

Gas Separation Membrane Made by Plasma Polymerization of 1,3-Ditrifluoromethylbenzene/CF₄ Mixture

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Synopsis

Plasma polymerization of 1,3-ditrifluoromethylbenzene (DTFMB)/CF₄ mixture was investigated by means of elemental analysis and infrared spectroscopy and the permeation properties of the formed plasma polymer films were examined. The plasma polymerization deposited films containing fluorine atoms, of which the concentration depended on the starting composition of the DTFMB/CF₄ mixture. The films were composed of fluorinated alkyl moieties with a small amount of fluorinated aromatic moieties and carbonyl moieties. The CF₄ addition to DTFMB caused the breaking down of aromatic rings. Permeation properties of the plasma polymer films depended on the starting composition of the DTFMB/CF₄ mixture, the discharge current, and the thickness of the deposited films. The permselectivity was enhanced by adding CF₄ and increasing the discharge current. Plasma polymer films prepared from DTFMB/CF₄ mixture containing 75 mol % CF₄ at a discharge current of 150 mA had a permselectivity of 5.0 and an oxygen permeation coefficient of 3.5×10^{-10} cm³ (STP) cm/cm² s cm Hg.

INTRODUCTION

Plasma polymers are of interest in applications as membranes for gas separation. Composite membranes plasma-polymerized from silicon and fluorine compounds and deposited on porous substrates have been reported as membranes used for oxygen enrichment process by many investigators.¹⁻¹⁵

In plasma polymerization, monomer molecules in a plasma state are fragmented, activated, and polymerized by the action of plasma, and thin films are deposited directly on substrate surfaces.¹⁶ The polymer formation process is completely different from the conventional polymerization methods such as radical and ionic. As a result, even when vinyl monomers are used as starting materials, the plasma formed polymers are not linear but somewhat branched and crosslinked. The degree of branched and crosslinked chains depends mainly on what monomer is used as a starting material and how much the electric energy is input into the plasma.

Gas separation membranes for oxygen enrichment require simultaneously high oxygen permeability and permselectivity. These qualities for typical polymers, generally, show a reverse relation. Polymers with a high permeability show low permselectivity and polymers with high permselectivity low perme-

ability. For polydimethylsiloxane, which is one of the most permeable polymers, the oxygen permeation coefficient (P_{O_2}) is $3.52 \times 10^{-8} \text{ cm}^3 \text{ (STP) cm/cm}^2 \text{ s cm Hg}$, and the permselectivity (P_{O_2}/P_{N_2}) is 1.94; on the other hand, for polyvinylacetate, which is one of the most permselective polymers, P_{O_2} is $2.25 \times 10^{-11} \text{ cm}^3 \text{ (STP) cm/cm}^2 \text{ s cm Hg}$, and P_{O_2}/P_{N_2} is 7.03.¹⁷ From a practical point of view for gas separation processes, we believe that permselectivity rather than permeability is the important factor because the slow permeation rate for polymers with high permselectivity could be avoided by thinning of membrane thickness. From the solution-diffusion model for gas permeation processes through polymer films it could be expected that the crosslinking of polymer chains brings about an increase in permselectivity and decrease in permeability.

In this study 1,3-difluoromethylbenzene (DTFMB) having affinity to oxygen molecules is used as a primary monomer for plasma polymerization, and tetrafluoromethane (CF_4) is used as a secondary monomer to accelerate crosslinking reactions. DTFMB is expected to give a high deposition rate in plasma polymerization because hydrogen atoms of DTFMB assist the polymer formation in a discharge state by dehydrofluorination.¹⁸ The plasma polymerization of DTFMB/ CF_4 mixture and effects of the CF_4 addition on permselectivity were investigated. The chemical composition of the formed polymers also was investigated by means of infrared spectroscopy and XPS.

