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Rational Molecular Design of PEOlated Ladder-structured Polysilsesquioxane Membranes for High Performance CO₂ Removal†

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Poly(methoxy(polyethyleneoxy)propyl-co-methacryloxypropyl) silsesquioxane membranes with different copolymer ratios were successfully fabricated via UV-induced crosslinking with mechanical stability. By selectively introducing polyethylene oxide (PEO) groups covalently bound to the ladder-structured polysilsesquioxane, we effectively suppressed the PEO crystallization, allowing for excellent CO₂/H₂ and CO₂/N₂ separations under single as well as mixed gas conditions.

Over the past several decades, the increase in CO₂ emissions arising from anthropogenic activities such as fossil fuel combustion, creation of biomass energy facilities, and mass chemical production has hastened the need for new materials to effectively mitigate the CO₂ emissions. In fact, CO₂ separation, capture, and sequestration have become crucial technologies for scientists to alleviate concerns over CO₂ emission-induced global warming.¹ While several methods of CO₂ separations are potentially feasible, membrane-based separations offer significant advantages because they require small footprints as well as less energy. Especially, membrane-based separations circumvent thermal requirements of other CO₂ capture alternatives such as distillation or aqueous amine-based absorption, markedly improving energy efficiency.

There have been diverse strategies for the development of gas separation membranes to achieve high performance CO₂ removal such as mixed matrix membranes (MMMs),² inorganic membranes,³ microporous organic polymer (MOP) membranes⁴ etc. Among them, polyethylene oxide (PEO)-

based membranes have been actively investigated due to the specific interaction between the dipole ethylene oxide group of PEO and quadrupole of CO₂.⁵ Unfortunately, PEO itself is a semi-crystalline polymer and comprises a high ratio of an impermeable crystalline phase, about 70%, resulting in a relatively low CO₂ permeability (i.e., 12 Barrer at 35 °C and infinite dilution).⁶ There have been various strategies to inhibit the drawbacks of PEO-based membranes including PEO-containing copolymers, PEO polymeric blends, crosslinked PEO-containing polymers and PEO hybrids.^{7–10} In most cases, the PEO-based membranes, however, melt at ambient temperature and their poor mechanical properties hamper their large-scale practical applications.

In order to overcome the trade-off between separation performance and mechanical strength, hybridization of PEO-based materials has been investigated. The initial approach based on the crosslinking of a polyether diamine with different organosilanes suffered from decrease in permeability with addition of tetraethoxysilane due to the reduction in the free volume as well as the increase in chain rigidity.¹¹ Another approach based on copolymerization of acrylate-based oligomers with 3-[tris-(trimethylsiloxy)silyl] propyl acrylate (TRIS-A) via UV-crosslinking sacrificed CO₂/light gas selectivity due to a strong non-polar nature of TRIS-A.¹² The Chung group extended the above protocol by additional blending of polyethylene glycol and observed that melting of PEO-based additives substantially increase the CO₂ permeability.¹³ A common theme among these methods was that the hybridization of PEO-based materials utilized the inorganic phases as secondary components, and the irregular inorganic structure led to inhomogeneous junctions between inorganic and organic phases.^{12, 14} As such, a new hybrid PEO-based material obtained through rational design of the thermal, mechanical, and gas transport properties equipped with controlled inorganic structure is much to be desired.

Polysilsesquioxanes (PSSQs) are a class of hybrid material with a chemical formula of (SiO_{1.5}R)_n, derived from trifunctional silanes through sol-gel chemistry.¹⁵ Ladder-structured PSSQs (LPSQs), while less known, consist of

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controlled, double stranded ladder-like structure, with the various organic functional groups radially stemming outwards.¹⁶ In this work, we successfully synthesized PEO-containing hybrid LPSQ materials by direct co-hydrolysis and condensation under basic conditions¹⁶⁻¹⁸ and fabricated free-standing, CO₂-selective LPSQ membranes via UV-crosslinking reaction (Fig. 1). The synthesis of our LPSQ/PEO hybrids enabled control over the copolymer composition in a homogenous phase, thus eliminating the agglomeration of inorganic phases. The effect of different copolymer ratios (i.e., methoxy(polyethyleneoxy)propyl: methacryloxypropyl = 40:60, 60:40 and 80:20 mol:mol denoted as LPPEOMASQ46, LPPEOMASQ64, LPPEOMASQ82, respectively) were investigated as related to CO₂ separation. The rational design of the various LPPEOMASQs originated from three meritable traits: (1) the inorganic rigid-rod Si-O-Si ladder structure giving rise to thermal and mechanical integrity, (2) PEO groups functionalized radially to the ladder-like Si-O-Si backbone for enhanced CO₂ solubility and suppressed crystallization, and (3) methacryloxypropyl groups for UV-curable function in order to obtain highly robust free-standing films. The structures of the LPPEOMASQs were confirmed by various characterization techniques including ¹H NMR, ²⁹Si NMR and FT-IR (Fig. S1, ESI[†]). Also, the UV-induced crosslinking process was confirmed by FT-IR (Fig. S2, ESI[†]) under mild conditions (3 J cm⁻²).

