Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2022

Supporting Information

Poly(benzyl ether)-type additive to engineer glassy polyimide membranes for enhanced gas separations

Jieun Park,[‡] Chang Oh Lee,[‡] Ji Woo Kim, Jin Hui Jo, Won Seok Chi,* and Hyungwoo Kim*

School of Polymer Science and Engineering, Chonnam National University, 77 Yongbongro, Buk-gu, Gwangju 61186, Korea

[‡]These authors contributed equally to this work

*Corresponding author e-mails: wschi@jnu.ac.kr (W.S.C.), kimhw@jnu.ac.kr (H.K.)

Contents

General Experimental	S1
Instrumentation	
Synthetic Procedures and Sample Preparation	
GPC Chromatogram	S6
¹ H NMR Spectrum	
Tensile Stress–Strain Curves	
FTIR Spectra	
Contact Angle Measurement	S9
SEM Images	
TGA and DSC Thermograms	S10
Gas Permeation Measurement	S11
Gas Permeation Properties	S13
Maxwell Model Prediction	S14
Gas Permeation Properties: Permeability and Selectivity	S14
Gas Permeation Properties: Diffusivity and Diffusivity-Selectivity	S15
Gas Permeation Properties: Solubility and Solubility-Selectivity	S15
Relevant Literature for Polymer Additives	S16
References	

General Experimental

All reactions were performed in flame-dried glassware under a positive pressure of nitrogen unless otherwise noted. Air-and moisture-sensitive liquids were transferred by syringe or stainless steel cannula. H₂, N₂, CH₄, and CO₂ gas cylinders in UHP grade (approximately 99.999%) were purchased from Daesung Synthetic Co., LTD. 6FDA-DAM:DABA (3:2) ($M_w = 210$ kDa, PDI = 2.50) was purchased from Akron Polymer Systems and used as received.

Instrumentation

Proton nuclear magnetic resonance (¹H NMR) spectra were recorded using MestReNova 400 MHz NMR spectrometers at 25 °C. Proton chemical shift are expressed in part per million (ppm, δ scale) and are referenced to tetramethylsilane ((CH₃)₄Si 0.00 ppm) or to residual protium in the solvent (CDCl₃, δ 7.26 ppm). Date are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances, br = broad peak), integration.

Molecular weights of polymers were analyzed by gel permeation chromatography (GPC) using an Shimadzu Prominence LC-20A instrument equipped with a differential refractive index detector (RID-20A) and an auto-sampler unit (SIL-20A). The column configuration consisted of a guard column (GVP-ODS, Shimadzu), a Phenogel linear column (pore size range 100–100000 Å; particle diameter, 5 μ m; size, 300 mm × 7.5 mm; Phenomenex) and a Phenogel column with a pore size of 100 Å (particle diameter, 5 μ m; size, 300 mm × 7.5 mm; Phenomenex). HPLC-grade THF was used as eluent with a flow rate of 1 mL min⁻¹ at 25 °C.

Uniaxial tensile tests were performed using a universal testing machine (UTM) (MCT-2150, A&D, Japan) with a 500-N load cell at 25 °C in air. Tensile samples for the mechanical testing were glued between two slide glass with a superglue for the measurement. Samples for the mechanical testing were prepared to have a size of (width \times length \times thickness) 5 mm \times 10 mm \times 0.05 mm for tensile testing. The samples were elongated at a rate of 10 mm min⁻¹ until broken. Then, stress-strain curves were recorded. Young's modulus was obtained from the initial slope of the stress-strain curve in the strain range of 0–10%.

Morphology was observed using a Carl Zeiss SUPRA 55VP scanning electron microscope (SEM) at an accelerating voltage of 2 kV. Before the measurement, the sample was dried in vacuum and coated with a thin platinum layer.

Density of films was determined at 25 °C using an electronic balance (Sartorius, Cubis® II Analytical) which was equipped with a density determination kit (Sartorius, YDK03).

Thermogravimetric analysis (TGA) was performed using TGAQ50 (TA Instruments) and samples were measured up to 800 °C at a heating rate of 10 °C min⁻¹ under an N_2 atmosphere.

Fourier-transform infrared spectroscopy (FTIR) were performed using an attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR, IFS66/S, Bruker, USA).

Water Contact angle measurements were conducted using a SurfaceTech GSA-X goniometer at 25 °C in air. The contact angle measurement was performed on a flat surface. The angles were measured immediately after dripping a water droplet on the surface of sample.

Differential scanning calorimetry (DSC) instrument (DSC823e, Mettler Toledo) was used to measure thermal properties. The samples were heated and cooled at a rate of 10 $^{\circ}$ C min⁻¹ under an N₂ atmosphere.