EXPERIMENTAL

Plasma Polymerization

The reactor for plasma polymerization is a capacitively coupled system operating at a frequency of 20 kHz. It consists of a bell jar (400 mm diameter, 470 mm height) with a monomer inlet, aluminum and mesh electrodes (150 × 150 mm), a glass plate (150 × 150 mm) for the mount stage of substrates, a vacuum system, and a magnetic enhancement set up. The relative position of these elements is schematically illustrated in Figure 1.

Experimental procedures for plasma polymerization were essentially the same as reported elsewhere.¹⁹ The reaction system was evacuated to approximately 0.13 Pa, and the substrate surfaces were exposed to an argon plasma for 10 min

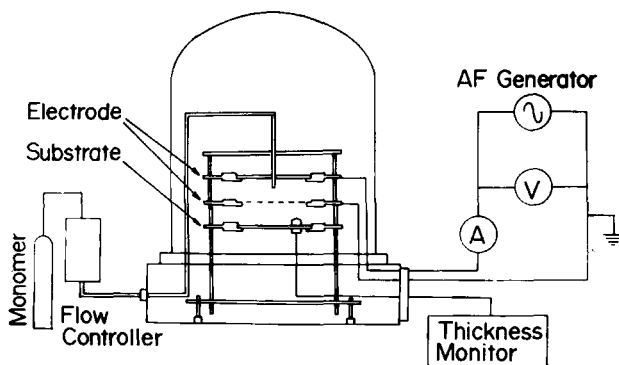


Fig. 1. Schema of reaction chamber for plasma polymerization.

to eliminate absorbed water. The system was again evacuated to 0.13 Pa, and then the monomer gas adjusted to a flow rate of 12 cm³ (STP)/min at 1.3 Pa was introduced into the reaction chamber. Electric power at 20 kHz audio frequency (AF) was applied between the aluminum and mesh electrodes. The plasma polymerization was performed at a constant AF current.

Ditrifluoromethylbenzene (DTFMB), perfluorobenzene (PFB) (purchased from Fluoro Chem. Ltd.), and tetrafluoromethane (CF₄) (purchased from PCR Research Chemicals, Inc.) were used as monomers without further purification.

Elemental Analysis

The C and H contents of the plasma polymers deposited were measured with a Yanagimoto TM-2 analyzer. The F content was determined by colorimetric analysis (Alizarine complex method).²⁰ Finally, the O content was deduced from the difference between sample weight and the sum of C, H, and F contents already determined.

IR and XPS Spectra

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

Plasma polymers deposited on silicon wafers were used as specimens for XPS measurement. Their XPS spectra were recorded with a Shimadzu electron spectrometer 750 employing Mg K_α exciting radiation at 8 kV and 30 mA. The Au core level at 84.0 eV was used for the calibration of energy scale. The C_{1s} core level spectra were deconvoluted with a Shimadzu data system ESCAPAC 760 computer.

Gas Permeation

Specimens used for the measurement of permeation properties were composite membranes, plasma polymers deposited on Millipore filter (VSWP 47, pore size 25 nm). The permeation rate of oxygen and nitrogen gases through the composite membranes were measured according to ASTM D 143V. The pressure at the inflow side was 7.8–19.4 × 10⁴ Pa (0.8–2.0 kg/cm²), and that at the outflow side atmospheric. The flux from the outflow side was measured at room temperature with a bubble flow meter.

The plasma polymer films deposited on the surface of a slide glass plate which was positioned near the Millipore filters during the plasma polymerization process were used for the estimation of the film thickness using interferometry. From the permeation rate and the film thickness data the permeation coefficient, P_{O_2} and P_{N_2} , were calculated with a mean error of less than 5%.

RESULTS AND DISCUSSION

Polymer Deposition Rate

The polymer deposition rate in the plasma polymerization of DTFMB was 12.9 μg/cm² min, which was faster than that for the plasma polymerization of PFB (2.3 μg/cm² min). The comparison indicates that DTFMB is more reactive

in a discharge state than PFB, which contains no hydrogen atoms itself. The four hydrogen atoms in the DTFMB molecule surely contribute to the formation of polymers in a discharge state.

