

## V.N.7 Fundamental Structure/Property Studies of Gas Separation Membrane Polymers

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### Objectives

Refinery, petrochemical, and natural gas industries, in particular, offer large opportunities for membranes, but they could benefit from more robust, higher performance membrane materials. The overarching goal of this fundamental, experimental research program is to systematically synthesize, characterize, and, ultimately, rationally tailor a novel class of polymeric membrane materials with the chemical and thermal stability as well as separation properties required for gas separation applications. This program will exploit and further develop our discovery that polymers prepared by thermal rearrangement of soluble aromatic polyimides (PIs) containing *ortho*-positioned functional groups, such as OH, exhibit unusually high gas permeability and selectivity values. Furthermore, early studies of this class of materials suggest that they are very robust chemically (i.e., insoluble in all known solvents) and resistant to plasticization, which would be important in, for example, olefin/paraffin separation or natural gas purification, where high concentrations of hydrocarbons dissolved in the polymer can compromise separation properties due to plasticization.

### Technical Barriers

Thermally rearranged polymers show promising separation characteristics for several gas pairs including CO<sub>2</sub>/CH<sub>4</sub>. The literature lacks substantive characterization studies of these materials for membrane applications, and therefore, a broad range of structure-functionality data must be compiled to develop a fundamental understanding of why these materials have property sets so far above those of other materials and to understand whether the fundamental, molecular-level characteristics that give these materials their high transport properties are general or specific to this class of polymers.

### Abstract

Work in 2012-2013 focused on studying gas permeability, diffusivity and solubility of polyimides and thermally rearranged (TR) polymers based on 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB) and 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA). To determine the effect of temperature on gas sorption, we studied H<sub>2</sub> sorption in the HAB-6FDA polyimide and 3 partially converted HAB-6FDA TR polymers. Increasing conversion increased gas solubility by approximately a factor of 2.6, which is similar to that of other nonpolar gases. Furthermore, in comparing H<sub>2</sub> sorption in HAB-6FDA with that of other polymers commonly considered for membrane applications, the HAB-6FDA TR polymers had the highest H<sub>2</sub> sorption. Similar studies are under way with other gases relevant for gas separations applications. We also investigated the effect of the size of the reactive leaving group and synthesis route on transport properties in TR polymers. In general, bulkier reactive leaving groups contribute to increased gas permeability in TR polymers compared to TR polymers synthesized from hydroxyl-functional leaving groups. Furthermore, we investigated samples with identical leaving groups but synthesized from two different routes. These tests showed that the leaving group on the polyimide has more of an effect on gas transport than that of synthesis route. We are also measuring mixed gas performance of these polymers and have found, in many cases, situations where CO<sub>2</sub>/CH<sub>4</sub> mixed gas selectivity is actually higher than the selectivity calculated based on pure gas permeability values. The fundamental basis for this observation is under investigation.

