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Supporting Information

A highly rigid and gas selective methanopentacene-based polymer of intrinsic microporosity derived from Tröger's base polymerization

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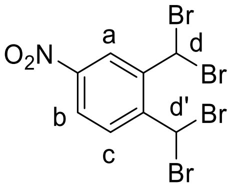
1. General methods and equipment.

Commercially available reagents were used without further purification. Anhydrous dichloromethane was obtained by distillation over calcium hydride under nitrogen atmosphere. Anhydrous *N*,*N*-dimethylformamide was bought from Aldrich. All reactions using air/moisture sensitive reagents were performed in oven-dried or flame-dried apparatus, under a nitrogen atmosphere. TLC analysis refers to analytical thin layer chromatography, using aluminium-backed plates coated with Merck Kieselgel 60 GF_{254}. Product spots were viewed either by the quenching of UV fluorescence, or by staining with a solution of Cerium Sulfate in aqueous H_2SO_4. Flash chromatography was performed on silica gel 60Å (35-70 micron) chromatography grade (Fisher Scientific). Melting points were recorded using a Gallenkamp Melting Point Apparatus and are uncorrected. ^{1}H NMR spectra were recorded in the solvent stated using an Avance Bruker DPX 400 (400 MHz) or DPX 500 (500 MHz) instruments, with ^{13}C NMR spectra recorded at 100 MHz or 125 MHz respectively. Low-resolution mass spectrometric data were determined using a Fisons VG Platform II quadrupole instrument using electron impact ionization (EI) unless otherwise stated. High-resolution mass spectrometric data were obtained in electron impact ionization (EI) mode unless otherwise reported, on a Waters Q-TOF micromass spectrometer. Low-temperature (77 K) N_2 adsorption/desorption measurements and CO_2 uptake and pore size distribution (273 K) of PIM powders, were made using a Quantachrome Instruments Quadrasorb Evo. Samples were degassed for 800 min at 120 °C under high vacuum prior to analysis. The TGA was performed using the device Thermal Analysis SDT Q600 at a heating rate of 10 °C/min from room temperature to 1000 °C.

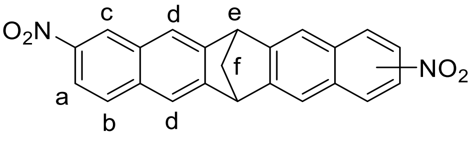
2. Monomer, intermediate and polymer synthesis

1,2-bis(dibromomethyl)-4-nitrobenzene[1] (2)



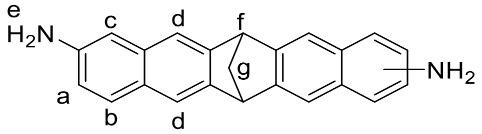
Under positive nitrogen flow, fitted with a gas trap to absorb evolved hydrogen bromide gas, 4-nitro-o-xylene **1** (15.1 g, 100 mmol) was dissolved in chlorobenzene (100 mL). The mixture was heated to reflux and irradiated with a halogen lamp, during which time bromine (67.20 g, 420 mmol) in a further 50 mL of chlorobenzene was added dropwise using a syringe pump over 4 hrs. Once cooled, saturated sodium hydrogen sulphate solution was added dropwise to the reaction mixture until effervescence ceased. The mixture was then washed twice with water, and the organic layer dried. Chlorobenzene was removed on the rotary evaporator to yield an oily yellow solid, which was recrystallised from hexane to give 1,2-bis(dibromomethyl)-4-nitrobenzene (**5**) as an off-yellow, powdery solid (34.50 g, 74%). Mp: 125-127 ºC (lit[1] 123-125 ºC); ν_{max} (cm^{-1}): 2929, 2359, 2320, 1450, 1339, 1136; ^{1}H NMR (601 MHz, DMSO-*d*$_6$) δ 8.55 (br s, 1H, H$_a$), 8.21 (dd, *J* = 8.7, 2.3 Hz, 1H, H$_b$), 7.94 (br s, 1H, H$_c$), 7.11 (br d, *J* = 30.3 Hz, 2H, H$_{d/d'}$); ^{13}C NMR (126 MHz, DMSO) δ 148.4, 143.4, 138.2, 132.7, 126.0, 124.4, 36.3, 36.1; LRMS (EI, m\z): calculated $C_8H_5Br_3NO_2^{\bullet}$ 383.79 found : 385.69 [M$^+$ - Br].