Figure 2 compares the polymer deposition rate in plasma polymerization of DTFMB/CF₄ and PFB/CF₄ mixtures as a function of CF₄ concentration. The polymer deposition rate in both mixture systems, as shown in Figure 2, decreased linearly with increasing CF₄ concentration: The polymer deposition rate in the plasma polymerization of DTFMB/CF₄ and PFB/CF₄ mixtures, when the CF₄ concentration was increased from 0 to 75 mol %, decreased from 12.9 to 5.0 $\mu\text{g}/\text{cm}^2 \text{ min}$, and from 2.3 to 0.6 $\mu\text{g}/\text{cm}^2 \text{ min}$, respectively. At the same time the plasma polymers deposited changed color from pale-yellow to yellow or brown, depending on the CF₄ concentration. This color change indicates that some modification of plasma polymers occurred by the addition of CF₄. The modification in chemical composition will be discussed in a later section.

Oxygen and Nitrogen Permeability

Plasma polymers formed from DTFMB/CF₄ mixtures and deposited on Millipore filters were used as composite membranes for permeation experiments. The oxygen and nitrogen permeation coefficients (P_{O_2} and P_{N_2}) and the permselectivity ($P_{\text{O}_2}/P_{\text{N}_2}$) of the composite membranes were examined to evaluate the plasma films.

Preliminary experiments showed that the starting composition of DTFMB/CF₄ mixture, the discharge current, and the plasma polymer thickness influenced the permeation properties. Figure 3 shows influences of CF₄ concentration on permeation coefficients (P_{O_2} and P_{N_2}). The CF₄ addition made the oxygen and nitrogen permeation coefficients (P_{O_2} and P_{N_2}) decrease and the permselectivity ($P_{\text{O}_2}/P_{\text{N}_2}$) increase simultaneously. The P_{O_2} value decreased from 6.1×10^{-9} to $3.5 \times 10^{-10} \text{ cm}^3 \text{ (STP) cm/cm}^2 \text{ s cm Hg}$, when the CF₄ content was increased from 0 to 75 mol %. The P_{N_2} value also decreased from 3.4×10^{-9} to $7.0 \times 10^{-11} \text{ cm}^3 \text{ (STP) cm/cm}^2 \text{ s cm Hg}$. The $P_{\text{O}_2}/P_{\text{N}_2}$ ratio, on the other

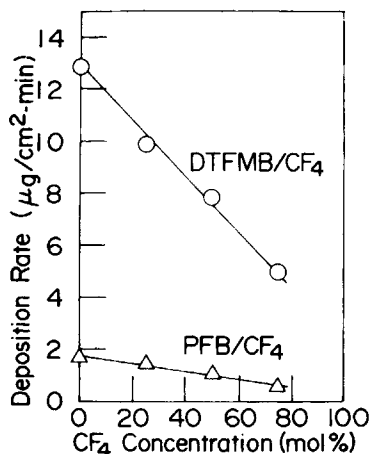


Fig. 2. Polymer deposition rate in plasma polymerization of DTFMB/CF₄ and PFB/CF₄ mixture as a function of CF₄ concentration.

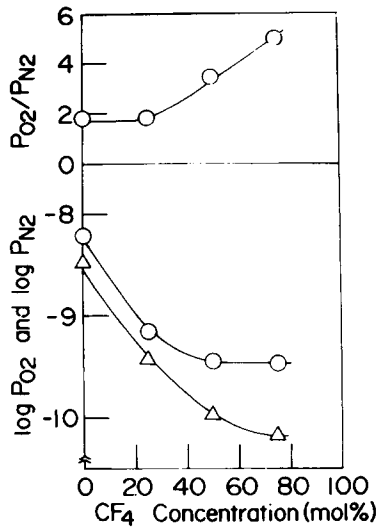


Fig. 3. Permeation coefficient (P_{O_2} , P_{N_2}) and permselectivity (P_{O_2}/P_{N_2}) for plasma polymer films prepared from DTFMB/CF₄ mixture as a function of CF₄ concentration: (○) P_{O_2} ; (△) P_{N_2} .

hand, increased from 1.8 to 5.0. From these results we conclude that the CF₄ addition is effective for the enhancement of the permselectivity.

