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The role of halogens in polychlorotrifluoroethylene (PCTFE) in membrane gas separations

Milad Yavari[a], Yoshiyuki Okamoto[b], Haiqing Lin[a,*]

[a] Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, NY 14260, USA
[b] Department of Chemical and Biomolecular Engineering, Tandon School of Engineering, New York University, Six MetroTech Center, Brooklyn, NY 11201, USA

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ABSTRACT

Halogenated polymers have emerged as interesting materials for membrane gas separation. Herein, we demonstrate that a combination of F and Cl substituents in polymers provide unexpectedly superior He/gas separation properties, as exemplified by polychlorotrifluoroethylene (PCTFE). PCTFE exhibits a He permeability of 26 Barrers at 35 °C and pure gas selectivity of He/H_2, He/CO_2, and He/CH_4 of 6.2, 53, and 1100, respectively. These selectivity values are among the highest reported for polymers, and the separation performance is very close to the Robeson's upper bounds. The effect of crystallinity in PCTFE on gas transport properties is discussed, and the gas transport properties in PCTFE are compared with other polyethylene (PE) analogues such as PE, polyvinyl chloride (PVC), polyvinylidene fluoride (PVDF), and polytetrafluoroethylene (PTFE). The effect of F and Cl substituents on gas solubility is also elucidated using a variety of hydrocarbons and halogenated liquids. The F substituents lead to unexpectedly high He solubility and exhibit unfavorable interactions with H_2 and CH_4, while the Cl substituents increase solubility parameter and size-sieving ability, both of which contribute to the superior He/gas separation properties (particularly He/H_2 and He/CH_4). The understanding of the role of F and Cl substituents of polymers in gas transport properties can be useful in designing high performance polymers for membrane gas separation.

1. Introduction

Polymers with high gas permeability and selectivity are of great interests for membrane gas separation, an energy-efficient gas separation technology [1–3]. However, there is a trade-off between gas permeability and selectivity, i.e., polymers with higher permeability exhibit lower selectivity, and vice versa [4–6]. Such a trade-off is ascribed to an intrinsic dilemma that polymers with higher free volume exhibit higher permeability but weaker size-sieving ability and thus lower selectivity [7,8]. An effective strategy to design polymers overcoming the trade-off is to incorporate functional groups that interact with gases, increasing solubility selectivity and thus permeability selectivity without significantly decreasing permeability [5,6,9–12].

Halogenated polymers have demonstrated interesting gas separation properties [13–19]. For example, perfluoropolymers have unfavorable interactions with hydrocarbons such as CH_4 and thus, they have been considered for N_2/CH_4 and CO_2/CH_4 separation [4,15,16,20,21], and they have unexpectedly high helium solubility, resulting in high He/N_2 and He/CH_4 separation performance [20–23]. The upper bounds for N_2/CH_4, He/H_2 and He/CH_4 separation in the Robeson's plots are governed by the amorphous glassy perfluoropolymers such as Hyflon® AD and Teflon® AF, which are copolymers of tetrafluoroethylene (TFE) and perfluorodioxlanes [4,20,21]. The TFE component provides high selectivity of He/CH_4 and He/H_2, while the perfluorodioxlane disrupts the TFE crystallization and provides high gas permeability. Recently, a series of copolymers of chlorotrifluoroethylene (CTFE) and perfluoro(2-methylene-4,5-dimethyl-1,3-dioxolane) (PFMDD) have been synthesized, and exhibit superior He/CH_4 and CO_2/CH_4 separation properties [20,21]. For example, a copolymer comprising 30% CTFE and 70% PFMDD shows He/CH_4 and CO_2/CH_4 selectivity of 480 and 48, respectively, which is very attractive for practical separations [24].

Despite the success in exploring these fluoropolymers for membrane gas separation, there lacks systematic understanding of gas transport properties in the polymers containing Cl and F substituents. In this work, we selected polychlorotrifluoroethylene (PCTFE) to elucidate the effect of F and Cl substituents on gas transport properties. There are few data on gas transport in PCTFE in the literature, though it is commercially available [25]. We systematically determine physical properties of PCTFE (including crystallinity and fractional free volume) and

* Corresponding author.
E-mail address: haiqingl@buffalo.edu (H. Lin).

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examine the effect of fluorine and chlorine groups on membrane gas separation properties. The effect of F and Cl on gas solubility is also elucidated using exampled halogenated organic liquids. Surprisingly, this simple polymer containing both F and Cl substituents demonstrates great potential for He/gas and H_2/CO_2 separation. Understanding the role of F and Cl substituents in the structure/gas separation property relationship is valuable to design advanced polymers with superior gas separation properties.

2. Experimental section

2.1. Materials

Thin films of PCTFE (under the tradename of HydroBlock® P600TR) were generously provided by Honeywell Performance Materials and Technologies (Pottsville, PA). Gas cylinders of N_2, Ar, H_2 and He with a purity of 99.999%, CH_4 and CO_2 (99.9%), and C_2H_6 (99.3%) were obtained from Praxair, Inc. (Tonawanda, NY).

2.2. Characterization of physical properties of PCTFE films

Density and thickness of the PCTFE films were determined using the geometric method. The weight was measured by an analytical balance, Model XS 64 (Mettler-Toledo, Columbus, OH), and the volume was determined using Accu-Pyc II 1340 Gas Pycnometer (Micromeritics Instrument Corporation, Norcross, GA). Films of about 0.3 g were used to achieve high accuracy of the volume measurement. Because the commercial films have uniform thickness, the thickness is calculated from the volume and known surface area.