2, 9(10)-dinitro-6,13-dihydro-6,13-Methanopentacene (4)



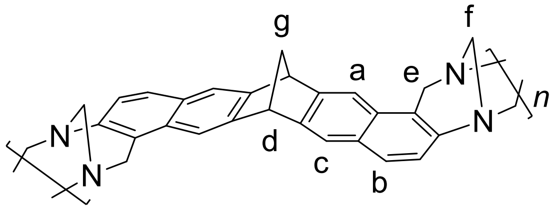
In flame dried apparatus fitted with a gas trap to absorb evolved hydrogen bromide gas, under nitrogen atmosphere 1,2-bis(dibromomethyl)-4-nitrobenzene (**2**) (44.00 g, 94.3 mmol) compound and norbornadiene (**2a**) (1.45 g, 15.7 mmol) were dissolved in dry DMF (400 mL). In a single portion, sodium iodide (94.00 g, 630 mmol) was added and stirred at 65 °C. As the reaction progressed a dark orange colour appeared. After approximately 16 hours the reaction mixture was poured into water. Powdered sodium hydrogen sulphate was added until the solution became light in colour. The solution was stirred until a light-yellow precipitate formed, which was collected by filtration and washed with water. The product was then dried thoroughly and purified by column chromatography on silica using DCM/Hexane 1:1 as eluent to give a yellow solid 2,9(10)-dinitro-6,13-dihydro-6,13-methanopentacene (**4**) as a light yellow solid (3.10 g; 50%). Mp: 166-168 ºC; ν_{max} (cm^{-1}): 3098, 2988, 2926, 2361, 1526, 1339; ^1H NMR (500 MHz, $CDCl_3$) δ 8.65 (m, 2H, H_a), 8.15 (m, 2H, H_b), 7.89 (m, 2H, H_c), 7.85 – 7.78 (m, 2H, H_d), 4.69 (m, 2H, H_e), 2.72 (m, *J* = 1.5 Hz, 2H, H_f); ^{13}C NMR (126 MHz, DMSO) δ 150.5, 148.2, 144.8, 134.9, 130.7, 129.2, 124.0, 121.7, 120.1, 118.7, 79.1, 78.9, 78.6, 49.9, 49.6, 49.3; HRMS (EI, m\z): calculated $C_{23}H_{14}N_2O_4$ 382.0948 found : 382.0959 [M +].

2, 9(10)-diamino-6,13-dihydro-6,13-Methanopentacene (5)



Under nitrogen atmosphere, 2, 9(10)-dinitro-6,13-dihydro-6,13-methanopentacene **4** (4.00 g, 10.5 mmol) was dissolved in degassed THF, to which was added a spatula of Raney nickel (approximately 50 mg) in water slurry. Dropwise, hydrazine monohydrate (10.0 mL, 200 mmol) was added to the refluxing mixture, which was then left overnight. The hot reaction mixture was filtered to remove Raney nickel, washed with 0.1 M sodium hydroxide solution and brine and dried over magnesium sulphate. Solvent was removed to afford the diamine, which was purified by column chromatography on silica using DCM \ ethyl acetate 70:30 as eluent, to give 2, 9(10)-diamino-6,13-dihydro-6,13-methanopentacene (**5**) as a pale orange solid (3.1g, 92%). Mp: 263-265 ºC; ν_{max} (cm^{-1}): 3327, 2990, 2359, 1622, 1510, 1371, 1339, 1269; ^1H NMR (400 MHz, DMSO-d_6) δ 7.40 (m, $4H_{b/d}$), 6.83 – 6.74 (m, $2H_a$), 6.71 (s, $4H_c$), 5.13 (s, $4H_e$), 4.44 – 4.34 (m, $2H_f$), 2.39 (s, $2H_g$); ^{13}C NMR (126 MHz, DMSO) δ 147.1, 146.8, 146.2, 146.2, 142.1, 141.8, 133.6, 133.5, 128.1, 124.5, 124.4, 119.1, 118.8, 117.1, 117.0, 116.9, 116.8, 107.1, 61.2, 49.7, 49.3, 48.9; HRMS (EI, m\z): calculated $C_{23}H_{18}N_2$ 322.1470 found : 322.1469 [M^+].

