Supporting Information

Rational Molecular Design of PEOlated Ladder-structured Polysilsesquioxane Membranes for High Performance CO_2 Removal

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Materials

3-methacryloxypropyltrimethoxysilane (MMATMS) (Shin Etsu, 98%) and 2-[methoxy(polyethyleneoxy)propyl]trimethoxysilane (PEGTMS) (Gelest, 90%) were vacuum distilled over CaH_2 prior to use. Potassium carbonate (99%, Sigma Alrich) was used as received. Poly(1-trimethylsilyl-1-propyne) (PTMSP) (Gelest, 95%) was dried at 100 ^oC for 12 hours under vacuum before use. Tetrahydrofuran (J.T. Baker, 99.5%), dichloromethane (J.T. Baker, 99.5%) and all other solvents and reagents were used as received. Igracure 184 (BASF) was used as received.

Instrumentation

Number averaged molecular weight (M_n), weight averaged molecular weight (M_w) distributions (M_w/M_n) of the polymers were measured by JASCO PU-2080 plus SEC system equipped with refractive index detector (RI-2031 plus), UV detector (λ=254 nm, UV-2075 plus), using THF as the mobile phase at 40 °C with a flow rate of 1 mL min^{-1}. The samples were separated through four columns (Shodex-GPC KF-802, KF-803, KF-804, KF-805). ^1H-NMR, ^{29}Si NMR spectra were recorded in $CDCl_3$ at 25 °C on a Varian Unity INOVA (^1H: 300 MHz, ^{29}Si: 59.6MHz). FT-IR spectra were measured using Perkin-Elmer FT-IR system (Spectrum-GX) using solvent cast films on KBr pellets. X-ray diffraction patterns were obtained with the 4C2 light source at Pohong Accelerator Laboratory with λ=1.542 Å. Nanoindentation measurements were conducted on a Hysitron Inc. TriboIndenter equipped with a Berkovich diamond tip. Thermal transition of LPPEOMASQs was analysed by performing differential scanning calorimetry (DSC, Q20 (TA instrument)). Samples were scanned two times from -70 ^oC to 100 ^oC with a heating rate of 10 ^oC min^{-1} under N_2 purge. It is noted that there was no significant change between first and second scan.

Synthesis of ladder-like poly(methoxy(polyethyleneoxy)propyl-co-methacryloxpropyl)silsesquioxane (LPPEOMASQ64)

In a 100ml RB, a reaction solution containing K_2CO_3 (0.04 g, 0.29 mmol), H_2O (4.8 g, 0.27 mol), and THF (8 ml) was first prepared. To the above reaction solution, a monomer mixture solution of 2-[methoxy(polyethyleneoxy)propyl]trimethoxysilane (25.2 g, 48 mmol) and 3-methacryloxypropyltrimethoxysilane (7.95 g,32 mmol) was added. After magnetically stirring for 5 days at 40 ^{o}C, excess THF was evaporated, and the reaction mixture extracted with MC and water several times. Drying the MC layers over anhydrous magnesium sulfate, filtering, and evaporating MC yielded LPPEOMASQ64 as a light brown, viscous liquid. ^{1}H NMR ($CDCl_3$, ppm): 0.35-0.45 (m, $Si(C\mathit{H}_2CH_2CH_2OCOCCH_2CH_3$, $SiC\mathit{H}_2CH_2CH_2O(CH_2CH_2O)CH_3$, 4H), 1.8-1.9 (m, $Si(CH_2C\mathit{H}_2CH_2OCOCCH_2CH_3$, $SiCH_2C\mathit{H}_2CH_2O(CH_2CH_2O)CH_3$, 4H), 1.95-2.05 (m, $Si(CH_2CH_2CH_2OCOCCH_2C\mathit{H}_3$, 3H), 3.15-3.3 (m, $Si(CH_2CH_2C\mathit{H}_2OCOCCH_2CH_3$, $SiCH_2CH_2C\mathit{H}_2O(CH_2CH_2O)CH_3$, 4H), 3.7-3.8 (m, $SiCH_2CH_2CH_2O(C\mathit{H}_2C\mathit{H}_2O)_{6\text{-}9}CH_3$, 30H), 4.08-4.16 (m, $SiCH_2CH_2CH_2O(CH_2CH_2O)C\mathit{H}_3$, 3H), 5.3-6.1 (m, $Si(CH_2CH_2CH_2OCOCC\mathit{H}_2CH_3$, 2H) ^{29}Si NMR (ppm): -65~-67 ppm, , -68~-70 ppm. M_w = 24.3 k. LPPEOMASQ46 and LPPEOMA82 were synthesized using the above procedure, only modifying the PEGTMS:MMATMS initial monomer feed ratio to 4:6 and 8:2, respectively.

