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Plasticization-Enhanced Hydrogen Purification Using Polymeric Membranes

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Polymer membranes are attractive for molecular-scale separations such as hydrogen purification because of inherently low energy requirements. However, membrane materials with outstanding hydrogen separation performance in feed streams containing high-pressure carbon dioxide and impurities such as hydrogen sulfide and water are not available. We report highly permeable, reverse-selective membrane materials for hydrogen purification, as exemplified by molecularly engineered, highly branched, cross-linked poly(ethylene oxide). In contrast to the performance of conventional materials, we demonstrate that plasticization can be harnessed to improve separation performance.

Hydrogen is produced primarily by steam reforming of hydrocarbons followed by the water-gas shift reaction, which yields a hydrogen product containing impurities such as CO2, H2S, and H2O (1). The hydrogen must be purified for further use, and based on the high volumes currently produced and the likelihood for this production to increase, even a small improvement in H2 purification efficiency could substantially reduce the costs. Membrane technology is attractive for molecular-scale separations because of inherent advantages such as high energy efficiency, excellent reliability, and a small footprint (2–5). The potential applicability of membrane technology relies strongly on the ability of membrane materials to exhibit high separation performance at practical feed conditions (e.g., with feed streams that contain high-pressure CO2 and impurities such as H2S and H2O).

Highly permeable and highly selective membrane materials are desired for CO2/H2 separation. Gas permeability P, which is the steady-state, pressure- and thickness-normalized gas flux through a membrane, is usually expressed as P = S × D, the product of gas solubility S and gas diffusivity D in the polymer matrix (6). Selectivity αA/B, which characterizes the ability of a membrane to separate gases A and B, is given by

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{S_A}{S_B} \times \frac{D_A}{D_B} \quad (1)$$

where $S_A/S_B$ is the solubility selectivity and $D_A/D_B$ is the diffusivity selectivity (6). The selectivity of CO2 over H2, $\alpha_{CO2/H2}$, reflects the tradeoff between favorable solubility selectivity (CO2 is more condensable than H2, and therefore, $S_{CO2}/S_{H2} > 1$) and unfavorable diffusivity selectivity (CO2 is larger than H2, so $D_{CO2}/D_{H2} < 1$) (7). In conventional polymeric membrane materials (8) and those based on carbon (4) and silica (9, 10), overall gas selectivity is dominated by diffusivity selectivity and, therefore, these materials are typically more permeable to H2 than to CO2. Consequently, the H2 product is produced in the permeate at low pressure, even though further downstream utilization requires H2 at high pressure. Expensive recompression of the H2 product hence eliminates the advantage of membrane technology relative to that of conventional separation technologies, such as pressure swing adsorption, that produce H2 at or near feed pressure (1, 2, 6). To minimize or avoid H2 recompression, optimal membrane materials should be reverse selective (i.e., more permeable to larger molecules, such as CO2, than to smaller molecules, such as H2). Here, we propose that to achieve very high CO2/H2 selectivity, a membrane must exhibit favorable interactions with CO2 to enhance solubility selectivity and have very weak size-seieving ability to bring $D_{CO2}/D_{H2}$ as close to 1 as possible. Guided by these material design principles, we prepared and characterized a family of highly branched polymers based on poly(ethylene oxide) (PEO) and found that these polymers display excellent CO2/H2 separation performance. Counterintuitively, the CO2/H2 selectivity and CO2 permeability improve as CO2 partial pressure increases (i.e., as CO2 concentration sorbed in the polymer increases). This is in contrast to the behavior of conventional, strongly size-selective materials, for which raising CO2 partial pressure typically decreases selectivity (11).

