Supplementary Materials: Membranes of Polymers of Intrinsic Microporosity (PIM-1) Modified by Poly(ethylene glycol)
Gisela Bengtson, Silvio Neumann, Volkan Filiz

S1. Synthesis of Monomers and Polymers

**Materials:** Most chemicals and solvents were delivered by Sigma Aldrich (Germany) and used as received. 5,5',6,6'-Tetrahydroxy-3,3',3'-tetramethyl-1,1'-spirobisindane (1) was purchased from ABCR (Germany), Maleimide-PEG-2000 (7a) from Specific Polymers (France) and Jeffamine®-600 from Huntsman (Germany), all as used as received. 2,3,5,6-tetrafluoro-1,4-dicyanobenzene (2) was donated from Lanxess (Germany) and sublimed twice at 80 °C and reduced pressure. K2CO3 was dried at 120 °C and milled.

**Synthesis within Paths 1, 2, 3, 4:**

- Preparation of PIM-1 by polycondensation reaction (upper part of Scheme 1) was performed either by low temperature method following Budd and McKeown [2] and applying 1:2:K2CO3 in molecular equivalents 1:1:2.04 (in paths 2, 3) or by high temperature method following [18, 21], applying identical amounts of the components at 150 °C and adding appropriate amounts of diethyl benzene to prevent a fast precipitation of the polymer. Reaction time is 0.5 h (PIM-1 in path 1).
- Preparation of 2,4,5-trihydroxybenzoic acid (THBA)-PEG-mono-esters (3a-c) and 3,4-dihydroxybenzoic acid (DHBA)-PEG-di-esters (5a-c) was performed by water extracting distillation of THBA resp. DHBA and PEG in boiling toluene in presence of catalytic amounts of p-toluene sulfinic acid. Reaction time 2 to 10 days, progress of reaction was followed by sampling, work up either by filtration/drying or by extraction, followed by evaporation of solvent under reduced pressure.

**Monomer synthesis example 1.** Preparation of 3b: 2.000 g (11.76 mmol) 2,4,5-trihydroxybenzoic acid (THBA) and 11.463 g (15.28 mmol) methoxy-PEG-750 were dissolved in toluene, 0.200 g (1.06 mmol) p-toluene sulfinic acid was added and the solution was refluxed in a Dean-Stark trap for 4 days. Progress of reaction was followed by sampling. After cooling the dark solution was poured in H2O, organic phase separated, dried and toluene was evaporated at reduced pressure. Yield 8.62 g brown oil 3b (80%). 1H (DMSO-d6) δ = 3.24 (s, 3H), 3.51 (s, ca. 70H), 3.70 (m, 2H), 6.70 (s, 2H), 9.8 (br, 3H) ppm. 13C (DMSO-d6) δ = 60.7 (OCH3), 63.9, 70.3 (OCH2), 109.1 (arCH), 119.7 (arCCOO), 138.9/146.0 (arCC-OH), 166.2 (C=O) ppm. FT-IR: 3294, 2867, 1709, 1609, 1452, 1347, 1088, 1034, 947, 846 cm⁻¹.

**Monomer synthesis example 2.** Preparation of 5b: 1.618 g (10.5 mmol) 3,4-dihydroxybenzoic acid (DHBA) and 4.990 g (4.99 mmol) PEG-1000 were dissolved in toluene, 0.17g (0.99 mmol) p-toluene sulfinic acid was added and the solution was refluxed in a Dean-Stark trap for 4 days. Progress of reaction was followed by sampling. After cooling precipitated 5b was filtered off, washed with toluene and dried at 50 °C/0.05 mbar. 2.5 g waxy brownish solid 5b (yield 40%). 1H (DMSO-d6) δ = 3.49 (s, ca. 90H), 3.72 (m, 2H), 6.82 (s, 2H), 9.8 (br, 3H) ppm. FT-IR: 3289, 2868, 1708, 1602, 1521, 1442, 1349, 1218, 1085, 946, 889, 839, 766 cm⁻¹.

- Polymers 4a-c and PIM(X)-b-PEO(Y) multiblock copolymers were prepared by low temperature method [2].

