Supporting Information

Structure and gas barrier properties of polyimide containing a rigid planar fluorene moiety and an amide group: Insights from molecular simulations

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1. Materials and instrumentation

1.1 Materials

2,7-Dinitro-9H-fluorene (FDN), palladium 10% on activated carbon (10% Pd/C), hydrazine monohydrate (N₂H₄•H₂O), 4-nitrobenzoyl chloride and ODA were purchased from Alfa-Aesar company and used as received. PMDA was purchased from Alfa-Aesar company and dried at 110 °C under vacuum for 6 h before use. Analytical grade absolute ethanol (EtOH), N,N-dimethylformamide (DMF), N-N-dimethylacetamide (DMAc), and pyridine (Py) were purchased from Sinopharm Chemical Reagent Co., Ltd. DMF was purified by distillation under inert nitrogen atmosphere. DMAc and Py were dried by 4A molecular sieve for a week before use. Absolute ethanol was used without further purification.

1.2 Instrumentation

All Nuclear Magnetic Resonance spectra (NMR) were recorded on a Bruker ARX400 MHz spectrometer. Samples were prepared as solution of 5~15 mg of compound in 0.5 mL of deuterated dimethyl sulfoxide (DMSO) using tetramethylsilane (TMS) as the internal reference. Mass spectra were measured on an AcquityUPLC/UPC2/Xevo G2-XS QTOFMS. Elemental analysis was carried out on a Vario EL cube Elemental Analyzer. Infrared spectra were recorded on a Nicolet iS10 Fourier-transform infrared (FT-IR) spectrometer. The molecular mass of the poly(amic acid) (PAA) was estimated by gel permeation chromatography on multi-angle laser light scattering (GPC-MALLS) system (Wyatt Technology Corporation). DMF is the eluent with flow rate of 1 mL/min and test temperature of
50 °C. WAXD were recorded by a Rigaku, Ultema III X-ray diffractometer using a Cu Kα radiation. Density was obtained with an ALFA MIRAGE SD-200L electronic density balance. The thickness of the films for density test was 20 μm.

Thermogravimetric analyses (TGA) were performed with a TA thermal analyzer (TGA55) under N₂ with a heating rate of 20 °C/min from 50 to 800 °C, and heated under flowing nitrogen (40 mL/min). The dynamic mechanical (DMA) spectra of the samples were obtained by using TA thermal analyzer (DMA Q850). The specimens were analyzed in tensile mode at a constant frequency of 1 Hz, amplitude of 20 μm, and a temperature range from 25 to 500 °C at a heating rate of 5 °C/min. Thermal mechanical analysis (TMA) was used to study the coefficient of thermal expansion of the film with a heating rate of 5 °C/min from 25 °C to 350 °C by TMA Q400 instrument under nitrogen.

Tensile test was performed on samples cut from 35–50 μm thick sheet and tested using SANS CMT6103 instrument according to GB/T16421-1996. The specimen size is 10×100 mm, Jaw separation is 50 mm. Jaw speed was first set to 2 mm/min, when elongation reached 1 mm, the Jaw speed was changed to 20 mm/min.

The oxygen permeability of a PI film was measured by Mocon (Minneapolis, MN), in accordance with ASTM-D 3985, using an OX-TRAN 2/21 ML instrument at 23 °C and 0 % RH. The moisture vapor permeability was measured using the model PERMATRAN-W® 3/33 of the Mocon Corporation (USA) at 90 % RH and 37.8 °C according to ASTM F-1249. The sample of 75 μm was fixed on an aluminum foil with the testing area of 5 cm².
Positron lifetime measurements were performed as follows: two identical samples with dimension of $1.5 \times 10 \times 10 \text{ mm}^3$ were sandwiched with a 10 $\mu$Ci $^{22}$Na positron source. The $^{22}$Na nucleus emits a 1.28 MeV $\gamma$-ray simultaneously (within a few ps) with the positron. The positron lifetime is determined from the time delay between the emission of the birth gamma (1.28 MeV) and one of the 0.511 MeV annihilation photons. Lifetime measurements were carried out using a fast-fast coincidence system with a time resolution of about 210 ps and a channel width of 12.6 ps. We have analyzed the lifetime spectra with the help of the data processing programs PATFIT. Before analyzing each spectrum, the positron source components (377 ps/11.75%, 1.04 ns/0.17%) were subtracted. The variance of the fits was around 1.1.
2. Details of molecular simulation

