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Permeation of Single and Mixed Gases through Composite Membranes Prepared by Plasma Polymerization of Fluorocarbon Compounds

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Abstract−The permeations of simple permanent gases and their mixtures through plasma-polymerized composite membranes were studied. Composite membranes were prepared by the plasma polymerization of fluorocarbon monomers such as pentafluorotoluene (PFT) and pentafluoropyridine (PFP) onto porous Celgard. For pure gases, the permeability coefficients were mainly affected by diffusivity rather than solubility. The permeability coefficient decreased as the kinetic molecular diameter of the penetrant molecules increased, and the permeability coefficients were independent of pressure. For mixed gases, the permeability coefficient was not affected by the composition of penetrants for the whole range of composition.

Key words: Permeation, Plasma Polymerization, Composite Membrane, Fluorocarbon

INTRODUCTION

From the beginning of the 1980s, permeation of gases in plasma-polymerized thin films has been studied by a number of groups [Oh et al., 1995a; Inagaki et al., 1986, 1987, 1990; Terada et al., 1986]. In particular, they have measured the permeabilities of oxygen and nitrogen and estimated the ideal selectivities between them. Some have reported that plasma-polymerized films prepared from fluorine-rich monomers show relatively high oxygen selectivity over nitrogen compared to other plasma polymers [Kim et al., 2000; Inagaki et al., 1986; Terada et al., 1986]. It has been suggested that the high selectivity of the plasma polymers is related to the high affinity of oxygen to fluorine-containing compounds. Only a few groups have studied the permeation behavior of plasma polymers for mixed gases. Inagaki et al., 1986 investigated the permeation behavior of oxygen-nitrogen mixture gases. They showed an entirely different trend of O_2 permeability compared to the trend in conventional polymer membranes. The permeability of oxygen and its permselectivity over nitrogen showed very high values in the region of low oxygen composition. They tried to explain their result with an assumption that, in the plasma polymer, the permeation of gases proceeds through an unknown route which is different from the permeation behavior in conventional polymers.

In this study, plasma-polymerized films were prepared from fluorine-rich monomers, and the permeation behavior of the plasma films for single gases and mixed gases was investigated.

EXPERIMENTAL

1. Materials

The monomers used for plasma polymerization were Pentafluoropyridine (PFP) and pentafluorotoluene (PFT). Both monomers were purchased from Aldrich and were used without further purification. Porous Celgard, supplied from Hoechst Celanese, was used as a substrate in plasma polymerization. The celgard sheet has an effective pore diameter of 0.05 μm and a porosity of 38%.

2. Plasma Polymerization

For the power source of plasma polymerization, 2.45 GHz microwave power is used. For the reactor body, a horizontal, 34 mm (I.D.) ×40 cm length pyrex glass tube with one sealed end, and the other, open end was used. A schematic diagram of the reactor system is shown in Fig. 1. The power was supplied to the reactor from the microwave power generator (Opthos Instrument, USA) through a wave guide connected to the power cable. The wave guide is installed horizontally to be in contact with the external surface of the reactor tube. To protect the power generator, the reflected power is guided into a dummy load by using a circulator. The open end of the tube is connected to the vacuum pump. The throttle valve and ball valve are installed between the reactor tube and the vacuum

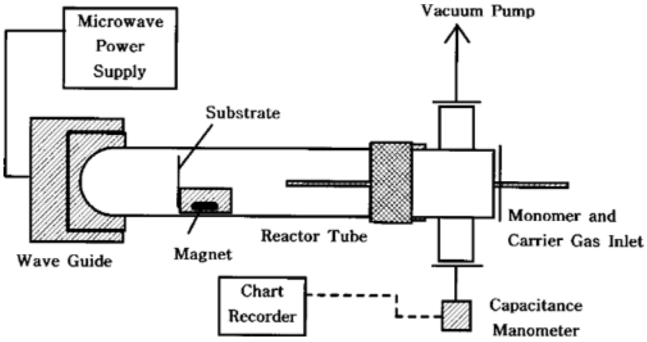

Fig. 1. Schematic diagram of the microwave plasma polymerization system.

