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Gas sorption and permeation in PIM-1

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ABSTRACT

Gas transport properties of PIM-1, i.e., the first "polymer with intrinsic microporosity," at 25 °C and different pressures were systematically studied. Permeability coefficients of 10 gases including He, H_2, N_2, O_2, CH_4, CO_2, C_2H_4, C_2H_6, C_3H_6 and C_3H_8 were conducted at 25 °C for five different upstream pressures (from 1 to 10 atm). The C_2 and C_3 hydrocarbons exhibited serious plasticization responses while the permeability coefficients of He, H_2, O_2, N_2, CH_4 and CO_2 decreased with the trans-membrane pressure as expected from the dual-mobility model. Sorption isotherms of all 10 gases were also determined using a dual-volume sorption cell at 25 °C up to a maximum pressure of 27 atm. The sorption isotherms followed the dual-mode sorption model. The logarithm of the solubility coefficients increased linearly with the critical temperature of the gas and the slope of this plot (0.018) was found to be comparable with values reported for other glassy polymers. Diffusion coefficients were calculated from the permeability and solubility data; the values for He, H_2, O_2, N_2, CH_4 and CO_2, increased with pressure as predicted by the dual-mobility model while those of the C_2 and C_3 hydrocarbon gases increased more strongly because of plasticization. Parameters from the dual mobility model, D_D and D_H, were significantly higher and their ratio, D_H/D_D was significantly smaller than those of previously reported polymers.

1. Introduction

Polymers of intrinsic microporosity (PIMs) are an interesting new class of materials believed to have interconnected regions of large interchain spacings, or free volume, that might be interpreted in some sense as "pores" (<2 nm) [1]. In any case, large surface areas, e.g., greater than 400 m^2 g^{-1}, have been measured using low temperature N_2 adsorption or BET-type techniques [2]. Unlike other microporous materials such as zeolites, active carbons or metal-organic frameworks (MOFs), PIMs are amorphous polymers that are soluble in many organic solvents including, but not limited to, chloroform, dichloromethane (DCM), tetrahydroforan (THF), *o*-dichlorobenzene and chlorobenzene [3]. Compared with acetylene-based polymers such as poly(1-trimethylsilyl-1-propyne) (PTMSP), PIMs have similarly high gas permeability values but are more selective. In addition, PIMs have better thermal and chemical stabilities than PTMSP because of the absence of vinyl and aliphatic groups. Therefore, the majority of the literature on PIMs has been aimed at membranes for gas separation and CO_2 capture in particular.

The structure of PIM-1 is given in Fig. 1; it is synthesized by the polycondensation reaction of 5,5,6,6-tetrahydroxy–3,3,3,3-tetramethyl–1,1′-spirobisindane with tetra-fluorophathalonitrile and is the first reported polymer of this type. PIM-1 is a glassy polymer with a very rigid and contorted backbone that results in a very high fractional free volume, FFV ~0.25, not observable T_g and large apparent BET surface area of ~800 m^2 g^{-1} [4]. To the best of our knowledge, most reported permeability data are for He, H_2, O_2, N_2, CH_4 and CO_2 [5–9], while very little data are available on permeation of hydrocarbon gases [10,11]. In addition, the reported gas solubility data of PIM-1 were mainly obtained by means of time lag and inverse gas chromatography experiments, which, at best, are complicated indicators of gas solubility in glassy polymers [5,6,8,12]. No sorption isotherms have been reported using the well-known dual volume sorption method. For glassy polymers, experimental sorption isotherms measured over a significant range of pressures have been useful for extraction of parameters like those of the dual sorption model and for more detailed analyses of gas permeability versus driving pressure. Extensive correlations of these parameters with the polymer free volume and the characteristics of the penetrant molecules have been made for a large number of glassy polymers, and it is of interest to examine PIM materials in the context of these prior correlations for other glassy polymers. Thus, the purpose here is to report sorption and permeation data over a wide range of

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pressures for a series of gases in PIM-1. These results should help achieve a better fundamental understanding of this class of polymers and aid evaluation of their potential for use in industrial separations.

