Gas Permeation Property of Polyaniline Films

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SYNOPSIS

We examined the influence of polyaniline (PAn)'s unit sequence and doping with low molecular weight dopants or polymer dopants on permeation property. It was found that CO_2 permeability was increased by the formation of a quinonediimine unit in PAn with the oxidation. CO_2 sorption amount of PAn was decreased by oxidation. The increase of CO_2 permeability with oxidation, therefore, resulted from the increase of diffusivity, which was attributable to morphological variation by the increase of a quinonediimine unit. The permselectivity of PAn films was found to be remarkably improved by doping. In particular, the selectivity value of the PAn film doped with polyvinyl sulphonic acid as a polymer dopant went up to over 2,000. This remarkable increase of selectivity was found to result in the increase of selectivity, depending on diffusivity. It was also found that the permselectivity of the PAn film doped by polymer dopants was surpassed, as compared with that doped by low molecular dopants. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Gas separation membrane systems have been interested, and various membrane materials have been investigated within the last decade. This interest is based on potential economic advantages[1-3] and environmental problems,[4] since separation systems are less energy intensive than more conventional methods. Recently polyimides with 2,2-bis(3,4-dicarboxyphenyl) hexafluoro-propane dianhydride have been reported as materials exhibiting both a high gas selectivity and permeability.[5-10] On the other hand, conducting polymers [including polypyrrole, polyaniline (PAn) et al.] have also attracted much interest as a new material, being a permselective membrane with an interesting performance.[11-13] M. R. Anderson et al. reported that a remarkable selectivity can be achieved by using redoped PAn for various gas pairs.[12] They reported that the high selectivities are achieved by decreasing the permeabilities of larger gases through controlled doping and redoping of the PAn film. This report shows that conjugated polymer is one of the most exciting materials for gas separation membranes.

In the present work, the influence of the structure and/or form of polyaniline (PAn) film (i.e., oxidized and reduced form) on the membrane permeability is examined. Furthermore, the membrane performance of PAn films doped with polymer dopants is also studied, as compared with that for PAn films doped by low-molecular weight dopants.

EXPERIMENTAL

Polymer Synthesis

Soluble and high molecular weight PAn[14,15] was obtained through chemical oxidative polymerization of aniline in an acidic aqueous solution (HCl-H_2SO_4) using ammonium peroxodisulphate as an oxidant in the range -5 to $-3°C$, followed by undoping with aqueous ammonia. An equimolar ratio of peroxodisulphate to aniline was used. The average molecular weight was evaluated by gel permeation chromatography (GPC) (HLC8020; Tosoh Corp.) with three consecutive columns (G5000H6, G4000H8, and G3000H8). Two eluents, 0.01 dm^{-3} LiBr/N-methyl-2-pyrrolidone (NMP) solution and NMP solvent, were used for comparison. Monodisperse polystyrene solutions were used as the standard. The weight average molecular weight (M_w) was 1.6 × 10^5.

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reduced form
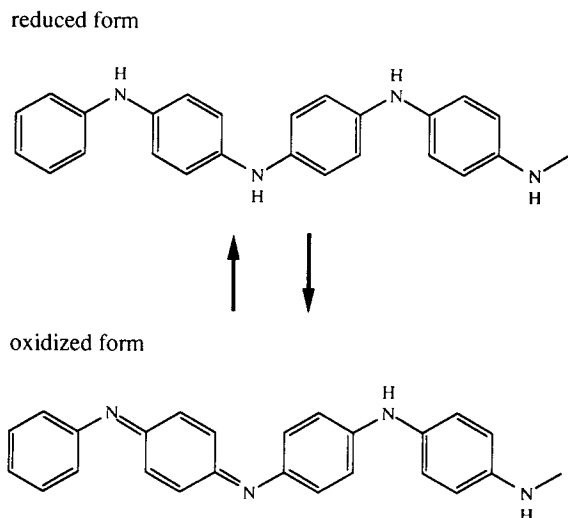
oxidized form

Figure 1 PAn unit sequence of reducted and oxidized form.

