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Carbon molecular sieve structure development and membrane performance relationships

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ABSTRACT

Characterization techniques beyond microscopy, scattering and spectroscopy approaches are needed to understand and improve sub-angstrom discrimination between penetrants in carbon molecular sieve (CMS) membranes. Here we use a method based on molecular scale gas diffusion probes to understand relevant membrane properties at the required level of detail. We further use this method to consider hypotheses about the evolution of structure responsible for fundamental properties of CMS materials derived from a high performance CMS precursor polymer, 6FDA:BPDA-DAM. While 6FDA:BPDA-DAM derived CMS membranes display a ~230% improvement in CO_2 permeability when compared to Matrimid® derived CMS formed under the same conditions, the CO_2/CH_4 *diffusional selectivity* for these two materials are very similar at 35 and 38.5, respectively. These results indicate a non-trivial connection between CMS precursor material structure and resulting performance. Linking hypotheses about structural changes likely to occur during pyrolysis with the probe data provides insights regarding transformation of the random coil polyimide into ultra-rigid CMS, with exquisite size and shape diffusion selectivity. The results provide a framework for understanding and tuning properties of this special class of materials with important technological advantages in energy-intensive gas separations.

1. Introduction and background

Carbon molecular sieve (CMS) materials [1–6] surpass the permeability versus selectivity "upper bound" trade-off [7–10] of solution-processable polymers and provide a platform for creating advanced membranes. It is generally accepted that CMS transport properties rely upon a slit-like pore structure consisting of a distribution of larger (~7–20 Å) micropores connected by smaller (<7 Å) ultramicropore windows [3,11–13]. This fact notwithstanding, understanding the evolution of precursor semi-flexible polymers into final CMS structures is at an early stage. Fig. 1a(i & ii) represent the CMS pore structure and bimodal distribution comprising micropores and ultramicropores. Fig. 1b is a popular representation of a CMS material derived from a hydrocarbon precursor but it also provides a starting point for discussion of more complex CMS materials derived from polyimide precursors in our work, such as shown in Fig. 2.

Making a connection between the representations of the bimodal distribution of pores in Fig. 1a and a more chemically-relevant structure such as that in Fig. 1b is desirable—but challenging. It is reasonable to connect these two representations by attributing ultramicropores to defects *within the plates* shown in Fig. 1b, while attributing the micropores to the spaces *between the plates*. Of course, the details of the plate structure in such a picture will be different in a simpler hydrocarbon versus a polyimide derived CMS. Unlike oxygen-containing cellulosic and purely hydrocarbon precursors, the presence of fluorine and nitrogen in the polymer backbone introduces additional factors affecting the ultimate properties of the final CMS versus the case in Fig. 1b. Moreover, differences will exist even between CMS derived from different precursor polyimides [1,15,16]; however, the general concepts and features should be similar, as is considered later in this discussion.

Previous work on CMS materials derived from Matrimid® and similar aromatic polyimide precursors noted the difficulties in using traditional characterization techniques, due to the amorphous nature of these materials [17–21]. Recent work on more complex