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Table 1. Kinetic molecular diameters and critical temperatures of the penetrant gases

Penetrants	Kinetic molecular diameters (Å)	Critical temperatures (K)
He	2.60	5.2
H_2	2.89	33.2
CO_2	3.30	304.2
O_2	3.46	154.6
N_2	3.64	126.2
CH_4	3.80	190.6

pump. Through the centerline of the reactor tube, a 1/4" O.D. tube is installed for the reactant gas supply. The open end of the tube is set to be 15 cm from the wave guide. The monomer is supplied into the reactor from external monomer bottle by evaporation through 1/4" teflon tube. The flow rate of the monomer is varied between 2 and 4 sccm. To sustain the plasma, carrier gas, argon, is mixed into the feed stream with the same flow rate of the monomer.

3. Film Thickness Measurements

The nominal thicknesses of the plasma-polymerized films are estimated by depositing plasma films onto glass slides under the same conditions as used to make the permeation samples. The thickness of the film on the glass substrate is measured by using a surface profilometer (Dektak IIA).

4. Penetrant Gases

We used single component gases (O_2, N_2, CO_2, CH_4) and their mixtures (O_2/N_2 and CO_2/CH_4 mixtures) with various compositions. The gas species used in this work, their kinetic molecular diameters and their critical temperatures are listed in Table 1. The gases are chosen to span a wide range of kinetic diameters and critical temperatures.

5. Permeation Measurements-Pure Penetrant

A schematic diagram of the permeation system is shown in Fig. 2. A plasma-polymerized membrane was charged in the permeation cell made of stainless steel. The permeation system consists of two sides that are separated by the membrane loaded in the permeation cell. One is designated as the upstream side and the other as downstream side. The plasma-coated side of the membrane is exposed to the upstream side. The downstream side volume is 96 cm^3 which is determined by a liquid filling method. Most of the system is submerged into a constant temperature bath at 35 °C.

Once a sample was loaded into the permeation cell, the cell was installed into the system and the whole system was evacuated below 0.1 torr by using the vacuum pump for at least 10 hours, usually overnight. At the beginning of the measurement, the upstream side was filled with the penetrant. During the measurement, the pressure at the upstream side was maintained around 1 atm, and the downstream side was isolated from the vacuum pump. The increase in the pressure of the downstream side was monitored with a pressure transducer (MKS, model 128A). The pressure at the downstream side was maintained below 2 torr throughout the run so that the pressure difference across the membrane was assumed to be equal to the upstream pressure. The pressure data were collected by using a personal computer via A/D interface connected to the pressure transducer. The permeation rate was determined from the slope of the linear portion of the downstream pressure increase with time. The slope was corrected for the system leak rate, which is typically less than 2% of the permeation rate. The corrected slope was then converted to the permeability coefficient by using the known area and the thickness of the membrane.

The permeability coefficient, P, of the penetrant is related to the measured permeation rate through the membrane, Q [cm^3 (STP)/sec] as shown in Eq. (1).

$$\frac{P}{\delta}=\frac{Q}{\Delta pA} \tag{1}$$

In Eq. (1), A is the unmasked area of the sample, Δp is the pressure difference of the penetrant across the membrane (assumed to be equal to the upstream pressure), P is the permeability coefficient of penetrant, and δ is the membrane thickness. The unit of P/δ is cm^3 (STP) cm^{-2} sec^{-1} $cmHg^{-1}$.

