

# Effect of Doping Treatment on Gas Transport Properties and on Separation Factors of Polyaniline Membranes

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## SYNOPSIS

Gas permeation experiments of H<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> were carried out with freestanding films of the conjugated polymer polyaniline (PANi). At first annealed to remove residual solvent, PANi membranes were doped (i.e., protonated) in a strongly acidic medium (HCl 4M), undoped in a basic medium (NH<sub>4</sub>OH 1M), and redoped in a slightly acidic medium (HCl 10<sup>-2</sup>M). Protonation and deprotonation kinetics were studied by elementary analysis. Gas permeation experiments were performed with the annealed, doped, undoped, and redoped PANi films. The gas transport mechanism was clearly influenced by the diffusivity factor and it obeyed a Fickian diffusion model. From the variations in permeability coefficients with the doping treatment, gases could be divided in two subgroups comprising H<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub> on one hand and N<sub>2</sub> and CH<sub>4</sub> on the other. After the doping–undoping–redoping process, gas fluxes were increased by 15% for the smaller gases and were decreased by 45% for the larger gases. As a consequence gas separation factors were approximately doubled for a gas pair involving the two subgroups and these were unchanged for a gas pair involving only one subgroup. The highest O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> selectivity coefficients were, respectively, equal to 14 and 78. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

It is essential to separate mixtures of gases for a wide variety of industrial applications and there is an increasing interest in membrane-based gas separations as energy efficient alternatives to cryogenic methods. Considerable effort has already been invested to introduce new polymeric materials that may present both high permeability values and high transport selectivities.<sup>1,2</sup> Recent results have attracted attention on electronically conducting polymers because large selectivity values have been reported by Anderson et al.<sup>3–5</sup> and by Martin et al.<sup>6,7</sup> The interest in using conducting polymers also lies in the fact that the film morphology can be modified after synthesis by a convenient doping process, which enables the optimization of a particular separation. Among the usual conducting

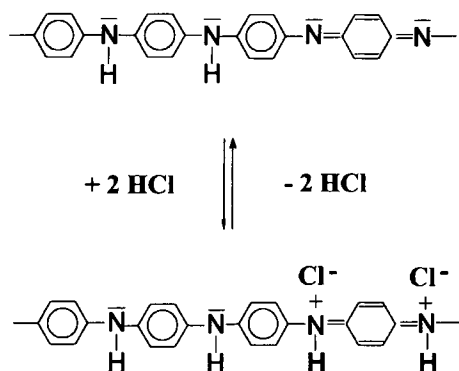
polymers (including polypyrrole, polythiophene, poly-paraphenylene, polyaniline, and their derivatives), polyaniline (PANi) is the most attractive one because of its air stability in both neutral and doped forms, its partial solubility (in the neutral form) in organic solvents such as *N*-methyl-2-pyrrolidone (NMP), and its simple acid–base doping chemistry in aqueous solutions. The aim of the present study was to determine the transport mechanism of gases through PANi membranes, to describe the variations in permeation and separation properties during a doping–undoping–redoping process, and to explain the microstructural modifications induced by the doping treatment.

## EXPERIMENTAL

### Materials

PANi in half-oxidized state (called polyemeraldine) was synthesized by chemical oxidation of aniline by

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**Figure 1** Polyemeraldine in (a) the base and (b) in the doped forms.

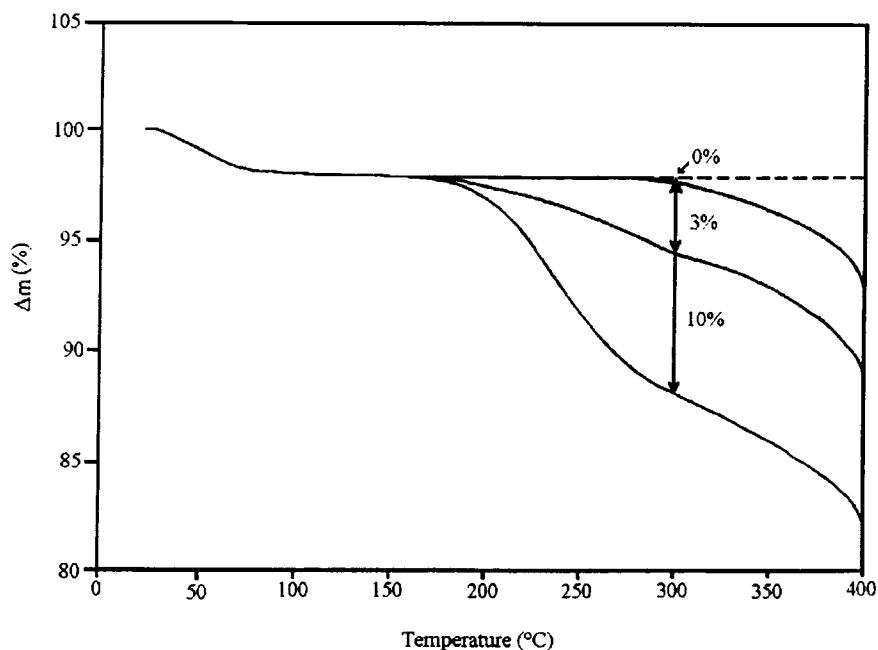
ammonium peroxodisulfate,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , in an acidic medium ( $\text{H}_2\text{SO}_4$ , 2M).<sup>8</sup> The polymer was deprotonated by immersion in a basic medium and it was purified by washing cycles in distilled water and in tetrahydrofuran. After drying under vacuum ( $T < 50^\circ\text{C}$ ,  $P < 1$  torr), a powder of polyemeraldine in the base form was obtained (Fig. 1).

