A highly permeable polyimide with enhanced selectivity for membrane gas separations

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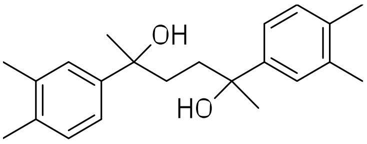
1. Experimental

1.1 Materials and methods. Acetic anhydride (Aldrich), acetone (Fisher), $AlCl_3$ (Alfa Aesar), benzene anhydrous (Aldrich), o-dichlorobenzene (*o*-DCB, Aldrich), DCM (Fisher), diethyl ether (Acros-Organics), 3,3'-dimethylnaphthidine (TCI), ethanol anhydrous (Alfa Aesar), hydrazine (Aldrich), $KMnO_4$ (Alfa Aesar), KNO_3 (Aldrich), Mg_2SO_4 (Fisher), mesytil oxide (Aldrich), N-methylpyrrolidon (NMP, Aldrich), Pd/C 10% (Aldrich), pyridine (Aldrich or Alfa Aesar), *o*-xylene anhydrous (Aldrich) were used as received.

^1H and ^{13}C NMR spectra were recorded with Bruker Advance DPX 400 Spectrometer (^1H: 400.13, ^{13}C: 100.61). All chemical shifts are reported as parts per million (δ, ppm). using tetramethylsilane (TMS) as internal standard. Infrared spectra were recorded in the range 4000-600 cm^{-1} using a Perkin-Elmer 1600 series FTIR instrument as a thin film deposited with $CHCl_3$ on polished NaCl plates. All absorptions are quoted in cm^{-1}. Mass spectra electron impact ionisation (EI) or were recorded on Fisons VG Platform II quadrupole instrument. GPC analyses were carried out on *Viscotek GPCmax* VE2001 with RI(VE3580) detector, using chloroform as eluent (columns: KF-805L SHODEX at ambient temperature and flow rate of 1 ml/min calibrated with a series of polystyrene standards with molecular mass up to 9.4 $x10^5$ g mol^{-1} with a narrow polydispersity.

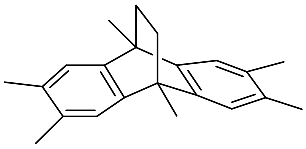
1.2. Synthesis

2,5-di(3,4-dimethylphenyl)hexane-2,5-diol



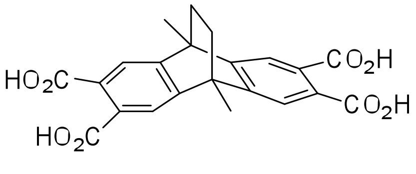
Following a literature procedure,[1] magnesium turnings (10.00 g, 411 mmol) and an iodine crystal (~5 mg) was suspended in dry tetrahydrofuran (200 ml) under a nitrogen atmosphere. With vigorous stirring, 4-bromo-1,2-dimethylbenzene (55.6 ml, 76.14 g, 411 mmol) was injected drop-wise and the mixture was refluxed until the magnesium was consumed. Under reflux, 2,5-hexanedione (24 ml, 23.48 g, 206 mmol) was injected drop-wise and the mixture was allowed to reflux for a further hour. The mixture was cooled to room temperature and then poured into crushed ice. The organic layer was extracted with diethyl ether and the solvent was removed under vacuum. The resulting yellow semi-solid was triturated in *n*-hexane and filtered to afford the desired product 2,5-di(3,4-dimethylphenyl)hexane-2,5-diol (64.1 g, 95%) as colourless crystals. Mp: 117 - 120 ºC; v_{max} (CH_2Cl_2/cm^{-1}): 3390 (br), 3018, 3018, 2971, 2921, 2864, 1506, 1451 ; ^1H NMR (500 MHz, $CDCl_3$): δ_H = 7.02 (s, 2H, Ar *H*), 6.94 (m, 4H, Ar *H*), 2.83 (s, br, 1H, O*H*), 2.72 (s, br, 1H, O*H*), 2.12 (m, 12H, 4 Ar CH_3), 1.73 (m, 2H, CH_2), 1.62, (m, 2H, CH_2), 1.37 (s, 3H, CH_3), 1.32 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C (ppm) =145.69, 145.44, 136.13, 134.54, 134.48, 129.46, 129.44, 126.27, 1216.23, 122.41, 122.35, 74.43, 74.31, 38.17, 37.94, 31.43, 30.45, 20.05, 20.03, 19.35, 19.32; TOF-HRMS (EI, *m/z*): calculated $C_{22}H_{30}O_2$ 326.255 found: 308.21 [M - H_2O^+].