6. Permeation Measurements-Mixed Penetrant

To measure the overall and individual permeability coefficients in mixed gas permeation, some modifications were made to the apparatus shown in Fig. 2. Fig. 3 is a schematic diagram of the mixed gas permeation system. Comparing Fig. 3 with Fig. 2, one notices two major changes: the addition of an extra port on the upper half of the permeation cell and the addition of a gas chromatography (GC) system (Hewlett-Packard Model 5880A). The port is added

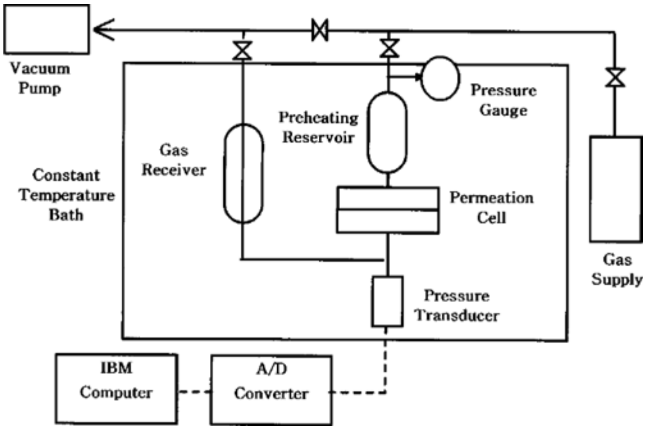

Fig. 2. Schematic diagram of the permeation system for pure penetrants.

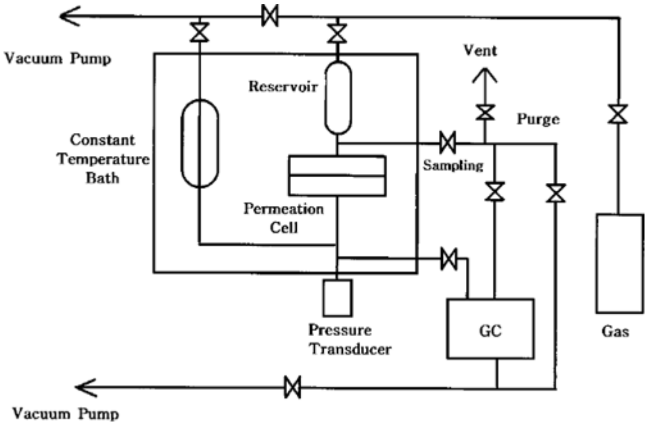

Fig. 3. Schematic diagram of the permeation system for mixed penetrants.

to allow the high pressure feed to flow across the upstream surface of the membrane. This is done to avoid any boundary layer effects at the membrane surface. Also, the purge ensures that the gas concentration at the surface does not differ from that in the bulk mixture as a result of permeation. The GC was used to measure the compositions of the penetrant and permeate. For this purpose, the upstream side and the downstream side were connected to the sampling loop of the GC. Helium was used as a carrier gas to sweep the sample loop into the GC. Two stainless steel columns with 1/8 inch diameter and 6 ft length were installed in the GC. One column was packed with silica gell, 80/100 meshes, and the other was with molecular sieve 5A, 80/100 meshes. The silica gell column was used for CO_2 and CH_4 detection, and molecular sieve 5A column was for O_2 and N_2 detection. The signals of the components were detected by the thermal conductivity detector (TCD). The oven and detector temperature were 100 °C and 250 °C, respectively.

The start of the mixed penetrant's permeation experiment is almost the same as that for the pure gas experiment. After the whole system including the sampling loop of the GC was evacuated for at least 10 hours, the upstream side of the membrane was filled with mixed penetrant gases and the penetrant was kept flowing across the upstream surface of the membrane throughout the experiment. For about 5 minutes, which is enough time to obtain the constant permeation rate, the downstream side was evacuated. Then the downstream side part was isolated from the vacuum pump and the permeate gas was accumulated. After the downstream side pressure was raised enough (higher than 5 torrs), the permeate was sampled and analyzed using the GC. With the pressure increasing rate, the overall permeability coefficient was estimated in the same way in the single gas permeation. Then the ideal selectivity ($\alpha_{A/B}$) between the two components A and B was estimated with the equation below:

$$\alpha_{A/B}=\frac{P_A}{P_B}=\frac{y_A/y_B}{x_A/x_B} \tag{2}$$

where y_A and y_B are mole fractions of component A and B in the permeate, and x_A and x_B are mole fractions of component A and B in the feed. With the data for the overall permeability coefficient and the permselectivity, the individual permeabilities were estimated.

