

Supporting Information

The Effect of Soft Nanoparticles Morphologies on Thin Film Composite Membrane Performance

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Experimental Details

Materials: Trimesoyl chloride (TMC, 98 %), benzyl alcohol (BA, 99 %), methanesulfonic acid (MSA, 97 %), poly(ethylene glycol) (PEG₄₀₀, $M_n = 400$ Da) were purchased from Sigma-Aldrich and used as received. Monomers oligo(ethylene glycol) methyl ether acrylate (OEGA) and di(ethylene glycol) ethyl ether acrylate (DEGA) were de-inhibited by percolating over a column of basic alumina. Pebax[®] 2533 was obtained from Arkema and used as received. Aminopropyl terminated polydimethylsiloxane (NH₂-PDMS-NH₂, $M_n = 5.0$ kDa; Gelest Inc.) and 2,2'-azobis(2-methylpropionitrile) (AIBN, 98%; Acros) were used as received. Deuterated chloroform (CDCl₃, 99.9 %) was purchased from Cambridge Isotope Laboratories, Inc. Triethylamine (TEA) and toluene were distilled from calcium hydride under argon. Tetrahydrofuran (THF) was distilled from benzophenone and sodium metal under argon. AR grade dichloromethane (DCM), diethyl ether (DEE), 2-propanol, *n*-butanol, *n*-hexane and other solvents were purchased from Chem-Supply Pty. Ltd. and used as received. The microporous polyacrylonitrile (PAN) substrate (6,000 MWCO) was purchased from SolSep BV and used without any further treatment.

Measurements: Gel permeation chromatography (GPC) using THF eluent was carried out on a Shimadzu liquid chromatography system equipped with a Wyatt DAWN-HELEOS MALLS detector (690 nm, 30 mW), Wyatt OPTILAB DSP interferometric refractometer (690 nm) and Shimadzu SPD-10AVP UV-Vis detector using three Phenomenex Phenogel columns (500, 104 and 106 Å porosity; 5 µm bead size) operating at 45 °C. THF was used as the eluent at a flowrate of 1 mL·min⁻¹. The molecular weights of all samples were determined using polystyrene standards. Dynamic Light Scattering (DLS) measurements were performed on a Wyatt DynaPro NanoStar DLS/SLS instrument with a GaAs laser (658 nm) at an angle of 90° and a temperature of 25 ± 0.1 °C. Stable spectra were obtained at sample concentrations of 1 mg·mL⁻¹. All sample solutions were filtered through 0.45 µm syringe filters. Proton magnetic resonance spectroscopy (¹H NMR) was performed using a Varian Unity (400 MHz) spectrometer, where the samples were dissolved in CDCl₃. X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance instrument with Cu Kα radiation (40 kV, 40 mA) and a nickel filter, and the samples

were exposed at a scanning rate of $2\theta = 0.02 \text{ }^\circ\cdot\text{s}^{-1}$ in the range of 3-70 $^\circ$. Scanning electron microscope (SEM) images were acquired using a FEI Quanta 200 ESEM FEG. Samples were pre-coated with gold using a Dynavac Mini Sputter Coater prior to imaging. X-ray photoelectron spectroscopy (XPS) analysis was performed on a VG ESCALAB 220i-XL spectrometer under ultra-high vacuum (6×10^{-9} mbar) to reveal the surface composition of the TFC membrane. A fixed photon energy (Al K α 1486.6 eV) was used. A survey scan was performed between 0 and 1200 eV with a resolution of 1.0 eV and pass energy of 100 eV. High resolution scans for C1s (276 to 296 eV) and O1s (522 to 542 eV) were also conducted with a resolution of 0.05 eV and a pass energy of 20 eV. Attenuated total reflectance infrared (ATR-FTIR) spectroscopy was performed on a Nexus 470 Fourier-Transform Infrared Spectrometer (Thermo Nicolet).

