Supporting Information

Rational Molecular Design of PEOlated Ladder-structured Polysilsesquioxane Membranes for High Performance CO₂ 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 CaH2 prior to use. Potassium carbonate (99%, Sigma Aldrich) was used as received. Poly(1-trimethylsilyl-1-propyne) (PTMSP) (Gelest, 95%) was dried at 100 °C 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 ($\lambda$=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). $^1$H-NMR, $^{29}$Si NMR spectra were recorded in CDCl3 at 25 °C on a Varian Unity INOVA ($^1$H: 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 $\lambda$=1.542 Å. Nanoindentation measurements were conducted on a Hysitron Inc. TribolIndenter 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 °C to 100 °C with a heating rate of 10 °C min$^{-1}$ under N2 purge. It is noted that there was no significant change between first and second scan.

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

In a 100ml RB, a reaction solution containing $K_2CO_3$ (0.04 g, 0.29 mmol), H2O (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 °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(CH$_2$CH$_2$CH$_2$OCH$_2$CH$_2$O)CH$_3$, 4H), 1.8-1.9 (m, Si(CH$_2$CH$_2$OOCCH$_2$CH$_3$, SiCH$_2$CH$_2$O(CH$_2$CH$_2$O)CH$_3$, 4H), 1.95-2.05 (m, Si(CH$_2$CH$_2$OOCCH$_2$CH$_3$, 3H), 3.15-3.3 (m, Si(CH$_2$CH$_2$OOCCH$_2$CH$_3$, 4H), 3.7-3.8 (m, SiCH$_2$CH$_2$O(CH$_2$CH$_2$O)$_{6-9}$CH$_3$, 30H), 4.08-
4.16 (m, SiCH$_2$CH$_2$O(CH$_2$CH$_2$O)CH$_3$, 3H), 5.3-6.1 (m, Si(CH$_2$CH$_2$OOCCH$_2$CH$_3$, 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 12 hours,
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 LPPEOMASQ 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 °C under vacuum to vitrify PTMSP and then further
dry was conducted at 110 °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 °C by using constant volume-variable pressure system. Also, permeation isotherm was carried out at the same system up to ca. 7 atm at 35 °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:

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

(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, $\Delta p$ 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:

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

(2)

In equation (2), $\theta$ 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 °C. The permeability ($P^*$) of mixed gas can be defined by following equations:

$$P_A^* = \frac{N_A l}{f_{A,\text{feed}} - f_{A,\text{permeate}}}$$  \hspace{1cm} (3)

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

The selectivity ($\alpha^*$), separation factor, of binary gas mixture can be expressed as follow:

$$\alpha_{A/B}^* = \frac{y_A/y_B}{x_A/x_B}$$  \hspace{1cm} (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). 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.](image)
**Table S1** $2\theta$ values and d-spacing of LPPEOMASQs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$X^a$ (2$\theta$ (°) / d-spacing (nm))</th>
<th>$Y^a$ (2$\theta$ (°) / d-spacing (Å))</th>
<th>$X^a$ (2$\theta$ (°) / d-spacing (Å))</th>
<th>$Y^a$ (2$\theta$ (°) / d-spacing (Å))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before Crosslinking</td>
<td>Before Crosslinking</td>
<td>After Crosslinking</td>
<td>After Crosslinking</td>
</tr>
<tr>
<td>LPPEOMASQ46</td>
<td>3.8° / 2.3 nm</td>
<td>21.5° / 4.15 Å</td>
<td>-</td>
<td>21.5° / 4.15 Å</td>
</tr>
<tr>
<td>LPPEOMASQ64</td>
<td>2.9° / 3.0 nm</td>
<td>21.5° / 4.15 Å</td>
<td>-</td>
<td>21.5° / 4.15 Å</td>
</tr>
<tr>
<td>LPPEOMASQ82</td>
<td>2.3° / 3.8 nm</td>
<td>21.5° / 4.15 Å</td>
<td>-</td>
<td>21.5° / 4.15 Å</td>
</tr>
</tbody>
</table>

$^a X$ 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 °C.
Table S2 Single gas permeation results for LPPEOMASQs at ca. 1 atm and 35 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Permeability [Barrer]</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>He</td>
</tr>
<tr>
<td>LPG64⁴</td>
<td>14.25 ± 0.42</td>
</tr>
<tr>
<td>LPPEOMASQ46</td>
<td>15.78 ± 0.97</td>
</tr>
<tr>
<td>LPPEOMASQ64</td>
<td>30.07 ± 0.07</td>
</tr>
<tr>
<td>LPPEOMASQ82</td>
<td>140.80 ± 18.55</td>
</tr>
</tbody>
</table>
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