RESULTS AND DISCUSSION

The operating conditions such as monomer flow rate, pressure and discharge power in plasma polymerization affect the structure and the gas permeation behavior of plasma-polymerized films [Cho et al., 1998; Kim et al., 1998]. The characterization of plasma polymers is difficult since the plasma polymers generally have highly crosslinked structure. Terada et al., 1986 showed that plasma-polymerized films did not contain any pores, which could be detected by scanning electron microscope (SEM). It is also well known that the plasma polymers have higher glass transition temperature than their decomposition temperature since they are crosslinked. The FT-IR spectra of the PFP and PFT plasma-polymerized films and the effect of operating conditions on the permeation behavior were reported previously [Oh et al., 1995b]. All the plasma films used here were prepared at the best operating conditions shown in the above reference.

1. Effect of Kinetic Molecular Diameter

When a penetrant permeates through the membrane, at first 1) the penetrant is dissolved (or adsorbed) at the upstream surface of the membrane, 2) it diffuses through the membrane, and finally 3) it is desorbed from the downstream surface. Hence, the permeability coefficient is related to diffusivity and solubility and is defined as

$$P=DS \tag{3}$$

where D is the diffusion coefficient and S is the solubility coefficient. The ideal selectivity α of the membrane is simply defined as the ratio of the permeability coefficients of the two penetrants, and is written by Eq. (4).

$$\alpha_{A/B}=\frac{P_A}{P_B} \tag{4}$$

Combination of Eq. (4) and (3) gives Eq. (5).

$$\alpha_{A/B}=\frac{D_A S_A}{D_B S_B} \tag{5}$$

The ratio D_A/D_B is the ratio of the diffusion coefficients and is often called the diffusivity or mobility selectivity. This term reflects the effect of the size or geometry of the penetrants related to the chain mobility and inter and intra molecular chain gaps of the polymer. The diffusivity selectivity for a gas with larger molecules over a gas with smaller molecules will always be less than one.

The ratio S_A/S_B is the solubility selectivity and reflects the relative sorption of gases. In general, the more condensable the component, the higher is its sorption. The condensability can be represented by critical temperature or Leonard Jones potential. The solubility selectivity of a gas with higher critical temperature over another gas with lower critical temperature is always greater than 1.

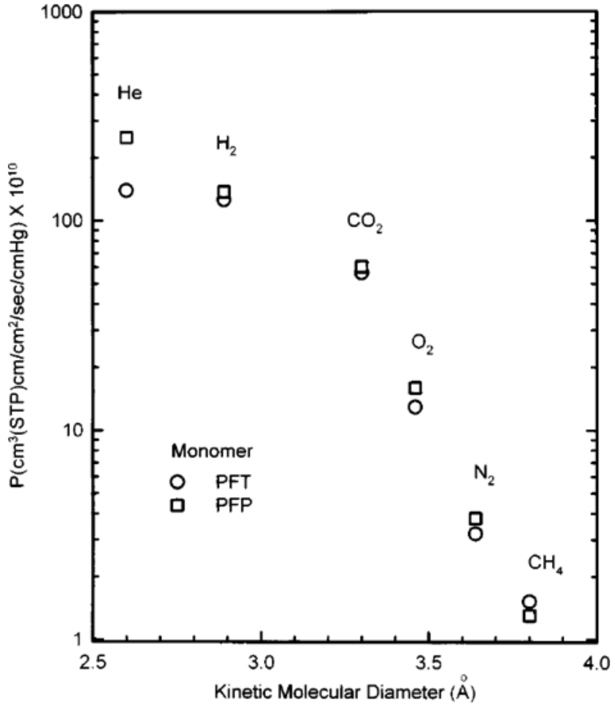

Fig. 4. Permeability coefficient vs. kinetic molecular diameter of gases for PFT and PFP plasma-polymerized films.

It was shown that the solubility selectivity determined the overall selectivity for polymers with high free volume and low crosslinking density [Inagaki et al., 1990; Terada et al., 1986; Nomura et al., 1984]. On the other hand, the diffusivity selectivity determined the overall selectivity for polymers with low free volume and high crosslinking density [Yamamoto et al., 1984; Sakata at al. 1987].

