

Plasma Polymerization of Perfluoro-2-Butyltetrahydrofuran/Methane and Perfluorobenzene/Tetrafluoromethane Mixtures and Gas Permeation Properties of the Plasma Polymers

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Synopsis

Plasma polymer films prepared from perfluoro-2-butyltetrahydrofuran (PFBTHF) and perfluorobenzene (PFB) were investigated by elemental analysis, infrared spectroscopy, and ESCA. The gas separation properties were also investigated to seek plasma polymer films with good permselectivity. Plasma polymer films from PFBTHF and PFB were composed of polymer chains with fluorinated moieties such as $\text{C}-\text{CF}_n$, CF , $\text{CF}-\text{CF}_n$, CF_2 , and CF_3 groups. Changes in the arc current as an operating condition for plasma polymerization showed less influence on the distribution of the fluorinated moieties but more influence on the permselectivity of the plasma polymer films formed. The permselectivity was improved by plasma polymerization in the PFBTHF/CH₄ or PFB/CF₄ mixture systems. The $P_{\text{O}_2}/P_{\text{N}_2}$ ratio for the plasma polymer films prepared from PFBTHF/CH₄ and PFB/CF₄ mixtures increased from 3.1 at 0 mol % CH₄ to 4.0 at 50 mol % CH₄ addition, and from 4.1 at 0 mol % CF₄ to 5.0 at 25 mol % CF₄ addition, respectively. The permselectivity of the plasma polymer films may be related to the crosslinkage and aggregation of polymer chains rather than the elemental composition.

INTRODUCTION

The gas permeability of polymer films, generally, is a product of solubility of gas at the film surface and diffusivity of gas molecules.¹ Both quantities are closely related to interaction between polymer chains and gas molecule and thermal motion of polymer chains.

Plasma polymerization is one of the processes yielding thin films. Thin films are directly deposited on substrate surfaces. Composite membranes, films plasma-polymerized from fluorocarbons or silicone compounds and deposited on porous substrates, are now beginning to find application in gas separation processes.²⁻¹⁴ Generally, chemical and physical properties of plasma polymer films, if prepared from the same starting materials (monomers), depend strongly on the operating conditions of plasma polymerization, such as the flow rate of monomer, the system pressure, the electric power for maintaining glow discharge, etc.¹⁵

Yasuda and his co-workers^{2,3} have emphasized the importance of the operating conditions of plasma polymerization to obtain plasma polymer films with good permselectivity. They used the W/FM parameter (J/kg) for representation of the operating conditions, where W , F , and M are the input

energy for glow discharge (J/s), the monomer flow rate (mol/s), and the molecular weight of the monomer (kg/mol), respectively. The W/FM parameter means the input energy per unit mass of the monomer.¹⁵ Plasma polymerization at extremely low or high W/FM values yielded plasma polymer films with less permselectivity, but polymerization at moderate W/FM values yielded films with good permselectivity. This observation is suggestive but complicated because changes in W/FM parameter induce somewhat alteration of the plasma polymer films formed in both chemical and physical properties.

The purpose of this study is to elucidate the effect of operating conditions on plasma polymerization, and also to seek an optimum condition to obtain plasma polymer films with good permselectivity. Perfluoro-2-butyltetrahydrofuran (PFBTHF) and perfluorobenzene (PFB) were used as starting materials for plasma polymerization. These compounds have been used as monomers for the preparation of gas separation membranes by plasma polymerization.^{2-9,11}

EXPERIMENTAL

Plasma Polymerization

The reactor system for plasma polymerization was a capacitively coupled system operating at a frequency of 20 kHz (af). It consisted of a bell jar (400 mm diameter, height 470 mm) with a monomer inlet, two parallel aluminum electrodes (150 × 150 mm) separated by a distance of 100 mm, a vacuum system, and a magnetic enhancement setup. Plasma polymers were deposited on the substrates mounted on a disk (320 mm diameter) positioned midway between the aluminum electrodes and rotating at 60 rpm by an electric motor. The details of the reaction chamber have been given in the literature.¹¹