Preparation of Free-Standing PAn Films

Free-standing PAn films were prepared by casting a PAn/NMP solution (10 ~ 12 wt %) on a glass plate, followed by drying at 130 ~ 150°C for 1 h. (Obtained PAn films were 20 ~ 30 μm in thickness.) These resulting free-standing and thin films, unlike the undoped PAn powder, are not soluble in NMP, probably as a result of crosslinking during high temperature exposure.

Oxidation and Reduction of Undoped PAn Film

The PAn's unit sequence of as-cast film is mainly composed of a p-phenylenediamine (reduced form), as shown in Figure 1. This form is changed to the unit sequence, which is composed of both a quino-nediimine (oxidized form) and a p-phenylene-diamine by oxidation. An oxidized PAn film was obtained by immersing into water at 60°C for 24 h. PAn film is oxidized by oxygen in water. Furthermore, this oxidized PAn film was reduced by immersing into phenyl hydrazine/diethylether solution
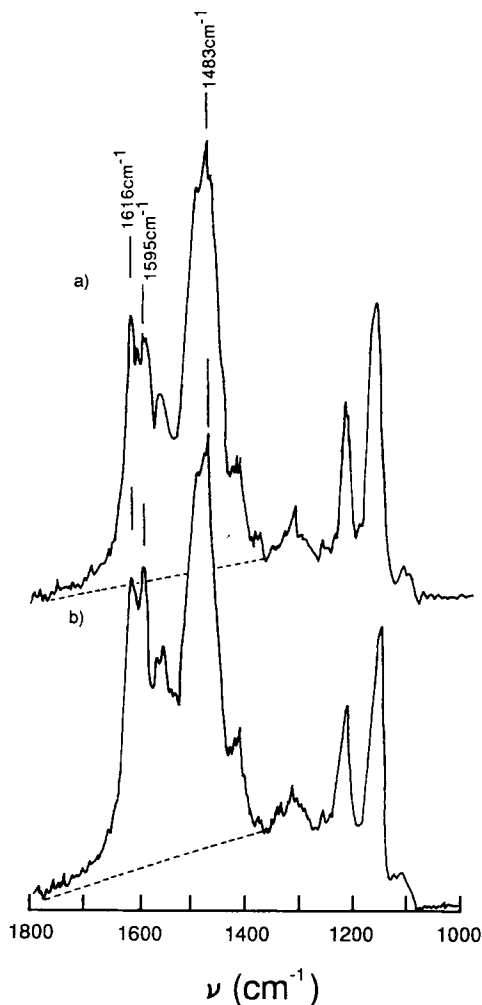
Figure 2 Raman spectra of (a) reducted PAn and (b) oxidized PAn, measured with 457.9 nm excitation at room temperature.

(conc.: 7×10^{-4} wt %) for 50 h. The more oxidized PAn film was obtained by immersing into p-qui-none/ethanol solution (conc.: 2 wt %) for 72 h.

The oxidized level of PAn film was measured using a laser Raman spectrophotometer (NR-1000; Nihon Bunko Kogyo K.K.), which used an Ar ion

Table I Doping Condition

Dopant	Solvent	Oxidant	Dopant Conc. (N)	Period
HCl	water	—	1.0	1 min ~ 24 h
MS	↑	—	↑	5 min ~ 552 h
PVSH	↑	—	0.43	5 min ~ 212 h
PISH	water/ethanol = 2/3	p-quinone (0.5 wt %)	0.1	3 h
PVS	water	—	↑	30 min

Table II   Influence of Oxidation or Reduction for As-Cast PAn Films on $\overline{P}CO_2$