Synthesis of the PIM-MP-TB



Under nitrogen atmosphere dimethoxymethane (1.0 mL, 11.0 mmol) was added to 2,9(10)-diamino-6,13-dihydro-6,13-methanopentacene (**5**, 0.700 g, 2.2mmol). The mixture was cooled to 0˚C in an iced water bath. Dropwise, trifluoroacetic acid (5.0 mL) was added (approximately 30% of the total volume) until a thick slurry was obtained. This was allowed to stir for around 30 minutes until most of the solid had dissolved. The remaining TFA was then added and the mixture was allowed to stir until the orange mixture became viscous (5 –6 hrs). The mixture was then poured slowly into iced ammonia solution, to precipitate fine strands of polymer. The aqueous mixture was stirred for several hours until the dark orange colour had dissipated throughout the polymer. Polymer was then filtered, washed with acetone and refluxed in methanol to remove water. Methanol was removed under suction and the polymer dried for several hours. The polymer was then dissolved in the minimum amount of chloroform by sonication. Polymer was reprecipitated by passing through cotton wool into methanol dropwise. Reprecipitation was repeated twice to obtain MP-TB as an orange solid (415 mg, 50%). ν_{max} (cm^{-1}): 2957, 2359, 2002 (br), 1603, 1497, 1202, 932; ^{1}H NMR (601 MHz, $CDCl_3$) δ 8.24 – 6.95 (m, 8H, Ha/b/c), 4.94 (s, 2H, Hd), 4.76 – 4.11 (m, 6H, He/f), 2.50 (s, 2H, Hg); ^{13}C SSNMR (101 MHz) δ 145. 9, 130.3, 127.0, 121.3, 112.8, 66.9, 56.3, 51.5; BET surface area = 743 m^2 g^{-1}; total pore volume = 0.5502 cm^{-3} g^{-1} for pores smaller than 466.5 Å (Radius) at (P/P_0) = 0.97890; TGA analysis: initial weight loss due to thermal degradation commences at ~ 430 °C with a 20 % loss of mass below 1000 °C.

3. Membrane preparation

Films were prepared by dissolving PIM-MP-TB (0.350 g) in chloroform (20 mL) and allowing solvent to evaporate slowly over 96 h in a Teflon dish. Methanol treatment was carried out prior to permeability measurements by soaking for 24 hours to remove residual solvent followed by drying for 24h in air.

4. Pure gas permeation

Pure gas permeation experiments were performed on a fixed volume/pressure increase instrument constructed by Elektro & Elektronik Service Reuter (Geesthacht, Germany). Permeation tests were carried out both on the as prepared MMMs and after methanol treatment. The feed gas pressure was set at 1 bar (the actual value was read with a resolution of 0.1 mbar); the permeate pressure was measured in the range from 0 to maximum, 13.3 mbar, with a resolution of 0.001 mbar. The gases were always tested in the same order (He, H_2, N_2, O_2, CH_4, and CO_2) and after each cycle, the N_2 and O_2 were repeated in order to evaluate eventually aging during the measurement. Feed pressure, permeate pressure, and temperature are continuously recorded during each measurement run. The temperature was controlled at a constant temperature of 35 ± 1 °C. Before the first measurement, the membrane was evacuated inside the cell with a turbomolecular pump for sufficient time (at least 1 h) in order to desorb all previously absorbed species. Between two subsequent measurements, the system was evacuated for a period of at least ten times the time lag of the previous species in order to guarantee the complete removal of the previous gas. Circular membranes, with an effective exposed surface area of 2.14 cm^2 were used. The pressure increase on the permeate side was recorded as a function of time from the moment that the membrane was exposed to the feed gas. The whole permeation curve takes the following form:

$$p_t = p_0 + (\mathrm{d}p/\mathrm{d}t)_0 \cdot t + \frac{RT \cdot A \cdot}{V_P \cdot V_m} \cdot p_f \cdot S\left(\frac{D \cdot t}{{}^{2}} - \frac{1}{6} - \frac{2}{\pi^2}\sum_{1}^{\infty}\frac{(-1)^n}{n^2}\exp\left(-\frac{D \cdot n^2 \cdot \pi^2 \cdot t}{{}^{2}}\right)\right) \qquad (1)$$

in which p_t is the permeate pressure at time t and p_0 is the starting pressure, typically less than 0.05 mbar. The baseline slope $(\mathrm{d}p/\mathrm{d}t)_0$ is usually negligible for a defect-free membrane. R is the universal gas constant, T is the absolute temperature, A is the exposed membrane area, V_P is the permeate volume, V_m is the molar volume of a gas in standard conditions (0 °C and 1 atm), p_f is the feed pressure, S is the gas solubility, D the gas diffusion coefficient, and ℓ the membrane thickness. The time lag method was applied to the recorded data to determine the gas diffusion coefficient.[1]

The permeability coefficient, P, is calculated from the following equation, describing the steady state permeation:

$$P_t = P_0 + (dp/dt)_0 \cdot t + \frac{RT \cdot A}{V_p \cdot V_m} \cdot \frac{p_f \cdot p}{\ell}\left(t - \frac{\ell^2}{6D}\right) \qquad (2)$$

the last term corrects for the so-called permeation time lag, *Θ*, which is inversely proportional to the diffusion coefficient of the gas:

$$\Theta = \frac{{}^{2}}{6D} \qquad (3)$$

the approximate gas solubility coefficient, *S*, was obtained indirectly as the ratio of the permeability to the diffusion coefficient by assuming the solution-diffusion transport mechanism:

$$S = P / D \qquad (4)$$

Permeabilities are reported in Barrer [1 Barrer=10^{-10} cm^3_{STP} cm cm^{-2} s^{-1} cm Hg^{-1}].

5. Mixed gas permeation

Mixed gas permeation experiments were carried out on a custom made constant pressure / variable volume instrument, equipped with a modified Millipore permeation cell (diameter 47 mm). The experiments were carried out at a feed flow rate of 100-200 cm^3 min^{-1} and a feed pressure of 0-5 bar (g), using EL-FLOW electronic Mass Flow Controllers (Bronkhorst) in the feed line and an EL-PRESS electronic back pressure controller in the retentate line. Argon (30 cm^3 min^{-1}) was used as the sweeping gas at ambient pressure. The actual temperature and pressure were recorded to convert the measured flow rates to standard temperature and pressure conditions (STP, 1 atm at 0°C). Highly permeable samples were masked with an adhesive aluminium tape with a smaller aperture to limit the total permeate flow rate and to keep the stage cut close to or below 1%.

The permeate composition was determined with a Mass Spectrometric device equipped with a quadrupole mass filter (Hiden Analytical, HPR-20 QIC Benchtop residual gas analysis system, max. 200 AMU) and a sampling capillary with a typical flow rate of ca. 10-20 cm^3 min^{-1} at ambient pressure, depending on the gas sampled. The electron ionization energy was 70 eV and the gases were detected with the SEM ion detector. Nitrogen was detected at 14 AMU to avoid overlap of N_2 with the CO fragments from CO_2 at 28 AMU in CO_2/N_2 mixtures; methane was detected at 15 AMU (as CH_3) to avoid overlap of the molecular CH_4 peak with the O fragment from CO_2 at 16 AMU in the case of CO_2/CH_4 mixtures. All sensitivity ratios were previously calibrated against the weaker ^{36}Ar isotope at 36 AMU (ca. 0.3% abundancy). During the permeation experiments, this signal was used as the internal standard for calculation of the gas concentrations in the sweep/permeate, and then the permeate flow rate.