X-ray diffraction (XRD) analysis was performed using a PANalytical X'Pert PRO MPD with Cu K α radiation (λ , 1.5406 Å) to determine the crystallinity of materials. The d-spacing values (d) were estimated following the Bragg's law (i.e., $d = \lambda/2 \sin \theta$). All experiments were performed at room temperature.

S3

Synthetic Procedures and Sample Preparation

Synthesis of the linear poly(benzyl ether) (PBE) additive:



Scheme S1. Synthetic routes to the poly(benzyl ether) additive.

The monomer was synthesized from the previous methods as reported by Yeung, Kim, Mohapatra, and Phillips.^{S1} To a flame-dried, round-bottom flask was added monomer (300 mg, 1.02 mmol, 1.00 equiv), and dry DCM (1 mL). The reaction mixture was cooled to 0 °C. Then, phenol (0.09 mg, 0.001 mmol, 0.001 equiv) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.15 mg, 0.001 mmol, 0.001 equiv) were added in sequence. The reaction mixture was polymerized at 0 °C for 4 h. Then, *tert*-butyldimethylsilyl chloride (TBSCl) (153.59 mg, 1.02 mmol, 1.0 equiv) and imidazole (83.25 mg, 1.2 mmol, 1.2 equiv) were added to the reaction mixture for the end-capping reaction. After stirring at rt for 24 h, the resulting mixture was precipitated in MeOH three times and filtered. The desired polymer was obtained as a white powder (60.1 %).

Film formation:

The matrix polymer 6FDA-DAM:DABA(3:2) (150 mg) was dissolved in THF (5 mL), and specific amounts of poly(benzyl ether) additive (0–4.5 mg) were separately dissolved in THF (1 mL). Both solutions were mixed together and additionally stirred for 10 min to

give a uniform mixture of two polymers, and the target concentrations of poly(benzyl ether) were set to be 0, 0.5, 1, 2, and 3 wt% with respect to the matrix polymer. Each mixture solution was poured onto a glass petri dish and covered with aluminum foil with a few holes to achieve slow evaporation. After storing in an oven at 45 °C overnight, the resultant polymer films were naturally detached from the petri dish and further dried in a vacuum oven under dynamic vacuum at 50 °C overnight to completely remove the residual solvent. This fabrication method resulted in flexible, transparent membrane films with a thickness of approximately 40–60 μ m.

GPC Chromatogram



Acquired by Sample Name Sample ID Vuli# Injection Volume Data Filename Method Filename Batch Filename Report Filename Data Processed	: System Administrator : HJP 210928 : JE : 1 : 10 uL : GPC 20210315 200bar.lcm : 210928 Jcb : DEFAULT.lsr : 28/9/2021 7:38:39 PM
---	--



Figure S1. GPC chromatogram of the linear poly(benzyl ether) additive (35 kDa).

¹H NMR Spectrum



Figure S2. ¹H NMR spectrum of the poly(benzyl ether) additive.

Tensile Stress–Strain Curves



Figure S3. Representative tensile stress–strain curves obtained from the 6FDA-DAM:DABA films that contain different amounts of the poly(benzyl ether) additive (0 wt%, gray; 0.5 wt%, light pink; 1 wt%, orange; 2 wt%, violet; 3 wt%, black).

Matrix	Additive	Elastic modulus (GPa)	UTS ^a (MPa)	Elongation at break (%)	Ref.
	pristine	0.1	14.9	7.8	
	PBE (0.5 wt%)	0.2	24.7	23.3	
6FDA-DAM : DABA	PBE (1 wt%)	0.5	30.9	10.5	work
	PBE (2 wt%)	0.6	43.2	44.4	
	PBE (3 wt%)	0.8	44.4	34.6	
	pristine	2.9	102	40	
PBI ^b	SA-SNP ^c (15 wt%)	>0.004	143	16	S 3
	SA-SNP ^c (20 wt%)	>0.004	138	9	
	pristine	2.7	73.9	n/a	
6FDA-DAM : DABA / PBI	2-Methylimidazole (5 wt%)	3.1	86.6	n/a	S 4
21211,121	2-Methylimidazole (9 wt%)	3.5	115	n/a	
	pristine	0.5	16.9	4.6	
	ZIF-8 (13 wt%)	0.7	18.6	4.0	
PIM-6FDA-OH ^d	ZIF-8 (33 wt%)	1.0	23.5	2.6	S5
	ZIF-8 (41 wt%)	0.8	12.3	1.8	
	ZIF-8 (52 wt%)	0.6	8.6	1.5	
PP	pristine	0.5	26.1	1071	66
LDPE pristine		0.3	16.6	616	86

Table S1. Comparison of mechanical properties of 6FDA-containing polyimide membranes when reinforced with various additives. The data from PP and LDPE are shown for comparison.