Membrane fabrication

Since LPPEOMASQs were viscous liquid states at room temperature, those did not need any solvents for the film formation. To crosslink LPPEOMASQs under mild UV irradiation, UV-induced crosslinking photoinitiator, Igracure 184 of 1 wt%, was added to proper amount of LPPEOMASQs. The dope solution was prepared by 20 ml vials lapped by Aluminium foil to avoid uncontrolled crosslinking by fluorescent light transmission. After rolling for 12hours, the prepared LPPEOMASQs were casted by a doctor's blade. The free-standing films were fabricated on a flat and clean hydrophobic film to measure single gas separation, which can give the information about inherent gas transport properties of LPPEOMASQs. Otherwise, LPPEOMASQs were coated on very thin PTMSP gutter layer supported by porous filter paper, since the free-standing LPPEOMSQ films were brittle due to the rigid double stranded siloxane structure. To prepare the PTMSP gutter layers, 4 wt% of dried PTMSP powder was dissolved in toluene by mixing on a roller for 12 hours. The porous filter paper was coated by PTMSP solution in Teflon ring at 110 ^{o}C under vacuum to vitrify PTMSP and then further dry was conducted at 110 ^{o}C for 12 hours. Crosslinking was conducted using Hitachi UV-lamp spot-cure system with total UV-output energy of 3 J cm^{-2}.

Single gas transport characterization

The purity of He, H_2, CO_2 and N_2 gases is 99.999% and that of O_2 and CH_4 was 99.995%. All tested gases in this work were purchased from Shin Yang Oxygen Co. (Seoul, Korea). The permeation tests were conducted at ca. 1 atm and 35 ^{o}C by using constant volume-variable pressure system.[1] Also, permeation isotherm was carried out at the same system up to ca. 7 atm at 35 ^{o}C for the H_2, CO_2 and N_2. For the gas permeation characterization, films were masked by Aluminum tape and attached on the downstream cell with epoxy treatment. The permeation cell was sealed by two different sized O-rings of upstream and downstream permeation cells and evacuated for at least 24 hours. Before each permeation test, the leak test was conducted to avoid overestimation of permeation rate. When upstream was pressurized, the pressure increasing rate in the downstream was monitored until it was reached to steady state (i.e., $(dp/dt)_{ss}$) as follow:

$$P = \frac{Vl}{RT\Delta pA} \times \frac{dp}{dt} \tag{1}$$

where P (Barrer, 1Barrer=10^{-10} cm^3(STP) cm cm^{-2} s^{-1} $cmHg^{-1}$) is permeability, V (cm^3) is permeate reservoir volume, l (cm) is membrane thickness, T (K) is temperature, Δp is pressure difference between feed side and permeate side, A (cm^2) is membrane area, R is ideal gas constant. Moreover, the apparent diffusivity (D) in Figure S7 was obtained from the time lag method:[2]

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

In equation (2), θ is the time lag of permeation, l is thickness of membrane.

Mixed gas transport characterization

For binary CO_2/N_2 and CO_2/H_2 (50/50 vol/vol) gas mixtures, mixed gas permeation tests were conducted by the constant-pressure variable-volume method at CO_2 partial pressure of ca. 3 atm and 35 ^{o}C.[3] The permeability (P*) of mixed gas can be defined by following equations:

$$P_A{*} = \frac{N_A \, l}{f_{A,\,feed} - f_{A,\,permeate}} \tag{3}$$

here, N *is* steady state flux, l is thickness of membrane, f_{feed} and $f_{permeate}$ are fugacity of feed and permeate side, respectively. The subscripts A and B are each component of gas mixture.