The powder was dissolved in NMP (1.5% w/v) and the macromolecular solution was spread on a glass plate. The NMP removal was undergone under reduced pressure ( $P \cong 10$  torr) and with a gradually increasing temperature from 60 to  $120^\circ\text{C}$ . A bright aspect, mechanically robust, 10–15  $\mu\text{m}$  thick PANi membrane was separated from the glass plate by immersion in water.

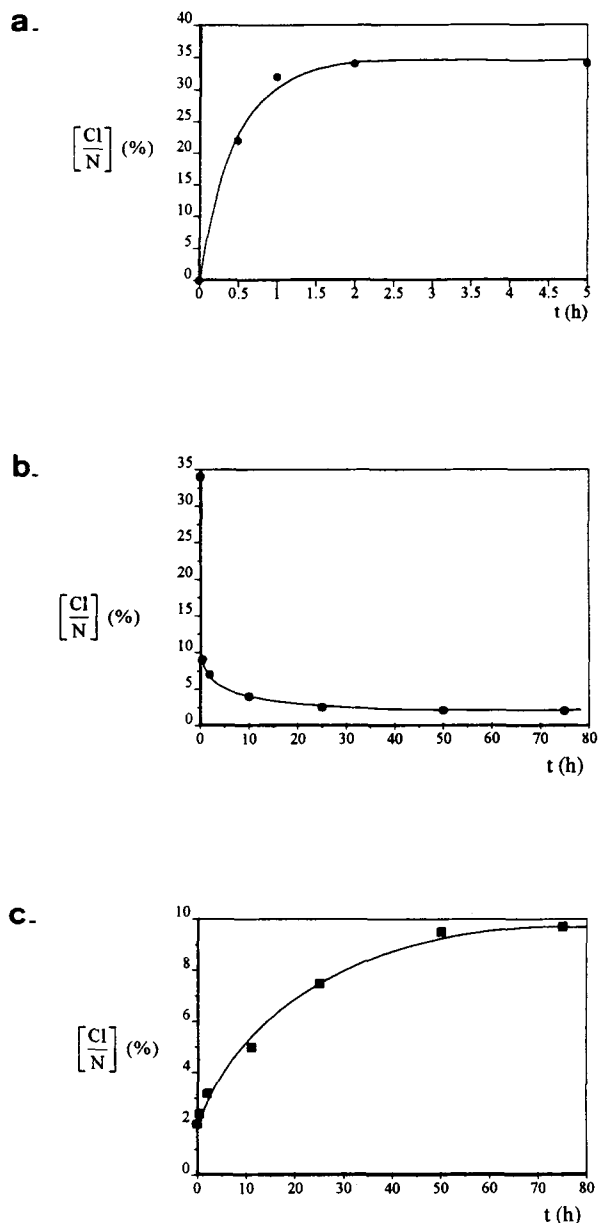
Because the as-cast membrane still contained 10% residual solvent, a process of annealing was settled and followed by thermogravimetric analysis (Fig. 2). Previous experiments performed at a temperature rise of  $0.5^\circ\text{C}/\text{min}$  have shown an important inflexion in the curve at  $300^\circ\text{C}$  before the degradation process begins. NMP weight losses were therefore measured between 150 and  $300^\circ\text{C}$ . After a 2-h curing at  $120^\circ\text{C}$  under dynamic pumping ( $P < 1$  torr), the NMP content decreased to 3% and it became negligible after a 5-h curing. As it previously described,<sup>9</sup> the permeability coefficients and the apparent diffusion coefficients increase for all gases by the removal of NMP from the film.

Following the method used by Anderson et al.,<sup>3–5</sup> the annealed membrane was doped (i.e., protonated) by immersion in a HCl 4M solution, undoped by similar treatment in a  $\text{NH}_4\text{OH}$  1M solution, and slightly redoped by a HCl  $10^{-2}\text{M}$  solution. The protonation and deprotonation kinetics were studied from elementary analysis by calculating the ratio  $[\text{Cl}/\text{N}]$  (Fig. 3).<sup>8</sup>

- The protonation kinetic is rather fast because 2 h are sufficient to reach a maximum rate of 34% [Fig. 3(a)]. This doping level is lower than the 50% protonation rate measured by Anderson et al.<sup>3–5</sup> or Martin et al.<sup>6,7</sup> Scanning electron microscopy photographs of our doped membrane cross sections nevertheless evidenced the



**Figure 2** Thermograms of as-cast (10%), partially annealed (3%), and completely annealed ( $\cong 0\%$ ) PANi membranes. Temperature rise of  $5^\circ\text{C}/\text{min}$ .