Fig. 4 shows the permeabilities of penetrants for PFP and PFT plasma-polymerized films, as functions of their kinetic molecular diameter. The result is very similar to that from the work of Oh et al., 1995b. In Fig. 4, the permeability coefficient decreased with increasing kinetic molecular diameter. It means that the greater the difference in molecular diameters between gas-pairs, the greater the ideal selectivities between the gas-pairs. However, the permeability was not dependent of the critical temperatures of the penetrants shown in Table 1. From the result, it can be presumed that permselectivities of the plasma-polymerized films from fluorine-rich monomers are mainly determined by diffusivity selectivity rather than solubility selectivity. The reason may be the result of the highly crosslinked and packed structure of the plasma polymers. The trend of permeability coefficient versus kinetic molecular diameter in our study was similar to that of conventional perflouropolymers [Pasternak et al., 1970, 1971].

2. Effect of Pressure

Sorption of gases through glassy polymers occurs both by dissolution (Henry's law mode sorption) and by adsorption (Langmuir mode sorption), which is characterized by the dual sorption model [Vieth et al., 1976]:

$$C = k_D p + \frac{C'_H bp}{1 + bp} \tag{6}$$

where, C is the equilibrium of the gas in the polymer, k_D the Henry's law solubility constant, b the Langmuir affinity constant, and C'_H the Langmuir capacity constant.

Pressure-dependent permeability coefficients can be explained by the partial immobilization model [Chiou et al., 1986], in which the gas molecules dissolved and adsorbed in the polymer both take part in the diffusion.

Fig. 5 shows the pressure dependence of gas permeabilities for PFT plasma-polymerized films. As shown in the figure, the permeabilities did not depend on pressure within an error limit of ±5% for all the gases, while the results for higher pressure above 40 psia were not shown since the thin plasma-polymerized films sometimes became broken at high pressures. The little pressure dependence of the permeability appears to be due to the rigid and cross-linked structure of the PFT plasma-polymerized film. Actually, PFT plasma-polymerized polymer is composed of C-F bonds stronger than C-H bonds in conventional polymers, since C-F bond energy (552 KJ/mol) is higher than C-H bond energy (338.3 KJ/mol). Therefore, the penetrating gas molecules adsorbed in the microvoids of the plasma polymer might not take part in the diffusion, that is, following the total immobilization model [Vieth et al., 1976], resulting in no pressure dependence of permeability coefficients. No pressure dependence of gas permeabilities has been observed for glassy polymers with high glass transition temperature such as polyimide and other plasma polymers [Stern et al., 1989; Inagaki et al., 1986]. The same trend was observed for the PFP plasma-polymerized films of which plots were not shown here.

3. Effect of Composition of Penetrant

The goal of this section is to see whether the permselectivity of the plasma polymer is ideal. If the permeabilities for each gas are independent of the composition of the penetrant gas mixture, then the permselectivity is considered to be ideal. In conventional poly-

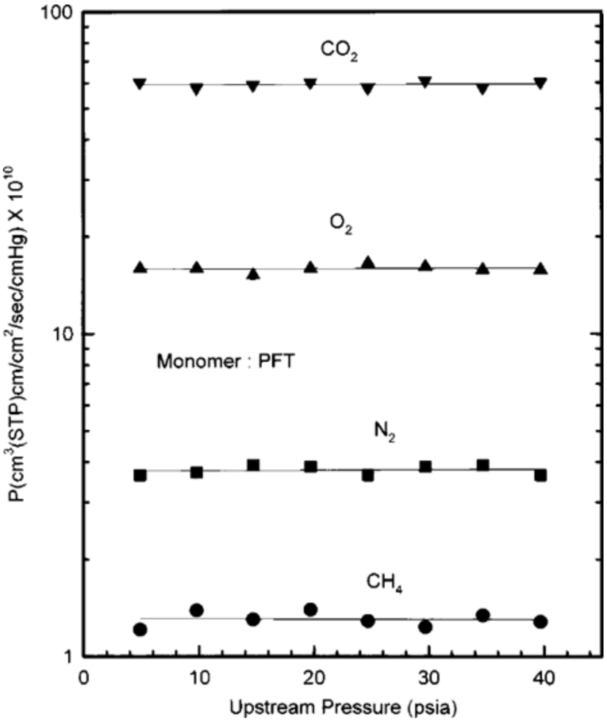

Fig. 5. Effect of pressure on the permeability of simple gases for PFT plasma-polymerized films.