Before each analysis, the membrane was flushed for at least 1 hour at both sides with two independent argon streams until the MS signal was sufficiently stable. Subsequently, two experiments were carried out. In the first experiment, the argon flux at the feed side was replaced by the pure gas or gas mixture at atmospheric pressure (absolute pressure 1 bar (a)) to determine the time needed to reach steady state permeation. In the second experiment, the feed pressure was stepwise changed from 1-6 bar (a) and back, with sufficiently long time intervals to reach steady state permeation in each step. The background signals were determined just before switching from argon to the gas or gas mixture at the feed side, and were subtracted from the measured signal during data processing.

All measured data were recorded with the MASsoft software package supplied with the mass spectrometer and with the FlowPlot software supplied with the pressure and mass flow controllers. The measured data were processed by a self-written elaboration program.

The mixed gas selectivity, $\alpha_{i/j}$ was calculated as the ratio of the individually calculated gas permeances (Π□) in the mixture:

$$\alpha_{\mathrm{CO_2/N_2}} = \frac{\Pi_{\mathrm{CO_2}}}{\Pi_{\mathrm{N_2}}} \qquad (5)$$

$$\alpha_{\mathrm{CO_2/CH_4}} = \frac{\Pi_{\mathrm{CO_2}}}{\Pi_{\mathrm{CH_4}}}$$

(6)

where the individual gas permeance, Π_i, of the ith species in the mixture is obtained as the ratio of its volumetric permeate flux, $J^{Permeate}$, to the partial pressure difference between the feed and permeate sides, Δp_i:

$$\Pi_i = \frac{x_i^{Permeate} J^{Permeate}}{x_i^{Feed} p^{feed} - x_i^{Permeate} p^{Permeate}} \qquad (7)$$

in which x_i is the mole fraction of the ith species, p^{Feed} and $p^{Permeate}$ are the total feed and permeate pressures, respectively. The permeate flux is the flow rate per unit area, defined as:

$$J_i^{Permeate} = \frac{Q_i^{Permeate}}{A} \tag{8}$$

The volumetric permeate flow rate, $Q^{Permeate}$, is calculated from the known Argon sweep flow rate and from the measured composition of the permeate/sweep mixture.

6. Gas adsorption

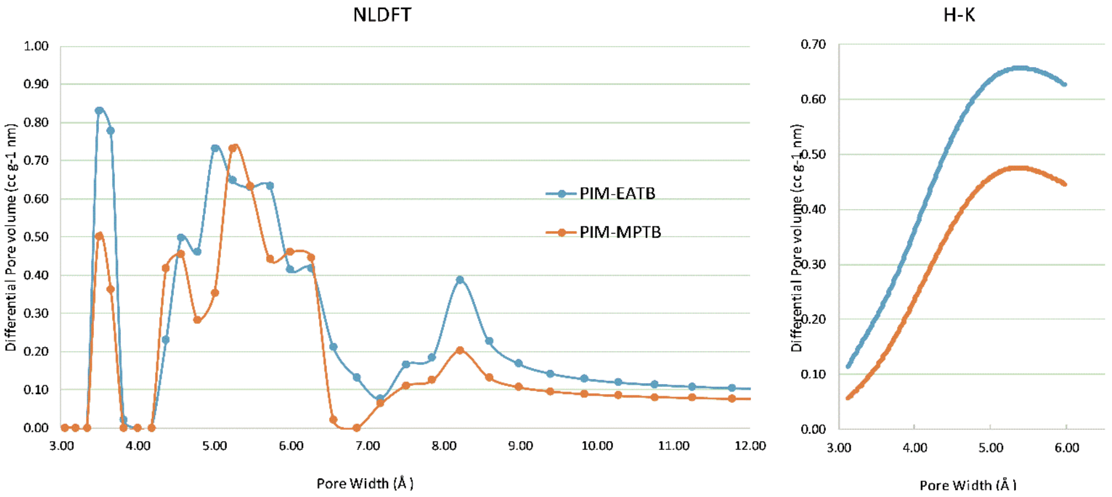


Figure ESI 1. NLDFT and H-K pore size distribution calculated from CO₂ uptake isotherms for PIM-EA-TB(Me) and PIM-MP-TB.