The selectivity (α*), separation factor, of binary gas mixture can be expressed as follow:

$$\alpha_{A/B}{*} = \frac{y_A/y_B}{x_B/x_B} \tag{4}$$

where y_A and y_B are the mole fraction of component A and B at permeate side, and x_A and x_B the mole fraction of component A and B at feed side, respectively.

By using back-pressure regulator (Tescom 44-1400), total pressure of feed side and permeate side was controlled and the pressure of permeate side was set to atmospheric level. The stage-cut, the ratio of permeate to feed flow rate, was maintained below 0.01 by controlling the flow rate of argon sweep gas using mass flow controller (Line Tech M3030VA), with a full scale of 10 cm^3(STP) min^{-1}. The permeated gas concentration was monitored by gas chromatography (GC, 490 Micro GC instrument (Agilent Technologies)) equipped with a thermal conductivity detector.

The structures of the LPPEOMASQs were confirmed by various characterization techniques. From ^{1}H NMR, only peaks corresponding to organic functional groups were observed, as both unhydrolyzed methoxy groups at 3.55 ppm and uncondensed silanol groups at 5.0 ppm were absent (See Figure S1a). ^{29}Si NMR analysis revealed the absence of T^2 peaks centered around -58 ppm and that all of LPPEOMASQs possessed fully condensed internal Si-O-Si structure as only the corresponding T^3 peaks were found for Si-PEO at -69 ppm, and Si-methacryloxypropyl at -67 ppm (See Figure S1b).[4] Moreover, the corresponding FT-IR spectra (Figure S1c) showed the characterization peaks of C=O, unsaturated vinyl C=C, and Si-O-Si at 1745 cm^{-1}, 1638 cm^{-1}, and 1050 cm^{-1}, 1100 cm^{-1}, respectively.