Synthesis of polymeric SNP-1 by condensation polymerization: The condensation polymerization of PEG₄₀₀ with TMC occurred under ambient condition. A typical procedure can be described as follows. PEG₄₀₀ (1.80 g, 4.5 mmol; 9.0 mmol of hydroxyl groups) was dissolved in a mixture of 50 mL of anhydrous THF and 4.2 mL of anhydrous TEA (3.05 g, 30 mmol) under dry nitrogen. TMC (0.584 g, 2.2 mmol) was dissolved in 10 mL of anhydrous THF and the solution was added dropwise to the PEG solution at 0 $^\circ\text{C}$ over 30 min under vigorous stirring. The mixture was then warmed to room temperature and stirred for a further 24 h. The precipitate of triethylamine hydrochloride was removed by filtration. The solution was then concentrated *in vacuo* (1 mbar) and the product was re-dissolved in 50 mL of DCM. The organic solution was then washed with H₂O (3 \times 50 mL), dried (anhydrous MgSO₄), filtered, concentrated and precipitated into cold DEE. After removal of DEE, the gel-like polymer was dried *in vacuo* (1 mbar) at 30 $^\circ\text{C}$. A colorless product, **SNP-1** with an isolated yield of 90% was obtained. ¹H NMR (400 MHz, CDCl₃, 25 $^\circ\text{C}$, δ_{H} ppm): 8.94-8.80 (*m*, 3H, ArH), 4.45-4.55 (*s*, 2H, -CH₂O(C=O)-), 3.40-3.80 (*m*, 4H, -CH₂CH₂O-).

Synthesis of single chain nanoparticle SNP-2 by ring-opening polymerization (ROP): The experimental details of the synthesis of benzyl dodecyl carbonotrithioate (BDC) and 4-(acryloyloxy)- ϵ -caprolactone (AC) are reported elsewhere.¹ Initially, a linear precursor (LP) was prepared *via* RAFT polymerization. AIBN (2.1 mg, 12.5 μmol), benzyl dodecyl carbonotrithioate (BDC) (12 mg, 31.2 μmol), oligo(ethylene glycol) methyl ether acrylate

(OEGA) (0.90 g, 1.87 mmol), di(ethylene glycol) ethyl ether acrylate (DEGA) (0.59 g, 3.12 mmol) and 4-(acryloyloxy)- ϵ -caprolactone (AC) (0.23 g, 1.25 mmol) were dissolved in toluene (5.1 mL), and the mixture was degassed by bubbling with N₂ for 45 min at 0 °C in an ice/H₂O bath. The reaction mixture was stirred at 80 °C for 15 h under N₂ and then cooled in an ice bath. The monomer conversion and percentage of lactone moieties in the polymer were determined to be 93 % and 19 %, respectively, by ¹H NMR spectroscopic analysis. The crude mixture was diluted with THF (5 mL) and precipitated into DEE : hexane (7 : 3, 100 mL), and the precipitate was isolated by centrifugation. This precipitation was repeated once more and the precipitate was dried *in vacuo* to afford **LP** as a yellow tacky liquid, 1.46 g (85%). M_n GPC = 49.4 kDa, M_w/M_n = 1.33. ¹H NMR (400 MHz, CDCl₃, 25 °C, δ_H ppm): 7.14-7.04 (m, 5H, ArH); 5.10-4.90 (m, 1H, -CHOC(=O)-); 4.60-4.52 (m, 2H, ArCH₂); 4.50-4.30 (m, 1H, -CHHOC(=O)-); 4.28-4.00 (m, 2H, -CH₂OC(=O)-, all other methylene protons from ester groups); 3.80-3.40 (m, 4H, -CH₂CH₂O-, ethylene glycol backbone, overlapping with 2H of -CH₂SC(=S)-); 3.00-2.40 (m, 2H, -CH₂C(=O)O-); 2.50-1.30 (m, 20H of -CH₂CH₃ overlapping with 4H of -CH₂CHO and 3H of polyacrylate backbones and 3H of methyl groups).

The synthesis of single chain SNP-2 can be described as follows. The LP (0.10 g; this equates to 73 μ mol of caprolactone), benzyl alcohol (1.0 μ L, 10 μ mol) and methanesulfonic acid (MSA, 1.3 μ L, 20 μ mol) were dissolved in 1 mL of CDCl₃, and the reaction mixture was left to react at 25 °C for 16 h. The reaction mixture was precipitated into DEE : hexane (7 : 3, 10 mL), and the precipitate was isolated by centrifugation. This precipitation step was repeated once more and the nanoparticles were dried *in vacuo*. M_n GPC = 35.6 kDa, M_w/M_n = 1.64. ¹H NMR (400 MHz, CDCl₃, 25 °C, δ_H ppm): 7.14-7.04 (m, 5H, ArH); 5.10-4.75 (m, 1H, -CHOC(=O)-); 5.05 (m, 2H, ArCH₂O); 4.65-4.50 (m, 1H, -CH₂OH overlapping with 2H of ArCH₂); 4.28-4.00 (m, 2H, -CH₂OC(=O)-, all other methylene protons from ester groups); 3.80-3.40 (m, 4H, -CH₂CH₂O-, ethylene glycol backbone, overlapping with 2H of -CH₂SC(=S)-); 2.50-1.30 (m, 20H of -CH₂CH₃ overlapping with 4H of -CH₂CHO and 3H of polyacrylate backbones and 3H of methyl groups). Additional data is reported elsewhere.¹

