

NOTE

Plasma Polymerization of Cyclic Perfluoroamines and Composite Membranes for Gas Separation

INTRODUCTION

Plasma polymerization is a film-forming process that deposits a thin film directly on the substrate surface. The polymer-growing reaction differs from that in conventional radical or ionic polymerizations and affords plasma polymers with highly crosslinked structures without repeating units.^{1,2} A wide variety of compounds can be used as monomers in plasma polymerization, even those without polymerizable functional groups under conventional methods. Membranes comprising a plasma polymer layer and a porous substrate have good potential for use in the separation process because plasma polymerization provides a pinhole-free, ultrathin polymer layer that gives a large permeate flux without lowering permselectivity.³

The properties of perfluoropolymers include high thermal stability, chemical resistance, and low surface energy. Plasma polymers of perfluorocompounds therefore have drawn much attention as to both preparation and application. The oxygen permeability of the fluoro plasma polymers has been investigated intensively on the basis of highly fluorinated compounds having high gas solubility.⁴⁻⁶ Perfluorotributylamine is reported to plasma-polymerize with polymer deposition on the substrates to give composite membranes that have a laminate structure and good oxygen permeability and selectivity.⁷

We applied plasma polymerization to the *N*-vinylated cyclic perfluoroamines such as pyrrolidine and morpholine and compared their polymerizability with *N*-ethylated ones. The oxygen and nitrogen permeabilities of the membranes that composed the plasma polymer layer and porous substrate also were evaluated.

(FVP) and perfluoro(*N*-vinylmorpholine) (FVM) were prepared by thermal decarboxylation of alkali-metal perfluoro(aminopropionate)s⁹ (see Fig. 1). Polycarbonate films with piercing micropores 0.015 μm in diameter (Nucleopore[®]) were used as the substrate for the composite membranes on which plasma polymers were deposited.

Plasma Polymerization

Plasma polymerizations were done in a reaction chamber: Samco International BP-1. The reactor consisted of a Pyrex bell jar 22 cm in diameter and 20 cm high and a pair of parallel SUS electrodes 8.0 cm in diameter that were fixed vertically 2.0 cm apart. The substrates to be covered by the plasma polymers were placed on the lower electrode which was cooled at 15–20°C during polymerization. The interior of the reactor was evacuated at 0.003 Torr. The gaseous monomer then was introduced into the reactor through inlet nozzles located at the bottom of the upper electrode to produce an internal pressure of 0.20 Torr. Radio-frequency power (13.56 MHz) of 50 W was supplied to generate the glow discharge. Polymer deposition rates were determined by weighing the glass slides covered with the plasma polymers. The thickness of the plasma polymer layer was measured by interferometry with a Wyko TOPO-3D surface profiler. Infrared spectra of the plasma polymers were obtained with KBr pellets covered by plasma polymers.

EXPERIMENTAL

Materials

Perfluoro(*N*-ethylpyrrolidine) (FEP) and perfluoro(*N*-ethylmorpholine) (FEM) were obtained as products of electrochemical fluorination of the corresponding methyl 2-aminopropionates.⁸ Perfluoro(*N*-vinylpyrrolidine)

Gas Permeability Measurement

The gas permeability of the composite membranes was evaluated with air (O_2 , N_2) at 25°C. The plasma polymer side of the membrane was maintained at atmospheric pressure, and the substrate side, at ca. 10^{-3} cmHg. The amounts of the permeated gases were measured by gas chromatography. The gas permeation rates, RO_2 and RN_2 in cm^3 (STP) $\text{cm}^{-2}\text{s}^{-1}$ cmHg^{-1} , were determined from the slopes of the time-permeate volume curves in the steady state.

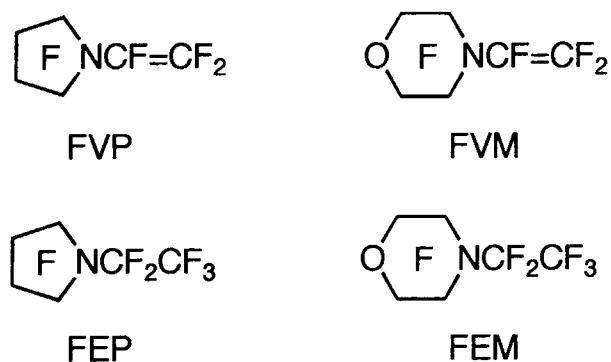


Figure 1. The monomer structures.