**Figure 3** Protonation and deprotonation kinetics of polyaniline films: (a) doping in HCl 4M; (b) undoping in  $\text{NH}_4\text{OH}$  1M; and (c) redoping in HCl  $10^{-2}\text{M}$ .

doping anion ( $\text{Cl}^-$ ) present in the bulk as well as in the surface area. The membrane structure allows the dopant acid diffusion up to the bulk, but it might have been densified by the different curing processes.

- The undoping in basic medium [Fig. 3(b)] and the partial redoping in a slightly acidic medium [Fig. 3(c)] are both kinetically low processes because a 50-h immersion is necessary to reach a plateau. The undoping treatment leaves an irreducible doping rate of 2%. That can be ap-

parent doping, because electron spectroscopy for chemical analysis experiments have evidenced some chlorine covalently bonded to aromatic rings. The redoping process leads to a 9.5% doping level, which is quite high regarding the very low concentration of the redoping solution.

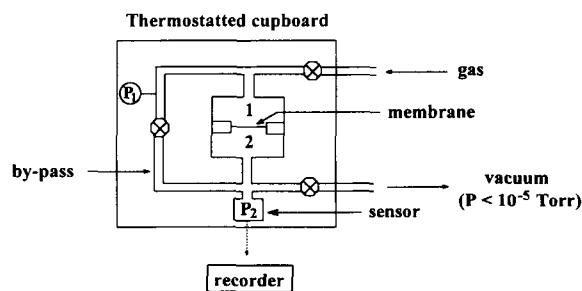
### Apparatus

Gas permeation experiments were carried out using the single-gas permeation method.<sup>10</sup> The freestanding film of PANi was settled between the upstream (1) and downstream (2) compartments of the permeation cell (Fig. 4). Before each experiment, a high vacuum pumping was performed during 48 h in order to strongly outgas the membrane and the downstream compartment walls. When the 3 bar gas pressure was introduced in the upstream part, the pressure increase,  $P_2$ , was measured in the downstream part by a Datametrics pressure sensor (range 10 torr). A 3-cm<sup>2</sup> surface of film was exposed to permeant gas and the downstream volume  $V_2$  was equal to 115.93 cm<sup>3</sup>.

### FUNDAMENTALS OF GAS PERMEATION

When a gas-free membrane is suddenly exposed to a pressure,  $P_1$ , of gas at the upstream side, gas molecules first adsorb at the polymer surface. Then the sorbed molecules penetrate into the polymer matrix and begin the process of diffusion-solution, which is commonly considered as the rate-limiting step for glassy polymers. After a certain period of time, the penetrant molecules reach the downstream side of the polymer film, desorb at the surface, and evaporate into vacuum as gas molecules.<sup>11,12</sup>

By measuring the downstream pressure,  $P_2$ , it is possible to determine the total amount  $Q_t$  of gas molecules having crossed the membrane at time  $t$ :



