

# Preparation of Ion Exchange Membranes by Plasma Polymerization. I

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## Synopsis

Plasma polymerizations of three kinds of amines,  $\gamma$ -aminopropylethoxydimethylsilane (APEMS), allylamine (AA), and pyrrole (PY), were investigated by IR and XPS analysis. Plasma-polymerized films were deposited on porous substrates, and ion exchange abilities of the composite membranes were measured. When APEMS were used as the monomer, the polymer retained the chemical structure of the monomer, amino groups. However, when AA and PY were used as the monomers, the plasma polymers contained a larger amount of amido structures than did the polymer of APEMS. Each membrane had ion exchange ability. In particular, the membrane prepared from APEMS showed superior ion exchange ability, anion permselectivity and conductivity, in acidic solutions. This property was attributed to the chemical structure of the polymer from APEMS retaining amino groups. The ion exchange properties of the membranes depended on the pH of the solution. In particular, the membrane of APEMS showed high membrane potential and low electric resistance only in a narrow pH region due to the weak basicity of amines and the hydrophobic property of the polymer.

## INTRODUCTION

It is well known that uniform, pinhole-free, thin films can be formed on various substrates by plasma polymerization.<sup>1,2</sup> The application of the plasma films to separation membranes was advanced: reverse osmosis membranes<sup>3</sup> and gas separation membranes.<sup>4,5</sup> On account of their thickness, these membranes show high permeability. In this paper, we have tried the application of plasma polymerization to the other type of separation membrane, ion exchange membranes.

For the ion exchange polymers, functional groups such as sulfo, carboxy, and amino groups are required, and the fundamental properties required for the ion exchange membranes are high ion conductivity, high ion exchange capacity, and high selectivity of cation or anion transference (large transference number).<sup>6-8</sup> The ion exchange membrane shows high conductivity owing to its thinness and high ion exchange capacity. The capacity and selectivity are dependent on the chemical structure of the membrane; the former depends on the concentration of the functional groups and the latter depends on the purity of the basic and acidic functional groups. However, it is difficult to control the chemical structure of the plasma polymers, since the polymer-forming process in plasma polymerization is complex.

Inagaki indicated the possibility of controlling the plasma polymerization reaction by selecting monomers which had reactive substituent groups.<sup>9</sup> In this paper, for the purpose of preparing anion exchange membranes, amines which possess reactive structures like double bonds and Si—C bonds were

used as the monomers, and the plasma-polymerized films were deposited on porous substrates. The ion exchange abilities of the composite membranes were examined.

## EXPERIMENTAL

### Material

The porous substrate used, was a porous polypropylene membrane (Cellgard 2400) 20  $\mu\text{m}$  thick with rectangular pores of a maximum size of  $2000 \times 200 \text{ \AA}$ .

The organic compounds used for plasma polymerization were  $\gamma$ -aminopropylethoxydimethylsilane (hereafter denoted APEMS, Shin-Etsu Silicon Chemicals, Co., Ltd.), allylamine (hereafter denoted AA, Nakarai Chemical Co., Ltd.), and pyrrole (hereafter denoted PY, Tokyo Kasei Co., Ltd.). They were used without further purification. Potassium chloride (Guaranteed Reagent, Nakarai Chemical Co., Ltd.) was used as an electrolyte. Adjustment of the pH of a solution was performed by adding a hydrochloric acid or a potassium hydroxide solution to the electrolyte solution. The pH of the solution was measured with a Horiba F-8AT pH meter. Concentration of both hydrochloric acid and potassium hydroxide solutions were adjusted to the same concentration of the electrolyte solution in each run.

### Plasma Polymerization

The apparatus and experimental procedures for plasma polymerization were the same as those reported in detail in previous papers.<sup>4,5</sup> The plasma system was constructed with a Pyrex glass chamber of bell-jar type, a monomer inlet, a rotary vacuum pump, a Pirany gauge, and a radio frequency power supply of 13.56 MHz with a matching network. The porous substrate and a glass slide were placed at a sample stage in the chamber. The system was evacuated to 0.01 Torr by the rotary pump. Vapor of the organic compound was introduced into the chamber, and the pressure was kept at an certain pressure by an appropriate opening of a needle valve in accordance with the evacuating speed of the pump. Under these conditions, plasma polymerization was initiated by loading the radio frequency electric power onto an electrode wound around top of the chamber. The plasma polymerization was continued for a certain length of time with the pressure being kept at the initial pressure by an appropriate opening of the needle valve. The plasma polymerization conditions for each monomer were shown in Table I.