In a recent review of the influence of primary chemical structure on CO2/H2 separation properties of polymers, ethylene oxide (EO) units were identified as the best chemical groups for such membranes because the polar ether oxygens in EO units interact favorably with CO2, resulting in high solubility selectivity (12). Polymers containing EO can be highly flexible, leading to weak size-seieving behavior and high diffusion coefficients, two factors which contribute directly to high CO2 permeability and high CO2/H2 selectivity (12, 13). However, pure PEO exhibits very low CO2 permeability [approximately 12 Barrers (14) at 35°C and infinite dilution] as a result of high crystallinity levels (7). Additionally, the presence of crystalline regions in pure PEO reduces polymer chain mobility in the amorphous phase and increases size-seieving ability, thereby decreasing CO2/H2 selectivity (12). To circumvent this limitation and effectively frustrate crystallization, short non-PEO segments are introduced into the polymer backbone to interrupt the EO repeat units. Chain branches containing short, noncrystallizable segments of EO are also introduced randomly into the chain backbone to further inhibit crystallinity. This leads to amorphous materials with higher gas permeability and higher CO2/H2 selectivity than semicrystalline PEO. Plasticization further improves their CO2/H2 separation properties, in contrast to the view that plasticization always reduces polymer membrane separation performance, as it does in the case of CO2/CH4 separation in natural gas purification (15). Moreover, all polymers are more permeable to CO2 than to H2 because CO2 has higher diffusivity (because of its smaller molecular size) and higher solubility (because of its greater tendency to condense) than CH4. In contrast, polymers that are more permeable to CO2 than to H2 are much rarer because the smaller size of H2 favors its permeation over that of the larger CO2.

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Our family of amorphous, high-molecular-weight, cross-linked, network copolymers was synthesized by photopolymerizing different composition ratios of poly(ethylene glycol) diacylate [PEGDA: CH$_2$=CHCOO(OC$_2$H$_4$)nOCCH=CH$_2$] and poly(ethylene glycol) methyl ether acrylate [PEGMEA: CH$_2$=CHCOOCH$_2$CH$_2$OCH$_2$] (16, 17). The resulting copolymer network has the general chemical structure shown in Fig. 1. PEGDA contains EO units in its backbone, and PEGMEA has pendant EO units. Cross-linked copolymer samples with 0 to 99 weight percent (wt %) PEGMEA and the balance PEGDA were prepared and characterized. Independent of the concentration of PEGDA and PEGMEA, the copolymers contain about 82 wt % EO. Increasing PEGMEA content increases fractional free volume and, in turn, CO$_2$ permeability and pure-gas CO$_2$/H$_2$ selectivity. However, at low temperatures (<0°C), materials with very high PEGMEA content (e.g., 91 wt %) crystallize, resulting in a substantial permeability decrease below 0°C. We extensively investigated the CO$_2$/H$_2$ permeation properties of the 70 wt % PEGMEA/30 wt % PEGDA copolymer at –20°C, 10°C, and 35°C with pure gases and three binary CO$_2$/H$_2$ mixtures of different compositions (16). We chose this temperature range not only because this copolymer does not crystallize over this range but also because this range is consistent with the operating temperature of some industrial processes currently used for H$_2$ purification (1). Additionally, to determine the effect of H$_2$O and H$_2$S impurities on CO$_2$/H$_2$ separation properties, the 91 wt % PEGMEA/9 wt % PEGDA copolymer was characterized at 22°C with a moisture-laden CO$_2$/H$_2$ mixture and a four-component, H$_2$S-containing gas mixture that mimicked the process of synthesis gas. In both pure- and mixed-gas studies, the PEGMEA/PEGDA films were physically stable at transmembrane pressure differences up to 21 atm (the maximum value explored in our study), and their gas permeability coefficients were independent of previous thermal and gas exposure history, as expected for rubbery polymers. Permeability coefficients were independent of film thickness, which varied from 70 to 500 μm.

Figure 2 shows the dependence of CO$_2$ and H$_2$ permeability coefficients on CO$_2$ partial pressure in the feed at different temperatures. As CO$_2$ partial pressure increases, CO$_2$ and H$_2$ permeabilities increase at all temperatures; the permeability rise is greater at lower temperatures because of higher CO$_2$ thermodynamic activity of the polymer by CO$_2$, which increases diffusivity at lower temperatures. Both pure- and mixed-gas permeabilities also follow the same trends, suggesting that the permeability increase is in large measure a result of increasing CO$_2$ partial pressure.