**Figure 4** Gas permeation apparatus.

$$Q_t = 22,400 \frac{P_2 \cdot V_2}{RT} \quad (1)$$

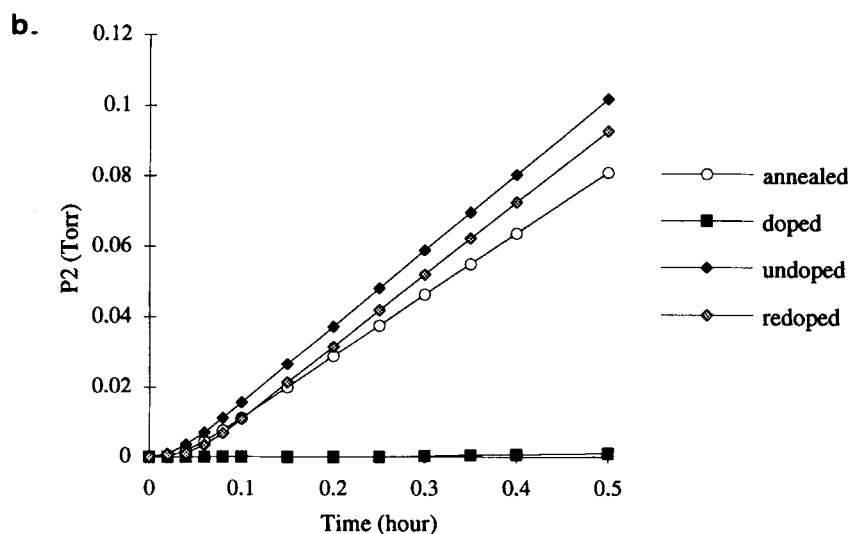
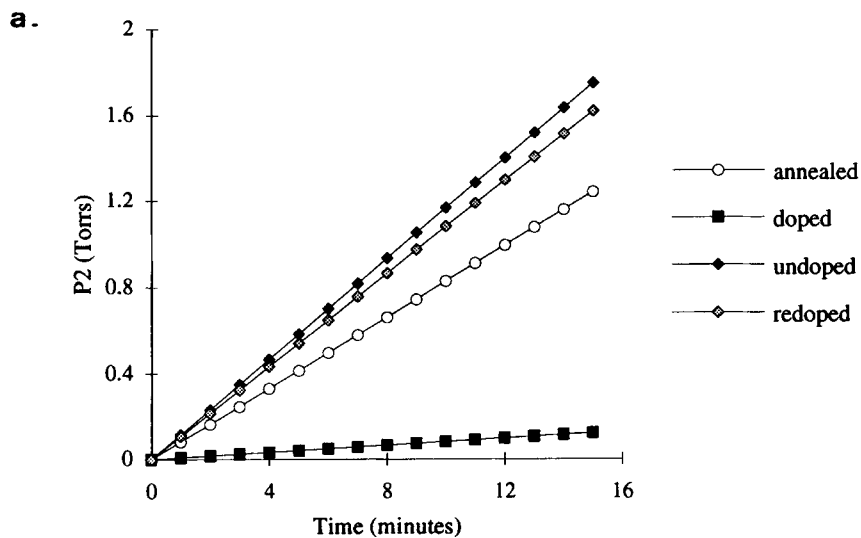
where  $V_2$  is the downstream volume and  $R$  and  $T$  have usual meanings. The gas flux across the membrane is defined as follows:

$$J = \frac{Q_t}{A \cdot t} \quad (2)$$

where  $A$  is the membrane surface exposed to the penetrant gas. From the first Fick's law,  $J$  can be related to the mean diffusion coefficient  $\bar{D}$ :

$$J = \bar{D} \frac{(C_1 - C_2)}{e} \quad (3)$$

where  $e$  is the film thickness and  $C_1$  and  $C_2$  are the equilibrium concentrations of the penetrant dissolved at the membrane upstream and downstream



**Figure 5** Gas permeation curves of the annealed, doped, undoped, and redoped films obtained with 3-bar upstream pressure for: (a) H<sub>2</sub>; (b) O<sub>2</sub>; (c) CO<sub>2</sub>; (d) N<sub>2</sub>; and (e) CH<sub>4</sub>.

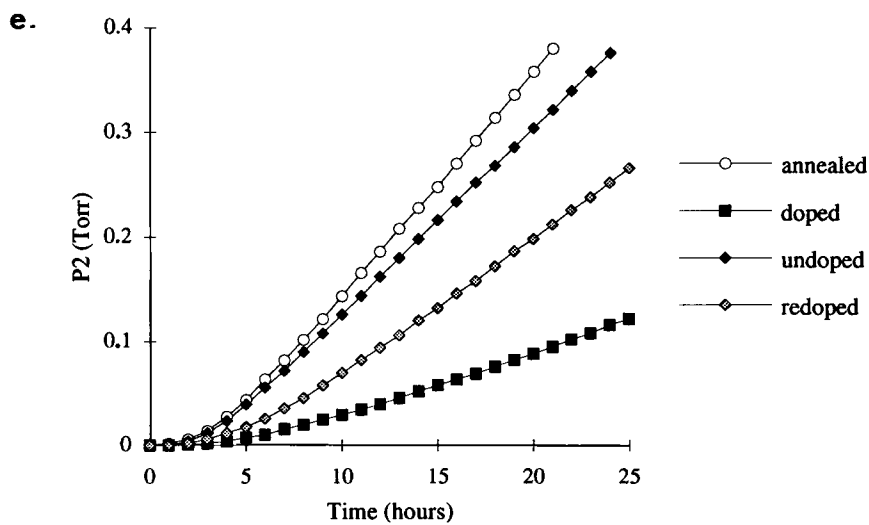
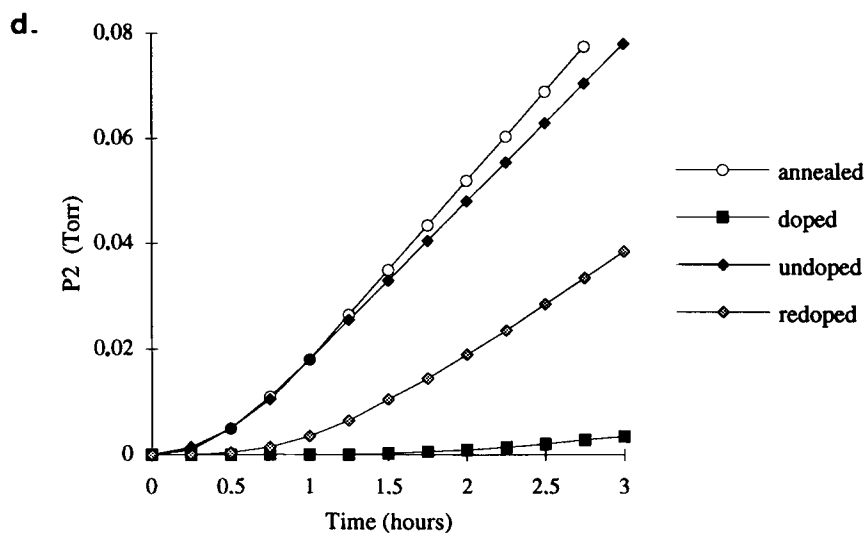
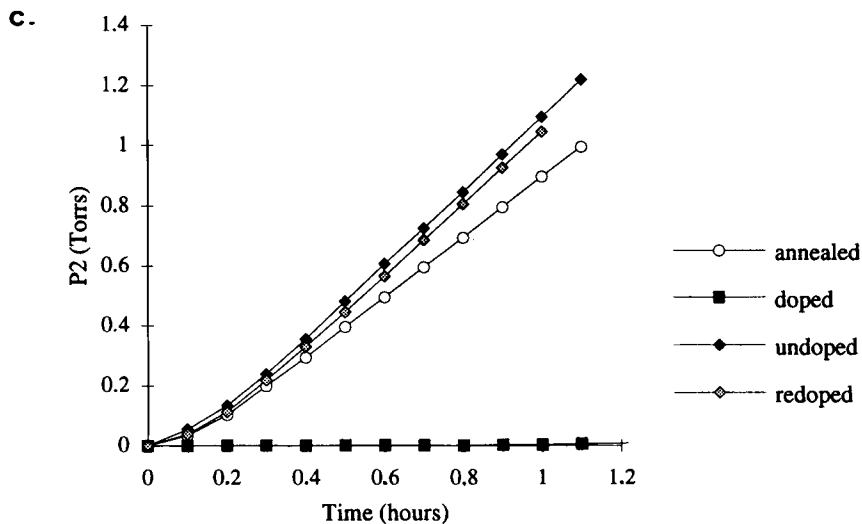