2,3,6,7,9,10-hexamethyl-9,10-dihydro-9,10-ethanoanthracene



Following a literature procedure,[1] 2,5-di(3,4-dimethylphenyl)hexane-2,5-diol (41.00 g, 126 mmol) was suspended in anhydrous toluene (150 ml) and cooled in an ice bath, under a nitrogen atmosphere. Aluminium trichloride (16.75 g, 126 mmol) was added in portions slowly over 30 min and the mixture was stirred for 1 h and then at room temperature for 1 h. The mixture was then refluxed for 24 h, cooled and poured into crushed ice. The organic layer was extracted with chloroform and the solvent was removed under vacuum. The residue was subjected to column chromatography (*n*-hexane) and the resulting green oil was crystallised from *n*-hexane to afford the desired product 2,3,6,7,9,10-hexamethyl-9,10-dihydro-9,10-ethanoanthracene (6.54 g, 18%) as colourless crystals: Mp: 226 - 227 ºC; ν_{max} (cm^{-1}): 2959, 2938, 2856, 1456; ^{1}H NMR (500 MHz, CDCl$_3$): δ_H = 7.40 (s, 4H, Ar *H*), 2.58 (s, 12H, 4 Ar CH_3), 2.28 (s, 6H, 2 CH_3), 1.97 (s, 4H, 2 CH_2); ^{13}C NMR (125 MHz, CDCl$_3$): δ_C = 144.58, 132.99, 122.11, 41.26, 36.57, 19.94, 18.75; TOF-HRMS (EI, *m/z*): calculated $C_{22}H_{26}$ 290.20 found: 290.20 [M$^+$].

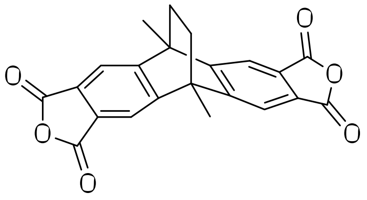
9,10-dimethyl-9,10-dihydro-2,3,6,7-tetracarboxyl-9,10-ethanoanthracene



Into a mixture of pyridine (100 ml) and deionised water (100 ml), 2,3,6,7,9,10-hexamethyl-9,10-dihydro-9,10-ethanoanthracene (4.17 g, 14 mmol) was added and the mixture was heated to reflux. Potassium permanganate (22.69 g, 144 mmol) was added in small portions, allowing for foaming between additions and the mixture was refluxed for 24 h. The black mixture was filtered hot and the manganese dioxide was washed with hot deionised water. The filtrate was cooled to room temperature and the solvent was removed under vacuum. The solid obtained was dissolved in deionised water and neutralized with concentrated hydrochloric acid to give a yellow precipitate. The solid was filtered, dried and recrystallized from tetrahydrofuran to afford the desired product 9,10-dimethyl-9,10-dihydro-2,3,6,7-

tetracarboxyl-9,10-ethanoanthracene (4.88 g, 83%) as an off white powder. Mp: 287 - 288 ºC; ν_{max} (CH_2Cl_2/cm^{-1}): 3100 (br), 2965, 1698, 1249; ^1H NMR (500 MHz, $(CD_3)_2SO$)): δ_H = 13.08 (s, br, 4H, 4 CO_2H), 7.56 (s, 4H, Ar *H*), 1.99 (s, 6H, 2 CH_3), 1.63 (s, 4H, 2 CH_2); ^{13}C NMR (125 MHz, $(CD_3)_2SO$)): δ_C = 169.18, 148.24, 131.01, 121.14, 42.49, 35.00, 17.92;

9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene-2,3,6,7-dianhydride



Under a nitrogen atmosphere, 9,10-dimethyl-9,10-dihydro-2,3,6,7-tetracarboxyl-9,10-ethanoanthracene (4.88 g, 12 mmol) was dissolved in acetic anhydride (200 ml). The mixture was refluxed for 12 h, cooled to room temperature and the acetic anhydride/acetic acid was removed under vacuum to give a black solid. The solid was recrystallized from tetrahydrofuran until pure to afford the desired product 9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene-2,3,6,7-dianhydride (2.03 g, 46%) as off white crystals. Mp: 340-355 ºC (dec); ν_{max} (CH_2Cl_2/cm^{-1}): 2959, 2863, 1838, 1778, 1286, 1236; ^1H NMR (500 MHz, $CDCl_3$): δ_H = 7.98 (s, 4H, Ar *H*), 2.21 (s, 6H, 2 CH_3), 1.83 (s, 4H, 2 CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 162.73, 153.71, 129.96, 118.26, 118.26, 44.34, 34.39, 18.46; TOF-HRMS (EI, *m/z*): calculated $C_{22}H_{14}O_6$ 374.08 found: 374.08 [M^+].