State of PAn	IQ/IBa	IQ/IBb	$\overline{P}CO_2$ [cm^3 (STP)cm/ cm^2 cmHg]	SCO_2 [cm^3 (STP)/ cm^3 cmHg]	DCO_2 [cm^2/s]	α $\overline{P}CO_2/\overline{P}CH_4$
As-case	—	—	7.9×10^{-12}	—	—	59
Oxidation 1	1.74	1.61	3.0×10^{-11}	—	—	45
Oxidation 2	—	—	8.8×10^{-11}	6.5×10^{-3}	1.4×10^{-8}	34
Reduction	1.39	1.40	2.0×10^{-11}	1.6×10^{-2}	1.3×10^{-9}	40

IQ: intensity of 1483 cm^{-1} band.
IBa: intensity of 1616 cm^{-1} band.
IBb: intensity of 1595 cm^{-1} band.
Oxidation 1: immersing into water.
Oxidation 2: immersing into p-quinone/ethanol solution.
$\overline{P}CO_2$: These were measured at 300 cmHg.
SCO_2: These were calculated using values at 300 cmHg in Fig. 3.
DCO_2: These were calculated using the equation; P = DS.

laser (GLG3300; NEC) for a light source while rotating the sample.

Doping

These doped PAn films were easily obtained by immersing the undoped films in solutions of protonic acid.[15] In this work, an oxidized PAn film was used as undoped film, and various protonic acids, e.g., HCl, methane sulphonic acid (MS), polyvinyl sulphonic acid (PVSH), polyisoprene sulphonic acid (PISH), and polyvinyl sulfate (PVS) were used as dopants. The immersing conditions are shown in Table I.

The conductivity of the doped PAn films was measured according to van der Pauw's method,[16] using the four-probe method. The doping ratio of obtained PAn films was determined by the increased weight of the PAn film.
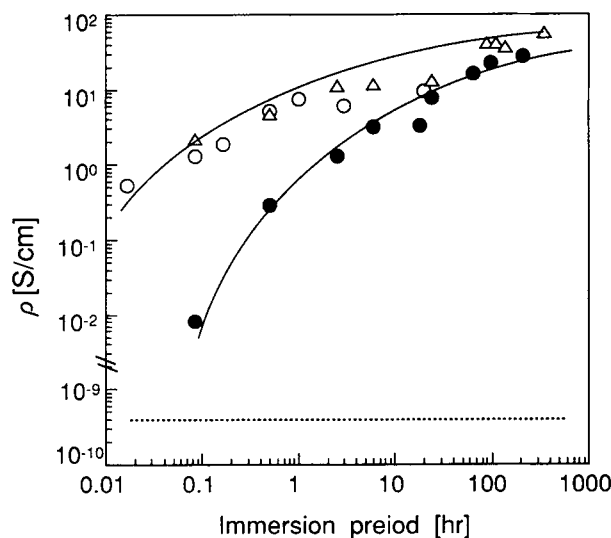
Average interchain spacing d-spacing of the PAn film before and after doping was obtained from wide-angle x-ray diffraction (WDXD) (RU-200B; Rigaku Co., Ltd.) measurements.

