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## New perfluoro-dioxolane-based membranes for gas separations

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## ABSTRACT

Perfluoropolymer membranes have found commercial use because of their unique gas separation properties and chemical resistance. To date, studies of gas transport in perfluoropolymers have been limited largely to variants of the commercially available polymers, Teflon<sup>®</sup> AF, Cytop, and Hyflon<sup>®</sup> AD. Here, we describe gas transport in composite membranes fabricated from copolymers of perfluoro(2-methylene-4,5-dimethyl-1,3-dioxolane) and perfluoro(2-methylene-1,3-dioxolane). These new perfluoro copolymer membranes have superior gas separation performance compared to the commercial perfluoropolymers for a number of gas pairs, including H<sub>2</sub>/CH<sub>4</sub>, He/CH<sub>4</sub>, N<sub>2</sub>/CH<sub>4</sub>, and CO<sub>2</sub>/CH<sub>4</sub>. For example, membranes based on 57 mol% perfluoro(2-methylene-1,3-dioxolane) show H<sub>2</sub>/CH<sub>4</sub> selectivity of 130 combined with a H<sub>2</sub> permeance of 700 gpu. These values far exceed an upper bound for commercial perfluoropolymers. The transport properties of the new perfluoro membranes depend strongly on the copolymer composition with increasing amounts of the efficient packing monomer perfluoro(2-methylene-1,3-dioxolane), yielding membranes with higher size selectivity and lower permeance.

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## 1. Introduction

Fluoropolymers have been recognized as having unique properties ever since the fortuitous discovery of poly(tetrafluoroethylene) [PTFE] in 1938 [1]. Among the valuable characteristics of fluoropolymers are extraordinary chemical and thermal stabilities, as well as useful optical, electrical, and surface properties [2]. These attributes stem from the strong carbon–fluorine bonds and the electronic structure of the fluorine atom, and are most prominent in fully fluorinated or perfluorinated polymers. As a result of their distinctive qualities, perfluoropolymers have found widespread commercial applications in the automotive, electronics, aerospace, chemical, specialty packaging, and medical industries [2–4].

The use of perfluoropolymers as gas separation membrane materials was initially hindered by the fact that early polymers like PTFE were semi-crystalline, resulting in relatively low gas permeability and an inability to process them by solution casting and coating methods used in the membrane industry [5]. This situa-

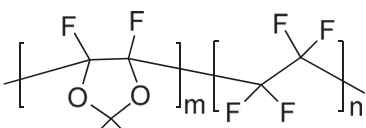
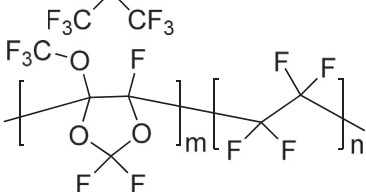
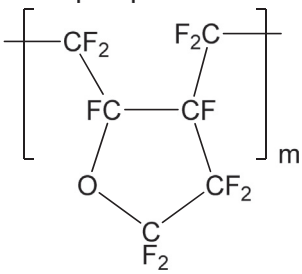
tion changed in the 1980s and 1990s with the development of amorphous, solvent-processable glassy perfluoropolymers available under the trade names Teflon<sup>®</sup> AF (DuPont) [6,7], Cytop (Asahi Glass) [8], and Hyflon<sup>®</sup> AD (Solvay) [9,10]. Over the past 25 years, the gas transport properties of these polymers have been studied extensively [11–21]. This work has shown that these perfluoropolymers have some unusual transport properties. For example, sorption of hydrocarbon gases and vapors in perfluoropolymers is anomalously low, and cannot be explained by regular solution theory or modern equation-of-state solubility models [22–24]. This attribute has been exploited to develop composite membranes that are resistant to hydrocarbon vapor-induced plasticization, which would have a detrimental effect on conventional membrane performance [25–27]. This swelling resistance feature has also been used in membrane-based solvent dehydration applications [28–30]. Additional interesting transport behavior in perfluoropolymers that has been noted in recent years includes low H<sub>2</sub>S sorption that is responsible for unprecedented CO<sub>2</sub>/H<sub>2</sub>S selectivities [31], low H<sub>2</sub> solubility that generates unique He/H<sub>2</sub> selectivities [32,33], and relatively high H<sub>2</sub>/CH<sub>4</sub> selectivities, again caused by solubility effects [22].

Recently, Robeson [34] re-examined the so-called upper bound relationship for membrane separations that he originally described in an influential 1991 paper [35]. He observed that in

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**Table 1**  
Chemical structures, glass transition temperature, nitrogen permeability, and O<sub>2</sub>/N<sub>2</sub> selectivity of Teflon AF, Cytop, and Hyflon AD.