PIM-PI-EA

Ethanol (10 mL) and triethylamine (1 mL) was added to the bisanhydride of 2,3,6,7-tetracarboxy-9,10-dimethylethanoanthracene (0.7364 g, 0.00197 mole) in a two-necked, round-bottom flask equipped with magnetic stirrer and a reverse Dean-Stark trap with condenser. The reaction mixture was heated gradually to 110 °C to give a highly viscous solution which was cooled to 60 °C. The Dean-Stark trap was drained and filled with the NMP/*o*-DCB (4:1 mixture). An equimolar amount of 3,3'-dimethylnaphthidine (0.6154 g, 0.00197 mole) and NMP/*o*-DCB (3 ml; 4:1 mixture) were added to the reaction mixture and the temperature was gradually raised up to 195 °C and kept at this value for approximately 20 h. Sufficient NMP/*o*-DCB (4-6 ml) was added whenever the reaction mixture became too viscous to stir during the next 120 h. The reaction mixture was cooled, diluted with $CHCl_3$ and the polymer precipitated into stirred methanol. The crude polymer was washed with methanol, collected by filtration and dried under reduced pressure at 120 °C. Purification was achieved by reprecipitation from $CHCl_3$ solution into methanol to provide a white solid product (1.18 g, 88% yield after second precipitation); ^1H NMR (250 MHz, $CDCl_3$) δ 7.99 (b s, 3H-Ar), 7.79-7.29 (m, 4H-Ar), 3.05-1.36 (m, 8H-CH_3, CH_2); IR (thin film/cm^{-1}): 1775; 1716 (imide); apparent BET surface area = 616 $m^2\ g^{-1}$; total pore volume = 0.46 $cm^3\ g^{-1}$ (p/p^o = 0.98 adsorption); micropore volume = 0.35 $cm^3\ g^{-1}$ (p/p^o = 0.1 adsorption) GPC: M_w = 343,000, M_n = 112,000; PDI = 3.0.

2. Procedures.

2.1 Gas permeability measurements. Film formation was achieved by preparing a solution of PIM-Trip-TB (0.35 g) in chloroform (20 mL) which was poured into a 9 cm circular Teflon mould. The film was allowed to form by slow solvent evaporation for 96 h. Prior to permeability measurements the films were soaked in methanol for 8 h to remove residual casting solvent and then dried in air. The density of the 72 mm film, measured by simple geometric means, was found to be 1.17 ± 0.04 g cm^{-3} after MeOH soaking. Gas permeation tests of single gases were carried out at 25 °C and at a feed pressure of 1 bar, using a fixed-volume pressure increase instrument, described elsewhere.[2] Before analysis the membrane samples were carefully evacuated to adsorbed species using a vacuum pump fitted with a trap to remove oil. The gases were tested in the following order: He, H_2, N_2, O_2, CH_4, CO_2. An effective membrane area of 2.14 cm^2 was used.

ESI Table 1. The gas permeabilities P_x, diffusivity D_x, solubility coefficient S_x and ideal selectivities α (P_x/P_{N_2}) for a methanol treated film of PIM-PI-EA of thickness = 72 μm with comparable data for a the same film obtained after 273 days given in parentheses. To allow a direct comparison, data from a methanol treated film of PIM-PI-SBI (180 μm), PIM-EA-TB (181 μm) and PIM-1 (128 μm), measured using the same equipment, are provided.