TABLE I  
Plasma Polymerization Conditions

Monomer	Pressure (Torr)	rf power (W)	Polymerization time (min)
APEMS	0.2	30	15
AA	0.1	50	20
PY	0.6	30	5

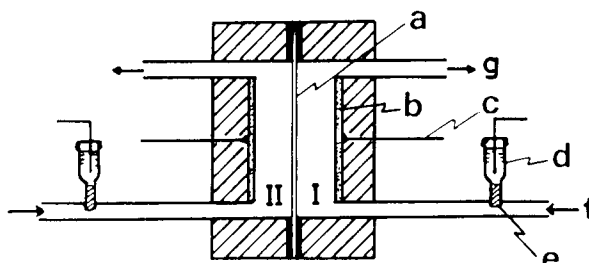


Fig. 1. A schematic diagram of a cell used for measuring the ion exchange properties of the composite membranes: (a) a membrane; (b) a platinum plate electrode; (c) a lead wire; (d) an Ag/AgCl electrode; (e) a KCl/agar salt bridge; (f) an inlet for electrolyte solutions; (g) an outlet.

### IR Measurement

Infrared spectra for each sample were obtained using a JEOL JIR-40X FT-IR spectrophotometer by the ATR method.

### XPS Analysis

XPS spectra of plasma polymers were recorded on a DuPont-Shimadzu ESCA 650B spectrometer.

### Measurement of Thickness

A plasma polymerized film was deposited on a glass slide and the thickness of the film was determined by using the multibeam interferometry method.

### Measurement of the Property of Ion Exchange

Ion exchange capacity was measured as follows. Each composite membrane with an area of  $10 \text{ cm}^2$  was soaked in 10 mL of hydrochloric acid solution adjusted to pH 3.83. The membrane was stored in the solution for 36 h, and the pH of the solution was measured. Appropriate correction for blank was made by measuring the change of the pH on the only porous substrate. The ion exchange capacity was determined from the variation of the pH.

The measurement of the properties of ion exchange were performed at  $25^\circ\text{C}$ . Figure 1 shows a cell constructed with two compartments in which electrolyte solution were introduced, platinum plates which were used as electrodes for measurement of electric resistance of membrane ( $R_m$ ), and Ag/AgCl electrodes which were used for measuring the membrane potential ( $E_m$ ). In order to moisten the membrane with water, the membrane was washed with ethanol, followed by water. The wet membrane was interposed between the compartments in order to separate them. The distance between the platinum electrodes was 4 mm, and the membrane area was  $1 \text{ cm}^2$ . The electrolyte solutions were introduced into the two compartments from the inlet respectively, and the solution in the two compartments was thoroughly replaced with new solutions before each measurement. The measurement of the properties of ion exchange was performed after stopping the flow of the solution.

### Measurement of Membrane Conductivity

Potassium chloride solution of 0.5 N adjusted to various pH (pH 2–12) was introduced into both compartments (I and II). The electric resistance between the two platinum plates was measured on a Yokogawa–Hewlett-Packard 4261A digital LCR meter. The measurement was made at 1 kHz. In a similar manner the electric resistance of the solution was measured without the membrane. The resistance of the membrane alone ( $R_m$ ) was calculated as the difference between the resistance values with and without membrane.

### Measurement of the Membrane Potential ( $E_m$ )

The Ag/AgCl electrode with an internal solution of saturated KCl was connected to the solution in each compartment by a salt bridge (KCl/agar) as shown in Figure 1. In order to correct the difference in the electrode potential between the two electrodes, the same solution was introduced into each compartment, and the potential between the two electrodes was compensated. The variation in  $E_m$  with pH was measured as follows. The KCl solutions of 0.1N and 0.01N, which were adjusted to the same pH as each other, were introduced into compartments I and II, respectively, and the potential between the two electrodes in each pH was measured with a Keithley 616 digital electrometer. When the potential of the solution in compartment I was higher than that in compartment II, the membrane potential was defined to be positive.

