

Supporting Information

AIMS: A new Strategy to Control Properties in Mixed-Matrix Membranes

Authors: Melanie Kitchin^{a,b}, Jesse Teo^b, Kristina Konstas^a, Cher Hon Lau^{a,b}, Christopher J. Sumbly^b, Christian J. Doonan^{*,a,b} and Matthew R. Hill^{*,a,b}

Affiliations:

a Manufacturing, CSIRO, Bayview Avenue, Clayton VIC, 3168, Australia

b Centre for Advanced Nanomaterials and the School of Chemistry & Physics, The University of Adelaide, Adelaide, SA, 5005, Australia

Experimental Details

Contents

1. Materials.....	2
a. MOP Synthesis.....	2
Synthesis of ^t Bu MOP, DEG-MOP, MOP-18.....	2
Synthesis of TEG MOPs.....	2
b. Fabrication of MOP-PTMSP membranes.....	2
2. NMR Spectra.....	3
3. Single gas permeability measurements.....	4
4. Scanning Electron Microscopy (SEM) and Focussed Ion Beam SEM (FIB-SEM).....	5
5. Wide-Angle X-ray Diffraction.....	6
6. Powder X-ray Diffraction.....	6
7. Viscosity Measurements.....	6
8. Mathematical Modelling.....	6

1. Materials

Polytrimethylsilylpropyne (PTMSP) was purchased from Gelest Inc. (Morrisville PA, USA) and used without purification. Chloroform was purchased from Sigma Aldrich.

a. MOP Synthesis

Synthesis of *t*Bu MOP, DEG-MOP, MOP-18

The *t*Bu MOPs was synthesised according to the preparation published by Li *et al.*¹

MOP-18 was synthesised according to Furukawa *et al.*²

The DEG MOPs were synthesised according to the preparation published by Tonigold.^{3,4}

Synthesis of TEG MOPs

The TEG MOPs were synthesised according to a modified preparation published by Tonigold.^{3,4}

TEG Isophthalic acid (TEG Linker)

Dimethyl 5-hydroxyisophthalate (200 mg, 0.95 mmol) was mixed with potassium iodide (270 mg, 1.62 mmol), potassium carbonate (140mg, 1.04 mmol) and 2-(2-(2-chloroethoxy)ethoxy)ethanol (0.3 mL) in acetonitrile (10 mL) and stirred at reflux for 72 hours. The reaction mixture was filtered before removal of the solvent in vacuo and addition of 1M HCl (10 mL). The product was extracted with ethyl acetate (20 mL x 2), dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (silica, 2:1 ethyl acetate:hexanes prior to saponification with KOH in 1:1 ethanol:water yielding an orange solid (154 mg, 52% over 2 steps). ¹H NMR (300MHz, DMSO) δ: 8.07 (1H, s), 7.65 (2H, s), 4.21 (2H, t, 4.2Hz) 3.78-3.50 (10H, m). Anal. Calc. C₁₄H₁₄O₈ C, 53.5; H, 5.77 Found: C, 53.2; H, 5.80.

TEG MOP

Equimolar solutions of the TEG ligand and copper(II) nitrate trihydrate in methanol form precipitate after adding two equivalents of the non-coordinating base 2,6-dimethylpyridine. (140mg, 0.45mmol) of TEG-isophthalic acid and (122 mg, 0.45 mmol) Cu(NO₃)₂·3H₂O yields 230 mg of TEG MOP.

Single crystals suitable for X-ray diffraction studies of the TEG MOPs were obtained by slow solvent diffusion of isobutanol into solutions of each MOP in DMSO.

b. Fabrication of MOP-PTMSP membranes

5 wt.%, 10 wt.%, 15 wt.%, 20 wt.%, 25 wt.% and 30 wt.% MOP-loaded PTMSP membranes were fabricated through a typical spin casting method. The following is an example, for 5 wt.% loaded film.