Figure 4 shows the typical influences of discharge current on the permselectivity for the plasma polymer films prepared from DTFMB/CF₄ mixture containing 75 mol % CF₄. The plasma polymerization at discharge currents less than 70 mA gave films with no permselectivity ($P_{O_2}/P_{N_2} = 1$), while the plasma polymerization at discharge currents more than 70 mA gave permselective films. The permselectivity (P_{O_2}/P_{N_2} ratio), as shown in Figure 4, increased with increasing discharge current and reached 5.0 at a discharge current of 150 mA. The plasma polymerization at discharge currents more than 150

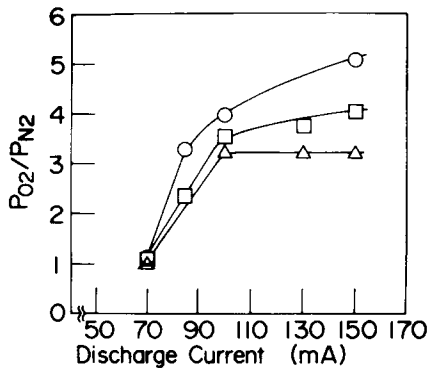


Fig. 4. Permselectivity (P_{O_2}/P_{N_2}) for plasma polymer films prepared from DTFMB/CF₄ mixture containing 75 mol % CF₄ as functions of discharge current and film thickness (nm): (△) 700; (□) 1000; (○) 1300.

mA was not attempted because of the capacity limitation of our power supply equipment.

The permselectivity also showed a dependency of plasma polymer film thickness (Fig. 4). The plasma polymer film prepared from DTFMB possessed a P_{O_2}/P_{N_2} ratio of 1.8 independent of the film thickness. On the other hand, the plasma polymer films prepared from DTFMB/CF₄ mixture containing 75 mol % CF₄ showed increases in P_{O_2}/P_{N_2} ratio from 3.1 at 700 nm to 5.0 at 1300 nm. Theoretically the permeation coefficient should be independent of the film thickness because the permeation coefficient is normalized to unit thickness (1 cm). The thickness dependency of the permeation coefficient suggests that the plasma polymer films are not homogeneous in the cross-sectional direction.

Nomura et al.¹ have discussed the film thickness dependency of permselectivity. Plasma polymer films deposited on porous substrates had two layers from the viewpoint of permeation action, a noneffective and an effective coating layer. The noneffective coating layer contains cracks because of internal tension between the crosslinked polymer networks, and the layer does not contribute to the separation process. The effective coating layer is a true layer contributing to the gas separation process.

Figure 5 shows SEM photographs of the cross section for the composite membranes coated with plasma polymers of the DTFMB/CF₄ mixture containing 75 mol % CF₄, which are the same specimens as used in the permeation experiment. We could see many craters at the surface of thin films (500–700 nm), but could see no craters at the surface of thicker films. The SEM results suggest that films deposited from the plasma polymerization of DTFMB/CF₄ mixtures tend to make cracks. Therefore, we speculate that the film thickness dependency of the permselectivity results from the creation of many cracks in the deposited films. The formation of cracks may be related to reactions between hydrogen atoms of DTFMB and CF₄ in a discharge state. Kay²¹ gave suggestive evidence that CF₄ in a discharge state reacted with hydrogen atoms of polyethylene and, then, fluorination occurred. Afterward, Yasuda²² extended the concept to a special mechanism [competitive ablation and polymerization (CAP)] of plasma polymerization. Therefore, it is not unreasonable that the hydrogen atoms of DTFMB predominantly react with CF₄ molecule in a discharge state and the formation of crosslinkages follows.

