

Precisely Tunable High Performance Carbon Molecular Sieve Membranes for Energy Intensive Separations

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discovery by our group that the presence of parts-per-million levels of oxygen enables exquisite control of permeability and selectivity in carbons. Finally, evaluation of the effects on separation performance for selected binary and ternary gas feeds is proposed to probe interactions between co-permeating components. These multicomponent gas studies, while difficult, provide valuable insights that are unavailable from single gas investigations alone.

To reach the goal, we need to design and synthesize precursor polymers with specific related structures; we need to tune pyrolysis protocols and atmospheres for optimization of CMS Properties; and finally, we need to compare the CMS membranes' gas separation performance to relate the performance with the structures and pyrolysis conditions.

Abstract

In our previous project of "Synthesis and analysis of polymers with high permeabilities and permselectivities for gas separation applications", we focused on rational discovery and development of robust crosslinked polyimide membrane materials for energy-efficient purification of natural gas, and investigated the following areas: (1) synthesis of 6FDA-based polyimides with comparable chemical structures; (2) thermal properties and chemical structures of the polymers; (3) CO₂-induced plasticization response vs. chemical structure of the polymers; (4) gas separation properties vs. chemical structure of the polymers; (5) sub-T_g thermal cross-linking of the polymer membranes, and (6) physical aging and CO₂ exposure effects on gas permeation properties of thin films.

The current project's focus is to study advanced carbon molecular sieve (CMS) membranes. The overarching goal is to develop an improved fundamental framework to guide the systematic understanding and formation of carbon molecular sieve membrane materials appropriate for important energy intensive separations. Determination and analysis of the effects on penetrant sorption and transport properties caused by systematic variations in precursor polyimide structures and pyrolysis protocols will be key thrusts of the work. A diverse but systematic set of dianhydride and diamine monomers will be used to explore effects of matrix rigidity and packing of precursor polyimides on final carbon properties. We will analyze diffusion selectivities in terms of activation energies and activation entropies to improve the understanding of discrimination on the basis of shape of the penetrants. A special focus will be upon the interaction of pyrolysis temperatures and pyrolysis atmospheres. This aspect of the work will expand on an important recent

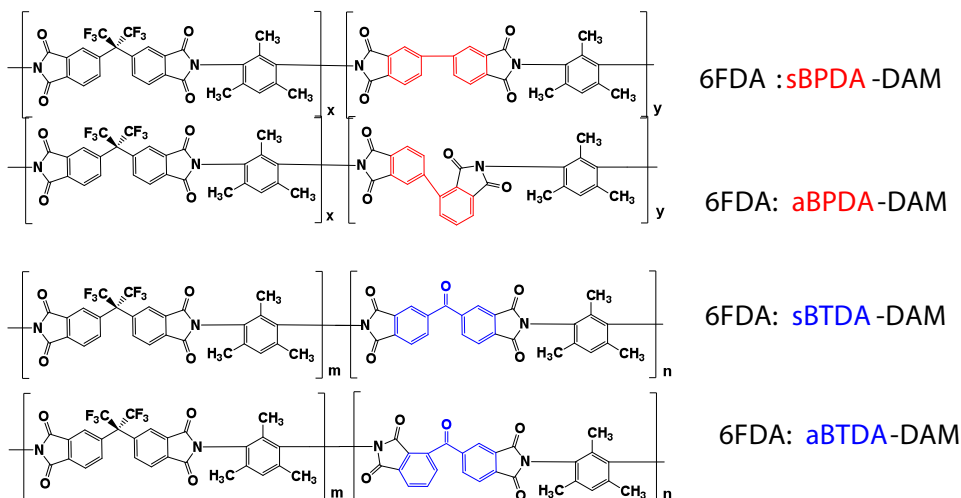
Progress Report

The 6FDA dianhydride and DAM diamine monomers provide starting points that we know yield a highly open and conveniently processable polyimide precursor, which can be engineered to adjust matrix rigidity and packing. We designed 6FDA-based polyimide copolymers by using a symmetrical (indicated by the "s" prefix) or an asymmetric (indicated by the "a" prefix) dianhydride. These irregular asymmetric dianhydrides provide packing inhibiting components, and should give higher permeability CMS structures vs. the CMS from symmetric structures. The structures of the polymers are given in scheme 1.