Membrane preparation: The cross-linked PDMS gutter layer was coated onto the PAN substrate as shown in Scheme 1. A typical example can be described as follows. In

separate vials, TMC (0.007 g, 0.0267 mmol) was dissolved in 0.35 mL of hexane (2.0 % w/v) and NH₂-PDMS-NH₂ (0.2 g, 0.04 mmol, 1 equiv.) was dissolved in 10 mL of hexane (2.0 % w/v). The two solutions were then mixed for 30 s and 1 mL of the solution was then spin-coated (1k rpm, 10 s) onto each PAN substrate (19.63 cm²) to prepare 10 substrates coated with the cross-linked PDMS gutter layer. The coated PAN substrates were dried *in vacuo* (1 mbar) at 25 °C over night and tested for their gas transport properties to ensure that there were no leakages before coating the selective layer. Pebax[®] 2533 was dissolved in a mixture of IPA/*n*-BuOH (3 : 1 vol. %) at 80 °C for 24 h to prepare the polymer solution (2.0 wt. % of Pebax[®] 2533). After cooling down the solution to room temperature, different amounts of the SNPs (SNP-1 and SNP-2) were added (0 to 50 wt. % relative to the amount of Pebax[®] 2533) and stirred at 50 °C for 30 min. The IPA/*n*-BuOH is a binary solvent which dissolve Pebax[®] 2533 and SNPs but does not damage the PDMS gutter layer or the microporous substrate. 1.5 mL of the mixture was then spin-coated (1,500 rpm, 20 s) onto the substrate that had been pre-coated with the PDMS gutter layer. The TFC membranes were then dried *in vacuo* (1 mbar) at 25 °C for 24 h and tested for their gas transport properties.

Gas permeation measurements: Single gas measurements of the TFC membranes were tested by an in-house built constant pressure variable volume (CPVV) apparatus shown in Figure S3. The TFC membranes were installed in a stainless cell and were tested for single gases (N₂ and CO₂) at 340 kPa and 35 °C. All data presented in this work were collected from at least three TFC membranes. PAN substrates that were pre-coated with PDMS gutter layer were also tested with the same gases under the same conditions to detect any leakages. The flow rates of the single gases were recorded manually with a digital flow meter (Agilent Technologies ADM 2000).

Mass transport theory: The mass transport in non-porous polymeric membranes follows the solution-diffusion mechanism that has been well documented in the literature.² The flux (J) of a single gas A can be calculated from equation (1):

$$J_A = P_A \left(\frac{\Delta p}{l} \right) \quad (1)$$

Where P_A is the permeability of gas A in Barrer, Δp is the pressure difference across the membrane in bar and l is the membrane thickness in μm .

The membrane permeance is defined as the permeability divided by the membrane thickness and has a unit of GPU. This permeance can also be expressed in terms of a total resistance to flow (R_T) by:

$$J_A = \left(\frac{P_A}{l} \right) \cdot \Delta p = \frac{\Delta p}{R_T} \quad (2)$$

In turn, the total resistance (R_T) to permeation through TFC membranes can be expressed as the sum of the resistances from the feed side boundary layer (R_F), the permeate side boundary layer (R_P), the membrane selective layer (R_{SL}) and the gutter layer (R_G) coated on the microporous substrate:

$$R_T = R_F + R_P + R_{SL} + R_G \quad (3)$$

The boundary layer resistances (R_F and R_P) arise from concentration gradients that are formed at the surface of the membrane in mixed gas systems. However, such concentration polarization is not possible for single gas permeation. Thus the total resistance to flow is related only to the respective thicknesses of the selective and gutter layers and their respective permeability:³

$$R_T = R_{SL} + R_G = \frac{l_{SL}}{P_{SL}} + \frac{l_G}{P_G} \quad (4)$$

The resistance to flow through the gutter layer ($R_G = l_G/P_G$) can be determined by measuring the flux through this layer prior to deposition of the selective layer. Equations (2) and (4) can then be used to determine the permeance and permeability through the selective layer, by measuring the flow through the combined TFC membrane. However, it should be noted that the estimation of the permeability is highly dependent on the accuracy in determining the thickness of the selective layer.