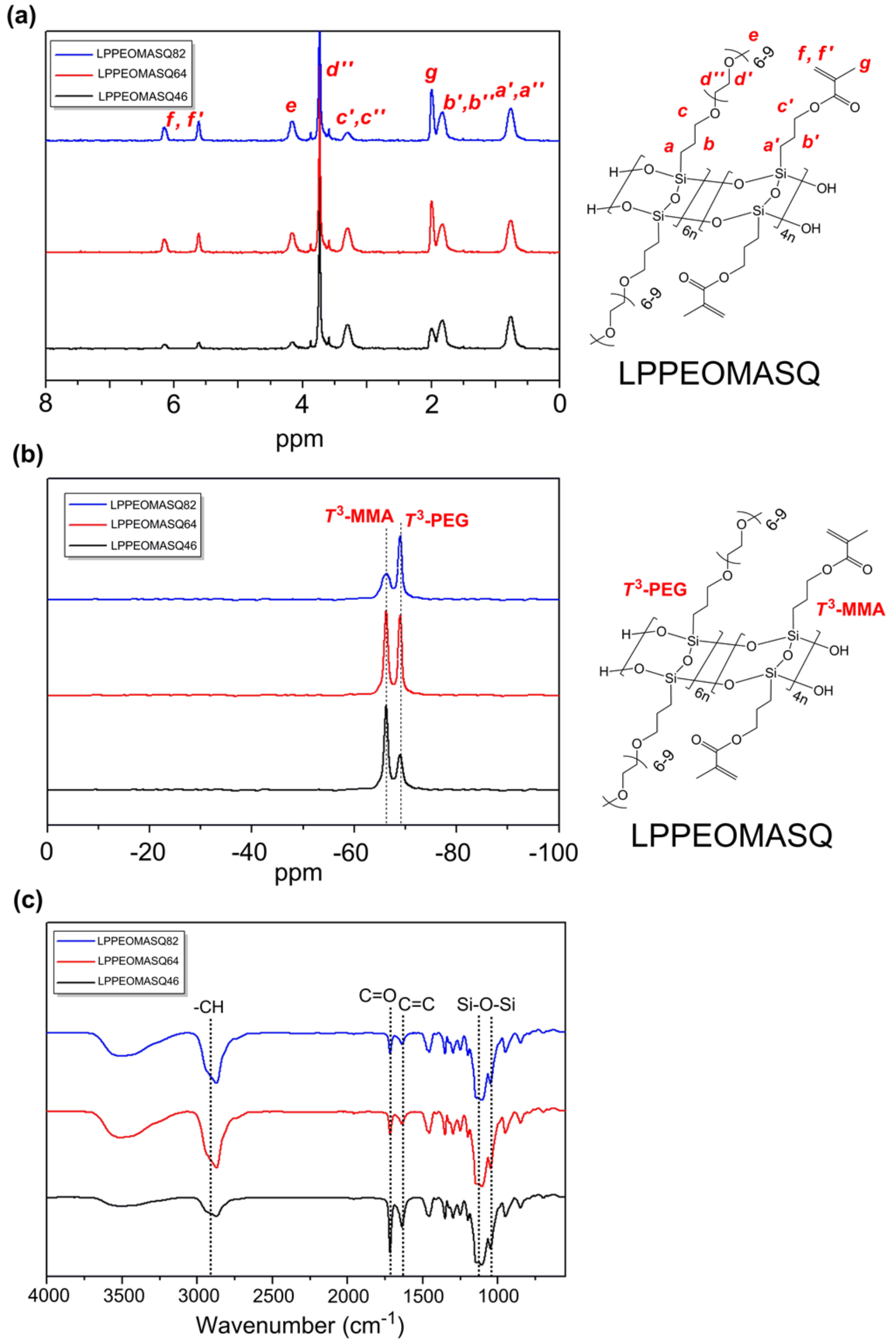

Fig. S1 Structural characterization of LPPEOMASQ series: (a) ^{1}H NMR, (b) ^{29}Si NMR, and (c) FT-IR spectra.

Also, the UV-induced crosslinking process (See Figure S2) was confirmed by comparing FT-IR spectra before and after UV-induced crosslinking for LPPEOMASQ membranes. As shown in Figure S2, the unsaturated C=C bonds in LPPEOMASQ64 centered at 1638 cm^{-1} completely disappeared after UV-exposure, validating that the presence of methacryloxypropyl groups allowed for the complete crosslinking under mild UV irradiation (3 J cm^{-2}).

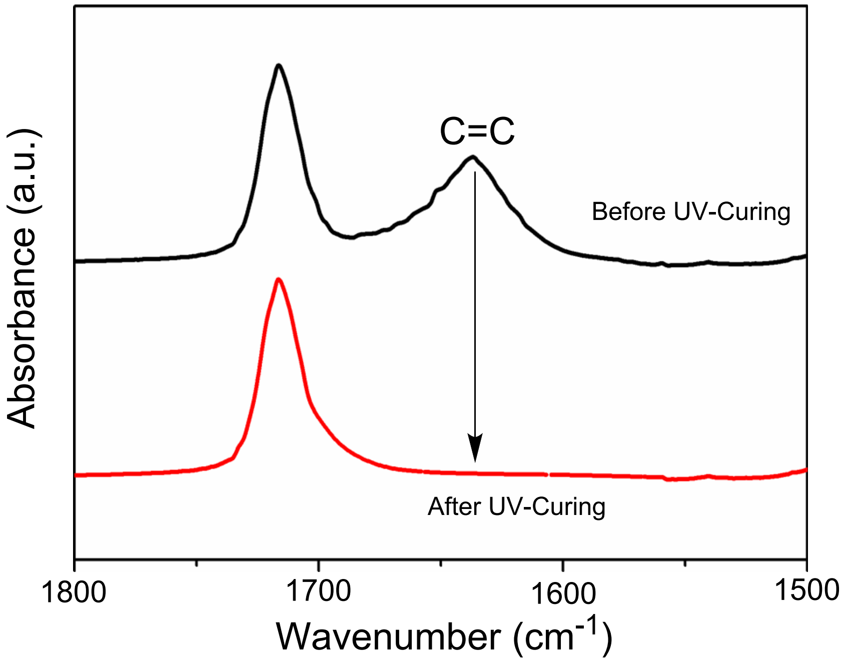

Fig. S2 FT-IR spectra for LPPEOMASQ64 before and after UV-induced crosslinking.