RESULTS AND DISCUSSION

Plasma polymerization is convenient for polymerizing perfluoro(*N*-vinylamine)s because they have little radical homopolymerizability due to steric hindrance around the vinyl group, whereas they copolymerize with vinylidene fluoride.¹⁰ The perfluoro(*N*-ethylamine)s also are thought to be nonpolymerizable by the usual method.

Results of the plasma polymerizations of the perfluoro(*N*-vinylamine)s, FVP and FVM, and the perfluoro(*N*-ethylamine)s, FEP and FEM, at 0.20 Torr and 50 W are shown in Figure 2. All the compounds gave plasma polymers in a film form under the conditions used. FVP showed the most rapid deposition of the polymer. The *N*-vinyl compounds, FVP and FVM, have larger polymer deposition rates than those of the corresponding *N*-ethyl ones, FEP and FEM. Compounds with the morpholine ring have smaller deposition rates than those with the pyrrolidine ring. These results are consistent with the general tendency in plasma polymerization that polymer deposition is enhanced by unsaturated bonds but reduced by oxygen atoms in monomer molecules.^{11,12} There was

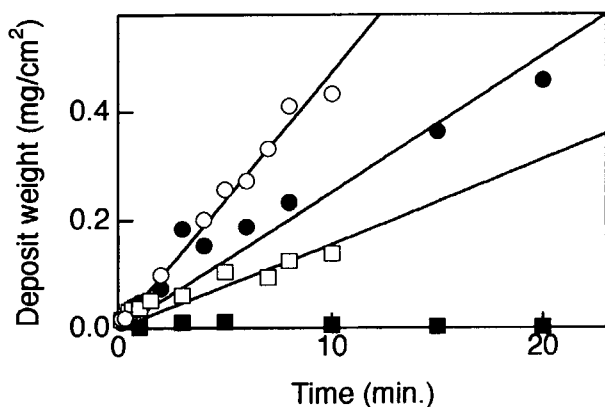


Figure 2. Polymer deposition rates of cyclic perfluoroamines at 50 W, 0.20 Torr: (○) FVP; (●) FVM; (□) FEP; (■) FEM.

Table I Elemental Composition of the Plasma Polymers

Plasma Polymer		C (%)	N (%)	C/N
FVP	Calcd ^a	24.42	4.75	5.14
	Found	28.72	7.07	4.06
FVM	Calcd ^a	23.17	4.50	5.15
	Found	27.95	8.89	3.14
FEP	Calcd ^a	21.64	4.21	5.14
	Found	27.10	7.74	3.50
FEM	Calcd ^a	20.65	4.01	5.15
	Found	17.27	7.57	2.28

^a Calculated for the monomer.

little initial deposition of the FEM polymer; moreover, the weight of the polymer decreased as the reaction proceeded. Low-power input (10 W at 0.20 Torr) improved the deposition of the FEM polymer, but the weight deposited became almost constant (ca. 0.01 mg/cm²) as the reaction progressed because of competitive ablation of the polymer in the glow discharge.¹³

The elemental compositions of the plasma polymers are shown in Table I. Except for FEM, all have larger carbon and nitrogen contents than those of the starting monomers, which is evidence of the elimination of fluorine atoms during polymerization. The C/N ratios in the polymers are smaller than those in the monomers, markedly so in the polymers of compounds with the morpholine ring. This is indicative that the carbon atoms are easily eliminated as CO or CO₂ as well as fluorocarbons such as CF₄. IR spectra showed that absorption due to the trifluorovinyl group in the FVP and FVM monomers was absent in their polymers, whereas absorption due to the

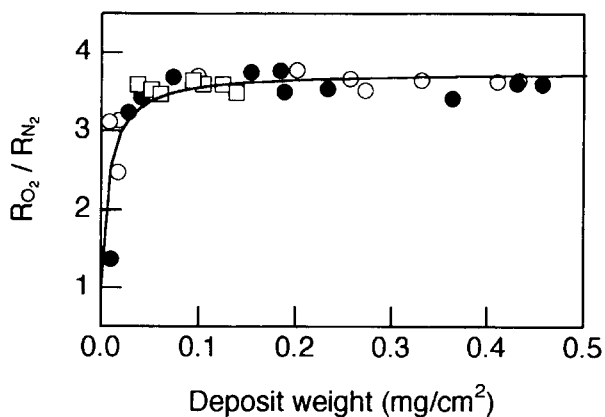


Figure 3. Separation factor for oxygen to nitrogen in composite membranes with a plasma polymer layer: (○) FVP; (●) FVM; (□) FEP.