**Polymerization example 3.** Preparation of 4b: 1st step (polycondensation to PIM-1): 1.021 g (3 mmol) 1, 0.600 g (3.0 mmol) 2 and 0.846 g (6.12 mmol) K2CO3 were dissolved in DMF, heated to 55 °C for 3 h. 2nd step (quenching polycondensation of PIM-1 with 3b): 0.012 (0.086 mmol) K2CO3 was added to the warm suspension of 1st step and stirred for 5 min, 0.0055 g (0.03 mmol) 2 was added and stirred for another 15 min, 0.059 g (0.064 mmol) 3b, dissolved in 1 mL DMF, was added and stirred for additional 30 min.
Final suspension was poured in H₂O, filtered and dried; re-precipitation from CHCl₃ solution in MeOH, drying in vacuo. 1.377 g yellow powder 4b (95% yield). SEC (MALS): M₅ = 52000 g/mol, Mₚ = 40500 g/mol. 

Polymerization example 4. Preparation of PIM(10)-b-PEO(1): 1st step (polycondensation to PIM-1): 1.02 g (3 mmol) 1, 0.66 g (3.3 mmol) 2 and 0.846 g (6.12 mmol) K₂CO₃ were dissolved in DMF, heated to 55 °C for 3 h, yellow suspension was poured in H₂O, filtered and dried; re-precipitation from CHCl₃ solution in MeOH, drying in vacuo, 1.34 g bright yellow powder (97%). M₅ (RI) 9400 g/mol, Mₚ 5000 g/mol. 2nd step (polycondensation of PIM-1 with 5b): 0.501 g (0.05 mmol) PIM-1 (from 1st step) and 0.0667 g (0.0503 mmol) 5b were suspended resp. dissolved in DMF, 0.161 g (1.171 mmol) K₂CO₃ was added, suspension was heated to 55 °C for 7 days; progress of reaction was followed by sampling. The final suspension was poured in H₂O, filtered off and the precipitate was dried; re-precipitation from CHCl₃ solution in MeOH, drying in vacuo. 0.374 g greenish yellow solid PIM(10)-b-PEO(1) (40%). SEC (MALS): M₅ = 99000 g/mol, Mₚ 70000 g/mol. 

-Preparation within Path 4

Preparation of 9,10-dibutylanthracene-2,3,6,7-tetrol (6) see [14,22]. After hydrolysis of methoxy to hydroxy groups by BBr₃, 6 was obtained as an off-white powder of mp. 218–220 °C.

Preparation of monomer 8a: Diels-Alder reaction of 6 and maleimide-PEG-2000 (7a) was accomplished in p-xylene, 24 h reflux, evaporation of xylene under reduced pressure. Light brown solid 8a (95%), mp. 46 °C. ¹H (DMSO-d₆) δ = 1.09 (t, 6H), 1.66 (m, 2H), 2.08 (m, 2H), 3.73 (m, 2H), 3.75 (m, 2H), 6.56 (s, 2H), 6.67 (s, 2H), 8.50 (s, 2H), 8.68 (s, 2H) ppm.

Preparation of monomer 8b: Maleimide-methoxy(polypropylene glycol) (7b) with PPO chain of ca. 600 g/mol, a viscous oil, was synthesized after [21] in 2 steps from Jeffamine®-M600 polyetheramine and maleic anhydride in 84% yield. ¹H (DMSO-d₆) δ = 1.03 (d, 27H), 3.25 (s, 3H), 3.29–3.51 (m, 31H), 6.97 (2s, 2H). FT-IR: 2974, 2871, 1710, 1455, 1375, 1094, 1014, 926, 832 cm⁻¹.