Permeability Measurements
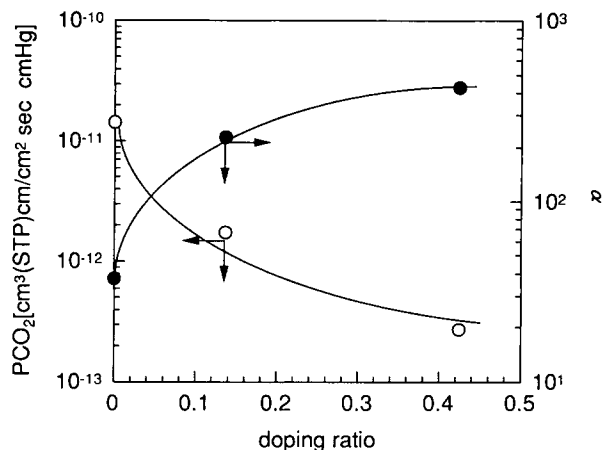
Gas permeability was measured using a gas permeation apparatus (GTR-10; Yanako Analyt-
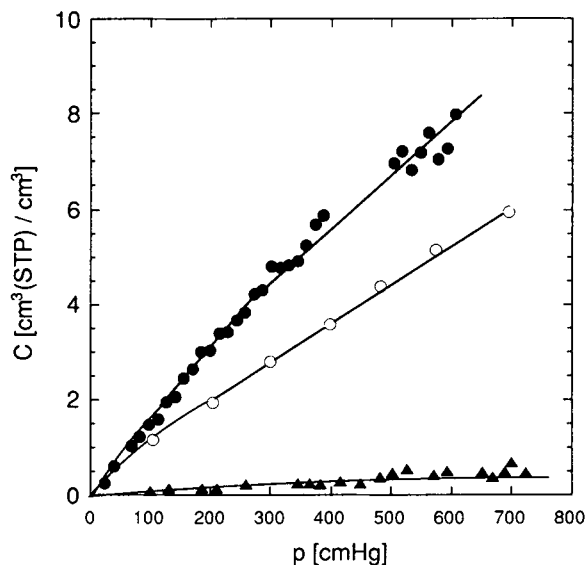
Figure 3   Sorption isotherms of reduced PAn (CO_2; ● and CH_4; ▲) and oxidized PAn (CO_2; ○) at 30°C.

Figure 4   Relationship between conductivity and immersing period of PAn film into dopant solutions: ○: HCl solution, △: MS solution and ●: PVSH solution.

Figure 5 Influence of HCl doping ratio on CO_2 permeability (PCO_2) and selectivity ($\alpha = \bar{P}CO_2/\bar{P}CH_4$). Pressure: 300 cmHg, measurement temperature: 30°C.
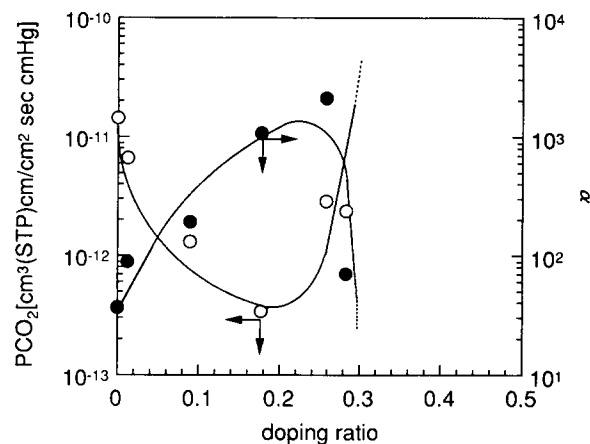
Figure 7 Influence of PVSH doping ratio on CO_2 permeability (PCO_2) and selectivity ($\alpha = \bar{P}CO_2/\bar{P}CH_4$). Pressure: 300 cmHg, measurement temperature: 30°C.

ical Instrument Corp.) with gas chromatography (G2800-T; Yanako Analytical Instrument Corp.).

Gas solubility was measured using a gas sorption apparatus (Belsorp-HP; Bel Japan Inc.).

RESULTS AND DISCUSSION

### Influence of PAn's Unit Sequence on Permeability

As shown in Figure 1, the unit sequence of as-cast PAns is mainly composed of a p-phenylenediamine. This form is changed to another unit sequence, which is composed of both a quinonediimine and a p-phenylenediamine, by oxidation. Figure 2 shows Raman spectra of (1) an oxidized PAn film (oxida-

tion 1) and (2) a reduced one and the ratio of intensity of quinondiimine stretching (1483 cm^{-1})[15] for that of benzene ring stretching (1595 cm^{-1} or 1616 cm^{-1})[15] is shown in Table II. Comparing the ratio, it was obvious that the quinonediimine unit was increased by oxidation.

