

Optochemical Sensor for HCl Gas Based on Tetraalkoxyphenylporphyrin Dispersed in an Acrylate Polymer Matrix

Heru Supriyatno¹, Katsuhiko Nakagawa² and Yoshihiko Sadaoka¹

¹Department of Materials Science and Engineering, Faculty of Engineering,
Ehime University, Matsuyama 790-8577, Japan.

²Department of Applied Chemistry and Biotechnology,
Niihama National College of Technology, Niihama 792-8580, Japan

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Tetraalkoxyphenylporphyrin-polymer composite films were prepared and examined for the detection of HCl gas. The sensing process is characterized by the following steps; the sorption of HCl to the polymer matrix ($\text{HCl}_{\text{gas}} \rightleftharpoons \text{HCl}_{\text{film}}$), and the diprotonation of the porphyrin ($\text{TPPH}_2 + 2\text{HCl}_{\text{film}} \rightleftharpoons \text{TPPH}_4^{2+} \cdot 2\text{Cl}^-$). Based on the λ_{max} of the Q band of the dicationic form of the porphyrin in acrylate polymers, the equilibrium constants of the diprotonation for all tetraalkoxyphenylporphyrins used are expected to be almost the same, i.e., the effect of the alkyl chain of the substituent is not observed, and those values are larger than that of tetraphenylporphyrin. The sensitivity is influenced by the polymer matrix and is of the order of butyl methacrylate > hexyl methacrylate > hexyl acrylate. A faster response to an increase in HCl was observed for the composite made from a polymer with a lower glass transition temperature, but the sensitivity decreased.

1. Introduction

Recently, various chemical sensors operating at room temperature have been proposed to measure the emission of gaseous pollutants at the ppm concentration level, e.g., the optochemical sensors based on porphyrin, which are a large class of compounds having a tetrapyrrolic macrocycle with side substituents.⁽¹⁻⁴⁾ There has been interest in the use of planar conjugated macrocyclic nitrogenous bases such as porphyrin as the detectors for

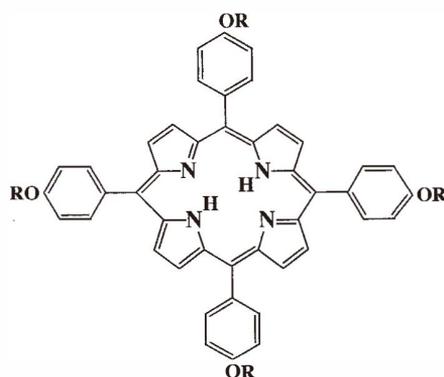
acidic gases.⁽²⁻⁴⁾ The use of tetraphenylporphyrin as a sensing material to detect some acidic gases has been attempted, however, its sensitivity to low concentrations of these gases is not high. In our previous studies,⁽⁵⁻⁶⁾ chemically modified tetraphenylporphyrins were used as HCl gas-sensing materials having preferable sensitivity as well as fast response and recovery behaviors. By substituting para-hydrogen of phenyl groups in tetraphenylporphyrin with a hydroxyl group, an increase in the pK for the diprotonation and the enhancement of the sensitivity were observed, suggesting that this material can be used to detect sub-ppm levels of HCl gas. However, the recovery time was very long, *e.g.*, to return to the initial state, the sample must be held in pure nitrogen for 3 days at room temperature. To improve the sensing characteristics, the use of tetraphenylporphyrin derivatives with the alkoxy group instead of the hydroxyl group is considered.

Polymer matrix and plasticizer are also important factors in obtaining high performance sensors. The addition of a plasticizer to the polymer matrix with a high glass transition temperature enhances the sensitivity as well as response behaviors, because it increases the mobility of the polymer chains, thus improving the gas permeability of the film. In our previous study it was confirmed that the plasticizer dioctylphthalate (DOP) added to ethyl cellulose polymer was significantly effective in enhancing the sensing characteristics.⁽⁶⁾ However, after several days the sensor showed some deterioration in sensitivity due to the phase separation of the plasticizer and ethyl cellulose. This fact is attributable to the difference in the solubility parameter between ethyl cellulose and DOP, as reported by Mills *et al.*⁽⁷⁾ Thus it is required that polymers used as a matrix contain no plasticizer. The use of polymers with a low glass transition temperature (T_g) should be considered, since the free volume will be enhanced, allowing easier diffusion of gas into the film. In this study, the effects of the substituents and the acrylate polymer matrices on HCl gas sensing characteristics were examined.