200 mg PTMSP was placed in a 20 mL vial with 5 g chloroform and an egg-shaped stirrer bar and stirred overnight. In a separate 20 mL vial, 10 mg *t*Bu MOP was placed in 5 mL chloroform and an egg-shaped stirrer bar. Each vial was closed and stirred for 24 hours under ambient conditions. Following this, the *t*-Bu MOP-chloroform solution was added to the vial containing the stirred PTMSP-chloroform solution, and the mixed solution stirred for a further 24 hours under ambient conditions. ~100 micron films were formed via solution casting at ambient conditions. The

membrane films were dried in a vacuum oven at 40 °C for 12 hours prior to single gas permeability measurements. Film thicknesses were measured using a Measumax digital micrometer.

The amount of each requisite MOP was changed to accord with the wt% dopant required, whilst the amount of PTMSP was kept constant at 200 mg:

10 wt.% = 20 mg MOP

15 wt.% = 30 mg MOP

20 wt.% = 40 mg MOP

25 wt.% = 50 mg MOP

30 wt.% = 60 mg MOP

2. NMR Spectra

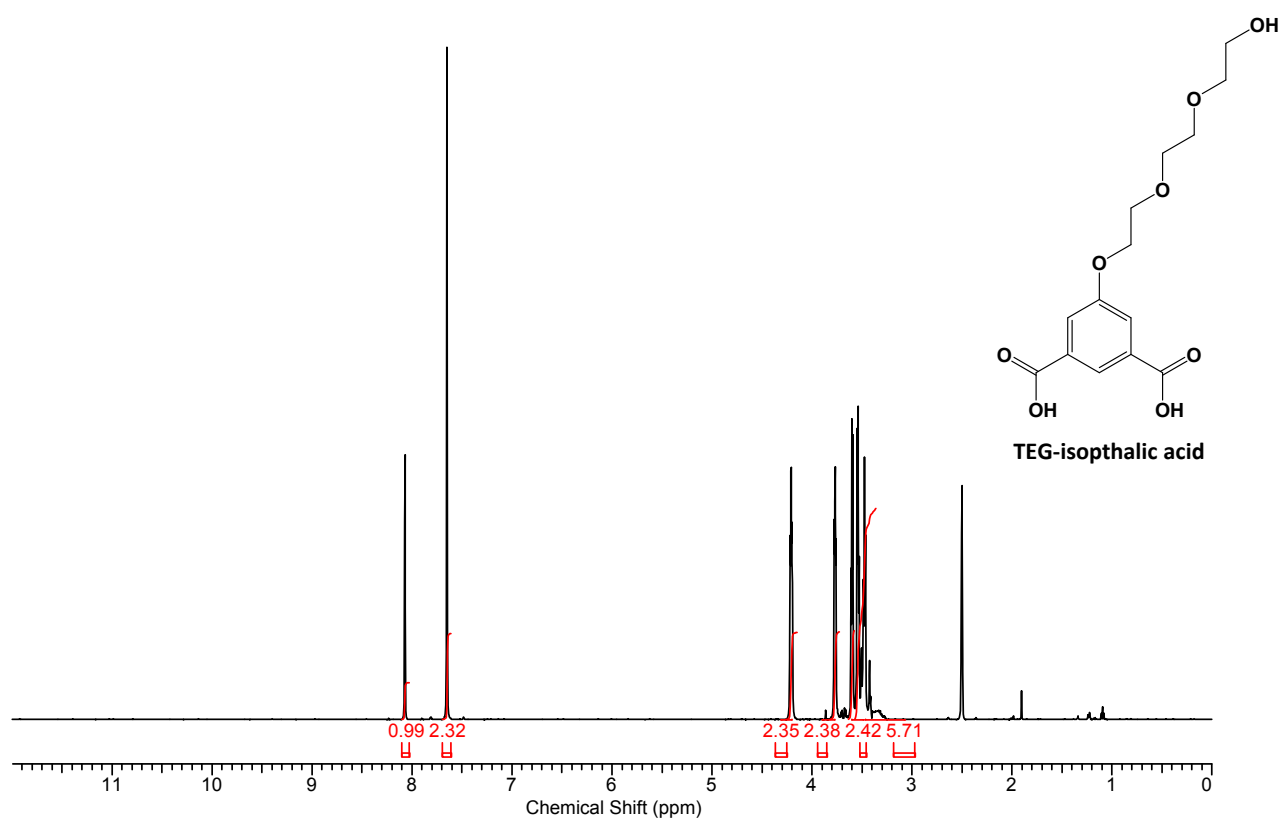


Figure S1. ¹H NMR (500MHz DMSO-d₆): TEG isophthalic acid

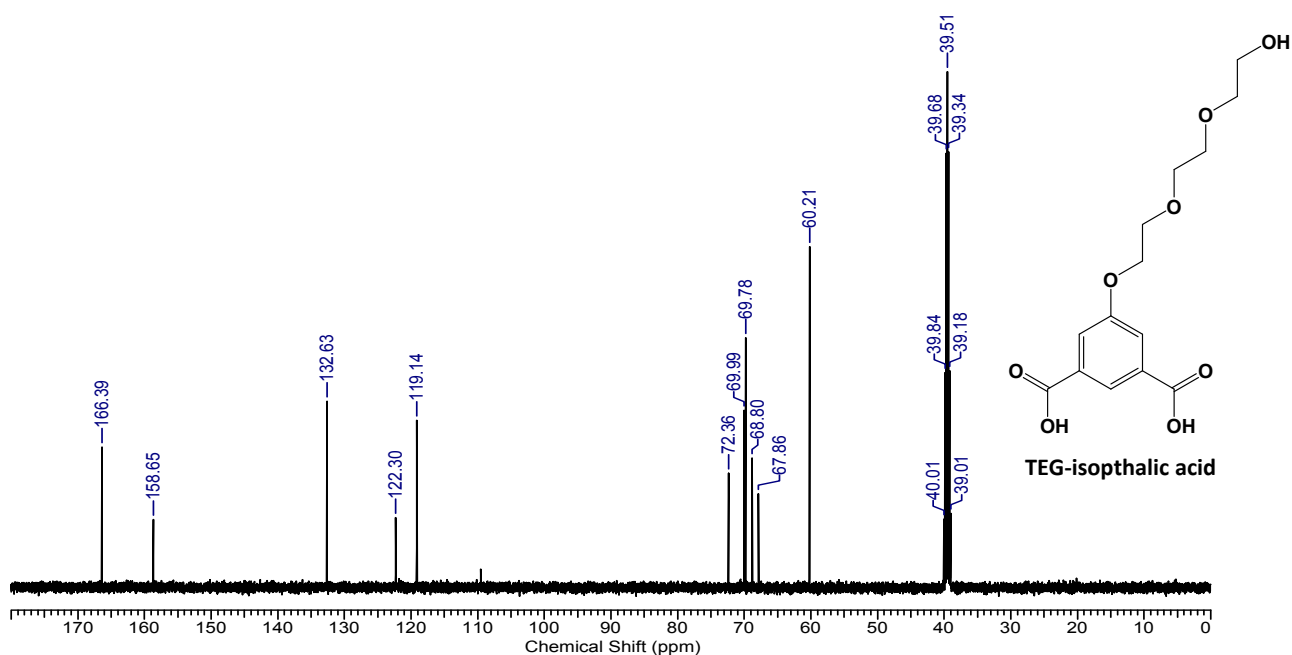


Figure S2. ^{13}C NMR (500MHz DMSO- d_6): TEG isophthalic acid

3. Single gas permeability measurements

The pure H_2 , N_2 , CH_4 and CO_2 permeabilities were determined using a constant volume and variable pressure method.⁵ Gas permeabilities at 2 at the moment were determined from the rate of downstream pressure build-up rate (dp/dt) obtained when permeation reached a steady state according to the following equation:

$$P = D * S = \frac{273 * 10^{10}}{760} \frac{VL}{AT \left[\frac{p_2 * 76}{14.7} \right]} \left(\frac{dp}{dt} \right)$$