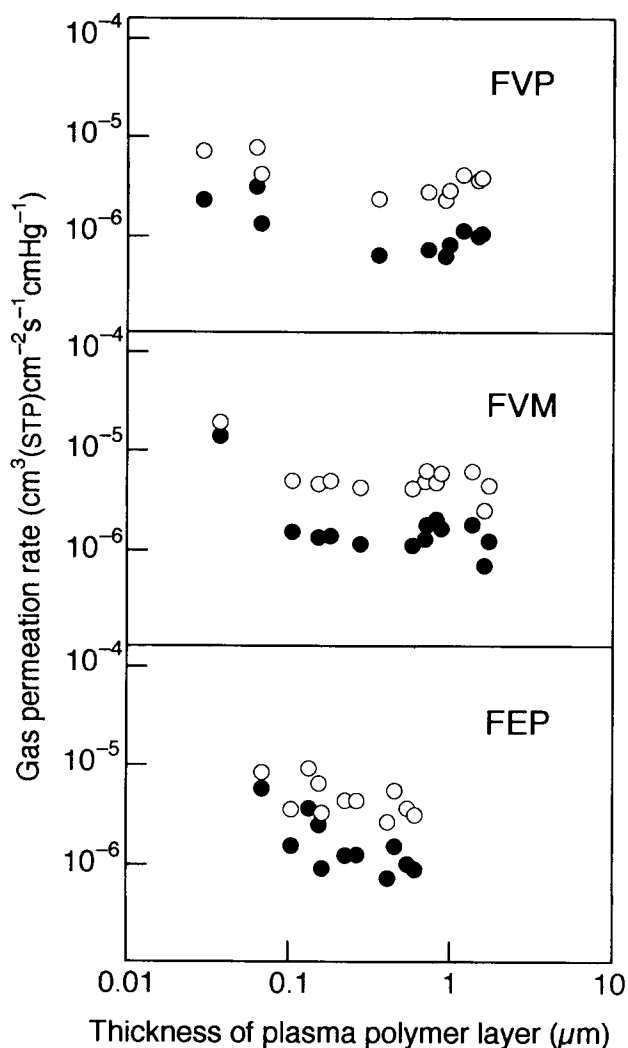


Figure 4. Relationship between the gas permeation rate in composite membranes and the thickness of the plasma polymer layer: (○) oxygen; (●) nitrogen.

trifluoromethyl group in FEM and FEP remained throughout polymerization. Vinyl polymerization therefore may occur to a degree, yielding linear segments in the polymers. Hydroxy and carbonyl groups present in the polymers are thought to have been incorporated on exposure to air after polymerization, the remaining active species on the polymer surface reacting with oxygen or moisture.

The oxygen and nitrogen permeabilities of the membranes composing the plasma polymer of FVP, FVM, or FEP and the porous substrate were measured using air. In Figure 3, the separation factors for oxygen to nitrogen, RO_2/RN_2 , are plotted against the weights of the plasma polymers. Permselectivity ($RO_2/RN_2 > 1$) appeared at 0.01 mg/cm^2 , a layer thickness of ca. $0.04 \text{ } \mu\text{m}$, consistent

with the substrate used having piercing pores $0.015 \text{ } \mu\text{m}$ in diameter. The permselectivity of the plasma polymers is 3.7, almost irrespective of the monomers, although there are slightly different elemental compositions depending on the monomer structure (Table I). The relationship between the gas permeation rates in the composite membranes and the thickness of the deposited polymer layer are shown in Figure 4. The oxygen permeation rates are $10^{-6} \text{ cm}^3 \text{ (STP) cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$. The oxygen and nitrogen permeation rates in these composite membranes do not decrease in inverse proportion to the thickness of the plasma polymer layer. This means that the apparent gas permeability coefficients of the plasma polymers, which are calculated from the permeation rates divided by the layer thicknesses, increase with thickness.^{7,14} The phenomenon seems pronounced in membranes with a plasma polymer layer of a *N*-vinyl compound. The reason why is not clear, but it may be due to the heterogeneous structure of the plasma polymers which include physical cracks at the surface, inside the layer, or both^{4,15} or to the very small surface porosity of the substrate used.^{14,16}

CONCLUSIONS

Cyclic perfluoroamines with an *N*-vinyl or -ethyl group plasma-polymerized in a glow discharge, giving polymers in film form. Perfluoro(*N*-vinylpyrrolidine), which had the vinyl group without an oxygen atom in its ring, gave the most rapid deposition of plasma polymer on the substrates. Membranes composed of plasma polymers and a porous support had oxygen permeation rates of $10^{-6} \text{ cm}^3 \text{ (STP) cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$ and oxygen permselectivity to nitrogen of $RO_2/RN_2 \sim 3.7$.

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