Table S1 2θ values and d-spacing of LPPEOMASQs.

Sample	***X***^{a} (2θ (°) / d-spacing (nm)) Before Crosslinking	***Y***^{b} (2θ (°) / d-spacing (Å)) Before Crosslinking	***X***^{a} (2θ (°) / d-spacing (Å)) After Crosslinking	***Y***^{b} (2θ (°) / d-spacing (Å)) After Crosslinking
LPPEOMASQ46	3.8° / 2.3 nm	21.5° /4.15 Å	-	21.5° /4.15 Å
LPPEOMASQ64	2.9° / 3.0 nm	21.5° /4.15 Å	-	21.5° /4.15 Å
LPPEOMASQ82	2.3° /3.8 nm	21.5° /4.15 Å	-	21.5° /4.15 Å

^{a} ***X*** indicates inter chain distance. ^{b} ***Y*** indicates intra chain-to-chain distance of LPPEOMASQs.

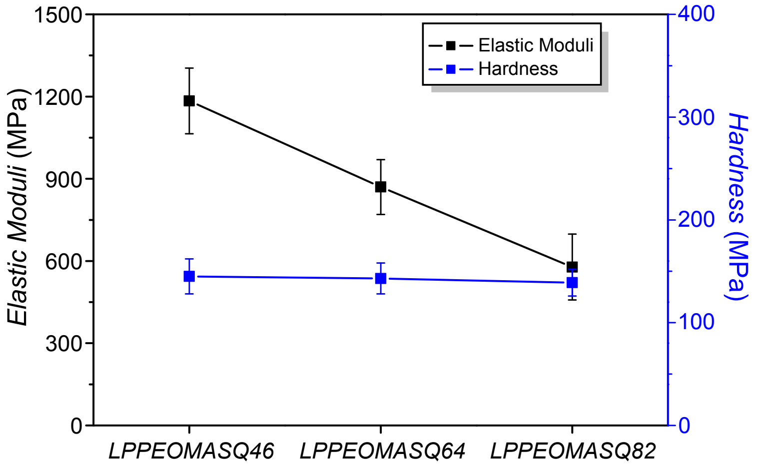

Fig. S3 Nanoindentation method-based mechanical properties for UV-crosslinked LPPEOMASQ membranes.

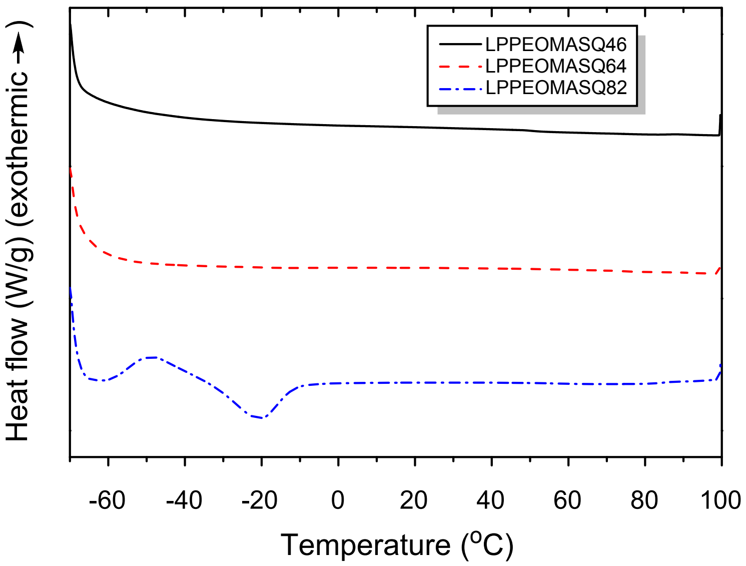

Fig. S4 DSC results of UV-crosslinked LPPEOMASQ membranes.

