Supporting information for

Systems membranes – combining the supramolecular and dynamic covalent polymers for gas-selective dynameric membranes

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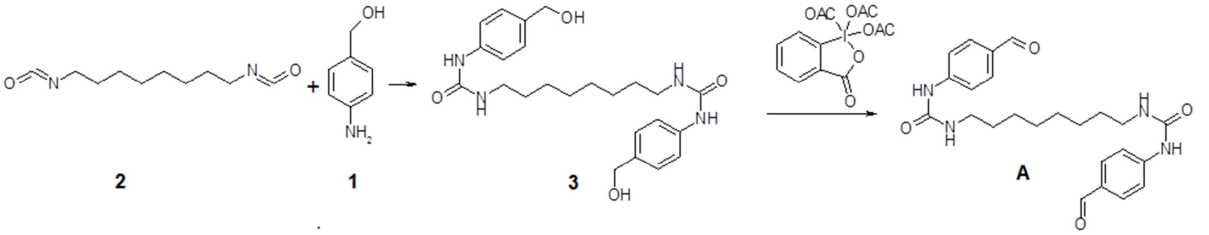
Materials and Methods: All reagents were obtained from Aldrich and used without further purification. All organic solutions were routinely dried by using sodium sulfate (Na_2SO_4). ^1H-NMR spectra were recorded on an ARX 300 MHz Bruker spectrometer in DMSO-d6 using the residual solvent peak as reference. FTIR measurements were performed with a Nicolet Nexus FT-IR spectrometer equipped with a ATR Diamant Golden Gate. SEM images were obtained with a Hitachi S-4500 apparatus, under a tension of 0.5-30 kV. X-ray powder diffraction measurements were performed with Cu-Kα radiation at 20°C using a Philips X’Pert Difractometer equipped with a Xcelerator detector.

General procedure for the synthesis of dialdehyde N,N'-hexane-1,6-diylbis (4-formylbenzocarboxamide), A. This synthesis has been performed in two steps:



Step 1: A mixture of 4-Aminobenzyl Alcohol (8.4 g, 68.4 mmol), **1** and 1,6-diisocyanatooctane (1eq, 5.2 mL, 32.3 mmol), **2** was heated overnight at reflux in acetonitrile. The pure compound **3** precipitating at room temperature as a white powder was filtered then washed with methanol and dried in an oven at 45°C. ^1H RMN (DMSO-d6, 300 MHz) : δ = 1,31 (t, 6H, ^2J=5,7 Hz), 1,56 (t,4, ^2J=6,6Hz), 3.2 (q, 4H, ^2J=6,0 Hz), 4,8 (d, 4H, ^2J=5,8 Hz), 5,7 (t, 2H, ^2J=6,0 Hz), 6,85 (s, 1H, ^2J=6,0 Hz), 7.2 (d, 2H), 7,62 (d, 2H), 9,80 (s, 2H). ^{13}C RMN (DMSO-d6, 75 MHz): δ = 27.0, 29.7, 31.3, 45.2, 68.5, 120.6, 127.7, 134.5, 137,9; HRMS (*m*/*z*): 429.24 $[M.H]^+$

Step2: The compound **3** was then oxidizing to dialdehyde **A**: The Dess martin reagent was dispersed in CH_2Cl_2. The compound **3** was dissolved in a minimum of DMSO and added drop by drop at the suspension. The reaction mixture was vigorously stirred for 3h and a saturated solution of $NaHCO_3$ / $Na_2S_2O_4$ (2 mmol/ mmol alcohol) was added and stirred for one more hour. The precipitated compound, A was than filtrated and washed several time in water, than in Et_2O and finally dried in a vacuum. ^{1}H RMN (DMSO-d6, 300 MHz) : δ = 1,31 (t, 6H, ^{2}J=5,7 Hz), 1,56 (t,4, ^{2}J=6,6Hz), 3.2 (q, 4H, ^{2}J=6,0 Hz), 5,7 (t, 2H, ^{2}J=6,0 Hz), 6,85 (s, 1H, ^{2}J=6,0 Hz), 7.7 (d, 2H), 7,8 (d, 2H), 9,80 (s, 2H). ^{13}C RMN (DMSO-d6, 75 MHz): δ = 27.0, 29.7, 31.3, 45.2, 68.5, 120.6, 127.7, 132.5, 144.0; 190.2; HRMS (*m*/*z*): 425.24 $[M.H]^{+}$

General procedure for the synthesis of dynameric thin layer membrane films P1-P4: 1 mmol, 0.43 g of the dialdehyde **A** (ex.: 0.30 g for x=34%) and 1 mmol of macromonomeric compounds (ex.: 1.1 g of PolyTHF, **1** 1.5g of polyPEG, **2** 2.5 g of Polydimesiloxane, **3** 3.5 g of poly*Me*PEG, **4** respectively) were solubilized in 80 ml of THF. The reaction mixtures were refluxed overnight under stirring. The mixture was concentred to almost the 10 mL and then the solutions were tape-casted onto PAN support slowly dried at 25°C for 1 day to supported thin-layer films of **P1-P4**. Finally these films were dried at 90°C in an oven for 2 more days.

