SUPPORTING INFORMATION

Volumetric properties and sorption behavior of perfluoropolymers with dioxolane pendant rings

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Membranes synthesis and fabrication

Poly(PFMD) and poly(PFMMD) were synthesized via radical polymerization from perfluoro-2-methylene-1,3-dioxolane and perfluoro-2-methylene-4-methyl-1,3-dioxolane, respectively.[1] The average molecular weight of poly(PFMMD), 1.0×10^6 g/mol, was determined using the Mark-Houwink method.[1] The molecular weight of poly(PFMD) cannot be determined, as it is not soluble in any solvents.[1]

Flat poly(PFMMD) films, about 50 μm thick, were fabricated via solution casting from a 5 wt% solution in hexafluorobenzene.[1] To ensure complete solvent removal, nascent membranes were first dried in air and then under vacuum at 80°C overnight. Poly(PFMD) films were prepared via compression molding at 250°C, due to the lack of polymer solubility in any solvents.

Table S1. *Relevant NELF model parameters and equations.*

symbol	property	definition
M_i	*Molar mass of species i*	
ρ_i	*Density of species i*	
ρ	*Density of the mixture*	
ω_i	*Mass fraction of species i*	
T_i^*	*Characteristic temperature of pure component i*	
p_i^*	*Characteristic pressure of pure component i*	
ρ_i^*	*Characteristic density of pure component i*	
Φ_i	*Volume fraction of species i at close packed conditions*	$\Phi_i = \frac{\omega_i / \rho_i^*}{\sum_i \omega_i / \rho_i^*}$
k_{ij}	*Binary parameter*	
r_i^0	*Number of lattice cells occupied by a molecule of pure component i*	
r_i	*Number of lattice cells occupied by a molecule in mixture*	
$\tilde{T}_i$	*Reduced temperature of pure component i*	$\tilde{T}_i = \frac{T}{T_i^*}$
$\tilde{p}_i$	*Reduced pressure of pure component i*	$\tilde{p}_i = \frac{p}{p_i^*}$
$\tilde{\rho}_i$	*Reduced density of pure component i*	$\tilde{\rho}_i = \frac{\rho_i}{\rho_i^*}$
$\tilde{T}$	*Reduced temperature of the mixture*	$\tilde{T} = \frac{T}{T^*}$
$\tilde{p}$	*Reduced pressure of the mixture*	$\tilde{p} = \frac{p}{p^*}$
$\tilde{\rho}$	*Reduced density of the mixture*	$\tilde{\rho} = \frac{\rho}{\rho^*}$
v_i^*	*Volume occupied by a mole of lattice site of pure component i*	$v_i^* = \frac{RT_i^*}{p_i^*}$
Mixing rules (for binary mixtures)		
T^*	*Characteristic temperature*	$T^* = \frac{p^*}{\frac{\Phi_1 p_1^*}{T_1^*} + \frac{\Phi_2 p_2^*}{T_2^*}}$
p^*	*Characteristic pressure*	$p^* = \Phi_1 p_1^* + \Phi_2 p_2^* - \Phi_1 \Phi_2 \left[p_1^* + p_2^* - 2(1-k_{12})\sqrt{p_1^* p_2^*} \right]$
ρ^*	*Characteristic density*	$\frac{1}{\rho^*} = \frac{\omega_1}{\rho_1^*} + \frac{\omega_2}{\rho_2^*}$
Relevant NELF model equations		
LF equation of state for pure penetrant		$\tilde{\rho}_1 = 1 - \exp\left[-\frac{\tilde{\rho}_1^2}{\tilde{T}_1} - \frac{\tilde{p}_1}{\tilde{T}_1} - \tilde{\rho}_1 \left(1 - \frac{1}{r_1^0} \right) \right]$

Pure penetrant equilibrium chemical potential	$$\frac{\mu_1^0}{RT} = r_1^0\left[-\frac{\tilde{\rho}_1}{\tilde{T}_1} + \frac{\tilde{p}_1}{\tilde{T}_1\tilde{\rho}_1} + \frac{1}{r_1^0}\ln\tilde{\rho}_1 + \frac{1-\tilde{\rho}_1}{\tilde{\rho}_1}\ln\left(1-\tilde{\rho}_1\right)\right]$$
Non-equilibrium chemical potential of species i in mixture	$$\frac{\mu_i^{ne}}{RT} = \ln\left(\tilde{\rho}\phi_i\right) - \left(r_i^0 + \frac{r_i - r_i^0}{\tilde{\rho}}\right)\ln\left(1-\tilde{\rho}\right) - r_i - \tilde{\rho}\frac{r_i^0 v_i^*}{RT}\left[p_i^* + \sum_{j=1}^{N_p+1}\phi_j\left(p_j^* - \Delta p_{ij}^*\right)\right]$$