^a Ultimate tensile strength
 ^b Polybenzimidazole
 ^c Sulfonated silica nanoparticles
 ^d Hydroxylated microporous polyimide

FTIR Spectra



Figure S4. FTIR spectra of the 6FDA-DAM:DABA films that contain different amounts of the poly(benzyl ether) additive (0 wt%, gray; 0.5 wt%, light pink; 1 wt%, orange; 2 wt%, violet; 3 wt%, black).

Contact Angle Measurement



Figure S5. Digital images of each water droplet on the surfaces of the 6FDA-DAM:DABA films that contain different amounts of the poly(benzyl ether) additive (a, 0 wt%; b, 0.5 wt%; c, 1 wt%; d, 2 wt%; e, 3 wt%). Average water contact angles are shown on top.

SEM Images



Figure S6. The obtained cross-sectional SEM images of (a) pristine 6FDA-DAM:DABA membrane and (b) that after incorporated with 1 wt% PBE.



Figure S7. The obtained SEM image from the 6FDA-DAM film when incorporated with 1 wt% poly(benzyl ether) additive measured at the magnification of 100000×.



TGA and DSC Thermograms

Figure S8. (a) TGA thermograms of PBE (sky blue), the matrix polyimide (gray), and the membrane with 1 wt% PBE (orange) as temperature increased at 10 °C min⁻¹. (b) DSC thermograms of the pristine membrane (black) and 1% PBE/6FDA-DAM:DABA (orange). The DSC thermograms were obtained during 1st cooling– 2^{nd} heating cycles with the rate of temperature change of 10 °C min⁻¹.

Gas Permeation Measurement

Estimation of fractional free volume:

Fractional free volume (FFV) of each reinforced membrane was estimated by a ratio of the free volume (V_f) to specific volume ($V = 1/\rho$) as follows:

$$FFV = V_f / V = (V - 1.3V_W) / V$$

where *V* and *V*_W indicate specific molar volume (cm³ mol⁻¹) and van der Waals volume (cm³ mol⁻¹) determined by the Bondi's group contribution method.^{S2}

Pure gas permeation measurement:

Pure gas permeation of H₂, N₂, CH₄, CO₂ was conducted using a custom-built, constantvolume, variable-pressure permeation system (Maxwell Robotics). The films were cut out to form a coupon with a specific active area. Of note, the thickness of the film was measure at least five times using a micrometer to calculate the average thickness of the film with small standard deviation. The film was attached to the impermeable brass disk (47 mm in outer diameter) with a hole located at the center using 5-minute epoxy glue. The active area of the film was enlarged by scanning the coupon image and measured by the Image J software. The coupon was loaded in a permeation cell and completely sealed. The permeation cell was located in the custom-built oven and temperature was kept at 35 °C using an air-heating circulator. The samples were under a dynamic vacuum condition at least 6 h to completely remove any residual molecules. The leak test was performed with all valve closed condition before running the permeation tests. The H₂, N₂, CH₄, and CO₂ gases were sequentially introduced by forming the pressure of 15 psi at upstream side, while the downstream pressure is under static vacuum. The gas permeation tests were performed when the permeation value was opened to allow the gas transport from upstream to downstream through the film.

Gas permeation parameter calculation:

The pure gas permeability was calculated using the following equation

$$P_{i} = \frac{Vl}{P_{2}ART} \left[\left(\frac{dP_{i}}{dt} \right)_{ss} - \left(\frac{dP_{i}}{dt} \right)_{leak} \right]$$

where P_i is the pure gas permeability, V is the downstream volume, l is the film thickness, P2 is the average downstream pressure, A is the film active area, R is the ideal gas constant, T is the temperature, $(dP_i/dt)_{ss}$ is the downstream gas pressure increasing rate in the steadsteady, $(dP_i/dt)_{leak}$ is the leak rate. As for the parameter unit, the pure gas permeability is in Barrer $(10^{-10} \text{ cm}^3(\text{STP}) \text{ cm} \text{ cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1})$, downstream volume is in cm³, film thickness is in cm, average downstream pressure is in cmHg, film active area is in cm², the temperature is in K, and the $(dP_i/dt)_{ss}$ and $(dP_i/dt)_{leak}$ are in cmHg/s. The ideal gas selectivity (α) was estimated as the ratio of two pure gas permeabilities (P_i/P_j) .