		N_2	O_2	CO_2	CH_4	H_2	He
PIM-EA-PI	P_x [Barrer]	369	1380	7340	457	4230	1580
		(131)	(659)	(3230)	(156)	(2860)	(1130)
	α (P_x/PN_2)	-	3.7	19.9	1.2	11.5	4.3
		(-)	(5.0)	(24.6)	(1.2)	(21.8)	(8.6)
	D_x ([10^{-12} m^2/s]	84	270	95	24	≥3360	≥5070
		(32)	(144)	(48)	(8.4)	(3581)	(5740)
	D_x/DN_2	-	3.2	1.1	0.29	40	60
			(4.8)	(1.6)	(0.28)	(120)	(191)
	S_x [cm^3 cm^{-3} bar^{-1}]	3.29	3.83	57.8	14.2	≤0.94	≤0.23
		(3.29)	(3.42)	(50.1)	(13.5)	(0.60)	(0.15)
	S_x/SN_2	-	1.2	17.6	4.3	0.29	0.07
			(1.1)	(15.2)	(4.1)	(0.18)	(0.04)
PIM-SBI-PI	P_x [Barrer]	340	1010	5910	550	2560	950
	α (P_x/PN_2)	-	3.0	17.6	1.6	7.6	2.8
	D_x [10^{-12} m^2/s]	78	224	97	29	≥3100	≥4600
	D_x/DN_2	-	2.9	1.2	0.37	39.7	59.0
	S_x [cm^3 cm^{-3} bar^{-1}]	3.3	3.4	45.6	14.05	≤0.6	≤0.16
	S_x/SN_2	-	1.03	13.8	4.3	0.18	0.05
PIM-1	P_x [Barrer]	823	2270	13600	1360	5010	1950
	α (P_x/PN_2)	-	2.8	16.6	1.7	6.1	2.4
	D_x [10^{-12} m^2/s]	186	512	226	79	≥4200	≥5500
	D_x/DN_2	-	2.8	1.2	0.42	23	30
	S_x [cm^3 cm^{-3} bar^{-1}]	3.3	3.3	45.2	12.9	≤0.9	≤0.25
	S_x/SN_2	-	1.0	14	3.9	≤0.27	≤0.08
PIM-EA-TB	P_x [Barrer]	525	2150	7140	699	7760	2570
	α (P_x/PN_2)	-	4.1	13.6	1.3	14.8	4.9
	D_x [10^{-12} m^2/s]	89.5	318	87	36	≥7000	≥10000
	D_x/DN_2	-	3.7	1.0	0.32	90	1
	S_x [cm^3 cm^{-3} bar^{-1}]	4.7	6.0	57.0	14.8	≤0.8	≤0.2
	S_x/SN_2	-	1.1	12.0	4.3	≤0.06	≤0.02

2.2. Sorption analysis

Nitrogen adsorption/desorption measurements at 77K were carried out using a Beckman Coulter SA3100 instrument with foreline filter and vacuum pump (10^{-3} mm Hg). Apparent surface areas were calculated by the multipoint Brunauer-Emmett-Teller (BET) method, sorption measurements were carried out under liquid nitrogen temperature and pure N_2 (99.999 %) was used as adsorbate.

Gas sorption experiments at 25 °C were performed gravimetrically using a self-developed sorption apparatus equipped with a calibrated McBain quartz spiral balance and with an automatic charge-coupled device (CCD, Sony) camera system detection of sample-target-point position. The detailed experimental procedure and a buoyancy testing were described previously.[3,4] The sample (flat membrane or powder in aluminium basket) was appended on the quartz spring by a tiny kanthal wire holder. The glass measuring chamber was evacuated before each measurement to a pressure lower than 10^{-3} mbar by a rotary oil pump (Trivac D4B, Oerlikon Leybold). A Leybold oil-mist filter eliminated (with 99.99% efficiency) contamination of the measuring chamber with oil vapours from the pump. The sorption experiments were performed at 25 ± 0.1°C and at the absolute pressure ranging from 0 to 8 bar. After the exposure of the sample to a particular gas at a known pressure, the elongation of the quartz spiral was monitored by an automatic optical system until the equilibrium state was reached. The average error of the mass determination reached approximately 30 micrograms.

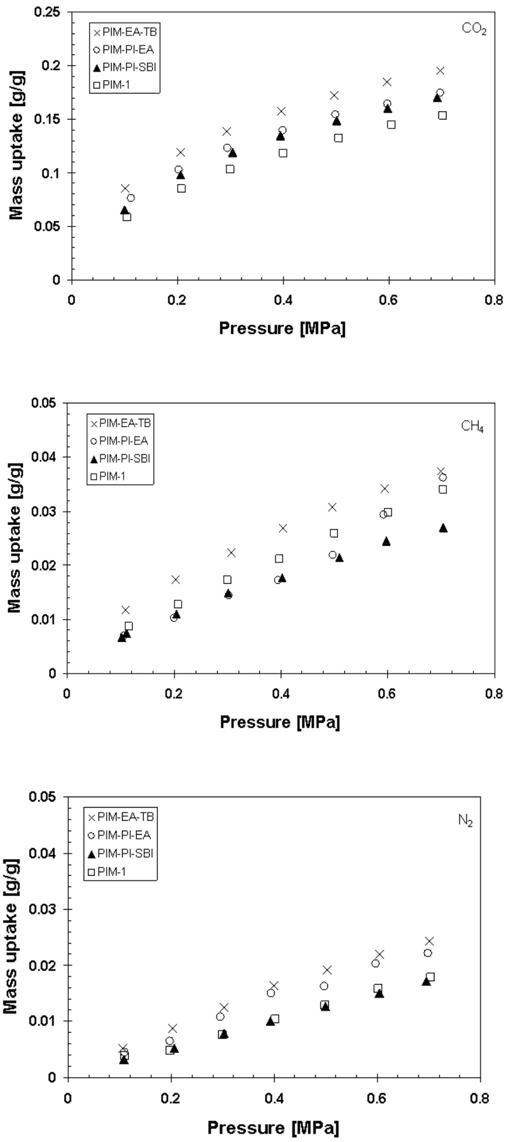
The experimental data were fitted by the dual mode sorption model which describes sorption of gaseous penetrants in glassy polymers:[5]