The permselectivity of the plasma films prepared from DTFMB/CF₄ mixture were compared with that of other plasma films prepared from PFB/CF₄, pentafluorobenzene (PnFB)/CF₄, and tetrafluorobenzene (TFB)/CF₄ mixtures, which have been reported in previous papers (Table I).²³ Table I indicates that (1) the CF₄ addition improves the permselectivity in all the mixture systems, (2) the plasma polymer films prepared from DTFMB/CF₄ mixture possess permeation coefficients comparable to those prepared from PFB/CF₄ and PnFB/CF₄ mixtures, and (3) the plasma polymer film prepared from a DTFMB/CF₄ mixture (5.0) is inferior in permselectivity to those prepared from PFB/CF₄ (7.2) and PnFB/CF₄ mixtures (5.5), but is superior to that prepared from a TFB/CF₄ mixture (3.4). DTFMB is a derivative of TFB and contains two CF₃ groups at position 1 and 3. From the comparison in permselectivity between the plasma polymer films prepared from a DTFMB/CF₄ and TFB/CF₄ mixtures, we recognize the contribution of CF₃ groups to permselectivity.

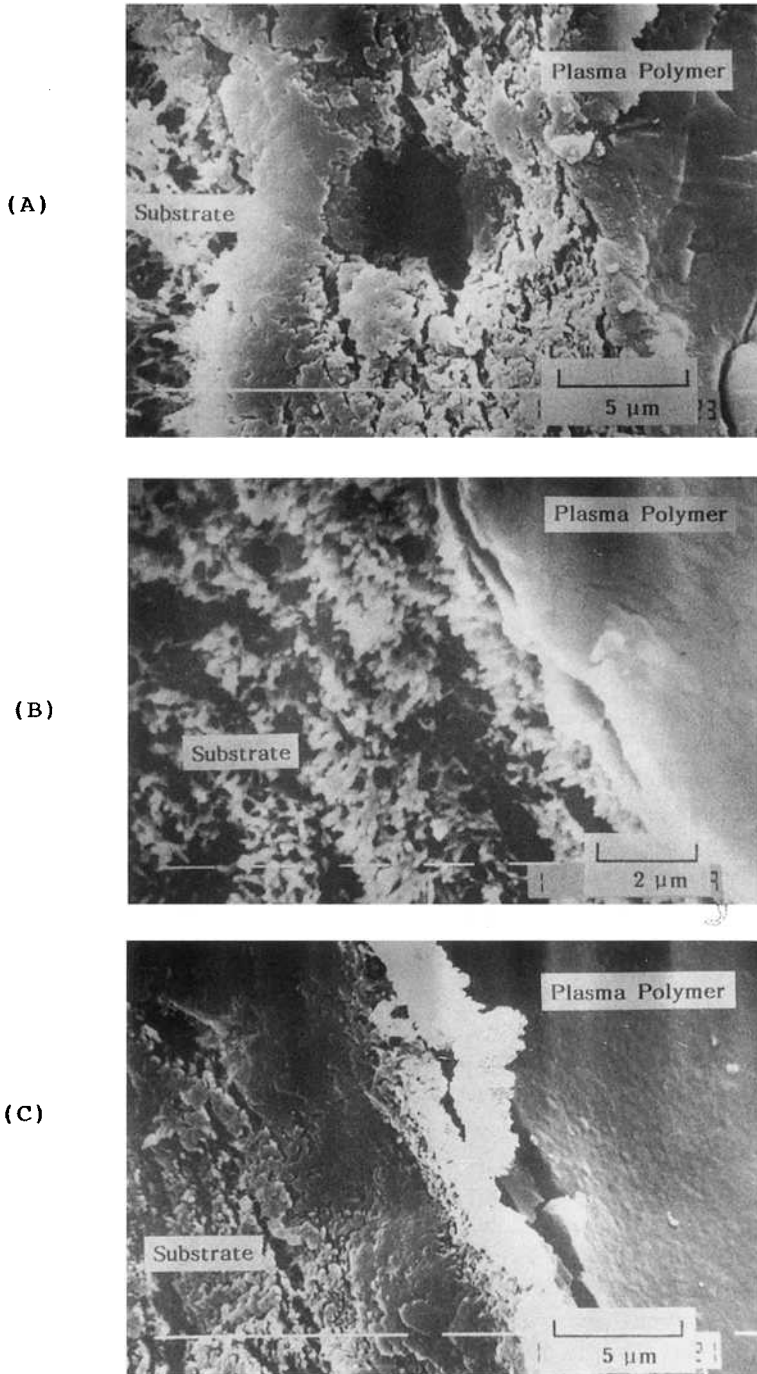


Fig. 5. SEM pictures of composite membranes coated with plasma polymers of DTFMB/CF₄ mixture containing 75 mol % CF₄; (A) 500; (B) 700; (C) 1300 nm thick.

TABLE I
Permeation Coefficient (P_{O_2} , P_{N_2}) and Permselectivity (P_{O_2}/P_{N_2}) of Plasma Films Prepared from DTFMB/CF₄, PFB/CF₄, PnFB/CF₄, and TFB/CF₄ Mixtures

Monomer mixture	CF ₄ concn (mol %)	Discharge current (mA)	Permeation properties		
			$P_{O_2} \times 10^{10}$ ^a	$P_{N_2} \times 10^{10}$ ^a	P_{O_2}/P_{N_2}
DTFMB/CF ₄	75	70	194	185	1.1 ^b
	75	100	16.6	5.5	3.0 ^c
	75	150	3.5	0.70	5.0 ^d
PFB/CF ₄	50	75	11.8	1.8	7.2
	75	75	1.0	0.47	2.1
PnFB/CF ₄	25	120	18.0	3.3	5.5
	75	120	3.31	1.13	2.9
TFB/CF ₄	25	120	1.84	0.54	3.4
	75	75	2.84	1.51	1.9

^a In cm³ (STP) cm/cm² s cm Hg.

^b Film thickness was 500 nm.

^c Film thickness was 1000 nm.

^d Film thickness was 1300 nm.

Chemical Composition