2. Background

2.1. Summary of prior gas permeability and solubility data for PIM-1

As listed in Table 1, the highest reported gas permeabilities for PIM-1 (films cast from chloroform) are almost three-fold greater than the lowest values (cast from THF). This variability is somewhat expected for polymers with such a high free volume. With its rigid backbone and low segment packing efficiency, it is difficult to achieve a stable solid state. Therefore, the gas transport properties of PIM-1 films are very sensitive to all prior history with the casting solvent as one source of this variability. Note that the gas permeability of PTMSP cast from different solvents also varies considerably. Bi et al. [13] reported that the CO_2 permeability of PTMSP was 70,200, 38,100 or 20,800 barrer when cast from cyclohexane, toluene or THF, respectively. They suggested that the casting solvent influences the molecular packing and the fractional free volume, FFV, and subsequently affects gas permeability. Similar effects of casting solvent appear to be at play for PIM-1. The CO_2 permeability of PIM-1 varies from 5000, 3500 to 2500 barrer when cast from chloroform, DCM and THF, respectively. Another factor affecting the PIM-1 permeability is the thermal history such as solvent removal conditions prior to the permeability measurement. A comparison of the data of Budd et al. [8,9] with this study for PIM-1 films prepared from chloroform is shown in Table 1, the permeability values for N_2 and CO_2 differ within 10%; those for He and H_2 are 100% higher in this report; and those for O_2 and CH_4 differ about 50%. In summary, gas permeability coefficients for PIM-1 are strongly affected by all aspects of the history of film preparation.

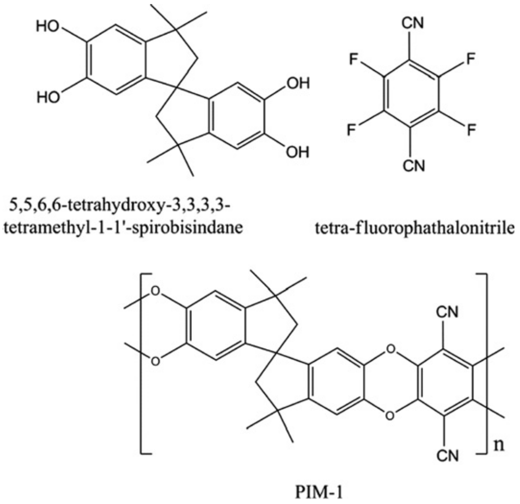

Fig. 1. Structures of monomers and PIM-1.

Table 2 compares the reported solubility coefficients of PIM-1 including those determined from this work. The values are quite comparable when films are cast from the same solvent, but they do vary significantly when cast from different solvents. The solubility coefficients of PIM-1 cast from chloroform and tested at 1 atm and 25 °C by Budd et al. are very similar to those found here. For highly soluble gases including CO_2 and CH_4, the differences between the data of Budd et al. and the current data are within 10%. For less soluble gases including He, H_2, O_2 and N_2, the prior work reports values that are 35% less than those found here. These discrepancies are consistent with the higher permeability values in this study. The solubility coefficients of PIM-1 decrease in the following order with casting solvent: THF > chloroform > DCM. Since PIM-1 is a glassy polymer, its gas sorption isotherm can be highly non-linear, e.g., as expected from the dual-mode sorption model, so its solubility coefficients will decrease with pressure which may help understand some of these differences.

2.2. Theory

Gas transport in a dense polymeric membrane is usually described by the solution-diffusion model [14–16] and involves the three steps: (1) the penetrant is sorbed into the upstream surface, i.e., the high pressure side of the film; (2) then diffuses to the low pressure side under a concentration gradient; and (3) desorbs from the film at its downstream surface, i.e., low pressure side. Sorption is assumed to be in equilibrium at the interface between the polymer and the gas phase. Fick's law governs the diffusion of penetrant within the film or membrane:

$$J = -D(c)\frac{\partial c}{\partial x} \tag{1}$$

where J, D, c and x are the steady-state flux of penetrant, the concentration-dependent diffusion coefficient, the penetrant concentration, and the position coordinate in the membrane, respectively. Average solubility, $\overline{S}$, and diffusion, $\overline{D}$, coefficients can be defined as shown below:

$$\overline{S} = \frac{c_h - c_l}{p_h - p_l} \tag{2}$$

$$\overline{D} = \frac{\int_{c_l}^{c_h} D(c)dc}{c_h - c_l} \tag{3}$$

where the subscripts h and l indicate the feed and permeate sides, respectively, and P is the partial pressure of penetrant in the external gas phases. With these definitions, Eq. (1) can be

Table 1
Gas permeability coefficients to PIM-1 reported by different groups.

Casting	Gas permeability, P (barrer)						Selectivity		Temp	Ref.
Solvent	He	H_2	O_2	N_2	CH_4	CO_2	O_2/N_2	CO_2/N_2		
THF	–	1300	370	92	125	2300	4.0	25	30	Budd [5]
DCM	1060	2330	790	240	360	3500	3.3	15	25	Staiger [6]
DCM	–	2696	712	166	472	3375	3.7	20.7	35	LFY[7]
Chloroform	760	1630	580	180	310	4390	3.2	24	25	Budd [8]
Chloroform	640	1450	680	240	440	4790	2.8	20	25	Budd[9]
Chloroform	1340	2936	969	252	320	5303	3.8	21	25	This study

All films were **not** soaked in methanol before testing.