



Gas separation membranes prepared with copolymers of perfluoro(2-methylene-4,5-dimethyl-1,3-dioxolane) and chlorotrifluoroethylene



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ABSTRACT

Several families of hydrocarbon polymers (polysulfones, polycarbonates, cellulose acetates, polyamides, and polyimides) have been established as common industrial gas separation membranes over the past three decades. Fluoropolymer membranes have found commercial use because of their unique gas separation properties in addition to their extraordinary chemical resistance and thermo-oxidative stability. To date, studies of gas transport in fluoropolymers have been limited largely to variants of the commercially available perfluoropolymers: Teflon[®] AF, Cytop[™], and Hyflon[®] AD. Here, we describe gas transport in composite membranes fabricated from copolymers of perfluoro(2-methylene-4,5-dimethyl-1,3-dioxolane) (PFMDD) and chlorotrifluoroethylene (CTFE). This poly(PFMDD-co-CTFE)-based membranes have far superior gas separation performance compared to the commercial perfluoropolymers for a number of gas pairs, including H₂/CH₄, He/CH₄, and CO₂/CH₄. The gas separation performance of the membranes depends strongly on the copolymer composition. Increasing the amount of CTFE up to 30 mol % in the copolymer increases the membrane selectivity and reduces permeance. The membranes based on 70 mol% PFMDD-30 mol% CTFE poly(PFMDD-co-CTFE) show H₂/CH₄ and He/CH₄ selectivities of 210 and 480, respectively, values that far exceed those possible with the known commercial perfluoropolymers.

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1. Introduction

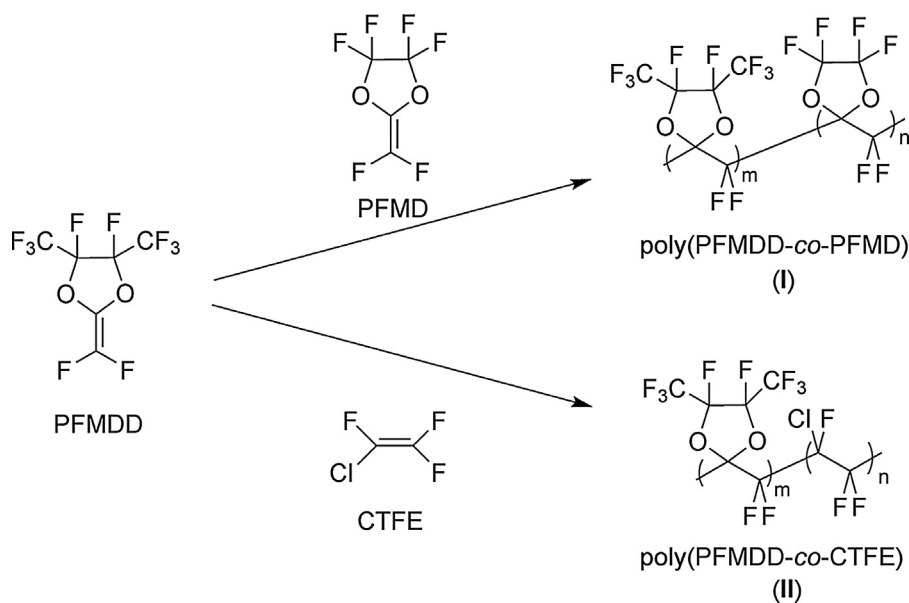
Polymeric gas separation membranes have become widely used for a variety of industrial gas separations applications over the past three decades and several polymers have been established as common gas separation membranes, including polysulfones, polycarbonates, cellulose acetates, polyamides, and polyimides [1]. Fluoropolymers as a new class of membrane material have attracted increasing interest due to their unique properties including the extremely high chemical resistance and extraordinary thermo-oxidative stability, improved separation performance as well as plasticization resistance [1,2]. The use of fluoropolymers for gas separations has drawn great attention ever since the development of commercial perfluoropolymers under trade names Teflon[®] AF, Cytop[™], and Hyflon[®] AD. These perfluoropolymers are amorphous and solvent-processable, resulting in relatively high gas permeability and the feasibility to process them by

solution casting and coating methods used in the membrane industry [3]. The gas transport properties of these commercial perfluoropolymers have been studied extensively over the past 25 years [4–13]. The perfluoropolymers have unique gas separation properties and in some cases they exceed the selectivity-permeability upper bound relationship originally described by Robeson [14]. However, new amorphous and solvent-processable fluoropolymers with higher selectivity are still highly desirable.