Figure 5 (Continued)

interfaces, respectively. As  $P_1 \gg P_2$  and thus  $C_1 \gg C_2$ ,  $J$  reduces to:

$$J = \bar{D} \frac{C_1}{e} \quad (4)$$

When the gas flux  $J$  is constant, the permeation steady state is established and the permeability coefficient  $Pe$  expressed in Barrer

$$1 \text{ Barrer} = 10^{-10} \frac{\text{cm}_{\text{STP}}^3 \text{ cm}_{\text{polym.}}}{\text{cm}_{\text{polym.}}^2 \text{ s cm Hg}}$$

is calculated from the following equation:

$$Pe = \frac{J \cdot e}{\Delta P} \quad (5)$$

where  $\Delta P$  is the pressure difference across the membrane. The permeability coefficient is the product of a mean diffusion coefficient  $\bar{D}$  (that is a kinetic factor) and a solubility-related function  $\bar{S}$  (that is a thermodynamic factor)<sup>2</sup>:

$$Pe = \bar{D} \cdot \bar{S} \quad (6)$$

The selectivity of a polymer membrane toward two different gases  $A$  and  $B$  is usually expressed in terms of an "ideal" separation factor  $\alpha_{(A/B)}$ , which is defined by the relation:

$$\alpha_{(A/B)} = \frac{Pe_{(A)}}{Pe_{(B)}} = \frac{\bar{D}_{(A)}}{\bar{D}_{(B)}} \cdot \frac{\bar{S}_{(A)}}{\bar{S}_{(B)}} = \alpha_D \cdot \alpha_S \quad (7)$$

where the factors  $\alpha_D$  and  $\alpha_S$  are known, respectively, as the "diffusivity selectivity" and "solubility selectivity." These factors represent contributions to the overall selectivity due to the differences in the diffusivities and solubilities of gases  $A$  and  $B$  in the polymer membrane.

Before reaching a constant flux of gas, the permeation process covers a transient state whose duration  $\theta$  is called the time lag and is defined by the following relation:

$$\lim_{t \rightarrow \infty} Q_t = J(t - \theta) \quad (8)$$

By plotting  $Q_t$  (or  $P_2$ ) versus  $t$ , the time-lag value is determined by extrapolation of the steady-state line on the time axis. If we assume the diffusion coefficient  $D$  does not depend on gas concentration, the second Fick's law can be solved:

$$Q_t = \left[ \frac{Dt}{e^2} - \frac{1}{6} - \frac{1}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp \left( - \frac{Dn^2\pi^2 t}{e^2} \right) \right] C_1 e \quad (9)$$

By calculating eq. (8) from eq. (9) and by comparison with eq. (4), we obtain the following relation:

$$J(t - \theta) = \frac{DC_1}{e} \left[ t - \frac{e^2}{6D} \right] \quad (10)$$

An apparent diffusion coefficient  $D_{\text{app}}$  can thus be calculated from the time-lag value  $\theta$ :

$$D_{\text{app}} = \frac{e^2}{6\theta} \quad (11)$$

As diffusion coefficients are generally a function of the penetrant concentration in glassy polymers,<sup>13</sup>  $D_{\text{app}}$  determined from eq. (11) has to be considered with care. Nevertheless this coefficient can be used for comparative purposes, for example, to indicate trends in the effects of structural changes in gas diffusivity.