Polymer	Chemical structure	Glass transition temperature (°C)	Nitrogen permeability (Barrer)	O <sub>2</sub> /N <sub>2</sub> selectivity
Teflon <sup>®</sup> AF2400		240	480 [20]	2.0[20]
Hyflon <sup>®</sup> AD60		134	24 [22]	2.9[22]
Cytop		108	5.0 [22]	3.2[22]

1 Barrer =  $10^{-10}$  cm<sup>3</sup>(STP) cm/(cm<sup>2</sup> s cmHg).

the cases where there were significant shifts in the upper bound position over the past 17 years, they were largely due to new transport data on perfluorinated polymers [34]. An analysis of the tradeoff data suggested that the exceptional performance of the perfluorinated polymers was mostly due to their unique solubility selectivities. In light of the position of the commercially available amorphous perfluoropolymers near the upper bound for several gas pairs, Robeson noted that “perhaps even improved results could be achieved with a detailed structure property study involving additional fluorinated monomers” [34].

Table 1 shows the chemical structures and a few relevant properties for Teflon AF, Cytop, and Hyflon AD. These commercial perfluoropolymers are either copolymers of perfluorodioxole rings and tetrafluoroethylene (Teflon AF and Hyflon AD) or a cyclic perfluoro homopolymer (Cytop). In general, the dioxole rings in these materials hinder polymer chain packing, yielding amorphous polymers with relatively high gas permeability. TFE is added to the copolymers to improve processability, and has the effect of lowering gas permeability and increasing size selectivity in Teflon AF and Hyflon AD. From the most permeable of these polymers (Teflon AF2400) to the least permeable (Cytop), the perfluoropolymers span about two orders of magnitude in nitrogen permeability. Compared to conventional glassy polymers used for membrane gas separations, such as polysulfone or Matrimid, the perfluoropolymers are much more permeable, but have lower size selectivity.

Other than the commercially available glassy perfluoropolymers, there are very limited gas transport data available for fully fluorinated polymers. Paul and Chiou [36] examined gas transport in dry Nafion<sup>®</sup> (a copolymer of tetrafluoroethylene and sulfonated perfluorovinyl ether) and found relatively high permeabilities and selectivities for several gas pairs (He/CH<sub>4</sub>, He/H<sub>2</sub>, and N<sub>2</sub>/CH<sub>4</sub>) compared to conventional hydrocarbon-based polymers considered for membrane applications. Nemser and Roman [11] reported gas permeability for a perfluorodioxolane-based polymer originally synthesized by DuPont in the late 1960s [37]. They found this polymer to be much less permeable than the Teflon AF copolymers

that were the focus of their study. Fitch et al. [38] examined gas transport in several grades of Viton fluoroelastomer as part of a study of barrier materials used in gaskets and seals. Prabhakar et al. [39] studied a perfluorinated elastomer copolymer of tetrafluoroethylene and perfluoromethyl vinyl ether and found unusually low hydrocarbon vapor solubilities that could not be explained by an equation-of-state model with simple mixing rules. The same perfluoro elastomer was studied by Merkel and Toy [31], and shown to have unusual H<sub>2</sub>S/CO<sub>2</sub> solubility selectivity compared to hydrocarbon-based polymers. Recently, Belov et al. [40] studied gas transport in poly(hexafluoropropylene) and a copolymer of this material with perfluoromethylvinyl ether. They found low solubilities of hydrogen-containing molecules in these polymers, resulting in high selectivities for some gas pairs (He/CH<sub>4</sub>, N<sub>2</sub>/CH<sub>4</sub>, He/H<sub>2</sub>).

These prior studies show that other fully fluorinated polymers generally share the interesting transport properties of the commercial perfluoropolymers. Such properties place perfluoropolymers near the upper bound for several gas pairs, particularly those involving hydrogen and hydrocarbons (e.g., methane). However, the existing commercial perfluoropolymers tend to fall into the high-permeability, modest-selectivity category of upper bound materials. It has been a long-standing goal to identify solvent processable perfluoropolymers with higher selectivities for industrially important gas pairs such as CO<sub>2</sub>/CH<sub>4</sub>, H<sub>2</sub>/CH<sub>4</sub>, and N<sub>2</sub>/CH<sub>4</sub>.

Here, we report gas permeances and selectivities for composite membranes based on new amorphous perfluoropolymers. These glassy perfluorinated materials are copolymers of perfluoro(2-methylene-4,5-dimethyl-1,3-dioxolane) and perfluoro(2-methylene-1,3-dioxolane). The synthesis and characterization of these new perfluoropolymers have been described previously [41–44], but to our knowledge, this is the first time these materials have been made into membranes and tested for gas transport performance. We have found that membranes made from some of these perfluoropolymers have superior gas separation performance compared to those prepared from the commercial perfluoropolymers (Teflon AF, Cytop, and Hyflon AD).

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