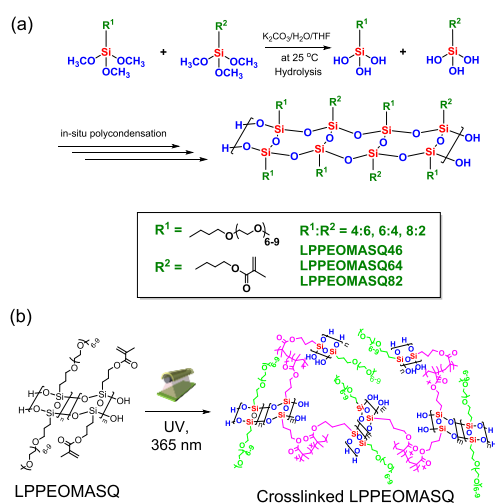


Fig. 1 (a) Synthesis of LPPEOMASQ, (b) UV-induced Crosslinking of LPPEOMASQ membranes.

The efficacy of PEO crystallinity suppression was verified by the absence of the general PEO crystalline peaks, 19° and 23° in the WAXD patterns (Fig. 2), implying that the rigid Si-O-Si backbone may effectively prevent the short PEO chains from forming impermeable crystalline phases.¹⁹ As expected, as-synthesized LPPEOMASQs revealed both the inter- and intra-chain-to-chain distance peaks at $2.3\sim 3.8^\circ$ and 21.5° , respectively (Table S1, ESI[†]).¹⁷ It was of great interest that the inter-chain distances increased with increase in PEO contents, implying that the LPPEOMASQ with a higher ratio of PEO to methacryloxypropyl groups may result in higher free volume. It may be attributed to the fact that the van der Waals (vdW) volume of the methoxy(polyethyleneoxy)propyl group was

greater than that of the methacryloxypropyl group (i.e., 205.0 cc/mol vs. 76.5 cc/mol) even in the case of lowest molecular weight of PEO. Choi et al.¹⁸ also observed that the intermolecular distance decreased with increase in copolymer ratio of phenyl to methacryloxypropyl groups in ladder-structured poly(phenyl-co-methacryl) silsesquioxanes, where the vdW volume of phenyl group is 45.85 cc/mol and that of methacryloxypropyl group is 76.5 cc/mol . The crosslinked LPPEOMASQs, however, gave only a single characteristic peak centered at 21.5° corresponding to the intra-chain-to-chain distance (i.e., 4.2 \AA) of a double stranded siloxane (Table S1, ESI[†]). The absence of intermolecular chain-to-chain distance peak reflects that the LPPEOMASQs were fully crosslinked amorphous network structure.

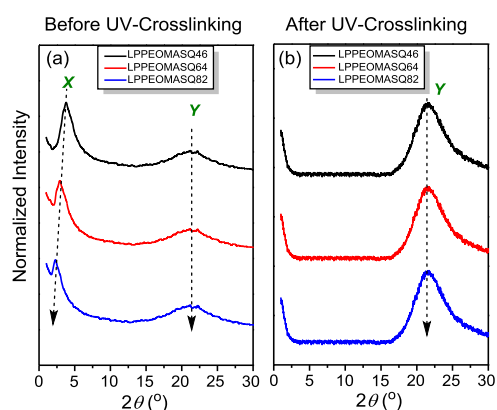


Fig. 2 XRD Patterns for LPPEOMASQ membranes; (a) before UV-crosslinking and (b) after UV-crosslinking.

For the practical application of gas separation membranes their mechanical and thermal properties are also critical. As shown in Fig. S3 in ESI[†], the nanoindentation method-based mechanical properties (i.e., elastic moduli and hardness) of all the UV-crosslinked LPPEOMASQs were comparable with those of conventional organic polymers and PSSQs, implying that the crosslinked LPPEOMASQs were quite robust and stable.^{20, 24} The crosslinked LPPEOMASQ82, however, became relatively brittle due to the shortage in the relative number of crosslinking groups, the methacryloxypropyl groups to the PEO groups.