The influence of PAn's unit sequence on permeation property was examined. Table II shows the permeation property of PAn film composed of various unit sequences. CO_2 permeability was increased by the formation of a quinonediimine unit with the oxidation. In particular, CO_2 permeability of PAn film oxidized using p-quinone as an oxidant was in-
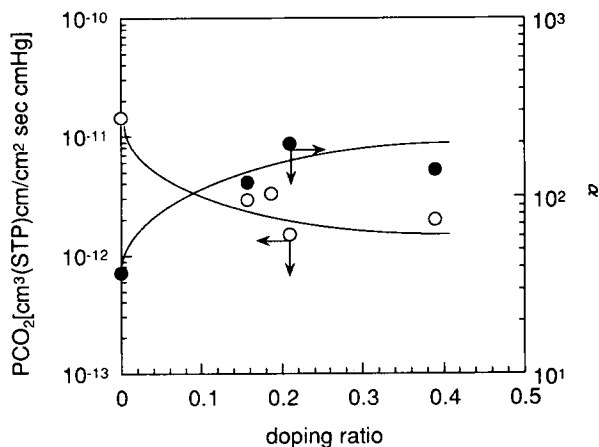
Figure 6 Influence of MS doping ratio on CO_2 permeability (PCO_2) and selectivity ($\alpha = \bar{P}CO_2/\bar{P}CH_4$). Pressure: 300 cmHg, measurement temperature: 30°C.
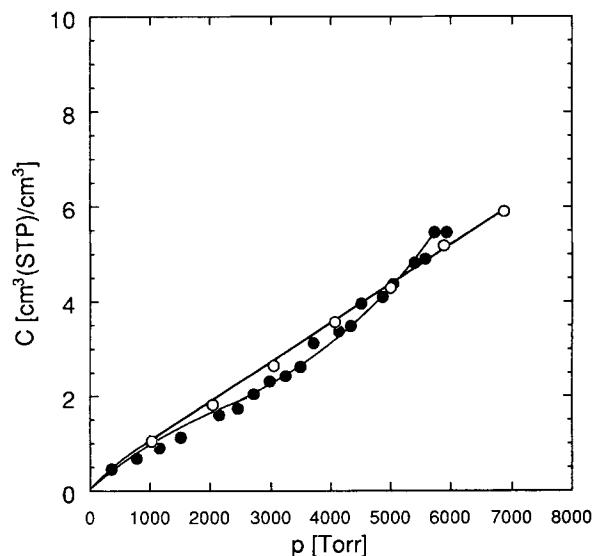

Figure 8 CO_2 sorption isotherms of undoped PAn (O) and PAn doped with PVSH (●) at 30°C.

creased about one order, as compared with that of as-cast film. It was also confirmed that the permeability of oxidized PAn film was decreased by reduction. Figure 3 shows the sorption isotherms of (1) an oxidized PAn film (oxidation 2) and (2) a reduced one. The isotherms were concave toward the pressure axis. Comparing the sorption isotherms, sorption amount of reduced PAn was larger than that of oxidized one. This difference in sorption amount may be attributable to the number of p-phenylenediamine units having amine groups whose affinity for CO_2 is very high on the basis of acid–base interaction. It was obvious that the increase of CO_2 permeability with oxidation results from the increase in diffusivity. The morphology, in which CO_2 gas can diffuse easily, may be formed by the increase of a quinonediimine unit in PAn. On the other hand, the selectivity ($\alpha = \bar{P}CO_2/\bar{P}CH_4$) was decreased by the increase of permeability with oxidation. This lowering may result in the decrease of selectivity, depending on diffusivity.