To clarify the reason why the permselectivity for plasma polymer films deposited from DTFMB was enhanced by the CF₄ addition, the chemical composition was investigated using elemental analysis, infrared spectroscopy, and XPS. The elemental composition for the plasma polymer films formed from DTFMB/CF₄ mixture depended strongly on the CF₄ concentration. The F/C atomic ratio determined by elemental analysis increased from 0.50 to 0.94 by a CF₄ addition of 75 mol %, and the H/C atomic ratio decreased from 0.33 to 0. These changes in elemental composition by the CF₄ addition suggest that fluorination and dehydrogenation occurred simultaneously during the polymer-forming process. The fluorination occurring in the DTFMB/CF₄ mixture system is compared with that in other mixture systems.

Table II summarizes the elemental composition for plasma polymer films prepared from PFB/CF₄, PnFB/CF₄, and TFB/CF₄ mixtures. This table has been reported in a previous paper.²⁴ The F/C atomic ratio of the starting monomers used for plasma polymerization is 1.0 for PFB, 0.83 for PnFB, 0.75 for DTFMB, and 0.67 for TFB; and that of their mixtures containing 75 mol % CF₄ is 2.0 for PFB/CF₄ mixture, 1.89 for PnFB/CF₄ mixture, 1.87 for TFB/CF₄ mixture, and 1.64 for DTFMB/CF₄ mixture. In spite of the differences in F/C atomic ratio among the starting monomers the plasma polymer films prepared from the four fluorinated benzenes possessed almost the same F/C atomic ratio (0.48–0.58). On the other hand, the plasma polymers prepared from mixtures containing 75 mol % CF₄ showed F/C atomic ratios widely distributed in ranges of 0.94–1.24. The magnitude of the F/C atomic ratio was: plasma polymers from PnFB/CF₄ mixture (1.24) > those from TFB/CF₄ mixture (1.10) > those from PFB/CF₄ mixture (1.09) > those from DTFMB/CF₄ mixture (0.94). This indicates that DTFMB is less reactive in fluorination with CF₄ than PnFB, TFB, and PFB.