Where:

P = permeability of a membrane to a gas (Barrer) ($1 \text{ Barrer} = 1 * 10^{-10} \text{ cm}^3 \text{ (STP)-cm/cm}^2 \text{ sec cm Hg}$)⁶

D = average effective diffusivity ($\text{cm}^2 \cdot \text{s}$)

S = apparent sorption coefficient/solubility ($\text{cm}^3 \text{ (STP)/cm}^3 \text{ polymer cmHg}$)

V = volume of the downstream chamber (cm^3)

L = film thickness (cm)

A = effective area of the membrane (cm^2)

T = experimental temperature (K)

p_2 = pressure of the feed gas in the upstream chamber (psia)

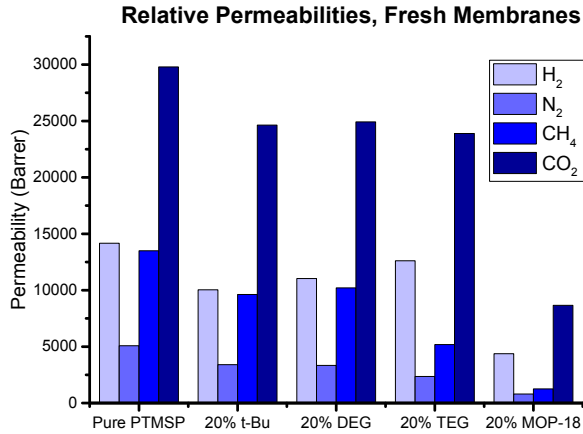


Figure S3: Relative gas permeabilities (H₂, N₂, CH₄, CO₂), fresh membranes.

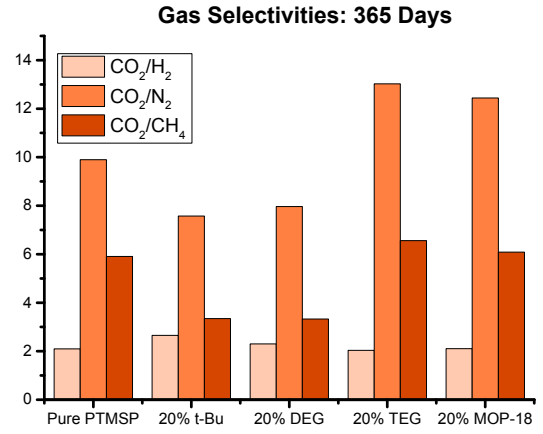


Figure S7: Gas Selectivities, aged membranes (365 days).

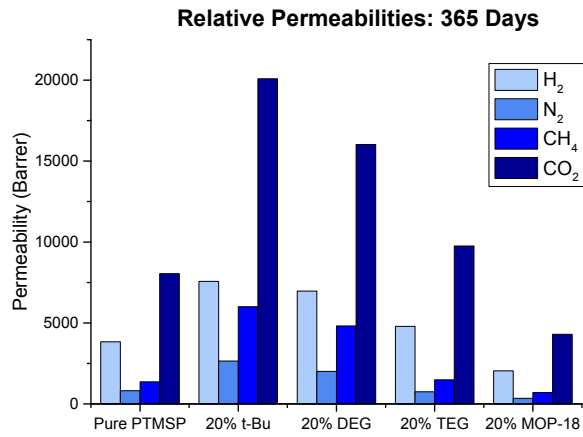


Figure S4: Relative gas permeabilities (H₂, N₂, CH₄, CO₂), aged membranes.