The experimental procedures for the plasma polymerization were essentially the same as reported elsewhere.¹¹ The reaction system was evacuated to approximately 0.13 Pa, and substrate surfaces were exposed to an argon plasma, which was operated at an argon flow rate of 14 cm³(STP)/min, a pressure of 1.3 Pa, and an af current of 50 mA, for 10 min to eliminate water adsorbed on the substrate surfaces. The system was again evacuated to 0.13 Pa, and then the monomer gases adjusted to a flow rate of 8 cm³(STP)/min at 1.3 Pa were introduced into the reaction chamber. The af power was turned on, and the plasma polymerization was conducted at a constant current of af power (30, 50, 75, 100, 120, and 150 mA).

Perfluoro-2-butyltetrahydrofuran (PFBTHF) (from Fluorochem), perfluorobenzene (PFB) (from Varsley Research Laboratories Co.), methane (CH₄) (from Takachiho Trading Co., Japan), and tetrafluoromethane (CF₄) (from PCR Research Chemicals) were used as monomers without further purification.

Elemental Analysis

The C and H contents of the plasma polymers were determined with a Yanagimoto TM-2 analyzer. The F content was determined by colorimetric analysis (alizarine complex method). The O content was a difference between the sample weight and sum of the C, H, and F contents determined.

IR and ESCA Spectra

IR spectra of the plasma polymers on KBr disks were recorded with a Nihon Bunko fourier transform infrared spectrometer FT/IR-3.

Plasma polymers (approximately 100 nm thick) deposited on silicon wafers were used for the measurement of ESCA spectra. ESCA spectra were recorded with a Shimadzu electrospectrometer 750 employing Mg K_{α} exciting radiation at 8 kV and 30 mA. The Au core level at 84.0 eV was used for calibration of the energy scale. The complex spectra were subjected to a curve-fitting procedure using a Shimadzu data system ESCAPAC 760. Gaussian distribution was assumed, and three parameters, the position and the height of the peak, and the full width at half-maximum (FWHM), were fitted to the observed spectra with a computer (ESCAPAC 760).

Gas Permeation

The permeation rates of oxygen and nitrogen gases through the composite membranes (Millipore filters, pore size 25 nm, coated with the plasma polymers) were measured at 20°C according to ASTM D143V. The pressure at the feed side was $7.8\text{--}19.6 \times 10^4$ Pa (0.8–2.0 kg/cm²), and that at the effluent side was atmospheric. The thickness of the plasma polymer films deposited on Millipore filters was estimated from SEM pictures (magnification of 5000) of the cross section of the composite membranes fractured in liquid nitrogen. From data of the permeation rate and the plasma polymer film thickness the permeability coefficients, P_{O_2} and P_{N_2} , were calculated with a reproducibility of $\pm 5\%$ tolerance.

It is well known that gas permeation properties of plasma polymers, generally, show a dependence of film thickness.² The polymer deposition of about 200 nm thick was required to fill up pores of the Millipore filter with plasma polymers. Plasma polymers prepared from PFBTHF/CH₄ mixture showed an almost constant selectivity (P_{O_2}/P_{N_2} ratio) independent of film thickness in the range from 200 to 600 nm thick, and those prepared from PFB/CF₄ mixture also showed a constant permselectivity in the range from 600 to 800 nm thick. Therefore, composite membranes used in this study for determination of gas permeation properties were Millipore filters coated with plasma polymers prepared from PFBTHF/CH₄ and PFB/CF₄ mixtures (ca. 200 and 700 nm thick, respectively).

RESULTS AND DISCUSSION

Polymer Deposition Rate and Permselectivity

Figure 1 shows the polymer deposition rate in plasma polymerization of PFBTHF and PFB, and the permselectivity (P_{O_2}/P_{N_2} ratio) as functions of the af current and the monomers used as starting materials for plasma polymerization. The polymer deposition rate in both plasma polymerizations of PFBTHF and PFB increased linearly with increasing of af current, and leveled off near 120 mA. This figure shows that the polymer-forming process below 120 mA is associated with the af current, but the process above 120 mA is saturated and is independent of the discharge current.