Moreover, glass transition temperatures (T_g) for all of the crosslinked LPPEOMASQ samples were absent, similar to previous LPSQs.^{17, 22} This is noteworthy, as the PEO groups were only tethered to the ladder-like Si-O-Si backbone, leaving it to be 'free-dangling', as opposed to previous reports of crosslinking with di-functional PEO monomers such as PEGDA, which commonly give T_g around -40°C . Furthermore, both LPPEOMASQ46 and LPPEOMASQ64 showed no discernible thermal transition between -70 and 100°C . Both crystallization temperature (T_c) and melting temperature (T_m) were, however, present at -49.5 and -20.4°C , respectively for LPPEOMASQ82, the highest PEO ratio LPPEOMASQs in this study (Fig. S4, ESI[†]). It is probably attributed to the shortage in the relative number of the crosslinker, the methacryloxypropyl to the PEO groups, failing to suppress the crystallization of all the PEO groups. Nevertheless, since the T_m of LPPEOMASQ82 was substantially

below room temperature, turning the PEO-phases liquid-like, LPPEOMASQ82 was hypothesized to have superior CO₂-selective gas transport properties over their copolymer counterparts.

Fig. 3 exhibits single gas CO₂, N₂ and H₂ permeation properties for all of crosslinked free-standing LPPEOMASQ membranes at 35 °C with different feed pressures. It was noted that the CO₂ component was characterized last to remove the complication of CO₂-induced plasticization and that the permeation results for the ladder-structured poly(phenyl-co-glycidoxypropyl) silsesquioxane (LPG64) were taken from our previous work for comparison.¹⁷ Also, our LPPEOMASQ membranes exhibit reverse-selective trends for CO₂/H₂ separations, similar to other PEO-containing membranes (Fig. 3b).⁹ As shown, both CO₂/N₂ and CO₂/H₂ separation performances were remarkably improved with an increase in PEO contents. Especially, the LPPEOMASQ82 membrane exhibited an exceptional increase in CO₂ permeability due to the melting of PEO crystalline phases, exceeding the most current CO₂/N₂ upper bound (i.e., CO₂ permeability of 1596.23 Barrer, CO₂/N₂ selectivity of 53.6 at ~7 atm and 35 °C).²³ Although the melting of PEO can be detrimental for the membrane formation, the structural integrity of the LPPEOMASQ82 membrane was retained due to the covalently bound inorganic-organic junctions of the ladder-like siloxane backbone to the PEO groups, further validated by the mechanical properties (Fig. S3, ESI[†]). The pressure-dependent permeabilities in our LPPEOMASQ membranes exhibited similar trends with those of rubbery polymers or typical PEO-based materials (Fig. S5, ESI[†]).^{6, 24} While the gas permeabilities of H₂ and N₂ in all of the LPPEOMASQ membranes were relatively constant regardless of feed pressure, CO₂ permeability increased with increase in feed pressure, improving both CO₂/N₂ and CO₂/H₂ separation performance (Fig. 3). Moreover, the CO₂ permeability as well as CO₂/N₂ and CO₂/H₂ selectivity was well preserved for several months, confirming the long-term stability of LPPEOMASQ membranes (See Fig. S6, ESI[†]).

Other single gas transport measurements (i.e., He, O₂, and CH₄) in crosslinked free-standing LPPEOMASQ membranes were also conducted at ~1 atm and 35 °C (Table S2, ESI[†]). As our previous work demonstrated that the permeation of all the gas penetrants in LPSQ membranes occurred through organic side chains by the solution-diffusion mechanism,¹⁷ we similarly expected that all of the gas penetrants would permeate through the organic functional groups in our LPPEOMASQ membranes. All of the LPPEOMASQ membranes involve the ether oxygen as well as the siloxane structure like the LPG64 studied previously,¹⁷ both of which contribute to improve CO₂ solubility, consequently exhibiting relatively high CO₂ permeability than all of other permanent gases.^{25, 26} As the relative content of PEO to methacryloxypropyl groups increased, the permeabilities for all the gases tended to increase due to the increase in fractional free volume (FFV) as well as the lower degree of crosslinking. As our XRD results in Fig. 2 demonstrated, a higher ratio of PEO to methacryloxypropyl groups showed an increase in the

intermolecular chain-to-chain distance, probably resulting in higher FFV even after UV-crosslinking. The higher FFV contributes to improve permeability, mainly due to the increased diffusivity (Fig. S7, ESI[†]). It is noted that the small sized gases (i.e., He or H₂) showed large inaccuracy of diffusivity especially for LPPEOMASQ64 and LPPEOMASQ82 due to the short time lag. In addition, the rubbery-like transport characteristics became more obvious for our LPPEOMASQ membranes with increase in PEO contents. As shown in Fig. S8 in ESI[†], the order of the extent for increase in gas permeability is as follows: H₂ < He < N₂ ~ O₂ < CO₂ < CH₄. Consequently, the CO₂ permeability as well as CO₂/N₂ and CO₂/H₂ selectivity increased with increasing PEO contents.