The measurement of the variation in  $E_m$  with the electrolyte concentration was carried out as follows. Each solution tested was adjusted to pH 3.9. The KCl concentration of the solution in compartment II was fixed at 0.01N in each run, and the KCl concentration in compartment I was changed to be in the range of 0.01–0.5N.

## RESULTS AND DISCUSSION

### Chemical Characterization

Figure 2 shows infrared (IR) spectra of the plasma polymers formed from APEMS, AA, and PY (hereafter denoted PAPS, PAA, and PPY respectively). On each spectrum, a broad absorption band around a wave number of  $3300\text{ cm}^{-1}$ , assigned to N–H stretch vibration derived from the structure of amine and or amid,<sup>10</sup> is observed, although the intensity of these bands is different from each other. These results indicate a possibility that each polymer contains amino groups. In the spectra of PAA and PPY, there appear the absorption bands at almost  $2200\text{ cm}^{-1}$  which are assigned to C≡N stretch vibration derived from nitriles, isonitriles, or isocyanic esters. On the other hand, the absorption of C≡N stretch vibration is not observed in the spectrum of PAPS. The formation of C≡N bonds indicates that, in plasma state, AA and PY are relatively apt to give rise to rearrangements and elimination reactions of hydrogen in comparison with APEMS. At almost  $1650\text{ cm}^{-1}$ , there are other characteristic absorption bands arising from a chemical structure containing nitrogen. These bands are assigned to C=O stretch vibration of amides and or —C=N— stretch vibration of imines. The

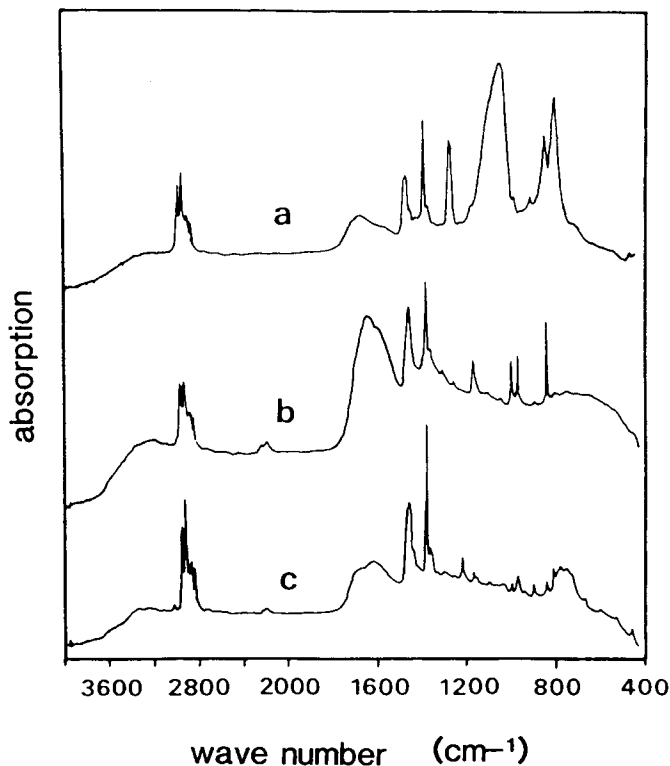


Fig. 2. Infrared spectra of the plasma polymers: (a) PAPS; (b) PAA; (c) PPY.

intensity of the absorption in the spectrum of PAPS is considerably weaker than those in the other spectra. Table II shows elemental ratios in the plasma polymers measured by XPS. It is found that oxygen exists in appreciable amounts in every polymer despite the absence of oxygen in the monomers AA and PY. These results suggest that each plasma polymer contains amide groups; however, PAPS retains the structure of amine compared with PAA and PPY. In the spectrum of PPY, there is a broad absorption band at around  $750\text{ cm}^{-1}$  which can be assigned out-of-plane C—H deformation vibration arising from a pyrrole ring. It is known that this absorption is the strongest in the spectrum of the monomer PY; therefore, PPY contains a small amount of the pyrrole ring because the intensity is weak in the spectrum of PPY. It is thought that the retention of the structure of the monomer in PAPS results

TABLE II  
Elemental Ratios in the Plasma Polymers Measured by XPS

Plasma polymer	N	C	O	Si
PAPS	1	9 (7) <sup>a</sup>	2 (1) <sup>a</sup>	2 (1) <sup>a</sup>
PAA	1	4 (3) <sup>a</sup>	1/5	—
PPY	1	6 (4) <sup>a</sup>	2/5	—

<sup>a</sup> Elemental ratios in the monomers.