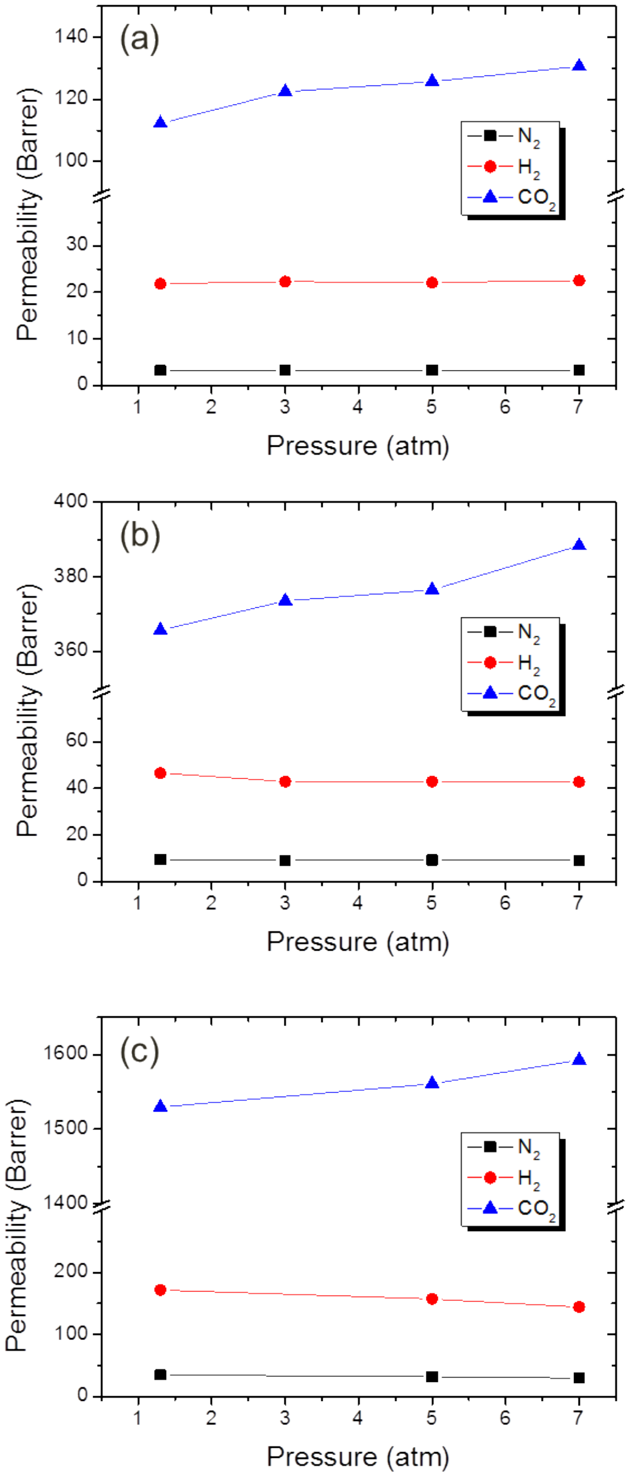

Fig. S5 Permeation isotherms for (a) LPPEOMASQ46, (b) LPPEOMASQ64, and (c) LPPEOMASQ82 at 35 °C.