Decreasing temperature typically decreases gas permeability as a result of a reduction in polymer chain mobility and, therefore, diffusivity at lower temperatures (6, 19). However, Fig. 2A demonstrates that decreasing temperature does not necessarily decrease CO$_2$ permeability, especially at high CO$_2$ partial pressure. For example, at a CO$_2$ feed partial pressure of 17 atm, the CO$_2$ permeability at –20°C is 410 Barrers, which is higher than that at 10°C (300 Barrers) and very similar to that at 35°C (440 Barrers). Thus, the permeability decrease that would normally accompany a temperature reduction is essentially offset by the increase in CO$_2$ solubility and the increased plasticization of the polymer by CO$_2$, which increases diffusivity at lower temperatures.

Decreasing temperature considerably increases mixed-gas CO$_2$/H$_2$ selectivity. As shown in Fig. 3, at a CO$_2$ partial pressure of 17 atm, mixed-gas selectivity increases from 9.4 to 31 as temperature decreases from 35°C to –20°C. Furthermore, the selectivity of 31 is accompanied by a CO$_2$ permeability of 410 Barrers, which is of orders of magnitude higher than that observed in conventional polymer membranes used for CO$_2$ separations (6). Facilitated transport membranes can exhibit high CO$_2$/light gas selectivity at low CO$_2$ partial pressure (~1 atm or less); however, the selectivity in these materials decreases strongly as CO$_2$ pressure increases (20–22). Such materials are often studied for low CO$_2$ partial pressure applications (e.g., removal of CO$_2$ from...
from breathing gas aboard spaceships) (20). However, they cannot operate at the high pressures required for hydrogen applications because they are often based on liquids supported in porous media, and the liquids typically cannot be maintained in the porous support when a large pressure difference is applied across the membrane (23, 24).

Mixed-gas selectivity is essentially independent of CO₂ partial pressure at 35°C and 10°C (Fig. 3). However, as CO₂ partial pressure increases at –20°C, mixed-gas CO₂/H₂ selectivity increases by 35%. In conventional size-sieving polymers, plasticization of the polymer by CO₂ or other condensable components results in mixed-gas selectivity values that decrease, often markedly, as CO₂ partial pressure increases (11) or when other strongly sorbing impurities such as higher hydrocarbons are present (25). For example, when the CO₂ partial pressure increased from 1 to 10 atm, the CO₂/CH₄ selectivity of a rigid, glassy, strongly size-sieving, aromatic polyimide decreased from 40 to about 11 (17).

We ascribe the mixed-gas CO₂/H₂ selectivity results for the PEGMEA/PEGDA copolymers to the inherent transport properties of these reverse-selective materials (3, 26). At high CO₂ partial pressures, these materials sorb considerable amounts of CO₂, leading to swelling and an increase in free volume, which presumably decreases the glass transition temperature (Tgs) (27–29) and weakens the size-sieving ability of the membrane (26).

Figure 4 presents a permeability/selectivity map for CO₂/H₂ separation. The upper bound line in the figure gives an estimate of the highest pure-gas selectivity possible for a given permeability in polymer-based materials at 25°C (8). Unlike separation based on strong size-sieving ability (where there is a strong tradeoff between permeability and selectivity (8, 30)), the positive slope of the upper bound indicates that high CO₂ permeability and high CO₂/H₂ selectivity may be achieved simultaneously. The PEGMEA/PEGDA copolymers we explored exhibit excellent separation performance for CO₂/H₂ mixtures, and decreasing temperature actually moves the CO₂/H₂ separation performance above the upper bound line. However, because this line is commonly established by permeation properties of polymers at or near 25°C (8), the upper bound may shift as temperature deviates from 25°C. Currently, there is no model to predict the temperature dependence of the upper bound, and there are not yet enough systematic experimental data available to provide clear evidence of its temperature dependence.

The effect of impurities such as H₂O and H₂S on CO₂/H₂ separation properties was investigated at 22°C with the 91 wt % PEGMEA/9 wt % PEGDA copolymer. Although this material crystallizes at about 0°C, it is wholly amorphous at the experimental temperature studied. Because it contains more PEGMEA, this copolymer is more permeable than the 70 wt % PEGMEA/30 wt % PEGDA copolymer. At 25°C, the infinite-dilution CO₂ permeability is 380 Barrers for the 91 wt % PEGMEA copolymer and 280 Barrers for the 70 wt % PEGMEA material. The addition of 0.33 mole percent (mol %) H₂O vapor (i.e., 100% relative humidity) to a feed gas containing a 1:3 mixture of CO₂:H₂ at 22°C and a feed pressure of 8.0 atm increased CO₂ permeability of the 91 wt % PEGMEA copolymer from 360 to 515 Barrers and its mixed-gas CO₂/H₂ selectivity from 7.8 to 12. We ascribe this change to plasticization by H₂O, which tends to improve CO₂/H₂ separation performance by a mechanism probably very similar to that by which higher CO₂ partial pressure increases CO₂/H₂ selectivity.