## Progress Report

### Hydrogen Sorption Polymers for Membrane Applications

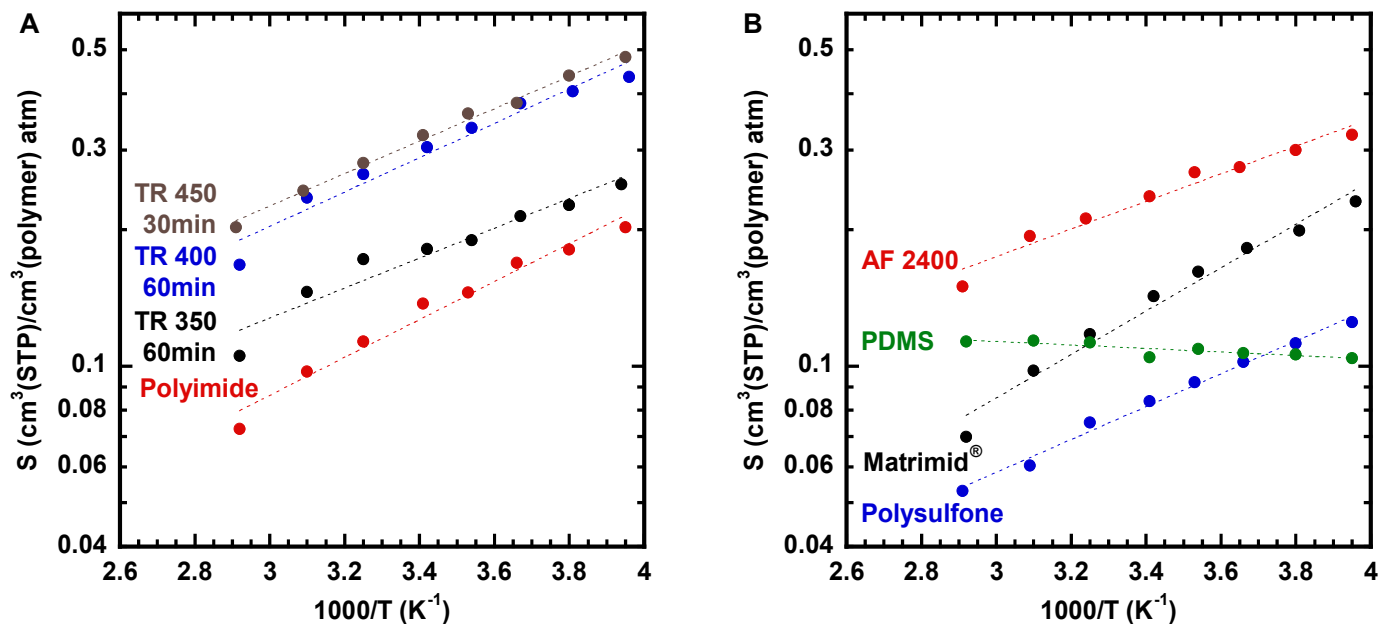
Hydrogen separation is used in many industrially significant gas separation applications such as oxo-chemical synthesis, refinery off-gas purification, and syngas ratio adjustment. However, because H<sub>2</sub> has a small kinetic diameter (2.89Å) and one of the lowest critical temperatures, T<sub>c</sub> (33K), the effect of polymer structure on hydrogen diffusion and solubility is difficult to determine because solubility is so low. Challenges in determining these fundamental gas transport parameters have hindered the polymer membrane field from advancing our understanding of polymer structure on hydrogen transport.

To investigate H<sub>2</sub> sorption, we used a high precision magnetic suspension balance to determine H<sub>2</sub> sorption as a function of temperature in a series of HAB-6FDA TR polymers with increasing conversion. As shown in Figure 1A, gas solubility increased by approximately a factor of 2.6 between the polyimide and most highly converted TR polymer (TR 450 30min), so the relative change in H<sub>2</sub> sorption as a function of thermal rearrangement is similar to that of other nonpolar gases such as O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub>. Notably, the increase in H<sub>2</sub> sorption does not track with increases in gas sorption for quadrupolar gases, such as CO<sub>2</sub>, whose solubility increases by a factor of 1.7 between the HAB-6FDA polyimide and TR 450 30min sample.

To broaden the framework of this study, we investigated H<sub>2</sub> sorption in other polymers commonly studied for membrane applications (c.f., Figure 1B). Matrimid<sup>®</sup>, which is of the same family of polymers as HAB-6FDA (i.e., polyimides), had nearly identical gas sorption to that of the HAB-6FDA polyimide. Amorphous Teflon<sup>®</sup> (AF 2400) had H<sub>2</sub> sorption between that of the TR 350 60min and TR 400 60min sample. Polysulfone had the lowest H<sub>2</sub> sorption, and poly(dimethylsiloxane) (PDMS), which was the only rubbery polymer considered, had a slightly endothermic enthalpy of sorption, as indicated by the negative correlation between gas solubility and 1000/T. From these results, accurate diffusion coefficients for H<sub>2</sub> sorption in these polymers can be determined. As we have shown for other gases in TR polymers, increases in gas permeability from thermal rearrangement for H<sub>2</sub> are largely a result of increases in gas diffusivity.