2. Materials and Methods

2.1 Chemicals

The dyes synthesized in this study were 5,10,15,20-tetrakis(methoxyphenyl)porphyrin, (TP(OCH₃)₄PH₂), 5,10,15,20-tetrakis(iso-propyloxyphenyl)porphyrin, (TP(OCH(CH₃)₂)₄PH₂), 5,10,15,20-tetrakis(butoxyphenyl) porphyrin, (TP(OC₄H₉)₄PH₂), and 5,10,15,20-tetrakis(2-ethylhexyloxyphenyl)porphyrin, (TP(O-2-EH)₄PH₂). The structure of the dyes is shown in Fig. 1. For comparison, 5,10,15,20-tetraphenylporphyrin (TPPH₂) and 5,10,15,20-tetrakis(hydroxyphenyl)porphyrin (TP(OH)₄PH₂) were also examined. As polymer matrices, hexyl methacrylate (HMA), butyl methacrylate (BMA), hexylacrylate (HA), and ethylcellulose (EC) were used. Their glass transition temperatures in K are : 268 (HMA), 293 (BMA), 213 (HA), and 318 (EC). The dye and polymer were dissolved in chloroform or a mixture of toluene : ethanol (8:2), then those solutions were mixed. Composite films for the sensor elements were prepared by coating these solutions on alumina substrates, and then heating them at 60°C in vacuum to remove the solvent.



R : CH ₃	(TP(OCH ₃) ₄ PH ₂)
CH(CH ₃) ₂	(TP(OCH(CH ₃) ₂) ₄ PH ₂)
C ₄ H ₉	(TP(OC ₄ H ₉) ₄ PH ₂)
CH ₂ CH(C ₂ H ₅)C ₄ H ₉	(TP(O-2-EH) ₄ PH ₂)

Fig. 1. The structure of substituted tetraphenylporphyrins (TP(OR)₄PH₂).

2.2 Optical measurements

The molar absorptivities of the dicationic forms of the porphyrins were determined in DMF-HCl solution and are summarized in Table 1 for λ_{max} of the Soret and Q bands. The spectra of the films that were about $5\mu\text{m}$ thick and formed on alumina plates were measured in reflection mode. Filtered light from a D_2/I_2 lamp (400–800 nm) was guided into a fiber, and the reflected light was collected and analyzed using a multichannel spectrophotodetector (MCPD-1000, Otsuka Electronics Co.). The spectrum (I_0) of the composite film was first measured in nitrogen flow and used as the standard reference for measuring the spectrum (I/I_0) of the film. The % reflectance is defined as $100 \cdot I/I_0$. Standard 11 ppm HCl gas diluted with nitrogen was obtained from Sumitomo Seika Co. All measurements were performed at 45°C . The HCl gas concentrations were controlled by mixing the standard gas with nitrogen. The element was placed directly in the gas stream. The chamber and gas-flow system were manufactured from poly-tetrafluoroethylene (PTFE). The total flow rate was controlled to $200\text{ cm}^3 \cdot \text{min}^{-1}$.

3. Results and Discussion

For dicationic forms, the full-width at half maxima (FWHM) of the Soret bands in both solution and film were examined. For the solutions with a concentration of $5 \times 10^{-9}\text{ mol/ml}$ or lower, the FWHM was 15–20 nm as shown in Table 2. For the composite films examined at a concentration of $1 \times 10^{-5}\text{ mol/g}$ (polymer), the FWHM was 32–44 nm and larger than those in the solution. Figure 2 shows the spectral changes in the TP(OCH₃)₄PH₂-

Table 1
Molar absorptivities ϵ of TP(OR)₄PH₂ in DMF.