The ideal single gas selectivity ($\alpha_{A/B}$) between two gases A and B can be expressed by the following equation:

$$\alpha_{A/B} = \frac{P_A}{P_B} \quad (5)$$

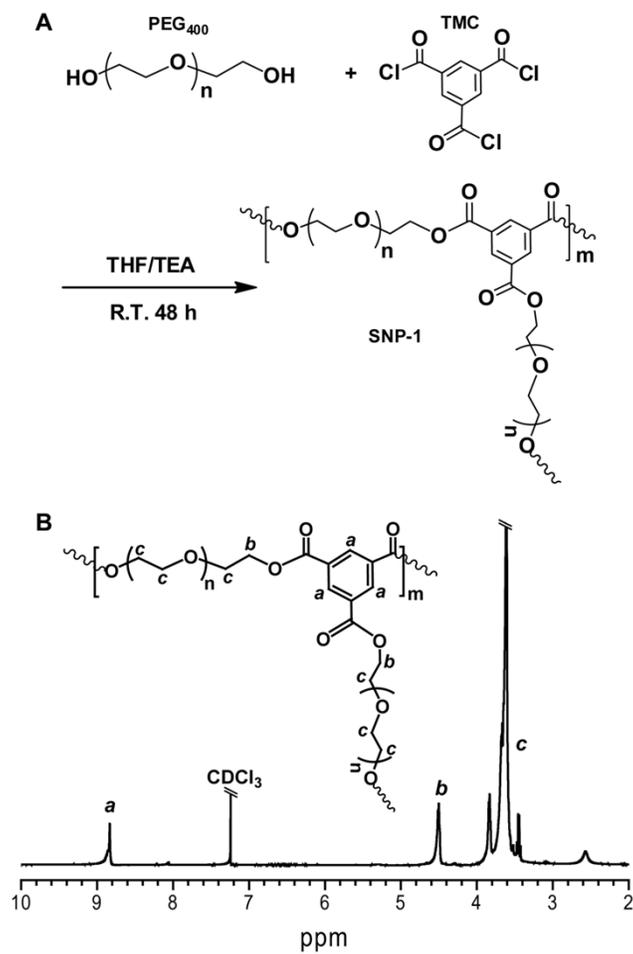


Fig. S1 (A) The synthesis of polymeric SNP-1 *via* condensation polymerization and (B) ^1H NMR spectrum of SNP-1 in CDCl_3 .