In the search for new, improved perfluoropolymers for gas separation membranes, we have previously prepared copolymers of perfluoro(2-methylene-4,5-dimethyl-1,3-dioxolane) (PFMDD) and perfluoro(2-methylene-1,3-dioxolane) (PFMD) (I, Scheme 1) [3]. The homopolymer of PFMDD is amorphous, while the homopolymer of PFMD is crystalline and does not dissolve in organic solvents. When PFMDD and PFMD are copolymerized, the resulting poly(PFMDD-co-PFMD) is amorphous when the content of PFMD is less than 70 mol%, and the amorphous poly(PFMDD-co-PFMD) exhibited superior gas separation performance for a number of important gas pairs [3]. We found that when the amount of the PFMD monomer in the copolymer is increased, the gas permeance shows a modest decline, but the size selectivity is

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Scheme 1. The chemical structures of monomers PFMD, PFMD, CTFE and copolymers poly(PFMDD-co-PFMD) and poly(PFMDD-co-CTFE).

dramatically increased. For example, the H_2/CH_4 selectivity of the membrane increases from 50 to 130 as the PFMD monomer content is increased from 26 to 57 wt%. This effect is rationalized by the fact that the absence of substituents on its 4 and 5 positions allows the PFMD monomer to pack more efficiently than PFMDD, giving a more ordered and tighter chain structure that is better for sieving gas molecules. The combination of PFMDD and PFMD in varied amounts allows the gas permeation properties of the resulting copolymer to be tuned very effectively.

In a continuing effort to identify highly selective fluoropolymers for gas separations, we aimed to prepare new fluoropolymers derived from copolymerization of the bulky PFMDD monomer and a small fluorinated monomer that might exhibit tight chain packing. Chlorotrifluoroethylene (CTFE) is the most widely used fluoroalkene after tetrafluoroethylene (TFE) [15–17]. CTFE is a smaller molecule than PFMD and is known to pack efficiently as a polymer. In fact, polychlorotrifluoroethylene (PCTFE) is highly crystalline and does not dissolve in most organic solvents including fluorinated solvents, and it is known as one of the best gas barrier materials [18]. CTFE is readily copolymerized with various vinyl monomers to yield novel copolymers [19,20]. We have previously prepared copolymers of a perfluoro dioxolane monomer with CTFE using a free radical initiator in bulk or in solution [21]. The polymers obtained are soluble in fluorinated solvents such as hexafluorobenzene and perfluoro-2-butyltetrahydrofuran (Fluorinert[®] FC-75). The films of the copolymers are flexible, chemically and thermally stable, and highly transparent.

Thus herein we describe a new fluoropolymer, the copolymer of PFMDD and CTFE (II, Scheme 1) for gas separation. The physical properties as well as the gas separation performance of the copolymers were investigated.

2. Results and discussion

The poly(PFMDD-co-CTFE) copolymers appear as white powder and the yield was about 80–90% based on the amount of PFMDD monomer in feed. The compositions of the copolymers can be estimated from ^{19}F NMR spectra, as shown in Fig. 1. The peak at ca. –80 ppm is assigned to the two $-\text{CF}_3$ groups located on the 4 and 5 position of the dioxolane ring of PFMDD unit; a group of broad and overlapped peaks from –100 to –130 ppm are attributed to the

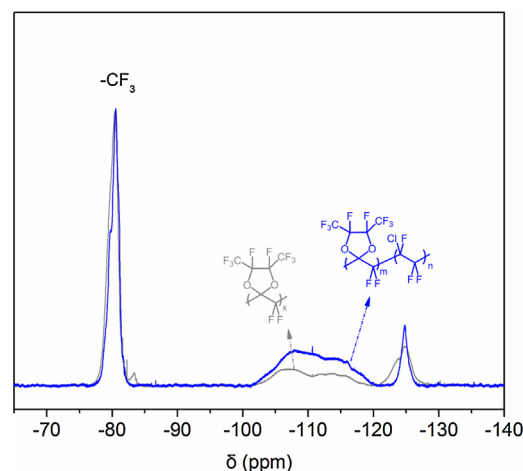


Fig. 1. The ^{19}F NMR (400 MHz) spectrum of poly(PFMDD-co-CTFE) (70 mol% PFMDD and 30 mol% CTFE) superimposed on that of the PFMDD homopolymer. The difference of peak integrals in the –100 to –130 ppm range is attributed to the presence of CTFE units in the polymer backbone.

$-\text{CF}_2-$ and $-\text{CClF}-$ units [22–24] on the polymer backbone as well as the two $-\text{CF}-$ groups of the dioxolane ring. By using the integrals of the $-\text{CF}_3$ peak and the region of –100 to –130 ppm from both the spectra of poly(PFMDD-co-CTFE) copolymer and the PFMDD homopolymer, the fraction of CTFE in the copolymers can be estimated.

Table 1 summarizes the compositions as well as other physical properties of four poly(PFMDD-co-CTFE) samples. The estimated CTFE content in the copolymers using the NMR data is 12 mol%, 17 mol%, 30 mol%, and 52 mol% for sample B1, B2, B3, and B4, respectively. The exact compositions of the corresponding samples were also determined by elemental analysis data. Using the Cl data, the CTFE content in the copolymers is calculated to be 10 mol%, 11 mol%, 28 mol%, and 50 mol% for sample B1, B2, B3, and B4, respectively. This indicates sample B1 and B2 are almost identical in composition, as verified by the same T_g value (152 °C). Since PCTFE has a lower T_g (75 °C) than that of PFMDD homopolymer

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