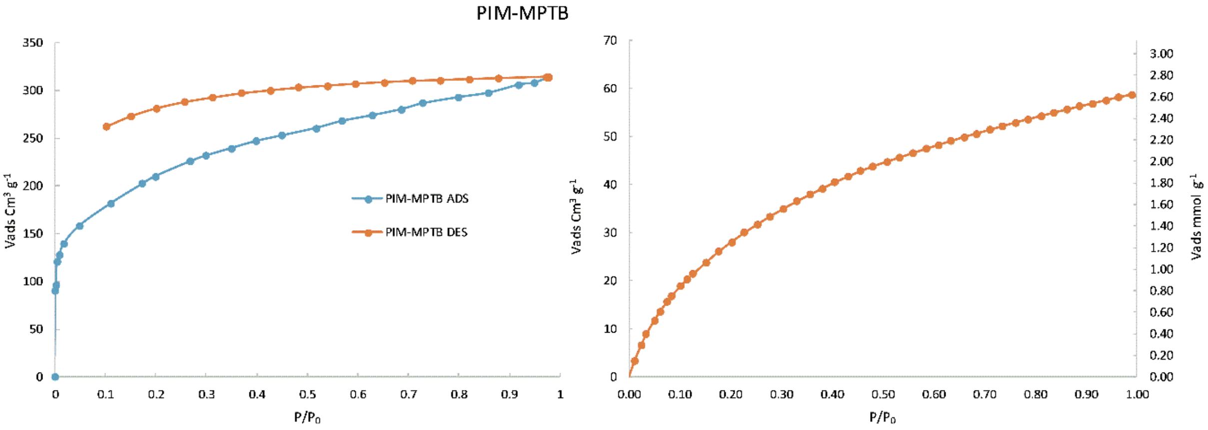


Figure ESI2. Nitrogen adsorption isotherm and CO2 uptake for PIM-MPTB

TGA curve of PIM-MP-TB

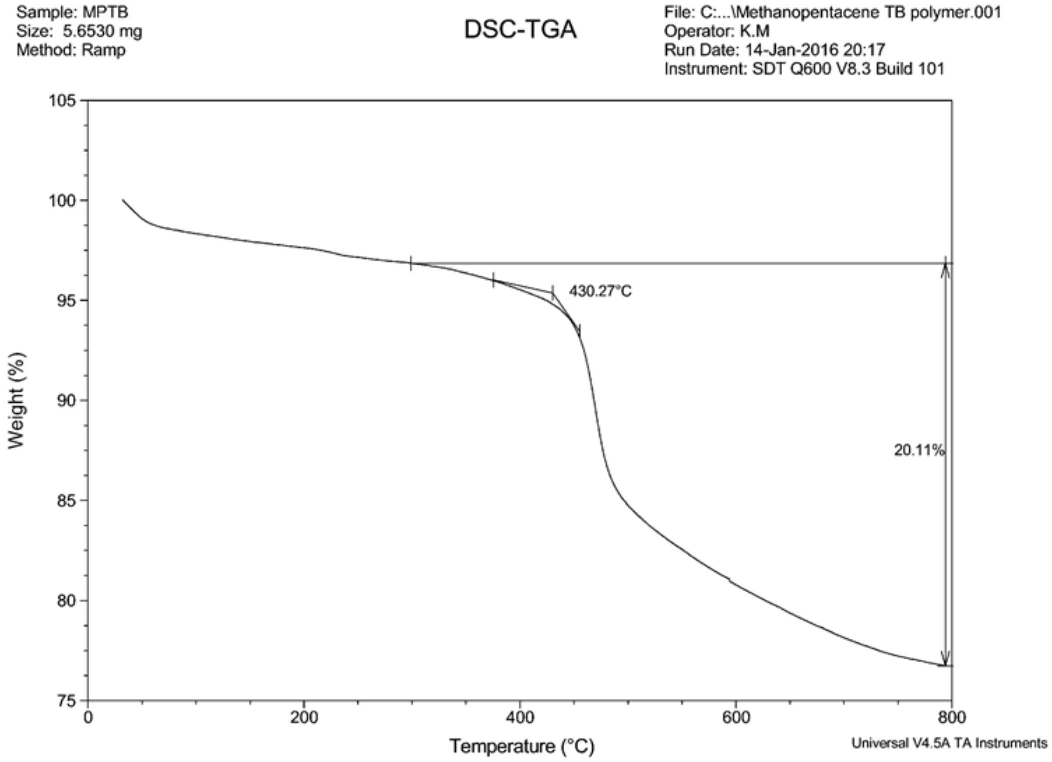


Figure ESI3. TGA curve of PIM-MPTB

7. Tables

Table ESI1 illustrates that the energy penalty paid in moving away from the minimum in dihedral angles 2 and 3 by 20° is considerably larger in MP than the other structural units. In addition to the proposed greater rigidity of MP relative to EA, it is also extended on each side by a further benzene ring (Figure 3a on the main text).

Table ESI 1. Difference in potential energy between MP and EA, triptycene and TB at – 20 ° and + 20 ° from the optimum angle.

	Difference in potential energy relative to MP / kJ mol^{-1}					
	Dihedral angle 1		Dihedral angle 2		Dihedral angle 3	
	-20 °	+20 °	-20 °	+20 °	-20 °	+20 °
EA	-4.6	2.5	7.9	13.8	33.7	45.0
Trip	-4.2	2.1	29.0	28.8	27.3	29.1
TB	-4.3	-2.3	26.6	27.1	27.9	42.4

Table ESI 2. Mixed gas permeabilities and selectivity of 110days aged **PIM-MP-TB** membrane using binary mixture CO_2/CH_4 (52.1:47.9).