2.1 Construction of polymer microstructures

Biovia Materials Studio software was employed to perform simulations in this study using the COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) forcefield.\textsuperscript{1,2} Initially, polymer chains containing 25 repeat units were built and geometry optimization was performed. Then, a periodic model of the PI, comprising of 5 polymer chains in cubic unit cell, was constructed and the total energy of the system was minimized using smart minimizing method. Annealing was performed by the NPT (constant number of particles (N), pressure (P) and temperature (T)) dynamics procedure through heating and cooling the system at 1 atm in the temperature range of 300 to 1000 K in steps of 50 K. Interactions of non-bond, van der Waals and electrostatic forces, were calculated using an atom-based summation method and an Ewald summation method, respectively. The annealed cell was later put through a stage-wise equilibration procedure. First the cell was heated to 1000 K, and then the temperature was decreased in several stages to 600 K in steps of 100 K. After this, the temperature was decreased in several stages to 400 K in steps of 50 K and then decreased to 300 K in steps of 25 K. Each stage consisted of two consecutive NVT (constant number of particles (N), volume (V) and temperature (T)) and NPT runs at 1 atm and a specific temperature. The aim of the procedure was to obtain a refined system that would relax at the experimental density of the amorphous
polymer at 1 atm and 300 K. Finally, the cell was relaxed by consecutive NVT (at 300 K) and NPT dynamics (at 1 atm and 298 K) to ensure that a constant density has been reached. Two criteria were used to determine the equilibrium of the system: (1) The density of the system remained stable for a long time; (2) the fluctuation of energy was lower than 10 %. The plots of density and energy versus simulation time in the last NPT for PI systems are shown in Figure S1 and Figure S2, respectively. It can be seen that the PI systems have reached equilibrium states. The equilibrated densities of Kapton and FAPPI systems are 1.41 and 1.50 g/cm$^3$, respectively, which are fairly close to the experimental densities (1.42 and 1.52 g/cm$^3$). In all runs, Nosé method was used for temperature control. In NPT runs, the pressure was controlled by Berendsen’s method. During these simulations, the cutoff for the nonbonded interactions was taken as 15.5 Å.

![Figure S1](image.png)

**Figure S1** Plots of density versus simulation time in the NPT simulation for Kapton and FAPPI.
Figure S2 Plots of energy versus simulation time in the NPT simulation for (a) Kapton and (b) FAPPI.
2.2 Free volume

The free volume was determined by a grid scanning method using the Connolly task. The void distribution was estimated by a method previously used for micro-crystalline materials. Specifically, the simulation cell was divided into three-dimensional fine grids with a size of approximately 0.25 Å. The void size at a grid was determined as the diameter of the maximum cavity that encloses the grid and additionally has no overlap with any polymer atom.

2.3 Radius of gyration

In order to study the molecular conformation behavior of polymer chains, the radius of gyration ($R_g$) of polymer chains were calculated. $R_g$ gives a sense of the size of the polymer coil and is defined as:

$$R_g^2 = \frac{\sum_{i=1}^{N} |r_i - r_{cm}|^2 m_i}{\sum_{i=1}^{N} m_i}$$

(1)

where $r_i$ and $r_{cm}$ represent the position vector of the $i$th atom and the center of mass of the polymer chain, respectively. $m_i$ is the mass of site $i$ and $N$ is the number of atoms. An NPT simulation of the equilibrated system was performed for 300 ps to determine the $R_g$.

2.4 Radial distribution functions

The radial distribution functions (RDF) refer to a measure of the probability that, given the presence of an atom at the origin of an arbitrary reference frame, there will be an atom with its center located in a spherical shell of infinitesimal thickness at a
distance $r$ from the reference atom. The RDF was calculated by the average of the static relationship of every given pair of particles AB using the following equation:

$$g_{AB}(r) = \frac{\langle n_{AB}(r) \rangle}{4\pi r^2 \Delta \rho_{AB}}$$

(2)

where $\langle n_{AB}(r) \rangle$ is the average number of atom pairs between $r$ and $r + \Delta r$, and $\Delta \rho_{AB}$ is the density of atom pairs of type AB.