TABLE II
Elemental Composition of Plasma Polymers Prepared from DTFMB/CF₄,
PFB/CF₄, PnFB/CF₄, and TFB/CF₄ Mixtures

Monomer mixture	CF ₄ concn (mol %)	Discharge current (mA)	Composition of monomer	Composition of polymers
DTFMB/CF ₄	0	100	CH _{0.50} F _{0.75}	CH _{0.33} N _{0.11} O _{0.12} F _{0.50}
	75	150	CH _{0.36} F _{0.16}	CN _{0.06} O _{0.02} F _{0.94}
PFB/CF ₄	0	120	CF	CH _{0.05} N _{0.02} O _{0.25} F _{0.48}
	75	120	CF ₂	CH _{0.18} N _{0.11} O _{0.06} F _{1.09}
PnFB/CF ₄	0	120	CH _{0.17} F _{0.83}	CH _{0.35} N _{0.11} O _{0.18} F _{0.58}
	75	120	CH _{0.11} F _{1.89}	CH _{0.17} N _{0.11} F _{1.24}
TFB/CF ₄	0	120	CH _{0.33} F _{0.67}	CH _{0.34} N _{0.02} O _{0.17} F _{0.49}
	75	120	CH _{0.22} F _{1.78}	CH _{0.21} N _{0.08} F _{1.10}

Figure 6 shows typical infrared spectra for plasma polymer prepared from DTFMB/CF₄ mixtures as a function of CF₄ concentration. The plasma films prepared from DTFMB showed strong absorption peaks at 1824 (C=O stretching vibration in C(O)F group), 1730, 1625 (C=O, CF₂=C), 1280 (C-F stretching vibration in fluorinated aromatic rings), 1180, 1145 (C-F stretching vibration in fluorinated alkyl groups), and 910 cm⁻¹ (CH out-of-plane deformation of one free hydrogen atom in aromatic rings); and weak absorption peaks at 3020 (CH stretching vibration of aromatic rings), 2920 (CH stretching vibration), 1335 (CH in-plane deformation of CH=CH groups), 840 and 802 cm⁻¹ (CH out-of-plane deformation of two adjacent free hydrogen atoms in aromatic rings). The appearance of the absorption peaks at 3020, 1335, 910, 840, and 802 cm⁻¹ means that the plasma polymers contain aromatic rings. Furthermore, the appearance of C-F stretching vibrations at 1280, 1180, and

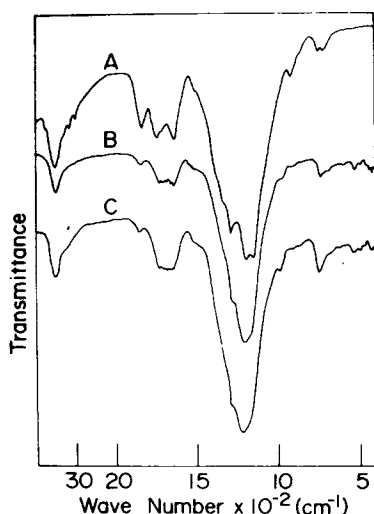


Fig. 6. IR Spectra of plasma polymers prepared from DTFMB/CF₄ mixture as a function of CF₄ concentration; (A) 0; (B) 50; (C) 75 mol % CF₄.

1145 cm^{-1} means the existence of two kinds of fluorinated moieties, aromatic and alkyl moieties. From these spectral results it can be assumed that the plasma polymer formed from DTFMB is a mixture of fluorinated alkyl and aromatic moieties and hydrocarbon moieties with carbonyl groups.