### Effect of Reactive Leaving and Synthesis Route Group on Transport Properties

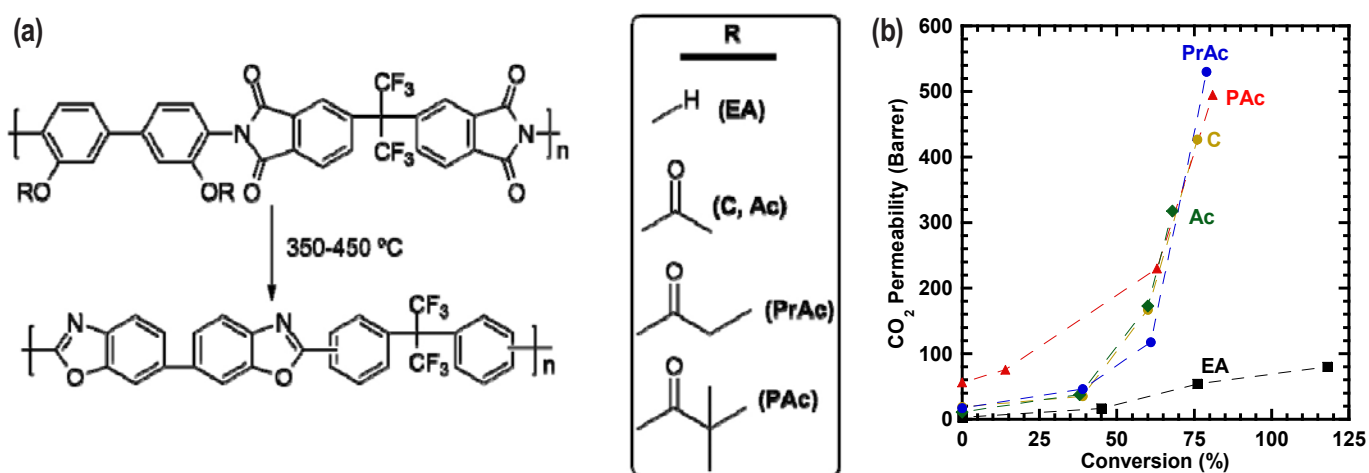
Thermal rearrangement occurs at elevated temperatures for precursor polyimides with reactive *ortho*-position functional groups. We have previously reported that there is an effect of precursor synthesis route and/or the reactive leaving group on TR polymer transport properties. To decouple these two variables, we pursued a unique organic synthesis approach to synthesize TR polymer precursors from identical synthesis routes but with different reactive



**FIGURE 1.** Hydrogen solubility in (A) HAB-6FDA as a function of thermal rearrangement, and (B) additional polymers frequently used for membrane applications. In Figure A, Polyimide stands for the HAB-6FDA polyimide, and partially converted TR polymers are represented by the temperature and time at which they have been rearranged. For example, TR 450 30min indicates a sample of HAB-6FDA that has been converted at 450°C for 30min. For Figure B, AF 2400 is amorphous Teflon<sup>®</sup> AF 2400 and PDMS is poly(dimethylsiloxane).

leaving groups. This synthesis approach was accomplished by first thermally imidizing HAB-6FDA to form a polyimide precursor with hydroxyl *ortho*-functionality. This precursor was chemically derivatized through a series of esterification reactions to synthesize an HAB-6FDA polyimide with variable reactive leaving groups.