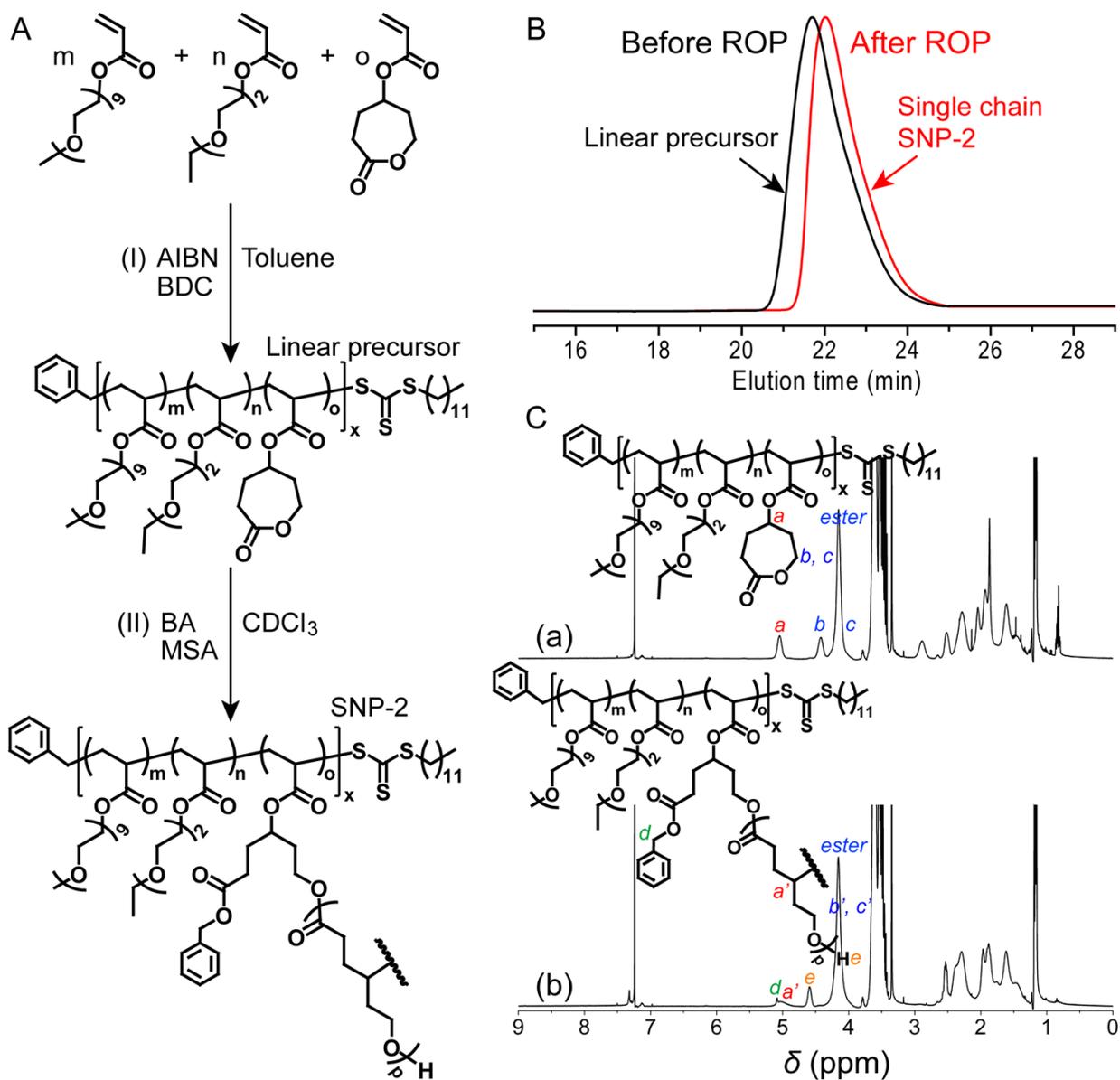


Fig. S2 (A) The synthesis of linear precursor (random copolymer) by RAFT polymerization (step I) and the preparation of single chain SNP-2 *via* ROP (step II). (B) GPC differential refractive index (DRI) chromatograms of linear precursor and the formed single chain SNP-2. (C) ¹H NMR spectra of linear precursor (a) and the single chain SNP-2 (b) in CDCl₃.

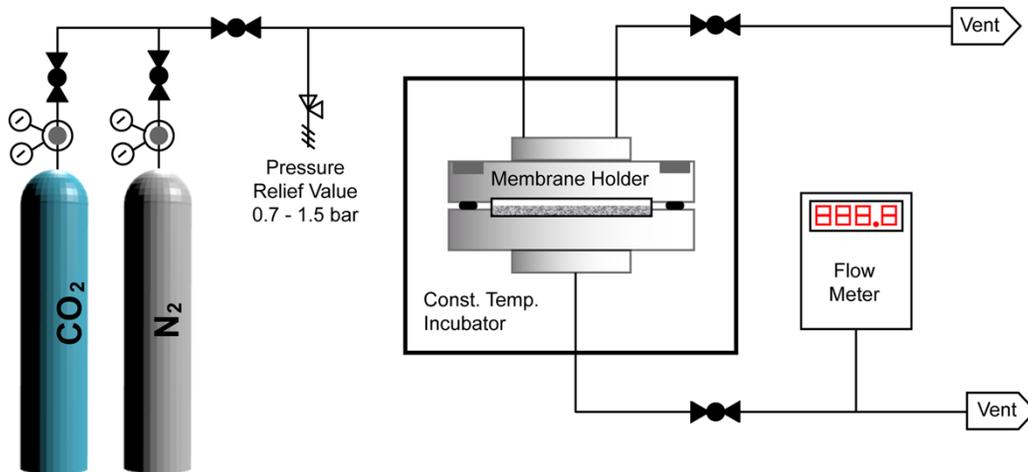


Fig. S3 Schematic diagram of apparatus for measurement of gas flow rate.