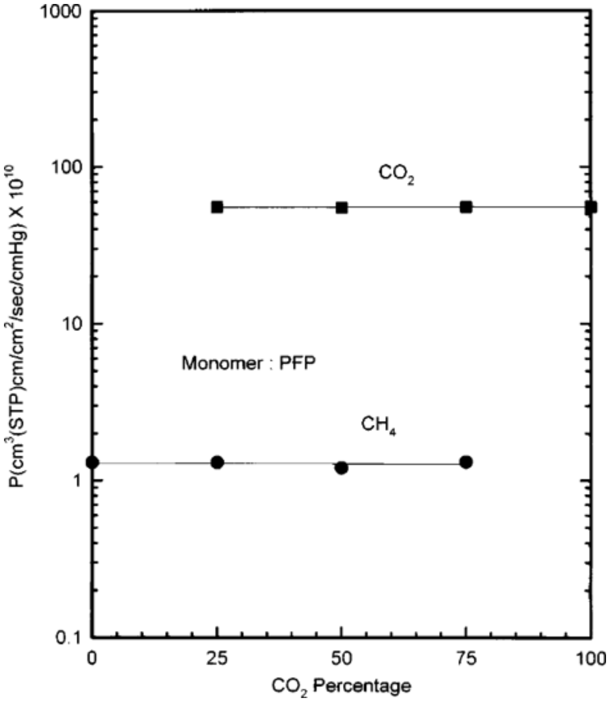

Fig. 6. Effect of penetrant composition on the permeability of CO_2/CH_4 mixture for PFP plasma-polymerized films.

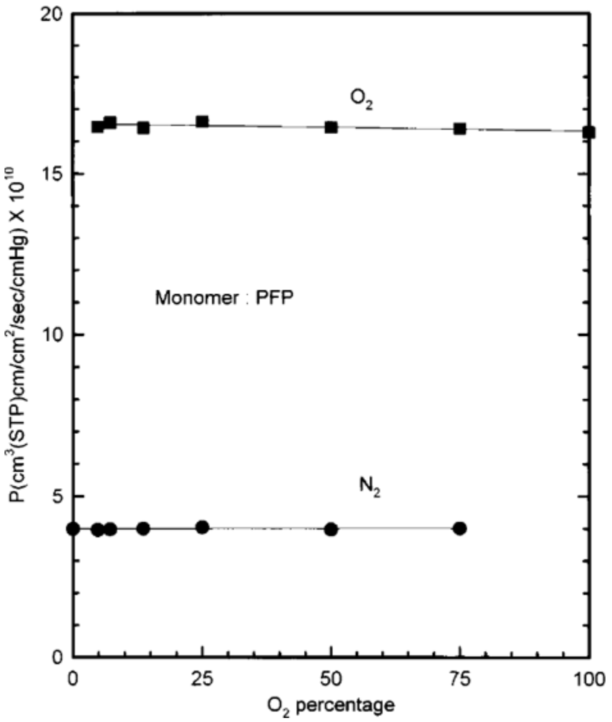

Fig. 7. Effect of penetrant composition on the permeability of O_2/N_2 mixture for PFP plasma-polymerized films.

