Supplemental Information

Dioxolane-based Perfluoropolymers with Superior Membrane Gas Separation Properties

Milad Yavari[1], Minfeng Fang[2], Hien Nguyen[1], Timothy C. Merkel[3], Haiqing Lin[1*], and

Yoshiyuki Okamoto[2*]

■ Thermal stability of poly(PFMD) and poly(PFMMD)

Thermal degradation of poly(PFMD) and poly(PFMMD) were investigated using a thermogravimetric analyzer (TGA, TA Instruments DSC SDT Q600, New Castle, DE). The system operated at a heating rate of 10 °C/min and a nitrogen flow of 100 ml/min. Figure S1 presents TGA curves of poly(PFMD) and poly(PFMMD). Both perfluoropolymers show thermal stability above 400 °C, which is comparable to polytetrafluoroethylene (PTFE) and other perfluoropolymers such as Teflon AFs and Hyflon ADs.[1, 2] The stability is ascribed to the strong C-F bond with low reactivity and the protection of the polymer main chains from degradation by fluorine atoms.[1]

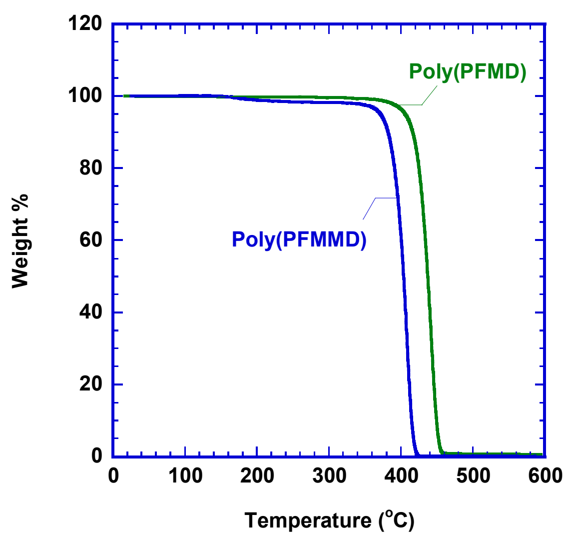

Figure S1. TGA curves of poly(PFMD) and poly(PFMMD) under N_2 atmosphere.

Gas transport properties in poly(PFMD) and poly(PFMMD)

Fig. S2a compares the pure-gas permeability of poly(PFMD) and poly(PFMMD) at 35 °C as a function of the penetrant critical volume. Poly(PFMMD) exhibits higher gas permeability and lower He/gas selectivity than poly(PFMD), as shown in Fig. S2b, because of the higher FFV in poly(PFMMD) (0.23) than poly(PFMD) (0.21).

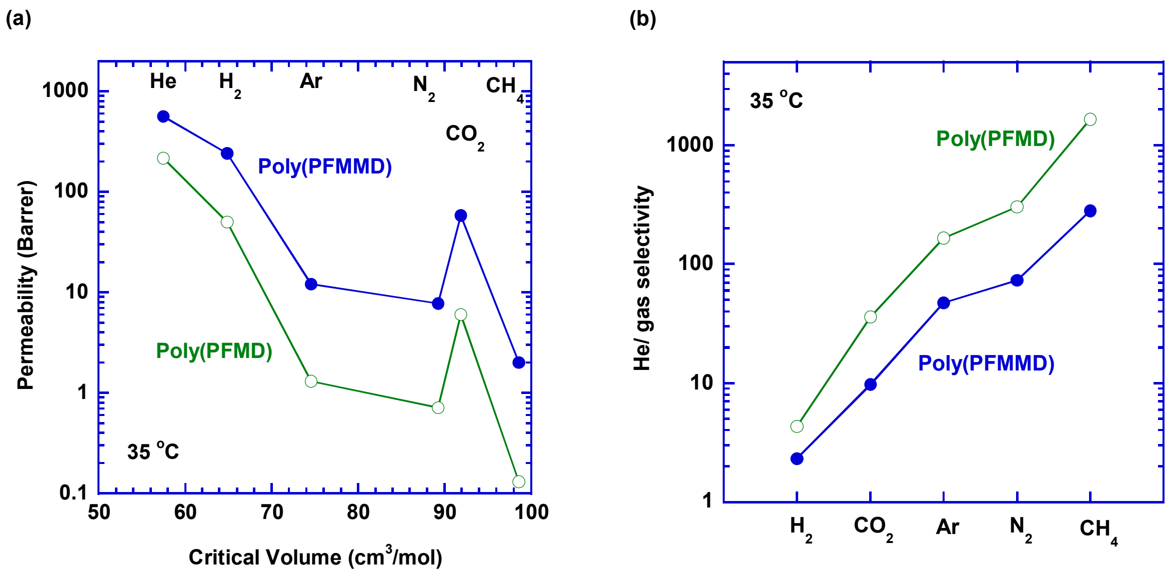

Figure S2. Comparison of (a) gas permeability and (b) He/gas selectivity at 35 °C in poly(PFMD) and poly(PFMMD).

The sorption of small molecules in glassy polymers is usually described by the dual-mode model using eq S1:

$$C_A = k_d p_A + \frac{C'_H b p_A}{1 + b p_A} \tag{S1}$$

where k_d is Henry's sorption coefficient, C'_H is the Langmuir capacity parameter representing the maximum amount of penetrant sorbed in the nonequilibrium excess free, and b is an equilibrium constant indicating the affinity between the penetrant and polymer.[3]

Table S1. Dual-mode sorption parameters including k_d (cm^3(STP)/cm^3 atm), C'_H (cm^3(STP)/cm^3), and b (1/atm) in poly(PFMD) and poly(PFMMD) at 35 °C.

Gas	Poly(PFMD)			Poly(PFMMD)		
	k_d	C'_H	b	k_d	C'_H	b
Ar	0.19	2.3	0.068	0.32	3.2	0.096
CO_2	0.93	5.4	0.20	0.64	15	0.096
CH_4	0.27	2.3	0.11	0.26	5.5	0.067
C_2H_4				0.45	8.9	0.15
C_2H_6	0.80	3.7	0.44	0.57	10	0.14

Table S2. Calculated gas solubility (cm^3 (STP)/(cm^3 atm)) in poly(PFMD) and poly(PFMMD) at infinite dilution and 10 atm using the parameters from Table S1.

Gas	Poly(PFMD)		Poly(PFMMD)	
	Infinite dilution	10 atm	Infinite dilution	10 atm
Ar	0.35	0.28	0.63	0.48
CO_2	2.0	1.3	2.1	1.4
CH_4	0.52	0.39	0.63	0.48
C_2H_4			1.8	0.98
C_2H_6	2.4	1.1	2.0	1.2

References:

1. Cox, J. M.; Wright, B. A.; Wright, W. W. Thermal degradation of fluorine-containing polymers. Part I. Degradation in vacuum. *J. Appl. Polym. Sci.* **1964,** 8 (6), 2935-2950.
2. Chemours™ Teflon® AF amorphous fluoroplastic, https://chemours.com/Teflon_Industrial/en_US/products/product_by_name/teflon_af/index.html.
3. Kanehashi, S.; Nagai, K. Analysis of dual-mode model parameters for gas sorption in glassy polymers. *J. Membr. Sci.* **2005,** 253 (1), 117-138.