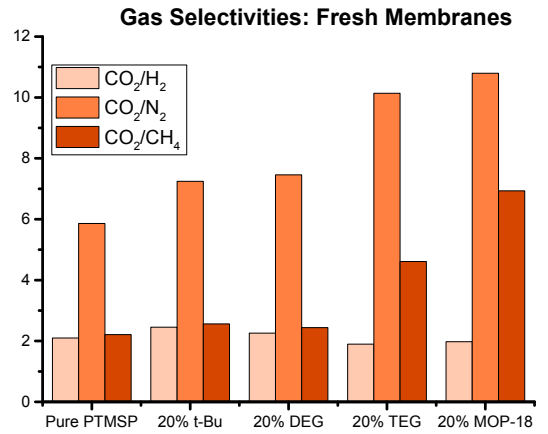


Figure S6: Gas selectivities, fresh membranes.

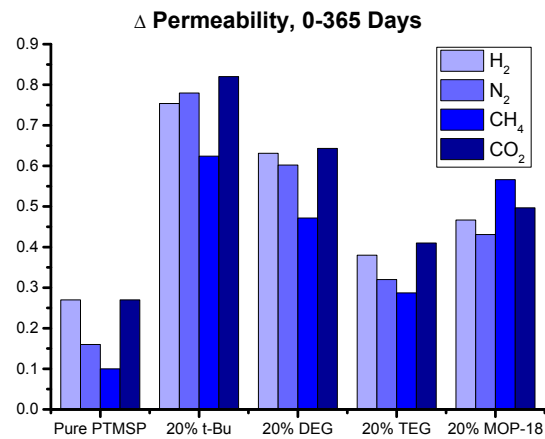


Figure S5: Change in gas permeabilities, 0-365 days.

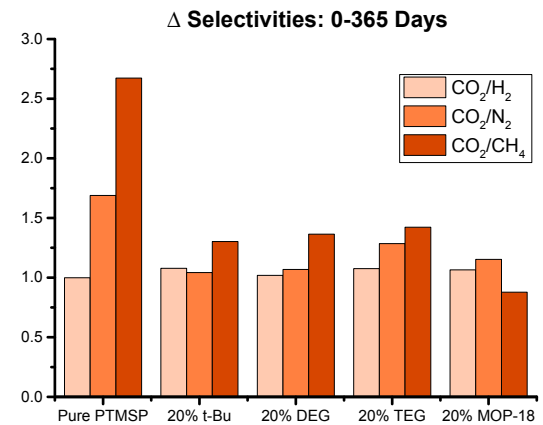


Figure S8: Change in gas selectivities, 0-365 days (H₂, N₂, CH₄, CO₂).

4. Scanning Electron Microscopy (SEM) and Focussed Ion Beam SEM (FIB-SEM)

All membrane films were cryo-fractured to achieve a clean break, before being mounted on cross-section SEM sample stubs. These sample stubs were then coated with iridium for elemental analysis through energy dispersive spectroscopy (EDS) during imaging.

Microscopy was performed on a JEOL JEM 2100F FEG TEM/STEM operated at 200 kV.

EDS spectra were obtained using a JEOL 50 mm² Si(Li) detector. X-ray maps (512*512) were obtained using 50-100 sweeps of the same area, drift correction and probe dwell times of 0.2 msec, resulting in total acquisition times of 30-60 minutes.