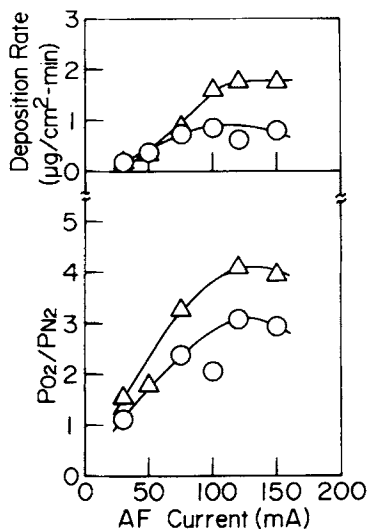


Fig. 1. Polymer deposition rate and permselectivity (P_{O_2}/P_{N_2} ratio) for plasma films prepared from PFBTHF and PFB as a function of the af current; (○) PFBTHF; (△) PFB.

The permselectivity (P_{O_2}/P_{N_2} ratio) for plasma polymer films prepared from PFBTHF and PFB, as shown in Figure 1, increased with increasing af current, reached a maximum, and then decreased. The maximum of the permselectivity appeared at an af current of 120 mA and was 3.1 for plasma polymer films prepared from PFBTHF and 4.1 for films prepared from PFB.

Nomura et al.² and Kramer and Yasuda³ pointed out that the permselectivity was closely related to the W/FM parameter. Plasma polymerization at low W/FM values before the polymer deposition rate was leveled off yielded plasma polymer films with good permselectivity. Our results summarized in Figure 1 show a similar dependence of permselectivity on the operating conditions. In this work af current was used instead of the W/FM parameter to represent the operating conditions because the magnitude of the af current corresponds roughly to the concentration of electrons which activate monomer molecules to be plasma-polymerized.

Generally, plasma polymerization show system dependence.¹⁶ Although our reaction system is different from the reactor used by Yasuda and his co-workers^{2,3} with respect to the shape and volume of the reaction chamber, the shape and area of the electrode, the frequency of the electric current for maintaining glow discharge, etc., similar dependence of permselectivity on operating conditions could be recognized. Therefore, this dependence is not an extrinsic phenomenon related to the reaction system used but an intrinsic phenomenon related to the polymer-forming reactions.

Chemical Composition of Plasma Polymer Films Prepared from PFBTHF and PFB

The magnitude of the af current to maintain glow discharge, as described in a previous section, influenced the permselectivity of the plasma films formed. To interpret the effect of af current, the chemical composition of the plasma

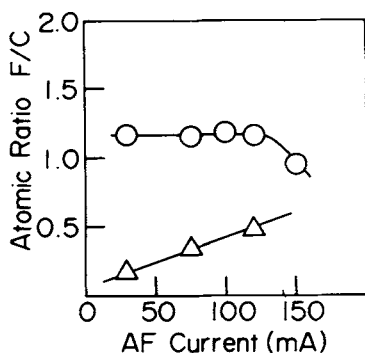


Fig. 2. Atomic ratio (F/C) of plasma films prepared from PFBTHF and PFB as a function of af current; (○) PFBTHF; (△) PFB.

polymer films, especially fluorine moieties, was investigated because of strong affinity of fluorine moieties for oxygen molecules.⁴ Many investigators^{2-6,10-13} have applied fluorine compounds for the preparation of gas separation membranes with good permselectivity.

Elemental analysis showed that plasma polymer films prepared from PFBTHF and PFB were mainly composed of carbon and fluorine atoms. The oxygen content for the plasma polymer films from PFBTHF was very low, e.g., the O/C atomic ratio for those prepared from PFBTHF at 120 mA was 0.01. It is not surprising because the elimination of carbon oxide or carbon dioxide occurs in glow discharge state when oxygen-containing monomers are plasma-polymerized.¹⁷ Figure 2 shows the atomic ratio (F/C) of the plasma polymer films prepared from PFBTHF and PFB as a function of af current. The F/C atomic ratio for the plasma polymer films prepared from PFBTHF was about 1.2, and the ratio for the plasma polymer films prepared from PFB was less than 0.5. The F/C atomic ratio for these plasma films was lower than that for the starting materials (PFBTHF, $F/C = 2$; PFB, $F/C = 1$). This indicates that fluorine elimination is accompanied with the polymer-forming processes.