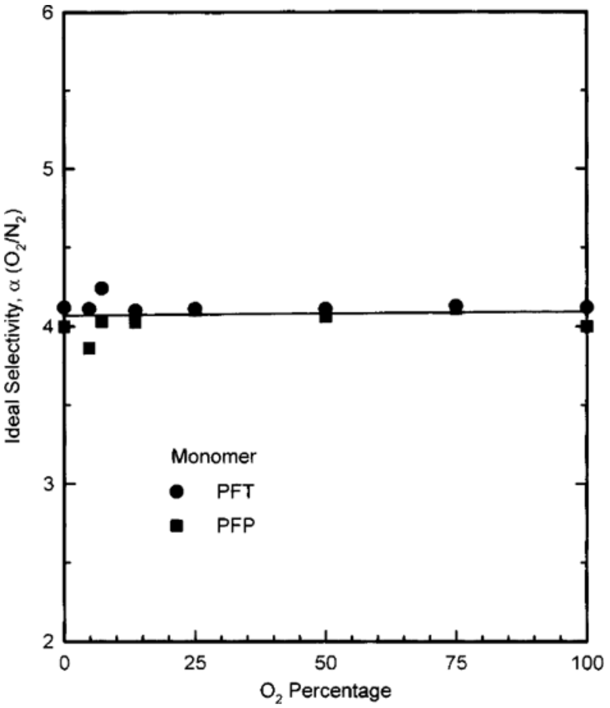

Fig. 8. Effect of penetrant composition on the selectivity of O_2/N_2 mixture for the plasma-polymerized films.

mers of which the permeability is dependent on pressure, the permeability is also dependent on the composition of the penetrant mixture. Several investigators have noted reduction in the permeability of each penetrant in mixed gas permeation for glassy polymers, compared to the corresponding permeability in pure gas permeation [Pye et al., 1976; McCandless et al., 1972]. Sanders and Koros, 1984 explained that the behavior could be due to a decrease in the solubilities, that is, the solubilities become smaller for mixed gases than for pure gases.

Fig. 6 and Fig. 7 show the effect of composition of penetrant on the permeability for CO_2/CH_4 mixtures and O_2/N_2 mixtures in PFP plasma-polymerized films. Fig. 8 shows the effect of composition on the ideal selectivity for O_2/N_2 mixtures. As shown in Fig. 6 and Fig. 7, the permeability coefficients were not affected by the penetrant compositions for the whole range of compositions. The same results were obtained for PFT plasma polymerized films; therefore, the ideal selectivities were not affected by the composition as shown in Fig. 8.

If the gas molecules adsorbed in the plasma polymer do not take part in the diffusion during the permeation process, as explained above, the permeability coefficients only depend on Henry's solubility constant (k_D) and diffusion coefficient (D), both of which are not a function of concentration. That would be a reason for no concentration dependence of gas permeability coefficients.

Inagaki et al., 1986 measured permeability of O_2/N_2 mixtures for plasma-polymerized films from perfluoromethylcyclohexane/methane mixture and hexafluoro-propane/methane mixture. They showed a great increase in the permselectivity of O_2/N_2 at low oxygen concentrations. The composition dependence in their study seems to result from the different chemical structure of their plasma polymers since their plasma polymers are composed of C-H bonds as well as C-F bonds, while PFP and PFT plasma polymers are mostly composed of strong C-F bonds.

CONCLUSIONS

Permselective composite membranes were prepared by the deposition of plasma-polymerized films from fluorine-rich aromatic compounds such as pentafluorotoluene (PFT) and pentafluoropyridine (PFP) on the substrates of porous Celgard. For pure gases, the permeability coefficient decreased with increasing kinetic molecular diameter of penetrants, and the permeability was not affected by the pressure. For binary mixtures, individual permeability coefficient showed the same value as that of the pure gas, that is, the permeabilities were not affected by the composition of penetrant mixtures.

NOMENCLATURE

A : effective membrane area [cm^2]
D : diffusion coefficient [cm^2/sec]
P : permeability coefficient [cm^3 (STP) cm/cm^2/sec/cmHg]
Δp : pressure difference [cmHg]
S : solubility coefficient [cm^3 (STP)/cm^3 polymer/cmHg]
Q : permeation rate [cm^3 (STP)/sec/cmHg]

Greek Letters

α : ideal selectivity
δ : thickness of the membrane [cm]

Subscripts

A : penetrant A

B : penetrant B
i : component i

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