$$c = k_D p + \frac{C_H bp}{1 + bp} \tag{1}$$

where c is the sorbate concentration, p the sorbate pressure, k_D is the Henry's law constant, C_H is the Langmuir (monolayer) sorption capacity constant and b is the Langmuir affinity constant.

The slope of the isotherms at low pressure defines the infinite dilution solubility, wich can be calculted from the dual mode parameters:

$$S_0 = \lim_{p \to 0} \frac{dc}{dp} = k_D + C_H\, b \tag{2}$$



ESI Figure 1. Sorption isotherms for CO_2 (top), CH_4 (middle) and N_2 (bottom) in the four methanol treated polymers PIM-1, PIM-PI-SBI, PIM-EA-TB and PIM-PI-EA.

3. Molecular Dynamics Simulation

The Materials Studio (5.0) software package (Accelrys Software Inc., CA, USA)[6] was used for this simulation. Amorphous polymer packings were constructed using the Theodorou/Suter method[7,8] as implemented in the Amorphous-Cell module. The molecular dynamics (MD) simulations were performed with the PCFF force field.[9,10]

3.1. Preparation of polymer models. A single repeat unit with assigned charge groups and subsequent energy minimization of PIM-PI-12 was prepared. For the minimization, a standard algorithm was employed, starting with a steepest descent stage, switching to conjugate gradient when the energy derivative reaches 1000 kcal mol−1 $Å^{-1}$ followed by a Newton–Raphson optimisation algorithm. For the final convergence a derivative of less than 0.001 kcal mol−1 Å−1 was accepted.

A single atactic homopolymer with 15 repeat units (1202 atoms) was constructed using random torsional angles and rapidly optimised (500 steps).

For the packing procedure, a general methodology for generating realistic models of membranes was used:[11]

1. Bulk amorphous polymer structures under periodic boundary conditions were prepared, where five polymer chains (total 6010 atoms) and spacer molecules were packed in an amorphous cell at a lower density (~30% of the final density), using the Theodorou/Suter chain-generation approach reproducing the natural distribution of conformation angles.[7,8] Several spacer molecules were introduced to avoid the artifacts of catenated rings spearings. This allows for a much more homogeneously packed chain configuration as well as for a more uniform free volume distribution within the matrix. The spacers, 100 methan and 500 argon molecules, were added randomly to the simulation box and were later removed in four steps. Each removal procedure was followed by energy minimization and NVT-MD (constant number of particles, volume and temperature) runs at 303 K combined with “scaling” of conformation energy terms and non-bonded interaction energy terms in the force field.
2. Simulated annealing NVT-MD runs at high temperatures followed by NVT dynamics at 303 K were used to further relax the polymer structure. The experimental density was reached by increasing the pressure using a set of NPT MD runs (constant number of particles, pressure and temperature).
3. Longer MD runs were performed for the final equilibration. We built a total three 3D models. The chosen boxes were checked by their densities deviation to the experimental densities and their stable total energy during the long MD runs. The general simulation conditions used were: a minimum image boundary condition to make the system numerically tractable and to avoid symmetry effects and a cut-off distance of 20 Å with a switching function in the interval 18.5–20 Å. Through the dynamics, the Andersen pressure control[12] and the Berendsen temperature control method[13] were used. The side length of the bulk models was about 4.2 nm. It is worth stating that small deviations in obtaining the

experimental density can occur for glassy stiff-chain polymer materials,[14] particularly if the models are rather large.

3.2. Free volume analysis. A free volume analysis, considering the size effect of gas molecules, was performed using the Visualizer module of the MS software package.[6] The van der Waals surface, defined as the surface that intersects with the vdW radii of the atoms in the given structure, was defined. Here the volume on the atom side of the surface (occupied volume) is used as the van der Waals volume. Then the accessible solvent surface is defined: the surface that is the locus of the probe center as the probe rolls over the scaled vdW surface. This surface describes a space that could, in principle, be occupied by a probe of the given radius and is only defined over externally accessible regions, where the volume on the side of the surface without atoms (the free volume) is used as the accessible free volume.

4. ESI References

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