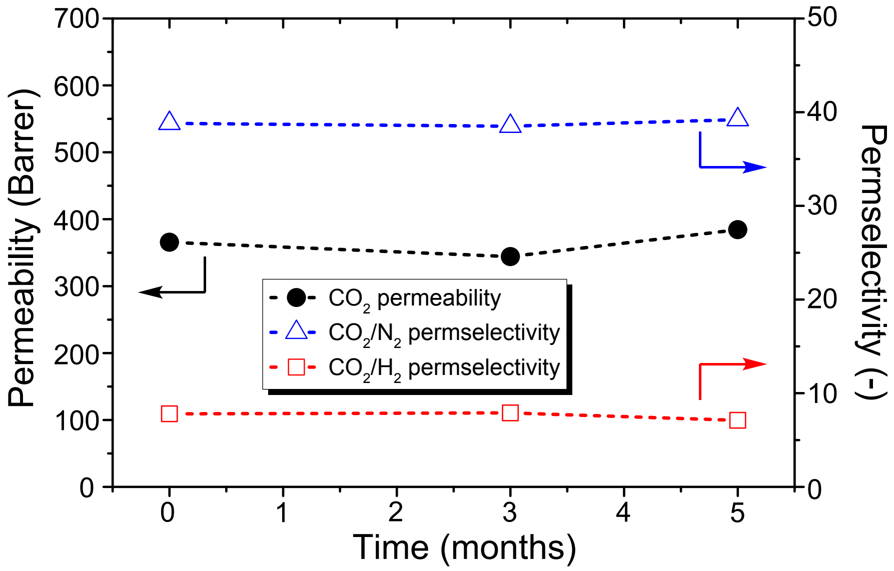

Fig. S6 Long-term stability tests of LPPEOMASQ64 measured at ca. 1 atm and 35 ^{o}C.

Table S2 Single gas permeation results for LPPEOMASQs at ca. 1 atm and 35 ^oC.

Sample	Permeability [Barrer]					
	He	H_2	CO_2	O_2	N_2	CH_4
LPG64[4]	14.25 ± 0.42	19.91 ± 1.03	47.88 ± 2.26	5.13 ± 0.23	1.57 ± 0.06	3.59 ± 0.18
LPPEOMASQ46	15.78 ± 0.97	21.85 ± 2.72	112.27 ± 4.07	8.60 ± 1.49	3.22 ± 0.85	8.44 ± 0.81
LPPEOMASQ64	30.07 ± 0.07	46.59 ± 1.39	365.67 ± 9.06	22.50 ± 0.20	9.42 ± 0.35	28.70 ± 0.39
LPPEOMASQ82	140.80 ± 18.55	171.51 ± 29.28	1529.69 ± 75.34	88.79 ± 10.01	34.86 ± 2.16	130.50 ± 19.42

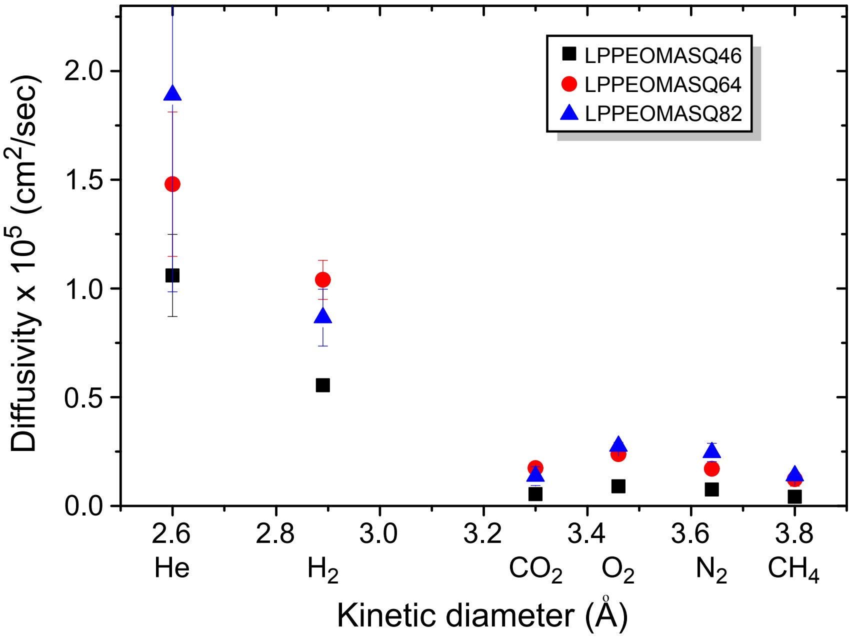

Fig. S7 Diffusivity of all gases in LPPEOMASQs tested at ca. 1 atm and 35 °C as a function of kinetic diameter of gas molecules.