The permeability can be de-convoluted into two factor (effective diffusivity and effective solubility) based on the solution-diffusion model following the equation

$$\mathbf{P} = \overline{D} \cdot \overline{S}$$

where \overline{D} is the effective diffusivity and \overline{S} is the effective solubility. As for the parameter unit, the \overline{D} is in cm²/s and \overline{S} is in cm³(STP)/cm³ atm.

The diffusivity can be calculated based on the time-lag method as following equation

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

where *D* is the diffusivity, *l* is the film thickness, and θ is the time-lag. As for the parameter unit, the diffusivity is in cm²/s, the film thickness is in cm, and the time-lag is in sec. The solubility can be estimated using the calculated permeability and diffusivity based on the solution-diffusion model. Additionally, diffusivity-selectivity and solubility-selectivity were estimated as the ratio of two diffusivities(D_i/D_j) and solubilities(S_i/S_j), respectively.



Gas Permeation Properties

Figure S9. Pure gas permeation properties for pure 6FDA-DAM and 6FDA-DAM:DABA films and 1% PBE/6FDA-DAM and 1% PBE/6FDA-DAM:DABA films at 15 psi and 35 °C with Robeson upper bound limits.

Maxwell Model Prediction



Figure S10. Maxwell model prediction for (1) impermeable (blue line) and (2) completely permeable (green line) filler and experimental data (black dot) for (a) H_2 permeability and (b) CO_2 permeability as a function of PBE volume fraction. The red highlight indicates that the PBE additive incorporated membrane surpasses the theoretical permeability from the Maxwell model.

Gas Permeation Properties: Permeability and Selectivity

Table S2. H₂, CH₄, N₂, and CO₂ permeabilities and CO₂/CH₄, CO₂/N₂, H₂/CH₄, H₂/N₂ selectivities at 15 psi and 35 °C of pure 6FDA-DAM:DABA polymeric film and PBE/6FDA-DAM:DABA polymeric blending membranes with various PBE weight loadings (0.5, 1, 2, 3 wt%)

Sample	P(H ₂) (Barrer)	P(CH ₄) (Barrer)	P(N ₂) (Barrer)	P(CO ₂) (Barrer)	P(CO ₂) /P(CH ₄)	P(CO ₂) /P(N ₂)	P(H ₂) /P(CH ₄)	P(H ₂) /P(N ₂)
6FDA- DAM:DABA	136	3.89	5.13	130	33.4	25.3	35	26.5
0.5 % PBE/6FDA- DAM:DABA	153	4.25	5.7	146	34.5	25.7	36	26.8
1% PBE/6FDA- DAM:DABA	219	4.79	7.2	180	37.6	25	45.7	30.4
2% PBE/6FDA- DAM:DABA	169	3.77	5.42	139	36.8	25.6	44.8	31.2
3% PBE/6FDA- DAM:DABA	153	3.94	5.49	135	34.3	24.6	38.8	27.8

Gas Permeation Properties: Diffusivity and Diffusivity-Selectivity

Table S3. CH₄, N₂, and CO₂ diffusivities and CO₂/CH₄, CO₂/N₂, diffusivity-selectivities at 15 psi and 35 °C of pure 6FDA-DAM:DABA polymeric film and PBE/6FDA-DAM:DABA polymeric blending membranes with various PBE weight loadings (0.5, 1, 2, 3 wt%). Of note, the time-lag of H₂ gas is extremely short that can result a not reliable diffusivity. Thus, we excluded H₂ diffusivity related data in the table. Of note, the unit of diffusivity is 10^{-8} cm²/s.

Sample	D(CH ₄)	D (N ₂)	D(CO ₂)	D(CO ₂) /D(CH ₄)	D(CO ₂) /D(N ₂)
6FDA-DAM:DABA	0.104	0.499	0.501	4.817	1.004
0.5 % PBE/6FDA-DAM:DABA	0.122	0.604	0.702	5.754	1.162
1% PBE/6FDA-DAM:DABA	0.125	0.598	0.781	6.248	1.306
2% PBE/6FDA-DAM:DABA	0.0964	0.394	0.536	5.560	1.360
3% PBE/6FDA-DAM:DABA	0.0839	0.415	0.492	5.864	1.186

Gas Permeation Properties: Solubility and Solubility-Selectivity

Table S4. CH₄, N₂, and CO₂ solubilities and CO₂/CH₄, CO₂/N₂, solubility-selectivities at 15 psi and 35 °C of pure 6FDA-DAM:DABA polymeric film and PBE/6FDA-DAM:DABA polymeric blending membranes with various PBE weight loadings (0.5, 1, 2, 3 wt%). Of note, the time-lag of H₂ gas is extremely short that can result in a not reliable solubility. Thus, we excluded H₂ solubility related data in the table. Of note, the unit of solubility is cm³(STP)/cm³ atm.