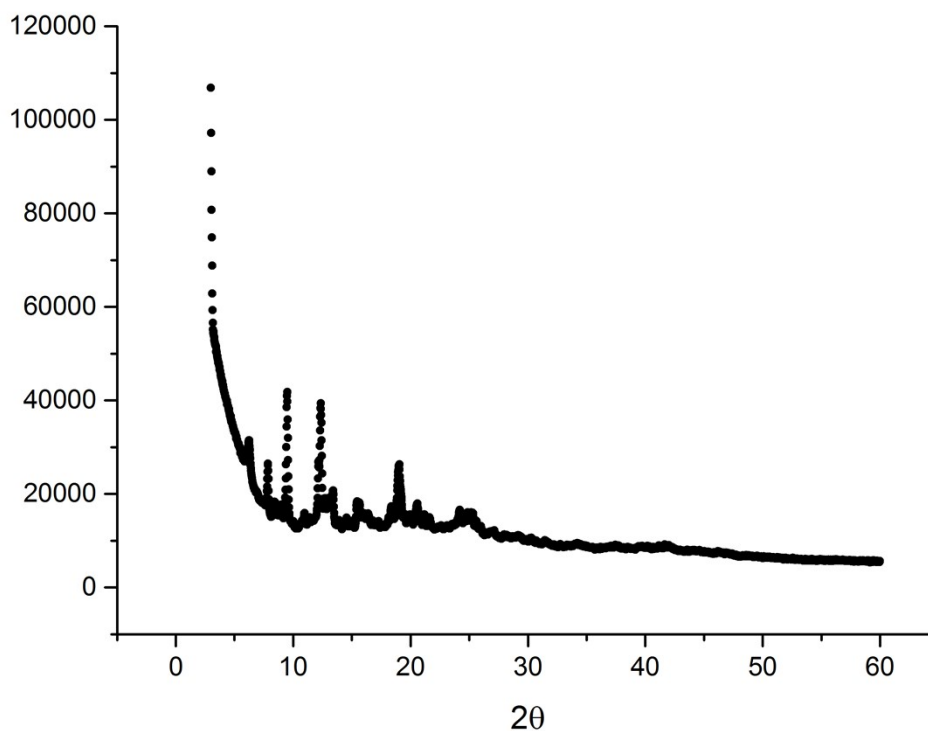
FIB SEM images were obtained at the MCN.

5. Wide-Angle X-ray Diffraction

Wide-angle X-ray scattering (WAXS) experiments were performed on the SAXS/WAXS beamline at the Australian Synchrotron, Clayton, Victoria, Australia. The synchrotron X-ray beam was 50 * 50 um in diameter and tuned to 11 keV with a typical flux of 10¹³ photons. Scattering patterns were acquired at 25C using an exposure time of 1 s. Lanthanum hexaboride was used to calibrate the WAXS Dectris – Pilatus 200K detector.

6. Powder X-ray Diffraction

Powder X-ray diffraction data was performed on the a Bruker D8 Advanced diffractometer (K- α radiation of copper was used as an X-ray source (X-ray wavelength of 1.54184 Å)). The angle of incidence θ of the X-rays was from 1° to 60° with a stepwise of 0.01° and a count time of 0.4 s.



7. Viscosity Measurements

Intrinsic viscosities of PTMSP and MOP-PTMSP solutions were measured using an Ubbelohde viscometer at 25 °C, and calculated based on the ATSM D445 standard. Chloroform was used as the solvent, and polymer concentrations were kept uniform at 2 wt.%.

8. Mathematical Modelling

Effective size calculations were used to calculate the size of the trimethylsilyl (TMS) side group of PTMSP and the pore window of the *t*-Bu-MOP. Effective size calculations consider the van der Waals radii of each atom, as defined according to Bondi.⁷

1. Li, J.-R.; Zhou, H.-C., *Nature Chemistry* **2010**, 2, 893-898.
2. Furukawa, H.; Kim, J.; Plass, K. E.; Yaghi, O. M., *J. Am. Chem. Soc.* **2006**, 128, (26), 8398-8399.
3. Tonigold, M.; Volkmer, D., *Inorganica Chimica Acta* **2010**, 363, (15), 4220-4229.
4. Tonigold, M. S. Ulm University, 2011.
5. Stern, S. A.; Gareis, P. J.; Sinclair, T. F.; Mohr, P. H., *J. Appl. Polym. Sci.* **1963**, 7, 2035-2051.
6. Stern, S. A., *J. Polym. Sci. Part A-2: Polym. Phys.* **1968**, 9, 1933-1934.
7. Bondi, A., *J. Phys. Chem.* **1964**, 68, (3), 441-451.