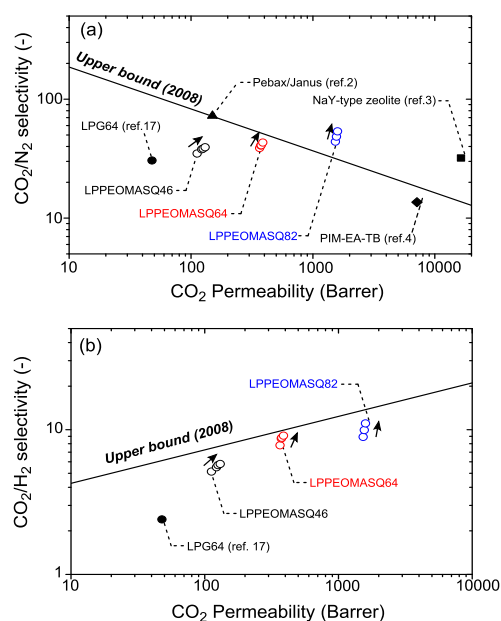


Fig. 3 Single gas permeation of (a) CO₂/N₂ and (b) CO₂/H₂ for LPPEOMASQ membranes in the upper bound plots (2008), with the arrows directing the increase in feed pressures from ~1 atm to 7 atm.

Moreover, by introducing a coating technique, further practical applications of LPPEOMASQs were possible. The permeation tests of single gas and binary CO₂/N₂ and CO₂/H₂ gas mixtures (50/50 vol/vol) were conducted on the coated LPPEOMASQ64 at CO₂ partial pressure of ~3 atm and 35 °C. The LPPEOMASQ64 was coated on the poly(1-trimethylsilylpropyne) (PTMSP) gutter layer to minimize the resistance, supported by porous filter paper (See Fig. S9, ESI[†]). The coated LPPEOMASQ64 still showed good single gas separation performances, although the permeability decreased for all of penetrants (See Fig. 4). As shown in Fig. 4 (a), the mixed CO₂/N₂ gas separation performance was depreciated compared to the corresponding single gas-based counterpart due to the strong competition between penetrants.²⁸ However, the mixed CO₂/H₂ gas separation performance was enhanced (See Fig. 4 (b)). Since the interaction between PEO and CO₂ is much stronger than H₂, H₂ transport was interrupted, decreasing H₂ permeability, consequentially improving the CO₂/H₂ separation factor.²⁹

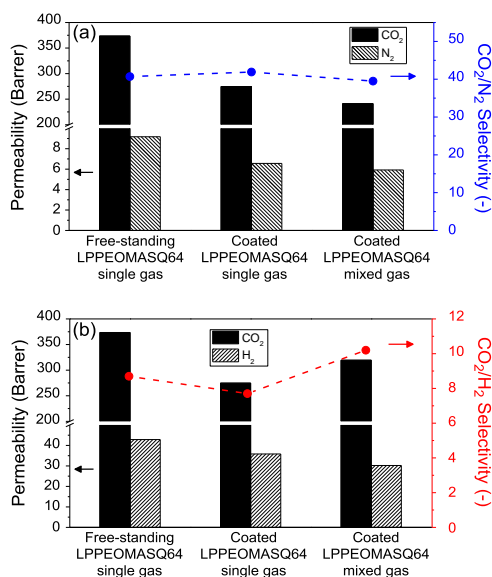


Fig. 4 Separation performance of free-standing or coated LPPEOMASQ64 membranes for single gas and binary gas mixture of (a) CO_2/N_2 (50/50 vol/vol) and (b) CO_2/H_2 (50/50 vol/vol) at CO_2 partial pressure of ~ 3 atm and 35°C .

In summary, the LPPEOMASQ membranes prepared by our rational molecular design achieved exceptionally high CO_2/N_2 and CO_2/H_2 separation performances, exceeding Robeson's most recent upper bounds, with good mechanical stability. The covalent bonding of PEO functional groups to the rigid siloxane structure effectively suppressed PEO crystallinity, allowing all the gases to permeate preferably through the amorphous and flexible PEO phase. Especially, as the copolymer ratio of methoxy(polyethyleneoxy)propyl to methacryloxypropyl increased up to 80/20 mol/mol, improvements in diffusivity for all the gas penetrants were pronounced, substantially enhancing the permeability. Moreover, coated LPPEOMASQ64 membranes still exhibited excellent gas separation performances, especially for CO_2/H_2 separations. Our current results suggest that the LPSQ can offer a new platform for advanced gas separation membranes.

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