To elucidate fluorine moieties of the plasma polymer films prepared from PFBTHF and PFB, IR and ESCA spectra were inspected. The specimens for the inspection were plasma polymer films prepared at af currents of 75 and 120 mA of which the permselectivity was 2.4 (at 75 mA), 3.1 (at 120 mA) and 3.3 (at 75 mA), 4.1 (at 120 mA), respectively. The four specimens showed similar IR spectra (Fig. 3). There were an intense absorption peak at 1230 cm^{-1} due to $C-F$ stretching vibration, broad absorption peaks at $1730-1650\text{ cm}^{-1}$ due to $C=O$ and $CF_2=C$ groups, and weak absorption peaks at 740 and 670 cm^{-1} ($C-F$) in the IR spectra. This indicates that the four plasma polymer films possess similar fluorine moieties.

ESCA spectra showed details of the fluorine moieties. Figure 4 shows ESCA (C_{1s} core level) spectra for the four plasma polymer films. The C_{1s} core level spectra are complex and involve at least four different C_{1s} features. The deconvolution divided the C_{1s} spectra into five C_{1s} features. They are components #1-#5 whose peaks positioned at $286.2-287.8\text{ eV}$ ($C-CF_n$), at $288.2-288.5\text{ eV}$ (CF), at $290.2-290.5\text{ eV}$ ($CF-CF_n$), at $292.3-292.5\text{ eV}$ (CF_2),

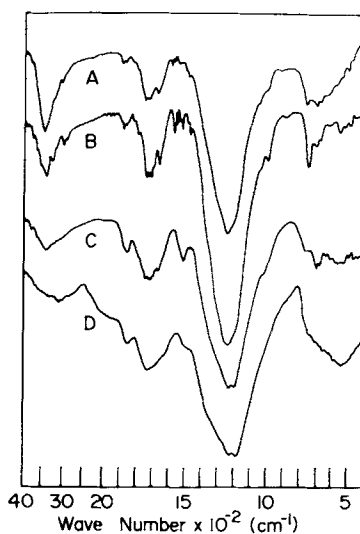


Fig. 3. IR spectra for plasma films prepared from PFBTHF and PFB as a function of the af current; (A) 75 mA (PFBTHF); (B) 120 mA (PFBTHF); (C) 75 mA (PFB); (D) 120 mA (PFB).

and at 294.4–294.5 eV (CF_3 and $\pi-\pi^*$ shake-up satellite). The relative peak area of these deconvoluted components is summarized in Table I. Table I indicates that (1) the plasma films prepared from PFBTHF and PFB are composed of similar carbon chains with five fluorine moieties, (2) there is some difference between the plasma polymer films prepared from PFBTHF and PFB in distribution of the five fluorine moieties and the plasma polymer films prepared from PFBTHF possess a larger amount of highly fluorinated moiety (CF_3 group) than those prepared from PFB, and (3) there is less effect of the af current on distribution of the fluorine moieties in the plasma polymerization of PFB but more effects in the plasma polymerization of PFBTHF.

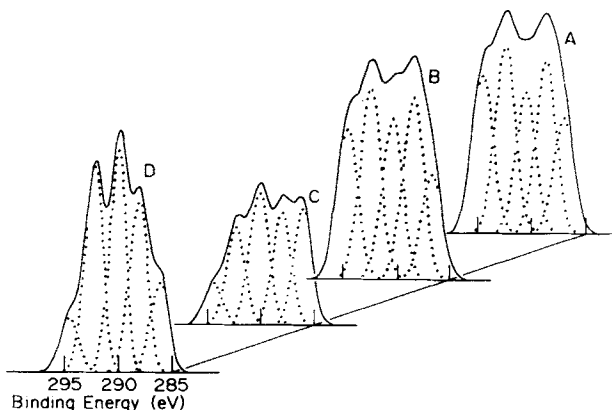


Fig. 4. ESCA (C_{1s}) spectra for plasma films prepared from PFBTHF and PFB as a function of the af current; (A) 75 mA (PFBTHF); (B) 120 mA (PFBTHF); (C) 75 mA (PFB); (D) 120 mA (PFB).