Sample	S(CH ₄)	S (N ₂)	S(CO ₂)	S(CO ₂) /S(CH ₄)	$\frac{S(CO_2)}{/S(N_2)}$
6FDA-DAM:DABA	2.84	0.781	19.7	6.937	25.224
0.5 % PBE/6FDA-DAM:DABA	2.65	0.717	15.8	5.962	22.036
1% PBE/6FDA-DAM:DABA	2.9	0.915	17.5	6.034	19.126
2% PBE/6FDA-DAM:DABA	2.97	1.05	19.7	6.633	18.762
3% PBE/6FDA-DAM:DABA	3.57	1.01	20.8	5.826	2.594

Relevant Literature for Polymer Additives

Ref	Sample	P(CO ₂) (Barrer)	CO ₂ /CH ₄
	6FDA-DAM:DABA	130	33.4
	0.5% PBE/6FDA-DAM:DABA	146	34.5
This work	1% PBE/6FDA-DAM:DABA	180	37.6
2	2% PBE/6FDA-DAM:DABA	139	36.8
	3% PBE/6FDA-DAM:DABA	135	34.3
	Matrimid/PBI(75/25 wt.%)	4.19	32.23
S 7	Matrimid/PBI(50/50 wt.%)	2.16	48.00
	Matrimid/PBI(25/275 wt.%)	0.58	59.79
	PI-10PS	2.33	47.5
	PI-15PS	2.32	47.3
	PI-20PS	2.90	8.53
CO	PI-25PS	4.29	8.94
38	PI-10PSVP	3.58	35.8
	PI-15PSVP	3.71	36.4
	PI-20PSVP	5.65	41.2
	PI-25PSVP	6.55	3.00
	Matrimid – 1:0	5.39	35.93
50	Matrimid – 1:0.2	7.51	21.72
39	Matrimid – 1:0.5	59.16	17.63
	Matrimid – 1:1	115.18	16.94
	PI-g-CD 200	56	31
	PI-g-CD 300	159	23
610	PI-g-CD 350	357	20
510	PI-g-CD 400	921	16
	PI-g-CD 425	4016	16
	PI-g-CD 450	8000	17
	6FDA-DAM:DABA(3:2)	158.9	37.8
S11	27% glycidol-modified	149.1	38.3
	41% glycidol-modified	95.6	39.1

Table S5. Literature comparison for polymer additive incorporated polyimide membrane for CO2/CH4 gas separation.

References

- (S1) K. Yeung, H. Kim, H. Mohapatra, and S. T. Phillips, J. Am. Chem. Soc., 2015, 137, 5324–5327.
- (S2) A. X. Wu, S. Lin, K. M. Rodriguez, F. M. Benedetti, T. Joo, A. F.Grosz, K. R. Storme,
 N. Roy, D. Syar, Z. P. Smith, *J. Memb. Sci.*, 2021, 636, 119526.
- (S3) Suryani and Y.-L. Liu, J. Memb. Sci., 2009, 332, 121–128.
- (S4) N. P. Panapitiya, S. N. Wijenayake, D. D. Nguyen, Y. Huang, I. H. Musselman, K. J. Balkus, Jr. and J. P. Ferraris, ACS Appl. Mater. Interfaces, 2015, 7, 18618–18627.
- (S5) X. Ma, R. J. Swaidan, Y. Wang, C.-e. Hsiung, Y. Han and I. Pinnau, ACS Appl. Nano Mater., 2018, 1, 3541–3547.
- (S6) Y. Li and H. Shimizu, ACS Appl. Mater. Interfaces, 2009, 1, 1650–1655.
- (S7) S. S. Hosseini, M. M. Teoh and T. S. Chung, Polymer, 2008, 49, 1594–1603.
- (S8) Z.-K. Xu, L. Xiao, J.-L. Wang and J. Springer, J. Membr. Sci., 2002, 202, 27–34.
- (S9) H.-Y. Zhao, Y.-M. Cao, X.-L. Ding, M.-Q. Zhou, J.-H. Liu and Q. Yuan, J. Membr. Sci., 2008, 320, 179–184.
- (S10) Y. Xiao and T.-S. Chung, Energy Environ. Sci., 2011, 4, 201–208.
- (S11) H. Eguchi, D. J. Kim and W. J. Koros, *Polymer*, 2015, 58, 121–129.