	Permeability, Barrer		
Total Pressure, bar	CO_2	CH_4	CO_2/CH_4 Selectivity, (-)
1	787	35	22
2	766	36	21
3	786	38	21
4	776	40	19
5	772	42	18
6	770	43	18

Table ESI 3. Mixed gas permeabilities and selectivity of 110days aged **PIM-MP-TB** membrane using binary mixture CO_2/N_2.

	Permeability, Barrer		
Total Pressure, bar	CO_2	N_2	CO_2/N_2 Selectivity, (-)
1	771	31	25
2	726	28	26
3	706	27	26
4	694	27	26
5	681	26	26
6	669	26	26

Table ESI 4. Chronological order of the permeation tests after different sample treatments.

Sample age (days)	**Experiment**
0	Pure gas, MeOH treated
1	Pure gas, thermally treated at 140°C for 4 h.
110	Mixed gas, 110 days aged
118	Pure gas, 118 days aged
370	Pure gas, 370 days aged

8. Molecular modeling

All simulations of the amorphous membrane models were carried out using the Material Studio package (version 7.0) of Accelrys[2] and the COMPASS force field.[3]

8.1 Model preparation

A MP-TB polymer chain of 15 monomer units (1388 atoms) was used as template chain for the adjacent initial packing with the Amorphous Cell module.