TABLE I
 ESCA (C_{1s}) Spectra for Plasma Polymer Films Prepared from PFBTHF and PFB

Monomer	AF current (mA)	Peak position (eV) and relative peak area (%)				
		Peak #1	Peak #2	Peak #3	Peak #4	Peak #5
PFBTHF	75	287.0 (15)	288.7 (23)	290.5 (18)	292.5 (24)	294.5 (20)
PFBTHF	120	286.8 (13)	288.5 (23)	290.5 (21)	292.5 (24)	294.5 (19)
PFB	75	286.1 (23)	288.0 (22)	290.2 (28)	292.3 (19)	294.4 (8)
PFB	120	286.2 (13)	288.2 (24)	290.2 (27)	292.3 (28)	294.5 (8)
Assignment		$\underline{C}-CF_n$	\underline{CF}	$\underline{CF}-CF_n$	\underline{CF}_2	\underline{CF}_3

From IR and ESCA results concerning the distribution of fluorine moieties of the polymer chains formed, we assume that the permselectivity of the plasma polymer films may be related to the crosslinkage and aggregation of plasma polymer chains rather than the chemical composition of plasma polymer chains.

Permselectivity of Plasma Polymer Films Prepared from PFBTHF/ CH_4 and PFB/ CF_4 Mixtures

The permselectivity, as assumed in the previous section, would depend on the polymer chain structure such as the crosslinkage rather than the chemical composition. It is well known that the polymer-forming reactions of perfluoro compounds in discharge state are accelerated by the addition of hydrocarbons to yield plasma polymer films having highly crosslinked polymer chains, and that a glow discharge of tetrafluoromethane initiates fluorination to yield fluorinated and crosslinked surfaces.¹⁸ If the assumption that the permselectivity is related to the polymer chain structure is true, the plasma polymer films prepared from PFBTHF/ CH_4 and PFB/ CF_4 mixtures will show an improvement in permselectivity.

Figure 5 shows the atomic ratio (F/C) of the plasma polymer films prepared from PFBTHF/ CH_4 and PFB/ CF_4 mixtures at an af current of 120 mA as a function of the mixture composition. The F/C atomic ratio for plasma polymer films prepared from PFBTHF/ CH_4 mixture, as expected, decreased linearly from 1.2 to 0.1 with increasing CH_4 concentration. On the contrary, the ratio for plasma polymer films prepared from PFB/ CF_4 mixture increased linearly from 0.5 to 1.1. Changes in F/C atomic ratio suggest that the polymer chain structure as well as the chemical composition could be modified by the CH_4 or CF_4 addition. Figure 5 shows oxygen and nitrogen permeability coefficients (P_{O_2} and P_{N_2}) as a function of the mixture composition. Large decreases in P_{O_2} and P_{N_2} values by the CH_4 or CF_4 addition could be observed for both plasma polymer films. Especially, for the plasma polymer films prepared from PFB/ CF_4 mixture containing 75 mol % CF_4 , the P_{O_2} value decreased 1/15 of that for the plasma polymer films from PFB, although the