As shown in Figure 2A, an HAB-6FDA polyimide can be converted to an HAB-6FDA TR polymer at elevated temperatures between 350°C and 450°C. Under these conditions, the reactive *ortho*-functional group, R, leaves the polymer. Regardless of which derivatized R group is used, upon thermal treatment, all forms of HAB-6FDA rearrange to form the polybenzoxazole (PBO) structure shown in Figure 2A. To compare the transport properties of TR polymers prepared from each of these derivatized precursors polyimides, we determined CO<sub>2</sub> permeability as a function of conversion for all of the derivatized products as shown in Figure 2B. Modifications to the leaving group of the polyimide change the CO<sub>2</sub> permeability for the unconverted samples. Upon conversion, samples with leaving groups that are bulkier than hydroxyl groups results in larger increases in CO<sub>2</sub> permeability. To compare transport properties of two polymers with identical leaving groups that were synthesized via diverse synthetic pathways, we compared the CO<sub>2</sub> permeability for two acetate-functional polymers, whereby the first was synthesized via the derivatization method described above (labeled Ac in Figure 2), and the second was synthesized via chemical imidization (labeled C in Figure 2). As shown in Figure 2B, there is almost no difference in CO<sub>2</sub> permeability between the samples of identical leaving groups but prepared from different synthesis routes. Therefore, the leaving group has a stronger influence on transport properties than the synthesis route.



**FIGURE 2.** (A) Thermal rearrangement of an HAB-6FDA polyimide to form an HAB-6FDA TR polymer. Various R groups will all theoretically rearrange into identical TR polymers. (B) Comparison of CO<sub>2</sub> permeability as a function of conversion for HAB-6FDA prepared with various leaving groups and prepared by multiple synthetic routes (i.e., C versus Ac).

## Future Directions

We are furthering our basic structure property studies by investigating the effect of light gas permeability and CO<sub>2</sub> as well as olefin/paraffin plasticization effects for several TR polymers with different functionality in the chemical backbone. In addition to the HAB diamine, we are investigating a fluorinated diamine known as APAF, and in addition to the 6FDA dianhydride, we are investigating a dianhydride known as ODP. Our plasticization studies for CO<sub>2</sub>/CH<sub>4</sub> separation have extended to mixed gas plasticization experiments, whereby we have investigated the effect of thermal rearrangement on plasticization to pressures of approximately 50 atm in 50:50 mixed-gas feeds and temperatures between 15°C and 70°C.

In our continued efforts to characterize the chemical and morphological features of TR polymers, we have begun a series of fractional free volume measurements using positron annihilation lifetime spectroscopy (PALS).

Finally, to provide a broader framework for comparing our H<sub>2</sub> sorption and diffusion data, we are determining helium sorption in TR polymers and a number of other polymers commonly used for applications in gas separation membranes.

## Publication list (including patents) acknowledging the DOE grant or contract

1. Smith, Z.P., Tiwari, R.R., Murphy, T.M., Sanders, D.F., Gleason, K.L., Gunawan, G., Paul, D.R., and Freeman, B.D., The Basis for Hydrogen and Helium Permselectivity in Hydrocarbon and Fluorocarbon Based Polymers. in preparation.

2. Sanders, D.F., Guo, R., Smith, Z.P., Stevens, K.A., Liu, Q., McGrath, J.E., Paul, D.R., and Freeman B.D., Influence of Polyimide Precursor Synthesis Route and ortho-Position Functional Group on Thermally Rearranged (TR) Polymer Properties: Pure Gas Permeability and Selectivity. in preparation.
3. Smith, Z.P., Tiwari, R.R., Murphy, T.M., Sanders, D.F., Gleason, K.L., Paul, D.R., and Freeman, B.D., Hydrogen sorption in polymers for membrane applications. *Polymer*, **2013**, in press, DOI: 10.1016/j.polymer.2013.04.006.
4. Sanders, D.F., Smith, Z.P., Ribeiro, C.P., Guo, R., McGrath, J.E., Paul, D.R., and Freeman, B.D., Permeability, diffusivity, and free volume of thermally rearranged polymers based on 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB) and 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA). *Journal of Membrane Science*, **2012**, 409-410.
5. Smith, Z.P., Sanders, D.F., Ribeiro Jr, C.P., Guo, R., Freeman, B.D., Paul, D.R., McGrath, J.E., and Swinnea, S., Gas sorption and characterization of thermally rearranged polyimides based on 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB) and 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA). *Journal of Membrane Science*, **2012**, 416.