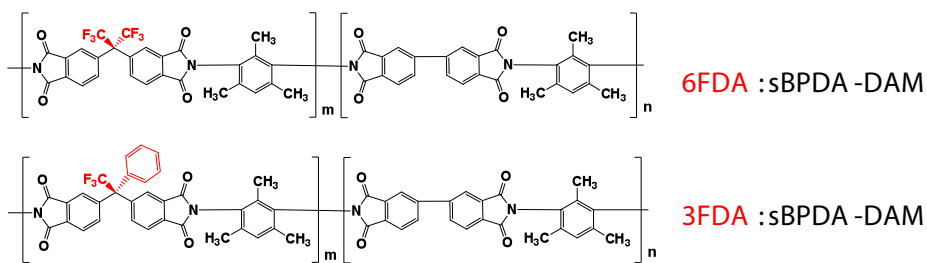
We will also compare 3FDA-based copolymers with 6FDA-based copolymers, examples are shown in Scheme 2.

We have synthesized symmetrical copolymers by condensation of the dianhydrides with the diamine, DAM. This is a two-step reaction in which the first step produces a high molecular weight polyamic acid (PAA) at low temperature (~5 °C), while the second step involves ring closure by releasing water to produce the chemical stable polyimide (PI). Chemical imidization was carried out for the PAA solution in the presence of beta picoline and acetic anhydride at ambient temperature for 24 h. The resulting polyimides were precipitated, washed with methanol, and dried at 210 °C under vacuum for 24 h. An example of the synthesis procedure is shown in Scheme 3.

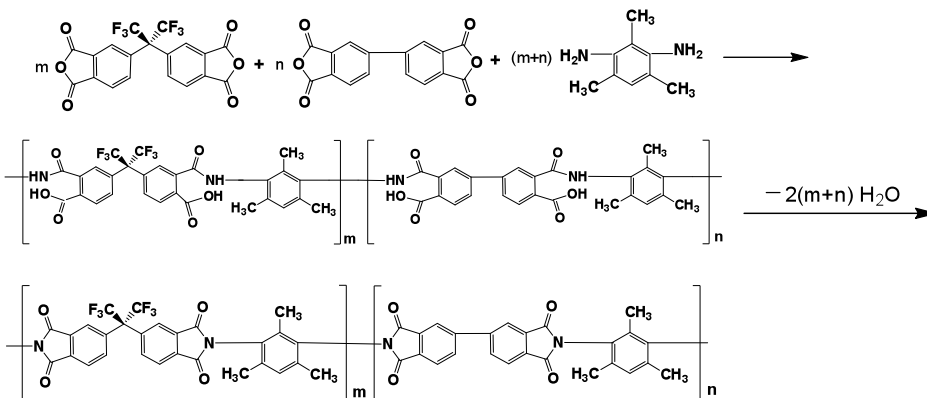
Synthesis of the asymmetrical copolymers is currently underway. Asymmetric dianhydrides are not common chemicals; however, we have successfully obtained samples from a specialty commercial supplier and are starting to characterize these samples. With the analytic results, we will make a decision to buy asymmetric dianhydrides



SCHEME 1. Chemical structures of symmetric and asymmetric copolymers



SCHEME 2. Chemical structures of 3FDA- and 6FDA-based copolymers



SCHEME 3. Synthesis of 6FDA:sBPDA-DAM copolymer

from a commercial source or to synthesize the asymmetric dianhydrides by ourselves.

Permeation performance of 6FDA:sBPDA-DAM membrane

6FDA:sBPDA-DAM(1:1) copolymer membrane was cast on a Teflon[®] covered glass plate from a THF solution

(~20 wt%) inside a controlled environment glove bag to promote slow evaporation of the solvent. A casting knife with a 12 mil clearance was used to draw the solution into a film of uniform thickness. After completion of the evaporation of THF solvent, the membrane was removed from the plate, and dried at 180 °C for 24 h under vacuum. The resulting polymer precursor membrane will be used for making CMS membrane.