## RESULTS AND DISCUSSION

### Experimental Data

Gas permeation experiments were carried out with the annealed, doped, undoped, and redoped PANi films (Fig. 5). The permeability and apparent diffusion coefficients were calculated from permeation curves and are listed in Table I.

Permeability coefficients considerably differ from one gas to another. The ratio in gas fluxes is equal to 30 between  $\text{H}_2$  and  $\text{O}_2$  and above 300 between  $\text{H}_2$  and  $\text{CH}_4$ . Apparent diffusion coefficients also strongly vary in function of the kinetic diameter: a factor of 100 can be calculated between  $\text{O}_2$  and  $\text{CH}_4$  diffusivities and a factor above 500 is found between  $\text{H}_2$  and  $\text{CH}_4$  diffusivities.

### Characterization of Gas Transport Mechanism

Before examining transport properties, we would like to specify that previous experiments<sup>15</sup> have evidenced that gas diffusivities do not vary a lot with gas concentrations above atmospheric pressure. Therefore the apparent diffusion coefficients measured for a 3 bar upstream pressure present a worthy physical meaning.

**Table I Permeability and Apparent Diffusion Coefficients of H<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> Through Polyaniline Films**

Gas	$\phi$ (Å) <sup>a</sup>	Film	$Pe$ (Barrer)	$D_{app}$ ( $\times 10^{-11}$ cm <sup>2</sup> s <sup>-1</sup> )
H <sub>2</sub>	2.34	Annealed	3.707	— <sup>b</sup>
		Doped	0.29	—
		Undoped	4.53	—
		Redoped	4.35	—
O <sub>2</sub>	2.92	Annealed	0.121	167
		Doped	0.01	5.1
		Undoped	0.15	223
		Redoped	0.142	130
CO <sub>2</sub>	3.23	Annealed	0.476	66.4
		Doped	0.035	4.5
		Undoped	0.568	77.5
		Redoped	0.547	44.2
N <sub>2</sub>	3.64	Annealed	0.019	13.5
		Doped	0.004	2
		Undoped	0.016	14.5
		Redoped	0.01	6.3
CH <sub>4</sub>	3.8	Annealed	0.013	1.6
		Doped	0.003	0.6
		Undoped	0.011	1.9
		Redoped	0.007	1.2

<sup>a</sup> From Kumens and Kwai.<sup>14</sup>

<sup>b</sup> The apparent diffusion coefficients of H<sub>2</sub> could not be determined because the permeation steady state is quite instantaneously established for this gas.  $D_{app}$  of H<sub>2</sub> is inferior to  $10^{-8}$  cm<sup>2</sup> s<sup>-1</sup>.

The permeation and previously described sorption measurements<sup>15</sup> allow the ordering of permeability, apparent diffusion, and solubility coefficients as follows:

$$Pe_{CH_4} < Pe_{N_2} < Pe_{O_2} < Pe_{CO_2} < Pe_{H_2}$$

$$D_{appCH_4} < D_{appN_2} < D_{appCO_2} < D_{appO_2} < D_{appH_2}$$

$$S_{N_2} \cong S_{O_2} < S_{CH_4} < S_{CO_2}$$

**Table III Relative Permeability Coefficients of Films, Calculated With Annealed Film as Reference**

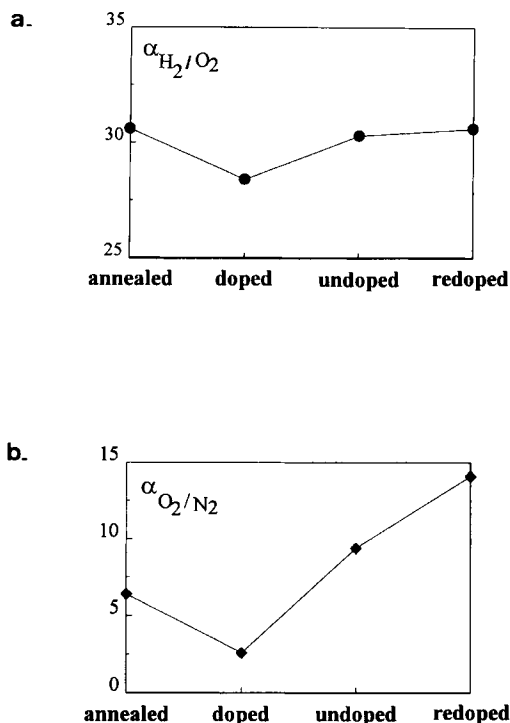
Gas	Film			
	Annealed	Doped	Undoped	Redoped
H <sub>2</sub>	1	0.078	1.22	1.17
CO <sub>2</sub>	1	0.073	1.19	1.15
O <sub>2</sub>	1	0.083	1.24	1.17
N <sub>2</sub>	1	0.21	0.84	0.53
CH <sub>4</sub>	1	0.23	0.85	0.54