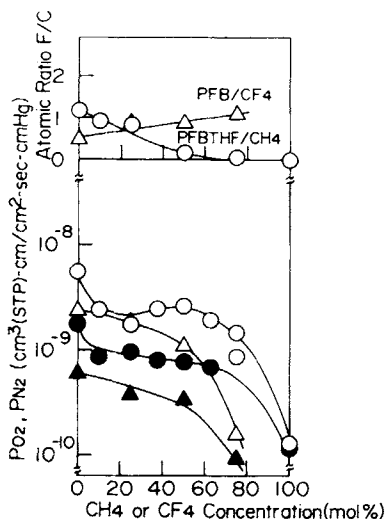


Fig. 5. Atomic ratio (F/C) and oxygen and nitrogen permeability coefficients (P_{O_2} and P_{N_2}) for plasma films prepared from PFBTHF/ CH_4 and PFB/ CF_4 mixtures as a function of the mixture composition; (○) P_{O_2} (PFBTHF/ CH_4); (●) P_{N_2} (PFBTHF/ CH_4); (△) P_{O_2} (PFB/ CF_4); (▲) P_{N_2} (PFB/ CF_4).

F/C atomic ratio increased about twice. This suggests the formation of crosslinkage by the CH_4 or CF_4 addition.

Large increases in the permselectivity by the CH_4 or CF_4 addition could be observed (Fig. 6). The P_{O_2}/P_{N_2} ratio for the plasma polymer films prepared from PFBTHF/ CH_4 mixture reached 4.0 at 50 mol % CH_4 addition, and the ratio for the plasma films prepared from PFB/ CF_4 mixture reached 5.0 at 25 mol % CF_4 addition. Taking the evidence that the plasma polymer films prepared from PFBTHF/ CH_4 mixture containing 50 mol % CH_4 possess less fluorine atom (F/C atomic ratio was 0.2) into account, we could speculate that the improvement of the permselectivity may be due to changes in polymer chain structure, probably crosslinkage, rather than changes in chemical com-

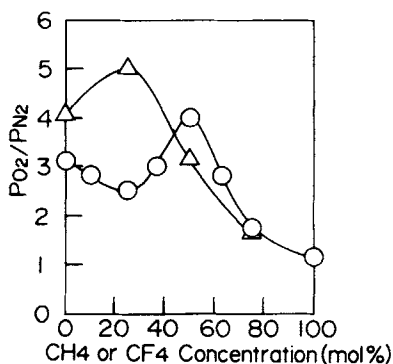


Fig. 6. Permselectivity (P_{O_2}/P_{N_2} ratio) for plasma films prepared from PFBTHF/ CH_4 and PFB/ CF_4 mixtures as a function of the mixture composition; (○) PFBTHF/ CF_4 mixture; (△) PFB/ CF_4 mixture.

position by the CH_4 or CF_4 addition. This speculation should be examined in the near future from the degree of crosslinked polymer chains, molecular weight of the crosslinkages, etc.

The high P_{O_2} value and $P_{\text{O}_2}/P_{\text{N}_2}$ ratio for the plasma polymer films prepared from PFBTHF/ CH_4 and PFB/ CF_4 mixtures (2.6×10^{-9} and 1.9×10^{-9} $\text{cm}^3(\text{STP}) \text{ cm}/\text{cm}^2 \text{ s cm Hg}$ and 4.0 and 5.0, respectively) indicate that these plasma films could be applicable as membranes for gas separation process.

In conclusion, we summarize results on plasma polymerization of PFBTHF and PFB and gas separation properties as follows.

1. Plasma polymer films prepared from PFBTHF and PFB are composed of polymer chains with fluorinated moieties such as $\text{C}-\text{CF}_n$, CF , $\text{CF}-\text{CF}_n$, CF_2 , and CF_3 groups. The distribution of the fluorinated moieties is less influenced by changing the af current as an operating condition for plasma polymerization of PFBTHF but more influenced in the plasma polymerization of PFB.

2. The magnitude of the af current influences the permselectivity of the plasma polymer films. The $P_{\text{O}_2}/P_{\text{N}_2}$ ratio for plasma polymer films prepared from PFBTHF and PFB increases from 1.1 (at an af current of 30 mA) to 3.1 (at 120 mA) and from 1.5 (at 30 mA) to 4.1 (at 120 mA), respectively.

3. The permselectivity of the plasma polymer films prepared from PFBTHF and PFB is improved by the CH_4 or CF_4 addition. The permselectivity of the plasma polymer films may be related to the secondary or higher structure of polymer chains rather than the primary structure.

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