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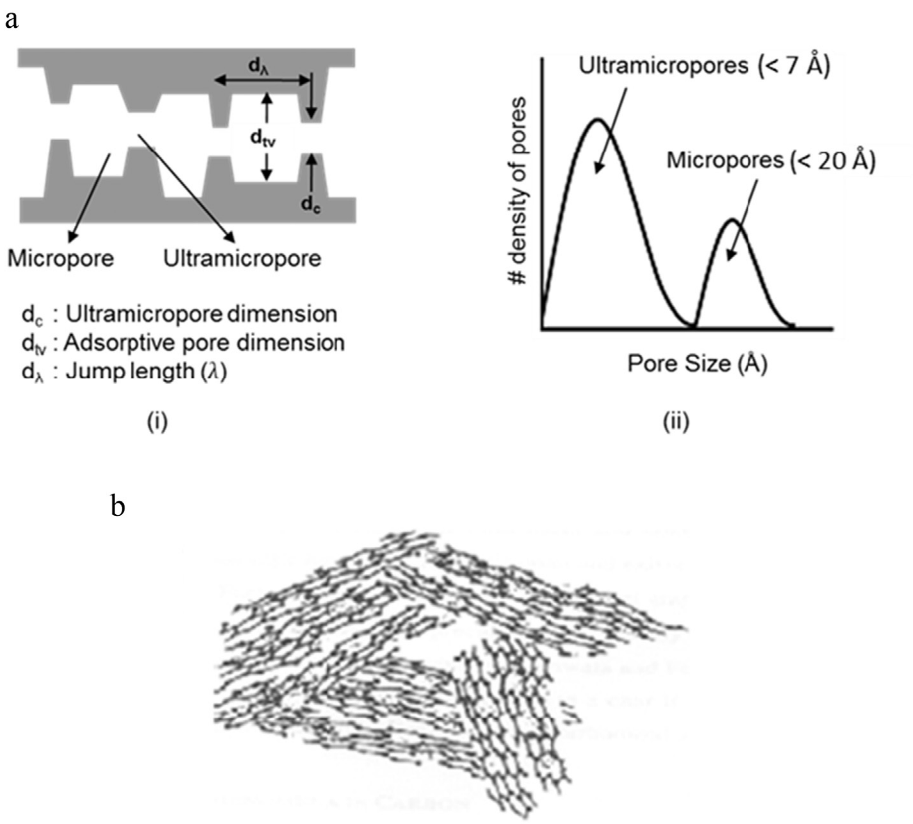

Fig. 1. a. CMS (i) Ideal “slit-like” pore structure and (ii) Bimodal distribution of pores [1]. b. Turbostratic carbon structure believed to represent some CMS materials [14].

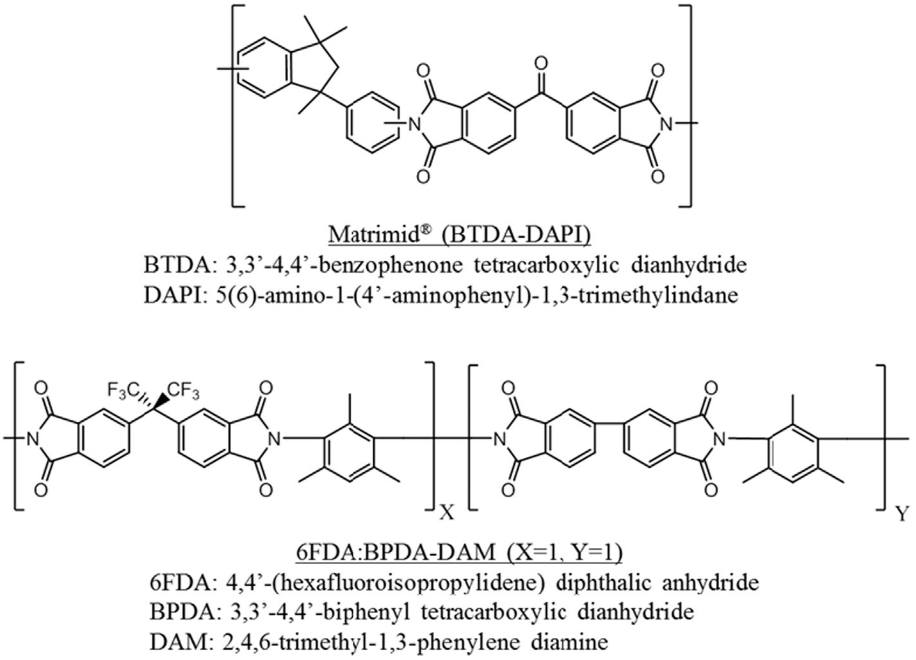

Fig. 2. Chemical structure of semi-flexible precursor polyimides Matrimid® and 6FDA:BPDA-DAM(1:1).

6FDA-based polyimide precursors further highlighted the disconnect between precursor physical properties and the resulting CMS materials. This recent work documented the lack of direct physical connection between free volume and x-ray “d-spacings” of polymer precursors and corresponding properties of CMS [22]. Considering these previous discussions, it is evident that this lack of a simple connection between the random coil precursor and the generally accepted slit-like structure of the final CMS, reminiscent