The 91 wt % PEGMEA copolymer was also evaluated with a four-component gas mixture composition representative (on a dry basis) of a synthesis gas stream produced by a commercial General Electric (formerly, Texaco) quench gasifier (31). This mixture contained 1.0% H₂S, 12.5% CO₂, and 35.7% H₂ in CO. The separation of H₂S from H₂, similar to that of CO₂ from H₂, requires reverse-selective membrane materials with weak size-sieving ability and a polar nature to interact more favorably with this acid gas. At a feed pressure of 7.8 atm, the copolymer had an H₂S permeability of 2500 Barrers and a mixed-gas H₂S/H₂ selectivity of 50. H₂S is considerably more soluble than CO₂ in polar polymers (32, 33), and this effect contributes to the much higher H₂S permeability than CO₂ permeability in the material. Additionally, CO₂ permeability and CO₂/H₂ selectivity remain unchanged in the presence of H₂S, indicating the robustness of this series of polymers for CO₂/H₂
Asymmetric Hydrogenation of Unfunctionalized, Purely Alkyl-Substituted Olefins

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Asymmetric hydrogenation of olefins is one of the most useful reactions for the synthesis of optically active compounds, especially in industry. However, the application range of the catalysts developed so far is limited to alkenes with a coordinating functional group or an aryl substituent next to the double bond. We have found a class of chiral iridium catalysts that give high enantioselectivity in the hydrogenation of unfunctionalized, trialkyl-substituted olefins. Because these catalysts do not require the presence of any particular functional group or aryl substituent in the substrate, they considerably broaden the scope of asymmetric hydrogenation.

A symmetric hydrogenation is one of the most widely used, most reliable catalytic methods for the preparation of optically active compounds (1–3). High enantioselectivity, low catalyst loadings, essentially quantitative yields, and mild conditions are attractive features of this transformation. Since the early 1970s, when the well-known L-DOPA (l-dioxyphenylalanine) process was established at Monsanto (3), hydrogenation has played a dominant role in industrial asymmetric catalysis (4). An enormous variety of chiral phosphines ligands has been developed, many of which induce very high enantioselectivity in rhodium- and ruthenium-catalyzed hydrogenations. However, despite great progress during recent decades, the range of olefins that can be hydrogenated with high enantiomeric excess (ee) is still limited. Both rhodium and ruthenium catalysts require the presence of a polar functional group next to the C=C bond, which can coordinate to the metal center. Hydrogenation of dehydro–amino acid derivatives or allylic alcohols are typical examples. With unfunctionalized olefins, these catalysts generally show low reactivity and unsatisfactory enantioselectivity. Therefore, their application is restricted to certain classes of properly functionalized substrates.

Some years ago, we introduced iridium complexes with chiral P,N ligands (ligands with coordinating P and N atoms) as catalysts that overcome these limitations (Fig. 1) (5–19). Various unfunctionalized aryl-substituted olefins can be hydrogenated with high enantioselectivity and high catalytic efficiency using catalysts of this type. Nonetheless, satisfactory

References and Notes
1. A. L. Kohl, R. B. Nielsen, Gas Purification (Gulf Publishing, Houston, TX, ed. 5, 1997).
14. 1 Barrer = 10⁻¹⁰ cm²(STP) cm⁻¹ s⁻¹ where STP is standard temperature and pressure.
16. Materials and methods are available as supporting material on Science Online.
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Fig. 1. Asymmetric hydrogenation of olefins with iridium catalysts 1 derived from chiral ligands 2 to 6. Abbreviations: cod, cycloocta-1,5-diene; BARf, tetrakis[bis-3,5-(trifluoromethyl)phenyl]borate.