For comparison, the gas separation performance was also tested for the polymer precursor membrane. Both pure gases and mixed gas were tested at 35°C with a feed pressure of 50 psia. The permeability is 282 barrers for He, 92.6 barrers for O₂, 24.3 barrers for N₂, 460 barrers for CO₂, 23 barrers for CH₄, 43.6 barrers for C₂H₄, 13.0 barrers for C₂H₆, 29 barrers for C₃H₆, and 2.2 barrers for C₃H₈. Selectivity is 12.3 for He/CH₄, 11.6 for He/N₂, 3.8 for O₂/N₂, 20.0 for CO₂/CH₄, 18.9 for CO₂/N₂, 4.0 for O₂/CH₄, 1.1 for N₂/CH₄, 3.3 for C₂H₄/C₂H₆, and 13.4 for C₃H₆/C₃H₈, respectively. For a mixed gas of CO₂/CH₄ (10/90), permeability was tested as 545 barrers and 23 barrers for CO₂ and CH₄, respectively, with a CO₂/CH₄ selectivity of 22.8; for CO₂/CH₄ (50/50) mixed gas, permeability was 493 barrers and 23.4 barrers for CO₂ and CH₄, respectively, with a CO₂/CH₄ selectivity of 21.

Preliminary results of CMS membrane from 6FDA:sBPDA-DAM precursor polymer

The CMS membrane was made through pyrolysis of the precursor membrane in a temperature and atmosphere controlled furnace. The final separation performance of a CMS membrane is influenced by the following parameters, including polymer precursor, pyrolysis temperature, thermal soak time, and pyrolysis atmosphere.

The thermal decomposition property was studied by TGA analysis. As shown in Figure 1, 6FDA:sBPDA-DAM(1:1) is stable until 450°C, then it starts to decompose. A weight loss of about 40wt% was found up to around 700°C in Argon. Beyond 700°C the weight loss is much smaller. Based on the decomposition behavior, the final pyrolysis temperatures were chosen as 500°C, 550°C, 675°C, and 800°C.

An example of a typical heating protocol for preparing CMS membranes at different pyrolysis temperature is

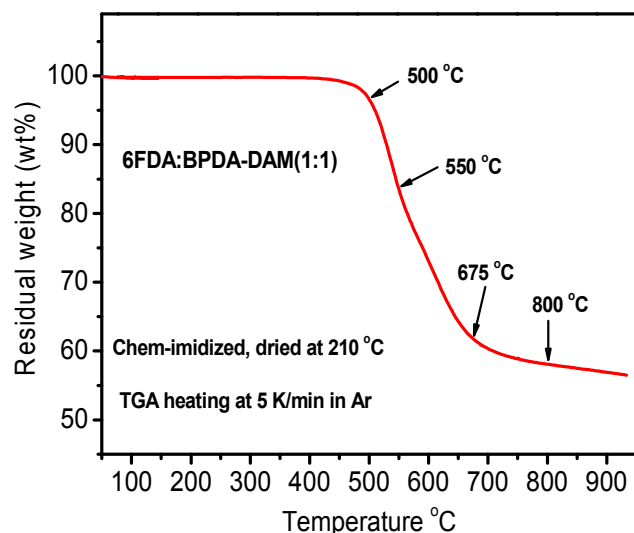


FIGURE 1. 6FDA:sBPDA-DAM copolymer TGA plot

shown in Figure 2. The polymer precursor membrane was heated from 50°C at 10 K/min to 250°C, followed by a rate of 3 K/min to a temperature of 15 degree below the final temperature, then heated at 0.25 K/min to the final temperature and soaked at that temperature for 2h in Argon with a flow rate of 200 mL/min. The furnace was then cooled down naturally to room temperature, and the resulting CMS membrane was used for gas permeation tests.

The gas separation performance was tested for CMS membranes, and the results were plotted against the experimental upper bound. As shown in Figure 3a, the 6FDA:sBPDA-DAM(1:1) precursor membrane showed a CO₂/CH₄ separation performance near the polymer upper bound, while the CMS membranes exhibited separation performance *greatly exceeding the upper bound*. CMS membranes from the lower pyrolysis temperatures, such as 550 °C, show quite high CO₂ permeability; however, the CO₂/CH₄ selectivity is not significantly increased. With the pyrolysis temperature increased to 675 °C, the CMS membrane shows both improved CO₂ permeability and CO₂/CH₄ selectivity. With an increase in final pyrolysis temperature, the CO₂/CH₄ selectivity increased, while the CO₂ permeability decreased. The CMS membrane pyrolyzed at 800°C showed quite lower permeabilities (not shown in the Figure).