Influence of Doping on Permeability

Figure 4 shows the conductivity of PAn film doped by various protonic acids as a function of the immersion period in dopant solutions. The increasing rate of PAn conductivity by a polymer dopant (PVSH) was slower than that by low molecular dopants. This difference resulted from the diffusivity of dopants into the PAn film, that is, it is difficult for a polymer dopant to diffuse into PAn film.
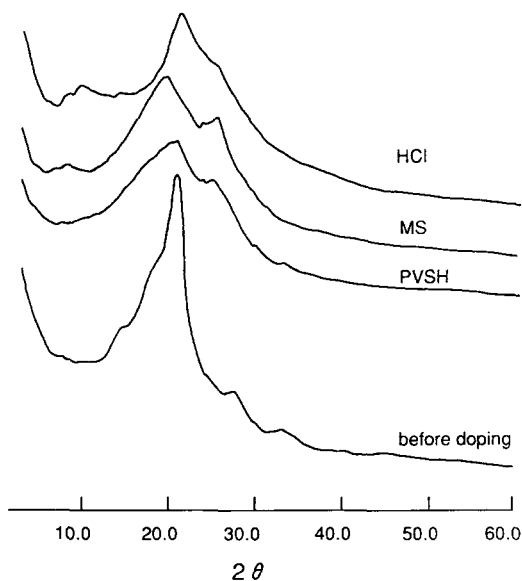
Figure 9 X-Ray diffraction patterns of PAn films doped various dopants and undoped PAn.

Figure 5 shows the variation of CO_2 permeability and selectivity ($\alpha = \bar{P}CO_2/\bar{P}CH_4$) of PAn films doped by HCl as a function of the doping ratio. The selectivity increased remarkably with the decrease of permeability. As reported by M. R. Anderson et al., a remarkable selectivity can be achieved by doping with HCl. However, the permeability is lower than that reported by them. This difference may be attributable to densification of PAn, that is, a soluble and high molecular weight PAn was used in this study.

The permeability and selectivity of PAn film doped by larger dopants (MS and PVSH) were examined for the purpose of improving permselectivity. Figure 6 and Figure 7 show the variation of CO_2 permeability of PAn films doped by MS and PVSH as a function of the doping ratio. The permselectivity of PAn film doped with MS could not improve, as compared with that doped with HCl. However, the selectivity was about 200, and this selectivity value was higher than the previously reported value (ex. about 60 for a fluorinated polyimide).[9,10] Furthermore, the permselectivity of PAn film doped with PVSH as a polymer dopant could improve remarkably, as compared with that doped by HCl or MS. CO_2 permeability decreased and α increased drastically with the increase of the doping ratio of PVSH, as shown in Figure 7. The selectivity value went up to over 2,000 from 37 at the undoping state. The permselectivity of the PAn film doped by PVSH was surpassed, as compared with that doped by low molecular dopants (HCl or MS).

Figure 8 shows the sorption isotherms of (1) PAn film doped with PVSH (doping ratio is 0.20) and (2) an undoped one. The isotherms were concave toward the pressure axis at a low pressure range. However, the isotherm of (1) exhibited an inflection point at high pressure and the sorption amount is greater. This phenomena may be a result of the PVSH being plasticized by the CO_2, because undoped PAn was not plasticized by the CO_2, as shown in Figure 3. Comparing these sorption isotherms, the remarkable difference in sorption amount of both PAn films was not found. It was suggested, therefore, that the remarkable increase of the selectivity results in the increase of selectivity was dependent on diffusivity.

The variation in d-spacing of PAn films doped with various dopants was examined using WAXD for the purpose of elucidating the structure change with doping. Figure 9 shows the diffraction pattern for various doped PAn film as compared with an undoped one. The patterns were assigned to an amorphous diffraction. The diffraction pattern for

Table III d-Spacing of PAn Films Doped with Various Dopants

| | Dopant | d-Spacing [A] | |
		Peak 1	Peak 2
Polymer dopant	PVSH	4.27	3.54
Low molecular	HCl	4.23	—[a]
Dopant	MS	4.57	3.54
	no	4.29	—

[a] As this peak could be observed as a shoulder but the center of the peak was not clear, the d-spacing could not be calculated.