The same procedure has been used for mixed **P3**/**P4** mixed polymers blends for which 1:1 mol:mol mixture of **P3** and **P4** blends has been used and then equilibrated at reflux in order to attain the exchange equilibrium between the components via imine reversible bonds.

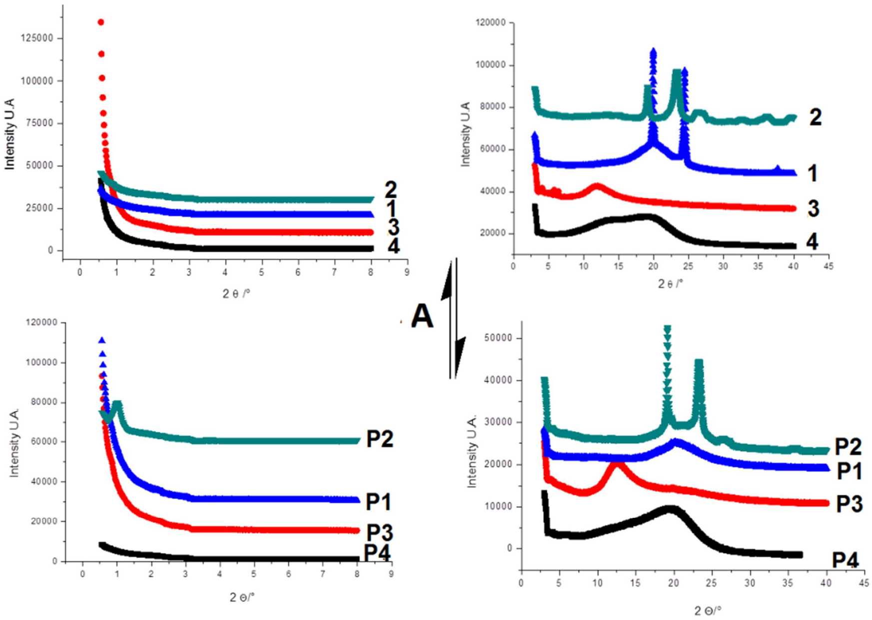


Figure 1S. XPRD patterns of **1-4** and **P1-P4** at left) low and right) high angles.