Compared with the precursor membrane, CMS membranes pyrolyzed at 500 °C had quite high C₂H₄ permeability with improvements in C₂H₄/C₂H₆ selectivity. CMS membranes pyrolyzed at 675 °C showed higher C₂H₄/C₂H₆ selectivity, while the C₂H₄ permeability was almost the same as the precursor membrane, as can be seen in Figure 3b.

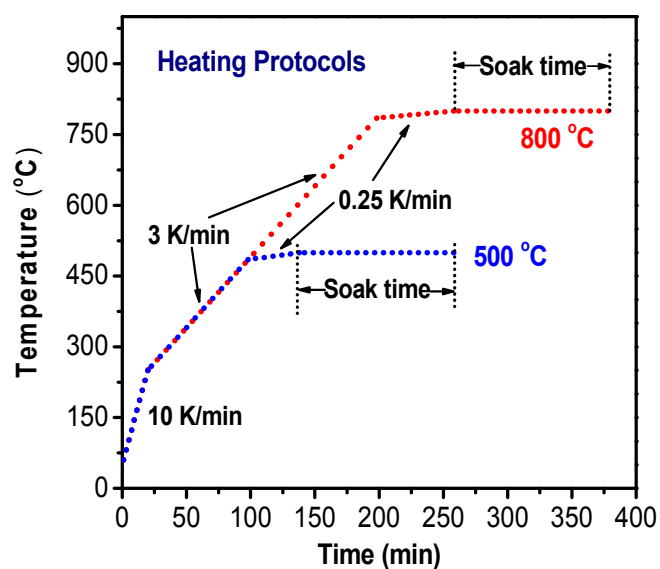


FIGURE 2. Example of pyrolysis protocols. Figure 1:6FDA:sBPDA-DAM copolymer TGA plot

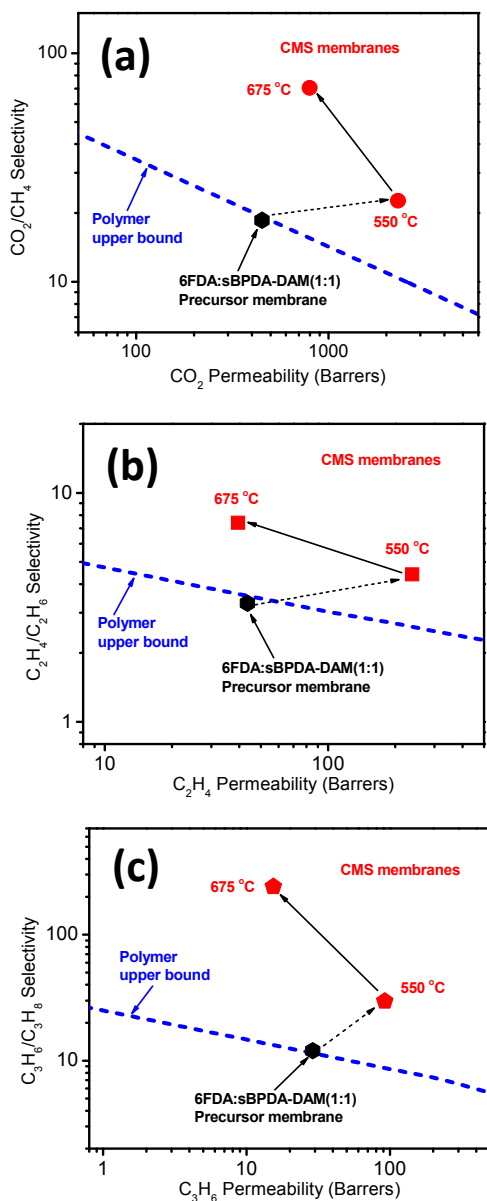


FIGURE 3. Performance of CMS membrane from 6FDA:sBPDA-DAM copolymer for separation of (a) CO_2/CH_4 , (b) $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$, and (c) $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$.

From Figure 3c, for the $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ pair the 6FDA:sBPDA-DAM(1:1) polymer precursor membrane showed a $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ separation performance on the polymer upper bound. The CMS membranes showed extremely good separation performance based on pure gas permeation tests, but we must also study mixed gases, since competition between the two penetrants can be strong for this more condensable pair. With an increase of pyrolysis temperature, the $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ selectivity increased markedly, although the C_3H_6 permeability decreased.