It was not until the CF_4 addition was 50 mol % CF_4 that the IR spectra stopped changing. The plasma polymers prepared from a DTFMB/ CF_4 mixture containing more than 50 mol % CF_4 showed a strong absorption peak at 1200 cm^{-1} (C—F stretching vibration in alkyl groups), weak absorption peaks at 1825 [C(O)—F] and 740 cm^{-1} (CF_3 groups),²⁴ and wide absorptions at 1730–1625 cm^{-1} . No absorption peak related to CH vibrations in aromatic groups could be observed. The absorption peak at 1280 cm^{-1} due to the C—F stretching vibration in fluorinated aromatic rings became weak in intensity and existed as a shoulder of the strong absorption peak at 1200 cm^{-1} . Therefore, from these spectral changes after CF_4 addition, we conclude that (1) the plasma polymers prepared from DTFMB/ CF_4 mixture are composed of fluorinated alkyl chains with small amount of fluorinated aromatic-moieties and carbonyl moieties and (2) the CF_4 addition breaks down aromatic rings.

XPS (C_{1s} core level) spectra for the plasma polymers prepared from DTFMB/ CF_4 mixture distributed widely in ranges of 283–296 eV and contained at least four components having different binding energies. The deconvolution process resolved these spectra into five components. We believe that the resolution was not good enough for discussion of details of fluorinated moieties because the C_{1s} spectra surely involve $\pi \rightarrow \pi^*$ satellite of aromatic rings. From this viewpoint we do not deal with the XPS spectra here.

The breakdown of fluorinated aromatic rings by the CF_4 addition may be related to the enhancement of permselectivity. The permselectivity, as shown in Figure 3, initiated an increase at 50 mol % CF_4 addition, and at the same time the breakdown of fluorinated aromatic rings occurred. It is not unreasonable that bulky aromatic rings in the plasma polymers contribute to increase in free volume, and as a result, bring about easy permeation and low permselectivity. Therefore, we could assume that the breakdown of aromatic rings brings about decreases in free volume and then increases in permselectivity. However, this assumption does not exclude the concept that the formation of crosslinkage by the CF_4 addition contributes to increase in permselectivity. It is not clear at the present time that either of the concepts is reasonable. This subject is important for seeking new separation membranes and will be dealt with in the near future.

CONCLUSION

This study provides important aspects on plasma polymerization of the DTFMB/ CF_4 mixture and on permeation properties of the plasma polymer films.

1. DTFMB is more reactive in a discharge state than PFB for deposition of plasma polymers. In plasma polymerization of DTFMB/ CF_4 mixtures, the polymer deposition rate decreases with increasing CF_4 concentration.

2. The polymer formation in plasma polymerization of DTFMB/CF₄ mixtures is accompanied with fluorination and dehydrogenation.
3. Plasma polymers prepared from DTFMB are composed of fluorinated alkyl and aromatic moieties and hydrocarbon moieties with carbonyl groups. Plasma polymers prepared from DTFMB/CF₄ mixtures are composed of fluorinated alkyl chains with a small amount of fluorinated aromatic moieties and carbonyl moieties. The CF₄ addition breaks down aromatic rings to form polymers.
4. Permeation properties of plasma polymer films prepared from DTFMB/CF₄ mixture are influenced by the starting composition of the DTFMB/CF₄ mixture, the discharge current, and the thickness of the deposited plasma polymer. The permselectivity is improved by adding CF₄ and increasing discharge current.
5. Plasma polymerization of DTFMB/CF₄ mixtures containing 75 mol % CF₄ at a discharge current of 150 mA yields membranes with a permselectivity of 5.0. The P_{O_2} and P_{N_2} values are 3.5×10^{-10} and 7.0×10^{-11} cm³ (STP) cm/cm² s cm Hg, respectively.

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