2.5 Diffusion coefficients

The diffusivity of gas molecules through PI was estimated by first inserting ten molecules of each gas into the equilibrated simulation box. Then, minimization of the potential energy was performed using “smart minimizing method” run. After this, the cell was put through annealing and stage-wise equilibration procedures using the same parameters as described before. The resulting structure was then equilibrated by NVT and NPT simulations at 298 K in order to ensure that its minimized total energy remained approximately constant with respect to the simulation time. An NVE simulation of the system was performed for 10000 ps. The diffusion coefficients can be calculated by means of the Einstein relation

$$D = \frac{1}{6N} \lim_{t \to \infty} \frac{d}{dt} \left( \sum_{i}^{N} |r_i(t) - r_i(0)|^2 \right)$$

(3)

where $N$ is the number of penetrants, $r_i(0)$ and $r_i(t)$ are the initial and final positions of the center of mass of penetrant $i$ over the time interval $t$, and $\langle |r_i(t) - r_i(0)|^2 \rangle$ is the averaged mean-square displacement (MSD) of
the penetrant. The diffusion coefficient was determined from the slope of MSD versus time data. In this work, MSD of H₂O and O₂ were calculated from the trajectories of ten penetrant molecules in the PI microstructures.

2.6 Determination of local mobility of polymer chains

The backbone MSD of PIs was determined to investigate the local mobility of PI chains. An NVE simulation of the equilibrated system was performed for 5000 ps.

2.7 Sorption isotherm

The equilibrated cell was used for grand canonical Monte Carlo (GCMC) simulations employing the standard Metropolis algorithm using the “Sorption Isotherm” module. Both the polymer framework and the penetrant molecules were treated as rigid bodies. The degrees of freedom of the system were accordingly specified by the center-of-mass position and orientation of the molecules. Metropolis sampling was used for inserting or deleting permeant molecules as well as accepting or rejecting their translational and rotational configurational moves. The COMPASS force field and force field assigned partial charges on atoms were used. A VTμ simulation was performed at each fixed pressure and 298 K. The pressure of the penetrant gas was varied from 10 to 3000 kPa. For each pressure value, 10⁵ equilibration steps were first performed to ensure proper relaxation of the polymer chains in response to the insertion of the penetrant molecule, following which 10⁶ steps of production run were carried out. The sorption isotherm can be obtained in the form of a plot of the concentration of sorbed gas, C, as a function of pressure at constant temperature. The solubility coefficient, S, is then obtained from the limiting
slope of the sorption isotherm at zero pressure as\textsuperscript{12}

\[ S = \lim_{p \to 0} (C/p) \quad (4) \]

where \( C \) is in units of \( \text{cm}^3 \text{(STP)}/\text{cm}^3 \text{(polymer)} \) and \( p \) is pressure.
3. Characterization and properties of monomers and polyimides

**Figure S3** $^1$H NMR (a), $^{13}$C NMR (b) and MS (c) spectra of FAPDN.
Figure S4 MS spectrum of FAPDA

Figure S5 FT-IR spectra of FAPDN, FAPDA and FAPPI.
**Figure S6** TGA curve of the FAPPI film.

**Figure S7** Photo image of the flexible FAPPI film.
4. Aggregation structures analysis by radial distribution functions

![Radial Distribution Functions graphs](image_url)

**Figure S8** Chain-chain intermolecular RDFs based on (a) all the carbon atoms in the benzene rings and (b) all the nitrogen atoms in the imide rings for FAPPI and Kapton.
5. Radius of gyration analysis

![Graph of Kapton](image)

![Graph of FAPPI](image)

**Figure S9** Time dependence of the radius of gyration $R_g$ for (a) Kapton and (b) FAPPI.
6. Gas diffusion

**Figure S10** Displacement of O\(_2\) and H\(_2\)O from their initial positions in Kapton and FAPPI. The curves of O\(_2\) and H\(_2\)O in FAPPI have been shifted vertically by 45 Å and 25 Å for better visualization.
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