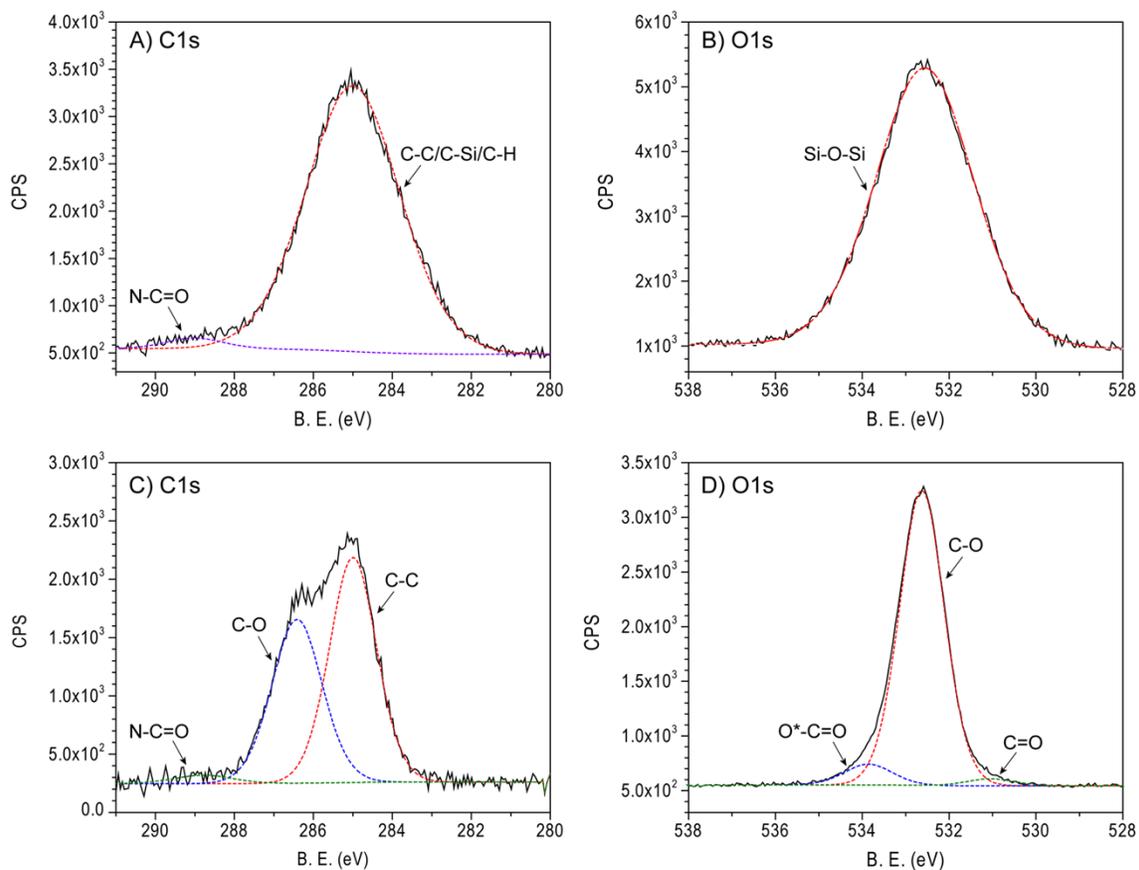


Fig. S4 High resolution XPS measurements of: (A-B) the PDMS gutter layer and (C-D) SNP-1 (50) TFC membrane with 50 wt % SNP-1 mass fraction.

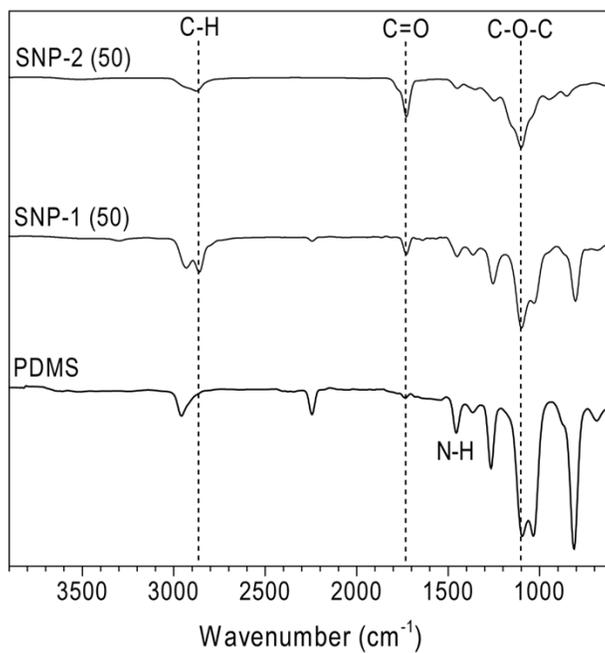


Fig. S5 ATR-FTIR spectra of the PDMS gutter layer, the SNP-1 (50) and SNP-2 (50) composite membranes.