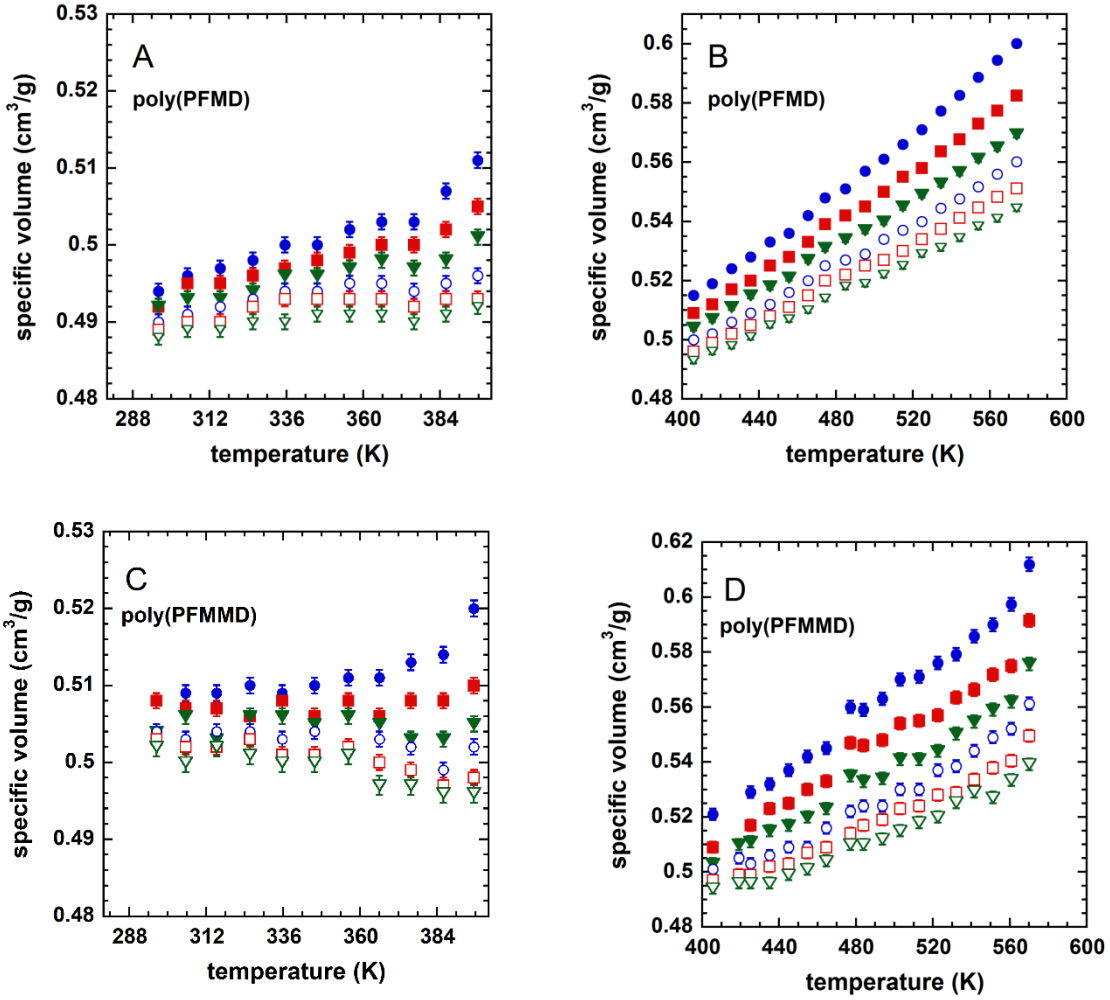

Figure S1. *Experimental pVT data for poly(PFMD) in the glassy (A) and rubbery region (B). Experimental pVT data for poly(PFMMD) in the glassy (C) and rubbery region (D). Experimental uncertainties are reported as well.*

Table S2. *Binary parameters and swelling coefficients estimated from the NELF analysis.*

penetrant	k_{ij}		k_{sw} (MPa^{-1})	
	poly(PFMD)	*poly(PFMMD)*	*poly(PFMD)*	*poly(PFMMD)*
Ar	*0.09 ± 0.02*	*0.07 ± 0.02*	*0*	*0*
CH_4	*0.045 ± 0.007*	*0.07 ± 0.01*	*0*	*0*
C_2H_6	*0.045 ± 0.004*	*0.09 ± 0.005*	*0.008± 0.0008*	*0.007± 0.0005*
C_2H_4	/	*0.08 ± 0.005*	/	*0*
CO_2	*-0.04 ± 0.005*	*-0.025 ± 0.01*	*0.007± 0.0005*	*0.005± 0.0002*

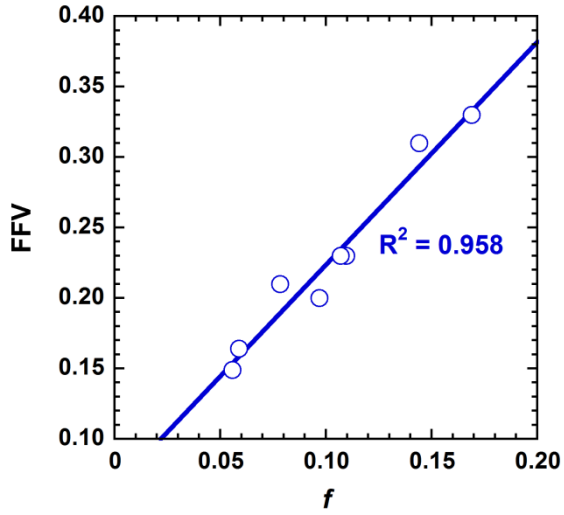

Figure S2. *FFV vs. f for several polymers.*

The definition of fractional free volume (FFV) is:

$FFV = (\hat{V} - \hat{V}_0)/\hat{V}_0$

where $\hat{V}$ and $\hat{V}_0$ are the polymer specific volume and the volume occupied by polymer chains, respectively. The lattice fluid definition of fractional free volume, *f*, is:

$$f = \frac{\rho_2^* - \rho_2^0}{\rho_2^*}$$

where ρ_2^* and ρ_2^0 are the lattice fluid characteristic density (i.e., the polymer density at 0K, where the chain packing is maximum) and the polymer density at room temperature, respectively.

Obviously *FFV* and *f* values do not match to each other, as they are defined and calculated in a completely different way. However, as shown in Fig. S2, they are linearly related.

References

1. Yavari, M.; Fang, M.; Nguyen, H.; Merkel, T. C.; Lin, H.; Okamoto, Y. Dioxolane-based perfluoropolymers with superior membrane gas separation properties. *Macromolecules* **2018**, *51*, 2489.