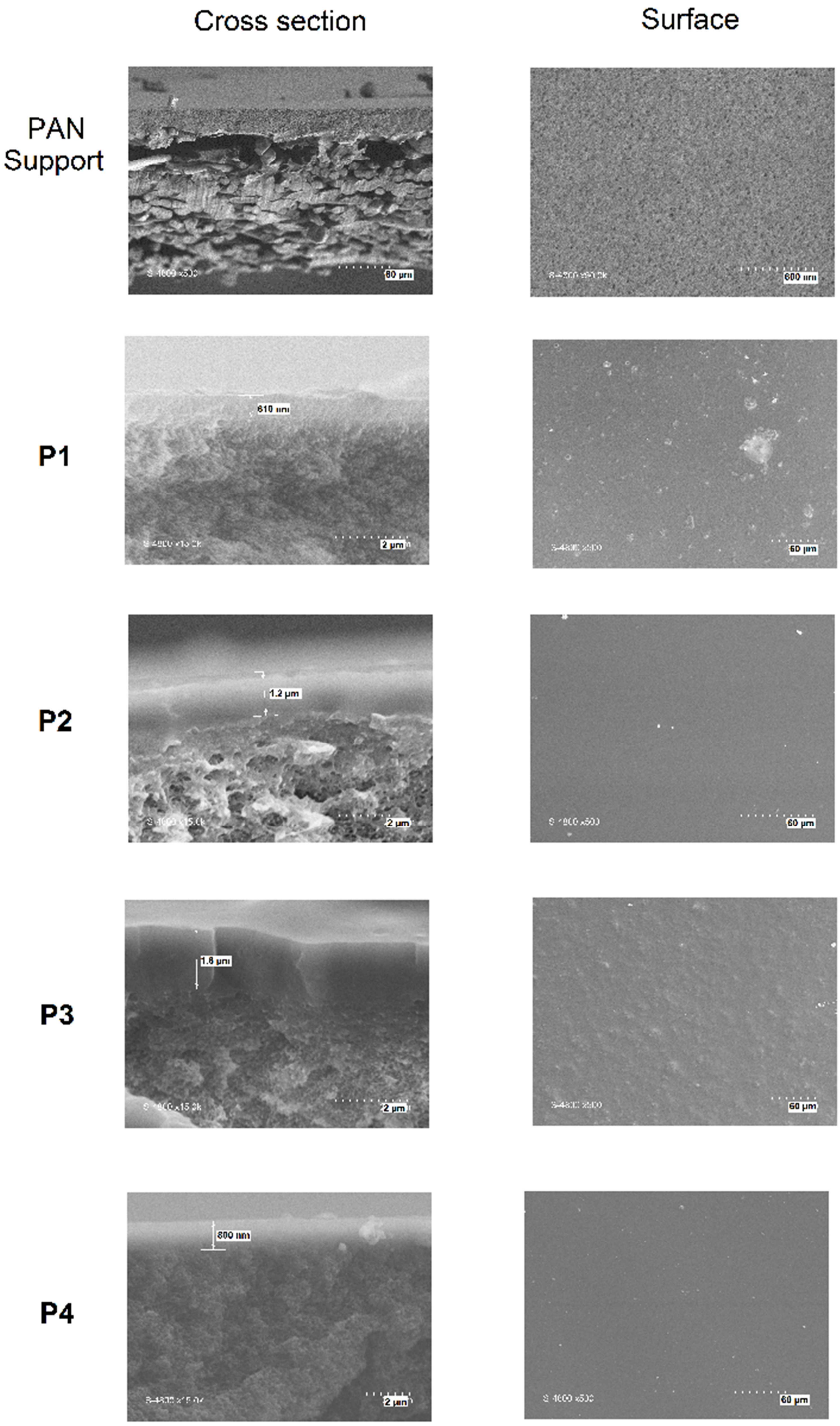
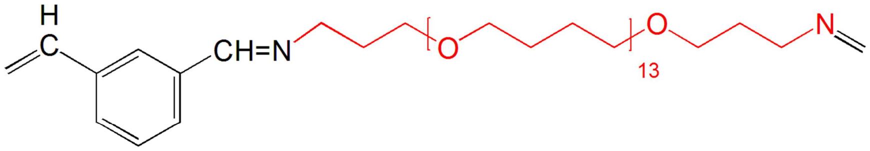
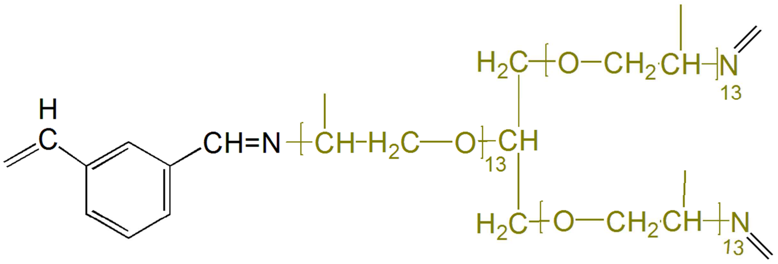


Figure 2S: SEM images of left) the cross-section and right) the surface of the Polyacrylonitrile PAN support and **P1-P4** thin-layer supported dynameric membrane films.



P5



P6

Figure 3S. Dynameric membranes **P5** and **P6** obtained via dynamic covalent imino-bonding of isophthalaldehyde non-structuring cores and linear polyTHF, **1** or cross-linked polyMePEG, **4** macromonomers.

Gas permeation and sorption experiments: Pure gas permeability of H_2, N_2, O_2, CH_4 and CO_2 of dense membranes were determined with a constant-volume/variable-pressure (time-lag) method at 30°C. The feed pressure was between 300 and 400 mbar for all gases, and the permeate pressure which did not exceed 15 mbar was recorded as a function of time. Before each gas permeation test, the permeation cell with the dense polymer membrane under study was under vacuum for 8-12 h (drying). Each measurement was repeated at least 2 twice for 2 membrane samples of the same composition. Diffusion coefficients were determined by the time-lag method. For fast gases like hydrogen the error of D is mainly based on the error of the time-lag, and thus, its error was determined less than 0.05s. Statistical error of the time-lag together with other experimental errors, the highest error for hydrogen diffusivity could be around 25%. The solubility coefficient is derived from the known permeability and diffusivity. The membrane active layer thickness was measured by a using Scanning Electronic Microscopy.