TABLE III  
Ion Exchange Capacity of the Plasma Polymer

Plasma polymer	Thickness (Å)	Ion exchange capacity (meq/cm <sup>3</sup> )
PAPS	2000	1.9 (31%) <sup>a</sup>
PAA	2200	4.8 (27%) <sup>a</sup>
PPY	4000	0.5 (3.4%) <sup>a</sup>

<sup>a</sup>The ratio of the polymer and the monomer in the equivalent weights when the specific gravity of the plasma polymer is 1.

from the absence of a double bond in the monomer which causes the re-arrangement reaction followed by changes of the chemical structure and from the existence of Si—C bond which has a low bond energy and is easily cleaved. Therefore, contrary to PAPS, PAA and PPY hardly retain the chemical structure of the monomers.

For the anion exchange polymer, the existence of C≡N and amide is undesirable, because groups are easily hydrolyzed and carboxylic groups with the ability of cation exchange are formed. It can be said that APEMS is a suitable monomer to retain the chemical structure and prepare the anion exchange polymer in this regard.

#### Ability of Ion Exchange

The ion exchange capacity and the thickness of the plasma polymerized films is shown in Table III. The capacity of PPY is considerably lower than those of the others. It is well known that the basicity of PY is so small that protonation on nitrogen does not occur even by strong acid because of the effect of aromaticity.<sup>11</sup> Therefore, the small ion exchange capacity of PPY is due to the small content of amino groups except a pirole structure. The ion exchange capacity of PAA is more than twice as great as that of PAPS. However, when compared with respective monomers, both PAA and PAPS retain about 30% of the amino group in the monomers; however, PAPS seems to be a little more retentive than PAA.

The membrane potential ( $E_m$ ) and the electric resistance ( $R_m$ ) of each membrane were plotted as a function of pH of the solution in Figures 3 and 4, respectively. In Figure 3, each membrane has positive membrane potential in acidic solutions (in the pH range below 5); therefore, it is found that each membrane has the ability of anion exchange. The membranes PAPS and PAA have high membrane potential at almost 50 mV. On the other hand, the membrane of PPY exhibits a lower membrane potential than the others. This lower potential of PY is attributed to its small ion exchange capacity. It is found that the  $E_m$  value of each membrane varies widely with pH. For each membrane, there is rapid decrease of  $E_m$  in different pH regions. The  $E_m$  of each membrane at high pH is opposite in potential to that at low pH. These results indicate that the membranes contain both basic and acidic functional groups.

In Figure 4, the  $R_m$  value of the membrane of PPY is almost constant and higher than those of PAPS and PAA at low pH. As to the membrane of PAPS