The permeability coefficients are ordered in the same way as the apparent diffusion coefficients. Nevertheless a comment has to be made concerning CO<sub>2</sub>: because the solubility factor of CO<sub>2</sub> is very high,<sup>15</sup> it significantly modifies the gas fluxes, which involves an inversion between the permeabilities and apparent diffusivities of CO<sub>2</sub> and O<sub>2</sub>. Apart from CO<sub>2</sub>, gas fluxes are only influenced by the gas kinetic diameter. In other terms the permeability coefficients are influenced by the diffusivity factors and do not depend on the solubility coefficients. This result is very interesting because it reveals that the permeability values are directly related to the amount of free volumes within the film and to the statistical repartition of these free volumes.

Another important observation can be made by comparing the ratio  $Pe/S$  with the apparent diffusion coefficient  $D_{app}$ . Results are for example presented for the redoped sample in Table II. The agreement between the calculated and apparent diffusion coefficients is very good for O<sub>2</sub>, CO<sub>2</sub>, and N<sub>2</sub>. Concerning CH<sub>4</sub>, the agreement is less convincing but CH<sub>4</sub> diffusivities are very low and therefore significantly less precise. As permeation and sorption results agree very well, we can conclude the relation:  $Pe = D \cdot S$  is verified. This result implies the gas

**Table II Comparison Between Ratio  $Pe/S$  and Apparent Diffusion Coefficient  $D_{app}$** 

Gas	Permeation (Redoped Film)		Sorption <sup>15</sup> (Redoped Powder)	Comparison	
	$Pe$ (Barrer)	$D_{app}$ ( $\times 10^{-10}$ cm <sup>2</sup> s <sup>-1</sup> )	$\left( \frac{S_{(3\text{ bar})}}{\text{cm}^3_{STP}} \right)$ ( $\frac{\text{cm}^3_{\text{polym}}}{\text{cm}^3 \text{ Hg}}$ )	$D_{\text{calcul.}} = \frac{Pe}{S}$ ( $\times 10^{-10}$ cm <sup>2</sup> s <sup>-1</sup> )	$\frac{D_{\text{calcul.}}}{D_{app}}$
O <sub>2</sub>	0.142	13	0.009	15.8	1.2
CO <sub>2</sub>	0.547	4.42	0.074	7.4	1.7
N <sub>2</sub>	0.01	0.63	0.01	1	1.6
CH <sub>4</sub>	0.007	0.12	0.019	0.37	3.1



**Figure 6** Variations in selectivity values with the doping-undoping-redoping treatment for (a) the  $H_2/O_2$  gas pair (same subgroup) and (b) the  $O_2/N_2$  gas pair (two different subgroups).

transport through PANi membranes obeys a Fickian diffusion model.

### Effect of Doping Treatment on Transport Properties: Correlation with Microstructure

The experimental data presented in Table I bring to the fore that transport properties are strongly decreased by the doping treatment. The introduction of chloride ions within the polymer decreases the number of free volumes, which is undoubtedly responsible for the decrease in gas diffusivities and therefore in permeability coefficients. After having undoped the membrane, transport properties are increased by the removal of doping ions. The partial redoping slightly decreases permeability and diffusivity values.

The variation in gas fluxes with the doping treatment are clearly evidenced by taking the annealed sample as a reference. Relative permeability coefficients were calculated for the doped, undoped, and redoped films and are listed in Table III.

Gases can be divided by a value at 3.3–3.4 Å into two subgroups comprising  $H_2$ ,  $CO_2$ , and  $O_2$  (the “smaller” gases) on one hand and  $N_2$  and  $CH_4$  (the “larger” gases) on the other. Within a subgroup, the

variations in the permeability values with the doping, undoping, and redoping treatment are strictly similar. After the doping cycle process, the permeability values of  $H_2$ ,  $CO_2$ , and  $O_2$  are increased by at least 15% whereas these of  $N_2$  and  $CH_4$  are decreased by 45%. It is worth noting that Anderson et al. have also evidenced that the doping-undoping-redoping process enhances the permeabilities of smaller gases and decreases the permeabilities of larger gases.<sup>3</sup> These authors suggest that the moderate redoping reduces the fluxes of larger gases by partially filling the large-sized free volumes. But this interpretation is not sufficient to explain why the permeability coefficients of larger gases are already decreased by 15% for the undoped film. The hysteresis phenomenon induced by the acid dopant diffusion during the doping process should have involved morphological modifications in the polymer structure and especially a shift of the statistical distribution of elementary free volumes toward smaller sizes. An attractive interaction between the  $N^+Cl^-$  dipoles (produced by protonation) could explain that macromolecular chains are brought closer to each other. Such an interaction would occur under the influence of the “electrostatic primary energy” that leads to the formation of multiplets in the polymer matrix.<sup>16</sup> These multiplets could also interact under the “residual energy of interaction” and condense into aggregates called clusters.