In every packing model, two polymer chains with a total of 2774 atoms were grown together under periodic boundary conditions at 298 K and at an initial density of 0.1 g cm^{-3}. Additionally, every simulation cell contained 400 randomly distributed Ar atoms as obstacles to avoid ring catenation during the chain growth. The procedure for packing and equilibration are described in detail elsewhere.[4] Amorphous polymer packings were constructed using the Theodorou/Suter method[5, 6] as implemented in the Amorphous-Cell module. The obstacle molecules were later removed. Each removal procedure was followed by the structure relaxation, applying a force field parameter-scaling scheme used by Heuchel *et al.*[4] Several hundred energy minimization iterations and several thousand NVT-MD steps (constant number of particles, volume and temperature) were used for each parameter set. After removing the obstacle molecules using a downscaling procedure, the packing models were equilibrated via a set of MD runs to increase the density. A long final NpT-MD run (constant number of particle, pressure and temperature) was applied in the final equilibration.[4] The procedure was repeated, eliminating the non-realistic boxes, until three realistic amorphous cells for each of the polymers were generated with side lengths of the packing cells of 32.09 Å and a final density of 1.088 $\pm$ 0.01 g cm^{-3}. The deviations from the experimental density of 1.13 g cm^{-3} is about 3.7%, which is quite usual for glassy stiff-chain polymer materials, particularly if the models are large.

9. Free volume

The fractional free volume (FFV) and free volume distribution (FVD) were calculated using the Hofmann – Heuchel method.[7] The theoretical FVD was compared with that obtained by Bondi's group contribution method,[8] describing the FFV as the ratio of the free volume, V_f, of a polymer (cm^3 g^{-1}) and the specific volume, V_{sp}, defined as reciprocal density:

$$FFV = {}^{V_f}\!/_{V_{sp}} \tag{8}$$

According to Bondi's method, the free volume can be estimated as:

$$V_f = V_{sp} - 1.3V_{vdW} \quad (9)$$

where the van der Waals volume V_{vdW} is calculated using a group contribution method, and a universal "packing coefficient", equal to 1.3, is used to convert the van der Waals volume of the repeat unit into the "occupied" volume.

The size distributions of the free volume elements accessible for penetrants of certain radius were also calculated using the program developed by Hofmann and Heuchel.[7] Free volume was determined by first superimposing a fine grid over the cubic packing. Then a test was performed at every point of the grid to determine if an overlap occurs between a hard spherical test particle (representing the penetrating molecule) and any atom of the polymer (represented also by a corresponding hard sphere). The result was a classification of grid points as "occupied" or "free". Subsequently, the connectivity of the "free" grid points was considered, and connected "free" grid points were collected into groups, which represented individual holes. This was done in two ways. In the first approach (named *V* connect), the topological criterion was that every point of a group had at least one next neighbour, which was also member of this group. This approach identified holes, which may be of complex shape and of large size. In a second approach, for every grid point, the shortest distance to a polymer atom is used to group points, and, among these distances, local maxima are defined by calculating the related gradient. Then, each grid point of the free-volume regions is assigned to its nearest local maximum. This approach is referred to as R_{max}. This method dissolves larger free-volume regions of elongated or highly complex shapes into smaller "local" regions, to come closer to the situation of PALS spectra, where the positron probe particle cannot completely sample very large holes of complex topology. In the present work, the calculation starts by the superimposition of a fine grid of about 0.5 Å over the cubic packing model. In both approaches, the number of lattice cells belonging to a hole times their cell volume was used as a measure for the volume of this hole. The obtained volume of each hole was converted to an equivalent sphere and the radius of this sphere is taken as a measure for the average linear dimensions of the respective hole. The positronium (Posi) particle is assumed to have the size of a hydrogen atom, i.e., the radius is assumed to be 1.10 Å. The other probes used were CO_2, N_2 and O_2 with a radius of 1.65, 1.73 and 1.82 Å, respectively.

10. Calculation of dihedral angle distributions

The structure of the polymer backbone has been defined by the dihedral angles between three successive chemical bond vectors. The Cartesian coordinates of the four consecutively bonded backbone atoms forming these bonds were used to calculate the dihedral angle θ. The dihedral angle was defined as the smallest angle between the two planes formed by the first three and last three atoms, with the most extended planar (trans) conformation leading to $\theta = \pm 180°$.

References

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