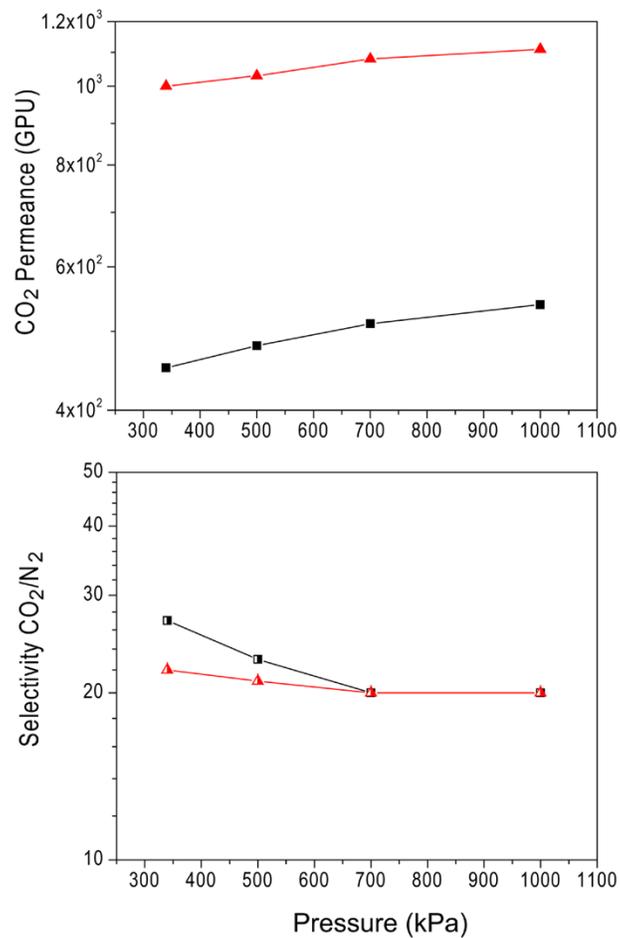


Fig. S6 CO₂ permeance and CO₂/N₂ selectivity of the Pebax[®] 2533 TFC membrane (black square) and SNP-1 (50) TFC membrane (red triangle) as a function of operation pressure tested at 35 °C.

Table S1. Gas separation performance of Pebax[®]/SNPs TFC membranes and their selective layers tested at 35 °C and 340 kPa.

Sample	SNP content (%)	TFC membranes ^a		Selective layer ^b			<i>l</i> ^c (nm)
		CO ₂ Permeance (GPU)	CO ₂ /N ₂ Selectivity	CO ₂ Permeance (GPU)	CO ₂ Permeability (Barrer)	CO ₂ /N ₂ Selectivity	
Pebax [®] 2533	0	414	23	509	158	25	310
SNP-1 (20)	20	514	23	642	202	26	315
SNP-1 (35)	35	673	23	846	275	25	325
SNP-1 (50)	50	920	21	1,240	397	24	320
SNP-1 (60)	60	1,170	16	1,930	618	20	320
SNP-2 (10)	10	507	23	615	200	26	325
SNP-2 (35)	35	564	26	702	225	30	320
SNP-2 (50)	50	601	28	757	250	33	330
LP (50)	50	1,280	15	2,210	641	19	290

^a The gas separation permeance of the TFC membranes.

^b The CO₂ permeance, permeability and CO₂/N₂ selectivity of the selective layers.

^c *l* is the thickness of the selective layer determined by SEM measurement.

Table S2. Gas separation performance of Pebax[®] 2533 and SNP1-50 TFC membranes as a function of feed gas pressure tested at 35 °C.

Pressure (kPa)	Pebax [®] 2533		SNP-1 (50)	
	CO ₂ (GPU)	CO ₂ /N ₂ Selectivity	CO ₂ (GPU)	CO ₂ /N ₂ Selectivity
340	415	23	920	22
500	442	23	948	21
700	470	20	994	20
1,000	496	20	1020	20

References

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