undoped PAn film was sharp, although there is no crystal structure in PAn. This pattern results from a relatively regular structure that depends on the rigidity of quinonediimine and/or p-phenylene-diamine units. This diffraction pattern for undoped PAn films was turned into a broader pattern, having two peaks by doping. The broad peaks was attributed to intersegmental interference.[5,17] The d-spacings can be calculated by applying the scattering angles (2θ) of the peak into the Bragg's equation,[18] $n\lambda = 2d \sin \theta$. The d-spacing determined in this manner is a measure of intersegmental distance of polymeric molecules.[17] The d-spacings from the WAXD data for various PAn film are shown in Table III. These values were smaller, as compared with those of a fluorinated polyimide (5.5 ~ 5.9 Å),[5] polyamide (5.5 Å),[19] polycarbonate (5.2 Å),[20] and so on. The d-spacings of the main peak (1) were not varied remarkably by doping except MS doping. The intersegment of the PAn film doped with MS may be widened by the bulkiness. However, the velures of the new peak (2) appeared by doping were smaller than that of main peak and were ca. 3.5 Å. This result suggested that a regular structure, which hinders the diffusion of CH_4 and increases the selectivity, was formed between PAn segments by doping, considering that

the kinetic diameters of CO_2 and CH_4 are 3.3 and 3.8 Å, respectively. The remarkably high selectivity of PVSH-doped PAn film may be attributable to such intersegments of PAn formed by doping as one of several factors.

As shown in Figure 7, the permselectivity of PAn film doped with PVSH fell rapidly with the increase of the doping ratio. This suggested that intersegment of PAn was disordered and formed defects by doping with PVSH, which is a larger dopant, over a certain amount.

Table IV shows the permselectivity of PAn film doped with various dopants. It is interesting that the membrane performance of PAn film doped with polymer dopants is satisfactory. In particular, the permeability of PAn film doped with polymer dopants is higher than that doped with low molecular dopants. These results suggest that polymer dopants as PVSH densified in the vicinity of the surface of undoped PAn film and formed a kind of asymmetric membrane, because it is difficult for a polymer dopant to diffuse inner PAn film, as shown in Figure 4. It seems, therefore, that remarkably high selectivity was attained in the vicinity of the film surface, and gases could diffuse easily the inner PAn film. As a result, the permselectivity of PAn film doped with polymer dopants surpasses those doped by low molecular weight dopants in comparison.

CONCLUSION

The influence of PAn's unit sequence on permeation property was examined, and it was found that CO_2 permeability was increased by the formation of a quinonediimine unit with the oxidation. The increase of CO_2 permeability with oxidation resulted from the increase of diffusivity, which was attributable to morphological variation by the increase of a quinonediimine unit.

Table IV   Effect of Doping of Various Dopants on Gas Permselectivity of PAn Film

	Dopant	M_w	Doping Ratio	E.C[a] [S/cm]	$\bar{P}CO_2$ [cm^3 (STO) cm/cm^2 s cmHg]	α $\bar{P}CO_2/\bar{P}CH_4$
Polymer	PVSH	1,500	0.23	7.8	2.9×10^{-12}	2.2×10^3
Dopant	PVS	24,000	0.03	3.3	1.2×10^{-12}	2.5×10^2
	PISH	40,000	0.06	4.8	2.3×10^{-12}	4.0×10^2
Low molecular	MCl	36.5	0.43	4.3	2.7×10^{-13}	4.3×10^2
Weight	MS	96.1	0.21	4.7	1.5×10^{-12}	2.0×10^2
Dopant						
	no	—	0	4×10^{-10}	$7.9 \times 10^{-12} \sim 1.4 \times 10^{-11}$	$59 \sim 37$

[a] Electric conductivity.

The permselectivity of PAn films was improved by doping. In particular, the selectivity value of PAn film doped with PVSH went up to over 2,000 from 37 at the undoping state. It was found that the permselectivity of the PAn film doped by polymer dopants surpassed those doped with low molecular weight dopants.

PAn films doped by polymer dopants indicate a higher potential for development of gas separation membrane.

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