Diels-Alder reaction of 6 and maleimide-PPO-600 (7b) conducted in p-xylene; 4 d reflux, evaporation of xylene under reduced pressure. 8b, dark brown oil (70%). ¹H (DMSO-d₆) δ = 1.04 (d, 33H), 1.65 (m, 6H), 1.91 (m, 2H), 2.08 (m, 2H), 2.65 (m, 2H), 3.25 (s, 3H), 3.37 (s, 31H), 6.58 (s, 1H), 6.68 (s, 1H), 7.06 (s, 2H), 8.58 (br, 2H), 8.69 (br, 2H) ppm. ¹³C (DMSO-d₆) δ = 14.6 (butylC-CH₃), 17.8 (PPO-CH₂), 23.7 (3-butyl-CH₂), 27.1/28.3 (2-butyl-CH₂), 45.5 (C₆-bicycle), 49.1 (CH-N), 58.8 (imidoC-CH), 68.3/72.8/75.1 (PPO-CH₂), 76.3 (PPO-OCH₂), 101.4/111.4 (arC), 134.3, 136.5, 142.4/143.0 (arC-CH₂), 176.7 (C=O). FT-IR: 3350, 2966, 2930, 2870, 1694, 1451, 1375, 1297, 1212, 1089, 1025 cm⁻¹.

Polymerization example 5. Preparation of PIM1-co-8a-1: 0.917 g (0.375 mmol) 8a, 4.978 g (14.625 mmol) 1, 3.001 g (15 mmol) 2 were dissolved in DMF, 4.229 g (30.6 mmol) K₂CO₃ was added at room temperature. The suspension was heated to 55°C for 3 days and worked up as in examples 3 and 4. Re-precipitation from CHCl₃ solution in MeOH, yield 7.644 g of yellow powder (99% based on 8a). SEC (MALS): M₅ 43000 g/mol, Mₚ 33800 g/mol. ¹H (CDCl₃) δ = 1.31/1.37 (PIM-1), 2.16/2.33 (PIM-1), 3.42 (PEO), 6.42/6.81 (PIM-1) ppm. FT-IR: 3054, 2865, 2240, 1445, 1310,1288,1263,1211, 1108, 1009, 874, 753 cm⁻¹.

S2 Gas Separation
Gas permeation measurements were carried out in a fixed-volume pressure-increase apparatus in the time lag mode (descriptions of the method in [5,16,17] and literature cited therein), applying the solution-diffusion model [15]. Permeate volume is 224 cm³, membrane area 13.8 cm², feed pressure 200–300 torr (26.6–40 × 10⁴ Pa).

Measurements in the time lag apparatus primarily give the permeability for result, calculated by the increase of pressure on the permeate side per time after reaching a “quasi” steady state. Permeability coefficients $P$ are calculated by eq. 1 ($V_p$ is the permeate volume, $l$ the actual membrane thickness, $A$ the membrane area, $p_f$ the feed pressure (constant) and $p_{p1}$ resp. $p_{p2}$ permeate pressures at different times). Permeability is expressed in Barrer [$1 \times 10^{-10}$ cm³(STP) cm cm⁻²s⁻¹cmHg⁻¹]).

$$P = \frac{V_p \times l}{A \times RT \times \Delta t \ln\left(\frac{p_f - p_{p1}}{p_f - p_{p2}}\right)}$$

(1)

Diffusivity coefficients $D$ are calculated by Equation (2) using the so called time lag $\theta$, the delay of pressure increase at start of every experiment, and the square of the membrane thickness $l$. Diffusivity is expressed in cm²/s.

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

(2)

The measured time lag $\theta$ of a PIM-1 membrane (thickness 80 µm, 30 °C) varies from ca. 0.1 (He and H₂), ca. 2 (O₂), ca. 6 (CO₂ and N₂) to about 16 s for CH₄. Although the time lag and permeability measurements are repeated several times, the experimental error for small gases like H₂ and He within the highly permeable PIM-1 membrane is considerable high and the results are not really reliable. Consequently, we concentrated on the results for the larger gas molecules under consideration being more reliable on account of their slower diffusion.

Following the solution-diffusion-model [15] permeability $P$ is the product of diffusivity $D$ and solubility $S$. Accordingly, the solubility coefficient $S$ is calculated by eq. (3), dividing $P$ by $D$.

Solubility unit is cm³/cm³·cmHg.

$$S = \frac{P}{D}$$

(3)