The above permeation results indicate that CMS membranes pyrolyzed at lower temperature have bigger

ultramicro pore size than the membranes pyrolyzed at higher temperature. There is a competition between the creation of pores and the reduction of pore size. The pyrolysis temperature can be grouped into two regions, the fast weight loss region and the slow weight loss region, as can be seen in Figure 4. With a pyrolysis temperature in the fast weight loss region, the creation of pores is dominant, while in the slow weight loss region, the reduction of pore size is dominant. It seems a pyrolysis temperature within the region where fast weight loss is ending while the slow weight loss is starting might yield the resulting CMS membrane with both good permeability as well as high selectivity.

The performance of CMS dense film membrane made from 6FDA:sBPDA-DAM(1:1) precursor membrane was influenced by aging time, as shown in Figure 5. The steady

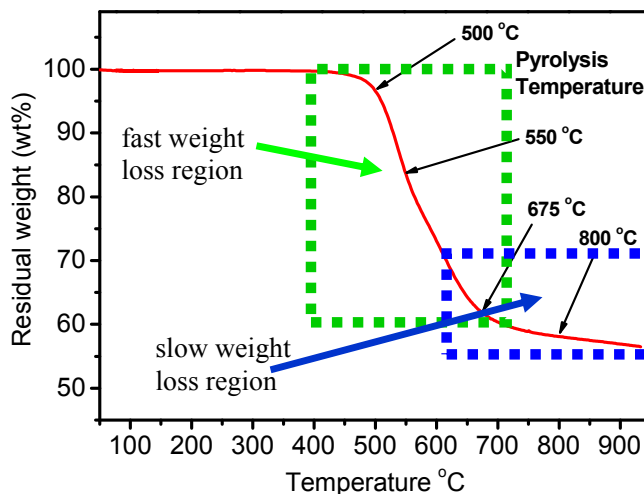


FIGURE 4. Wt. loss rate vs. CMS ultramicro pore development

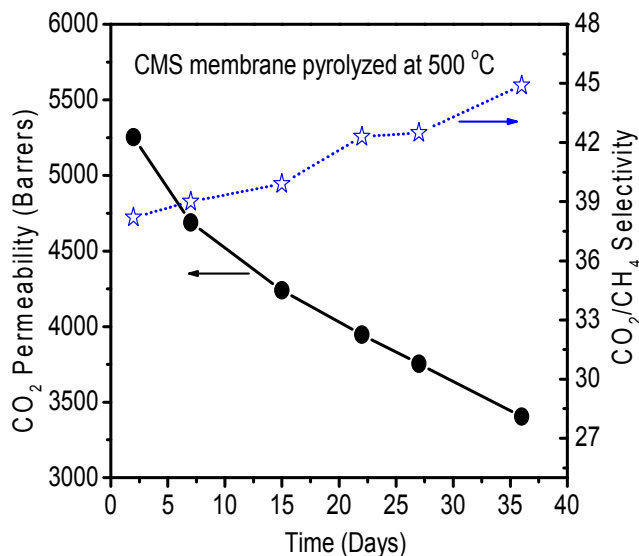


FIGURE 5. CO_2 permeability vs. aging time

state was not reached in one month for a CMS membrane pyrolyzed at 500°C. This response appears to be somewhat related to aging phenomena seen in conventional glassy polymers, and our goal is to accelerate the aging to enable focusing on the intrinsic stable properties of the high performance carbon glass. We will report more on this topic in our next update.

Publication list (including patents) acknowledging the DOE grant

Publications Under DE-FG02-04ER15510 (2011-2012)

1. W.J. Koros and R.P. Lively, “*Water and beyond: Expanding the spectrum of large-scale energy efficient separation processes*”, *AIChE Journal*, 58(9) 2624-2633, 2012.

2. Wulin Qiu, Liren Xu, William J Koros, “*Effects of Polymer Precursors and Pyrolysis Conditions on Carbon Molecular Sieve Membranes for Gas Separation*”, **40th Annual NATAS (North American Thermal Analysis Society) Conference**, Orlando, FL, United States, August 10–15, 2012.

3. Wulin Qiu, Chien-Chiang Chen, Liren Xu, William J Koros, “*6FDA-Based Polyimide Membranes with Different Chemical Structures for Gas Separation*”, **NAMS (The North American Membrane Society) 2012 meeting**, New Orleans, LA, United States, June 9–13, 2012.