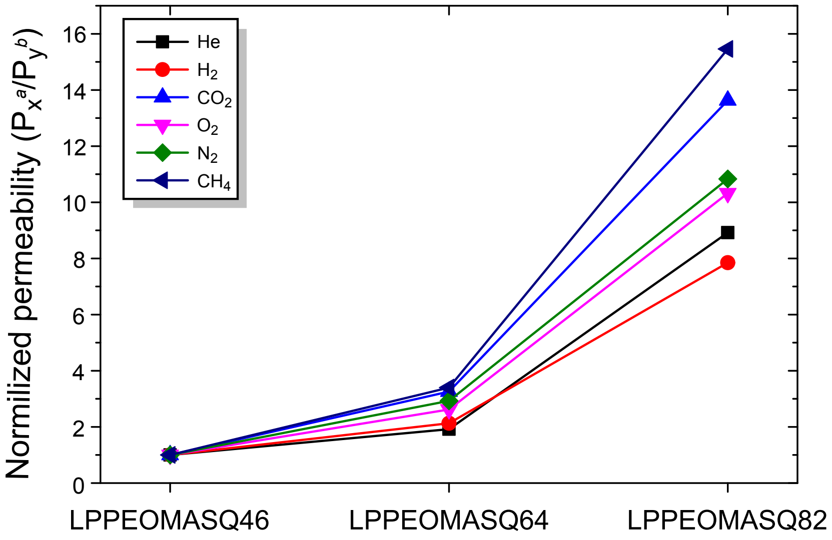

Fig. S8 Normalized single gas permeability for LPPEOMASQs as a function of PEO ratios.

[a] P_x is the permeability of LPPEOMASQ46, LPPEOMASQ64 and LPPEOMASQ82. [b] P_y is the permeability of LPPEOMASQ46.

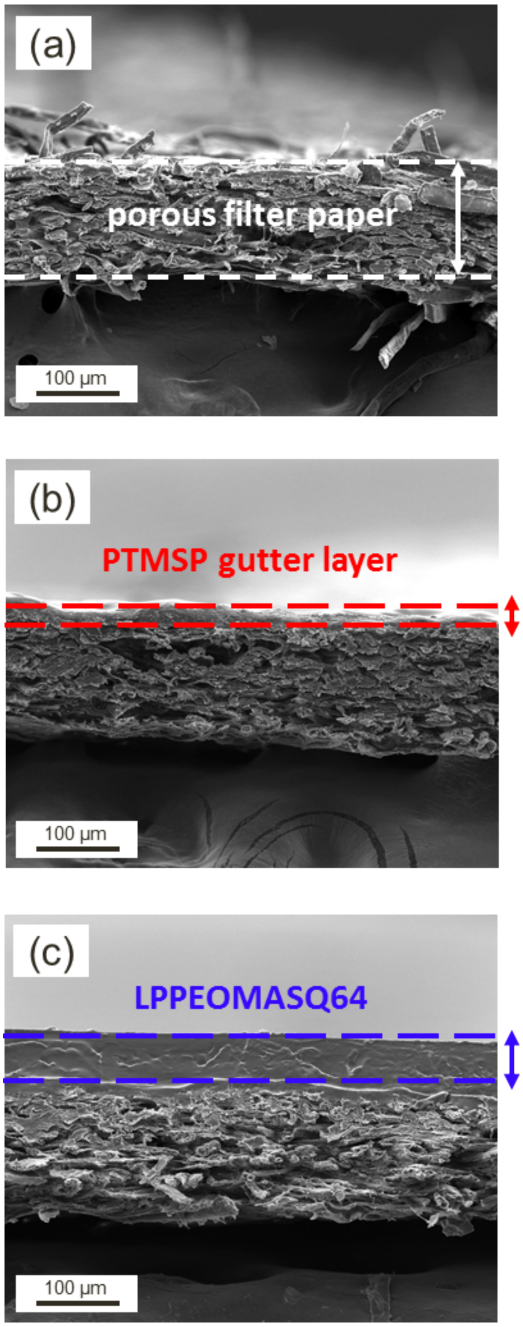

Fig. S9 Cross-sectional SEM images of coated LPPEOMASQ64 film: (a) pristine porous filter paper, (b) PTMSP gutter layer and porous filter paper, and (c) LPPEOMASQ64 with a PTMSP gutter layer on porous filter paper.

References

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