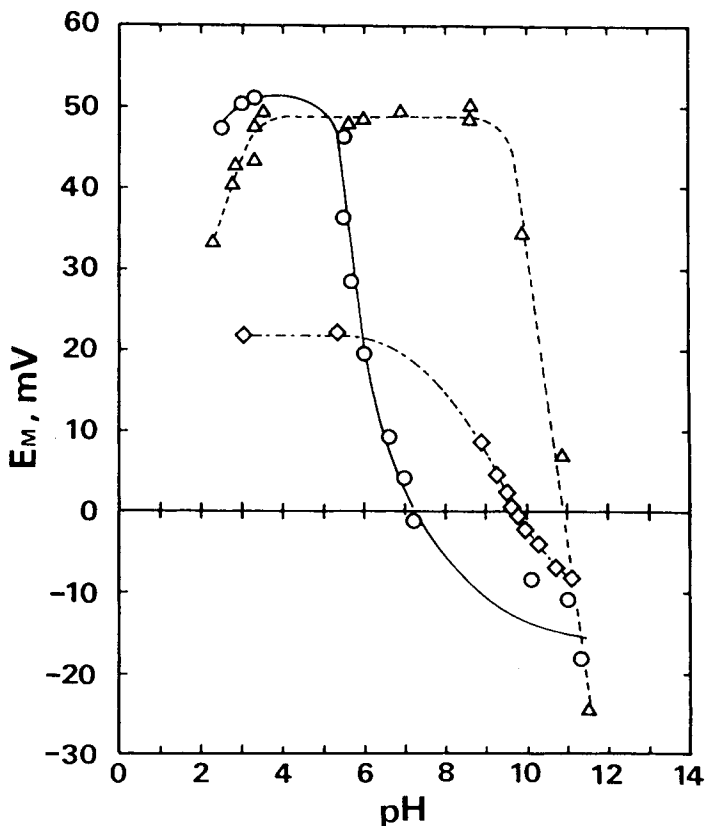


Fig. 3. The effect of the pH on the membrane potential ( $E_m$ ) of the composite membrane: (○) PAPS; (△) PAA; (◇) PPY.

and PAA, the values vary widely with the pH. Particularly, for the membrane of PAPS, there is a rapid rise of  $R_m$  between pH 5 and 8, and  $R_m$  in an alkaline region increases by about 4 orders of magnitude over  $R_m$  in an acidic region. The rapid decrease of  $E_m$  and increase of  $R_m$  of PAPS occur almost in the same pH region. The low membrane potential and the high resistance at high pH are attributed to weak basicity of the amino groups in the membrane of PAPS. In comparison with PAA and PPY, the pH region in which the membrane of PAPS shows high  $E_m$  and low  $R_m$  is very narrow. It is known that  $\text{pK}_a$  of conjugate acids of amines ( $-\log[B] \cdot [H_3O^+]/[BH^+]$ ) is about 10; however, when organic solvents, like methanol, are added to the solution, the basicity of amine decreases.<sup>11</sup> Therefore, showing high  $E_m$  and low  $R_m$  in the narrow region is presumed to be due to a low degree of swelling in water. Contact angles of each membrane were measured with distilled water and 0.1N of hydrochloric acid solution. These results are shown in Table IV. The contact angle of PAPS in a neutral condition is more than  $90^\circ$ , and even in an acidic condition, in which ammonium salt formation is expected, it is near to  $90^\circ$ , too. It is found that PAPS is a hydrophobic polymer even if ammonium salts are formed in the polymer. It is thought that the hydrophobic property arises from containing dimethylsilane structure, and the membrane of PAPS

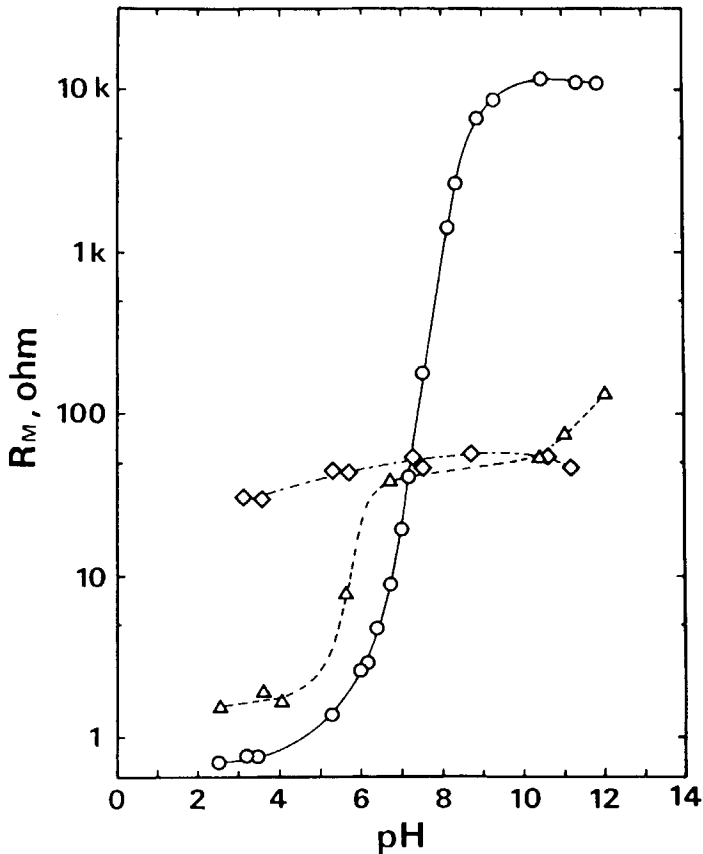


Fig. 4. The effect of the pH on the electric resistance ( $R_m$ ) of the composite membrane: (○) PAPS; (△) PAA; (◇) PPY.

shows high  $E_m$  and low  $R_m$  only in the narrow region of pH because of the hydrophobic property.