An Ultima IV X-ray diffractometer (Rigaku Corporation, Tokyo, JP) with CuKα radiation (with a wavelength of 1.54 Å) was used to characterize the PCTFE films at a scanning range of $5-50^{\circ}$ and a scanning rate of 0.5°/min. The obtained Wide-angle X-Ray Diffraction (WAXD) spectra were analyzed using Rigaku PDXL software 4.2.2 to estimate the crystallinity.

Differential scanning calorimetry (DSC, Q2000, TA Instruments, New Castle, DE) was used to determine thermal transitions of the PCTFE films. The measurement was performed at a heating rate of 10 °C/min from 25 °C to 250 °C under a nitrogen gas flow of 50 ml/min. Universal Analysis 2000 software was used to determine glass transition temperature (T_g), melting temperature (T_m), and heat of crystallization and melting.

2.3. Determination of pure-gas permeation and sorption properties

Pure-gas permeability of CH_4, N_2, Ar, CO_2, H_2, and He through PCTFE films was determined using a constant volume/variable pressure apparatus at 35 °C [26,27]. A PCTFE film masked using an aluminum tape with an active area of 2.0 cm^2 was mounted in a permeation cell (Millipore Corporation, Bedford, MA). The steady-state rate of pressure increase in the downstream with a known volume was used to calculate gas permeability. Gas permeability (P_A) has units of Barrers, where 1 Barrer = 10^{-10} cm^3(STP) cm/(cm^2 s cmHg).

Pure-gas solubility of CH_4, Ar, CO_2 and C_2H_6 in PCTFE films was determined using a dual-volume and dual-transducer apparatus based on a pressure decay method [26,28]. Polymer films were placed in a sample cell and evacuated overnight. A known amount of gas was then introduced into the sample cell, and the pressure in the sample cell decreased due to the gas sorption by the polymer. The gas solubility (S_A) can be calculated using the following equation:

$$S_A = C_A/p_A \tag{1}$$

where C_A is the concentration of the sorbed gas (cm^3 (STP)/cm^3 polymer) in the polymer at an equilibrium pressure of p_A (atm). The determined solubility of CH_4, Ar, CO_2 and C_2H_6 has an uncertainty less than 10%, which was estimated based on error propagation and analysis [29]. The sorption of He, H_2 and N_2 was too low to determine using this method [26].

Within the framework of the solution-diffusion mechanism, gas diffusivity (D_A, cm^2/s) in PCTFE can be calculated using the following equation [30]:

$$D_A = P_A/S_A \tag{2}$$

3. Results and discussion

3.1. Fractional free volume and crystallinity in PCTEF

Gas transport properties in polymers are influenced by polymer morphology, such as fractional free volume (*FFV*) [31] and crystallinity in volume percentage (φ_c) [28,32,33]. The *FFV* of the amorphous phase polymer can be estimated using the following equation [31,34]:

$$FFV = 1 - \rho_a V_o \tag{3}$$

where ρ_a is the density of amorphous PCTFE, and V_o is the specific occupied volume at 0 K, which can be estimated as 1.3 times of van der Waals volume [34]. Based on a value of 2.077 g/cm^3 for ρ_a [35], the *FFV* in PCTFE is estimated to be 0.170.

Polymer crystallinity can be estimated using three methods, i.e., density, heat of melting from the DSC, and WAXD spectrum [28]. The φ_c values from these three methods are described below.

First, the φ_c can be estimated from the polymer density (ρ_P) using Eq. (4) [28]:

$$\varphi_c = \frac{\rho_P - \rho_a}{\rho_c - \rho_a} \times 100\% \tag{4}$$

where ρ_c is the density of crystalline phase (2.187 g/cm^3) [35]. Based on the density value of 2.137 g/cm^3 determined from the geometric method in this study, the φ_c has a value of 54%.

Second, the φ_c can be estimated from the DSC curve shown in Fig. 1. As temperature increases from 25 °C to 250 °C, the polymer exhibits a T_g of 63 °C, a crystallization peak at 89 °C, and a melting peak at 211 °C. These thermal transitions are consistent with those reported in the literature [36–38].

The φ_c value can be estimated from the heat of melting using the following equation [28,39,40]:

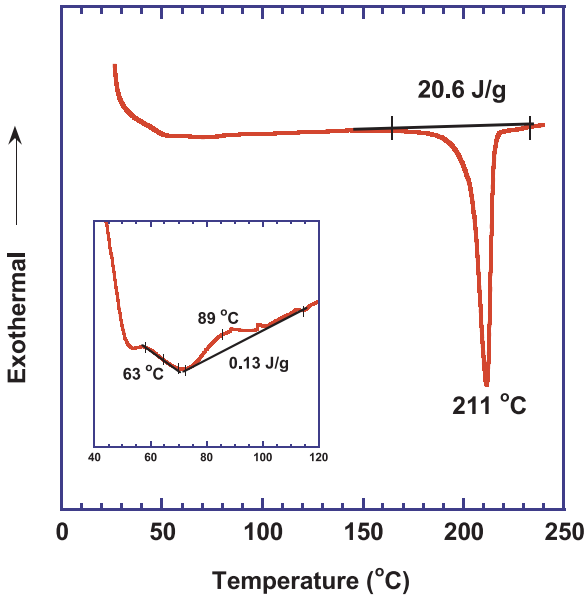

Fig. 1. The first heating scan of DSC thermogram for PCTFE films. The inset shows the thermal transitions of T_g and crystallization.

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