### Consequence on Gas Selectivities and Comparison with Literature

The separation factors of gas pairs involving the two subgroups made up of  $H_2$ ,  $O_2$ , and  $CO_2$  and  $N_2$  and  $CH_4$ , will be significantly improved by the doping cycle process. However the selectivity of a gas pair involving only one subgroup will be unchanged. These results are illustrated in Figure 6 and some selectivity values are listed in Table IV. For a gas pair involving the two subgroups, the separation factor is approximately doubled by the process of doping-undoping-redoping. This gain in selectivity is interesting because the separation factors obtained for the redoped sample are high compared to the values commonly provided in the literature.<sup>17</sup> As a matter of fact, the interesting separation factors obtained with PANi come from the fact that permeability coefficients of  $N_2$  and  $CH_4$  are extremely low. Because the number of large-sized free volumes is very poor in the polymer matrix, a small variation in this number during the doping process involves a great improvement in gas selectivities.



**Table IV** Selectivity Values for H<sub>2</sub>/N<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/CH<sub>4</sub>, and H<sub>2</sub>/O<sub>2</sub> Gas Pairs in Function of Doping Treatment

$\alpha_{(A/B)}$	Annealed	Doped	Undoped	Redoped	$\frac{\alpha_{\text{redoped}}}{\alpha_{\text{annealed}}}$
H <sub>2</sub> /N <sub>2</sub>	195	73	283	435	2.2
O <sub>2</sub> /N <sub>2</sub>	6.4	2.5	9.4	14.2	2.2
CO <sub>2</sub> /CH <sub>4</sub>	36.6	11.7	51.6	78.1	2.1
H <sub>2</sub> /O <sub>2</sub>	30.6	29	30.2	30.6	1

The selectivity values presented in this study are compared in Table V with the values proposed by Anderson et al.<sup>3-5</sup> and by Martin et al.<sup>6,7</sup> for free-standing films of PANi treated by HCl doping acid.

Table V shows that our selectivities are quite comparable with those of Martin, but we did not succeed in reproducing the exceptional separation factors proposed by Anderson et al. We should nevertheless remember that the permeability coefficients of N<sub>2</sub> and CH<sub>4</sub> are very low and have to be determined with great care to get suitable accuracy.

## CONCLUSION

Gas permeation experiments of H<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> were carried out on annealed, HCl 4M doped, NH<sub>4</sub>OH 1M undoped, and HCl 10<sup>-2</sup>M redoped PANi membranes. The permeability coefficients are influenced by the diffusivity factors and depend therefore on the statistical distribution of free volumes in the polymer matrix. Despite different affinities with PANi, all of the analyzed gases obey a Fickian transport model.

The heavy doping treatment involves a strong decrease in gas fluxes and diffusivities, but transport properties are mostly regained by the removal of chloride ions when undoping in a basic medium. The variations in permeability coefficients with the doping-undoping-redoping process allow the division

of gases into two subgroups comprising H<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub> (the smaller gases) and N<sub>2</sub> and CH<sub>4</sub> (the larger gases). The relative variations are indeed strictly similar within a subgroup. After the doping-undoping-redoping treatment, the gas fluxes are increases by 15% for the smaller gases and are decreased by 45% for the larger gases. This result can be explained by the partial filling of large-sized free volumes under moderate redoping and by a hysteresis phenomenon due to the strong treatment with doping acid.

As a consequence, gas selectivities are modified by the doping cycle process because the separation factor is approximatively doubled for a gas pair involving the two subgroups, whereas it is unchanged for a gas pair involving only one subgroup. The highest O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> selectivities are, respectively equal to 14 and 78. Such high separation factors are due to the very low permeability coefficients of N<sub>2</sub> and CH<sub>4</sub> through PANi. Indeed, as the number of large-sized free volumes in the polymer matrix is very poor, a small variation in this number involves great improvements in separation factors. By reporting our separation factors in the selectivity versus permeability curves presented by Koros,<sup>18</sup> it turns out the redoped PANi factors are interesting for the separation of N<sub>2</sub>, but these are not particularly attractive for the separation of CH<sub>4</sub>. Despite its low permeability to gases, the redoped PANi membrane may therefore be considered as a promising material for the separation of N<sub>2</sub>.

**Table V** Comparison Between the Selectivity Values

	Anderson et al.			Martin et al. Ref. 7 36% Doped Film	Present Study Redoped Film
	Ref. 3 Redoped Film	Ref. 4	Ref. 5 Redoped Film		
O <sub>2</sub> /N <sub>2</sub>	30	53 (Undoped)	27	14.9	14.2
CO <sub>2</sub> /CH <sub>4</sub>	336	146 (Redoped)	—	54.3	78.1

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