On the other hand, the contact angles of PAA is relatively small, particularly in acidic condition. These results indicate that PAA is more hydrophilic than PAPS. The fact that PAA shows high  $E_m$  near to 50 mV in wide pH range between 3 and 10 is attributed to this property. In Figure 3 the  $E_m$

TABLE IV  
Contact Angle of the Plasma Polymer

Plasma polymer	Contact angle (°)	
	with water	with acid <sup>a</sup>
PAPS	92	84
PAA	77	26
PPY	95	62

<sup>a</sup> Contact angle with acid was measured after the membrane was soaked in 0.1N hydrochloric acid solution.



TABLE V  
The Ratio of Acidic Groups and Basic Groups and the Transference Number ( $t_-$ )

Plasma polymer	$R_m$ at pH 11 ( $\Omega$ )	$R_m$ pH 3 ( $\Omega$ )	Ratio (base/acid) [ $R_m(\text{pH}11)/R_m(\text{pH}3)$ ]	$t_-$ at pH 3.9
PAPS	12k	0.75	1600	0.99
PAA	75	1.6	46.8	0.94
PPY	50	32	1.6	0.76

value of PAA at a pH less than 3 is lower than that at a pH between 3 and 10. In Figure 4,  $R_m$  at a pH less than 3 is smaller than that in the other regions. These phenomena are attributed to the excess content of water in polymer by swelling.

From the ratio of  $R_m$  values at pH 11 and 3 in Figure 4, where the membrane shows opposite  $E_m$ , the ratio of acidic and basic functional groups in each polymer was calculated and shown in Table V. PAPS has almost basic groups only, and PPY has both basic and acidic groups equally.

Figure 5 shows the relationship between the  $E_m$  values of PAPS and PPY at pH 3.9 and activities of ions ( $a_i$ ) in the solutions. An approximately linear relationship exists between  $E_m$  and  $\log a_i$  for each polymer. Transference numbers for anion ( $t_-$ ) were calculated from the slopes of these linear lines. The  $t_-$  of PPY was determined from the  $E_m$  value in Figure 3. These values are shown in Table V. PAPS and PAA show a high  $t_-$ , of over 0.9, in particular the  $t_-$  of PAPS is very high (0.99). It is found that the membrane of PAPS has excellent anion permselectivity in an acidic region. On the other hand, the membrane of PPY is less permselective than the others due to its small  $t_-$ .

### CONCLUSION

As mentioned above, a plasma polymer containing amino groups can be formed. In particular, when APEMS was used as the monomer, the plasma

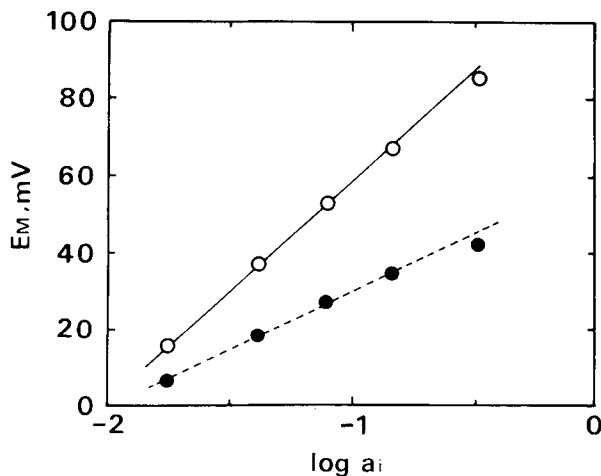


Fig. 5. The relationship between the membrane potential ( $E_m$ ) of the composite membrane and the activity of ion ( $a_i$ ) in the solution; (○) PAPS; (●) PPY.

polymer retained the chemical structure of the monomer, amino groups. The membrane of PAPS was hydrophobic even in acidic conditions. The membrane showed anion exchange ability only in acidic conditions; however, this property must be improved by quaternization of amino groups in the polymer. Ion exchange properties of quaternized plasma polymer will be reported in a subsequent paper.

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