \( D \) \( \times 10^{-12} \text{cm}^2 \text{m} \text{s}^{-1} \text{cmHg}^{-1} \) | \( S \) \( \times 10^{-3} \text{cm}^3 \text{m}^{-2} \text{d}^{-1} \text{cmHg}^{-1} \) | \( P \) \( \times 10^{-10} \text{cm}^3 \text{m}^{-2} \text{d}^{-1} \text{cmHg}^{-1} \) |
|------|-------------------------------------------------|---------------------------------|---------------------------------|
| DABPI| 1.7 4.82                                        | 0.41 0.045                     | 0.70 0.22                      |
| AAPPI| 1.0 2.53                                        | 0.18 0.031                     | 0.18 0.078                     |

* Units of \( (10^{-4} \text{cm}^3 \text{m}^{-2} \text{s}^{-1}) \).
* Units of \( \text{cm}^3 \text{STP} \text{m}^{-3} \text{cmHg}^{-1} \).
* Units of \( (10^{-8} \text{cm}^2 \text{cm}^{-3} \text{s}^{-1} \text{cmHg}^{-1}) \).
solution coefficients of O₂ and H₂O in AAPPI are low, it follows that the corresponding permeability coefficients are also low in this PI, which is interpreted to mean that AAPPI exhibits high barrier performance. Compared with DABPI, AAPPI has more amide structure, which will form more interchain hydrogen bonds, increase the stack density and crystallinity of the chain, and reduce the free volume and chain mobility, in order to improve the barrier performance. This high-performance PI has tremendous potential for use in microelectronics and other advanced packaging applications.

Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

ORCID iDs

Duxin Li https://orcid.org/0000-0002-9548-9181

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