No.	TPPH derivatives	Soret band	Q band
1	TPPH	384600	45400
2	TP(OH) ₄ PH ₂	293400	72500
3	TP(OCH ₃) ₄ PH ₂	202800	45100
4	TP(OC ₄ H ₉) ₄ PH ₂	267500	58300
5	TP(O-2-EH) ₄ PH ₂	359500	77600
6	TP(OCH(CH ₃) ₂) ₄ PH ₂	281300	62800

Table 2
Full-width at half maximum (FWHM) for dicationic forms of TP(OR)₄PH₂ at the Soret band.

A. in solution (DMF)

No.	TPPH derivatives	FWHM (nm)	
		5×10^{-9} mol/ml	1×10^{-9} mol/ml
1	TPPH	16.96	15.72
2	TP(OH) ₄ PH ₂	19.81	19.45
3	TP(OCH ₃) ₄ PH ₂	17.73	17.86
4	TP(OCH(CH ₃) ₂) ₄ PH ₂	18.55	18.30
5	TP(OC ₄ H ₉) ₄ PH ₂	17.97	17.84
6	TP(O-2-EH) ₄ PH ₂	18.66	17.86

B. in film

TPPH ₂ derivatives	FWHM of various composite films (nm)			
	HA	HMA	BMA	EC
TP(OCH ₃) ₄ PH ₂	43.7	42.3	33.8	25.4
TP(OCH(CH ₃) ₂) ₄ PH ₂	32.4	36.6	33.8	23.9
TP(OC ₄ H ₉) ₄ PH ₂	36.5	39.4	33.8	23.9
TP(O-2-EH) ₄ PH ₂	32.4	33.8	33.8	22.5

HMA composite film upon exposure to HCl gas at 45°C. The reflectance at 458 nm (Soret band) and 694 nm (Q band) decreased with increasing HCl concentration. Simultaneously, the reflectance of the Soret band of the neutral form at 420 nm increased. The absorption bands appearing at 458 and 694 nm were assigned to the dicationic form. The normalized absorbance changes with HCl gas concentration for the Soret and Q bands of the dicationic forms are shown in Figs. 3 and 4, respectively. In this case, the absorbance was estimated from the peak height at λ_{\max} of the Soret and Q bands. In appearance, the Soret band is more sensitive than the Q band for HCl gas. The difference in the calibration curves may reflect the difference in the FWHM of each band. The FWHM of the Soret band is apparently smaller than that of the Q band, as shown in Fig. 2. The normalized absorbance changes as a function of HCl gas concentration, i.e., the calibration curve, for the TP(OCH₃)₄PH₂-polymer composite are shown in Fig. 5. The calibration curve was influenced by the polymer species.

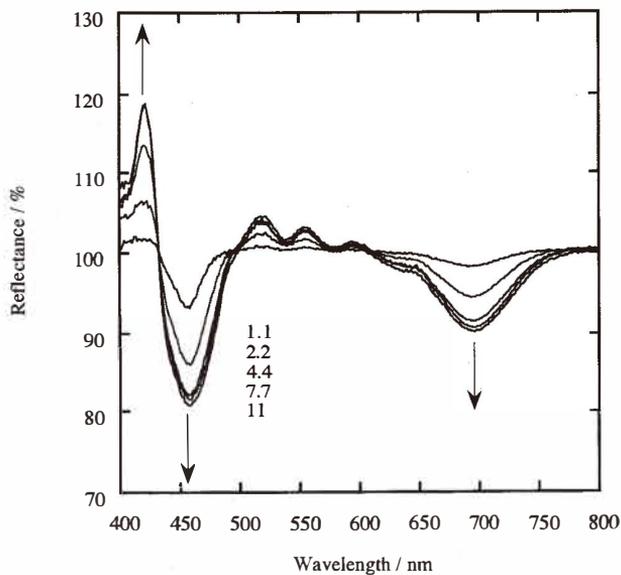


Fig. 2. Spectral changes of TP(OCH₃)₄PH₂-HMA composite films upon exposure to HCl at 45°C. TP(OCH₃)₄PH₂: 1×10^{-5} mol/g-HMA. HCl concentrations in ppm are shown in the figure. The arrows indicate the direction of the spectral changes with HCl.

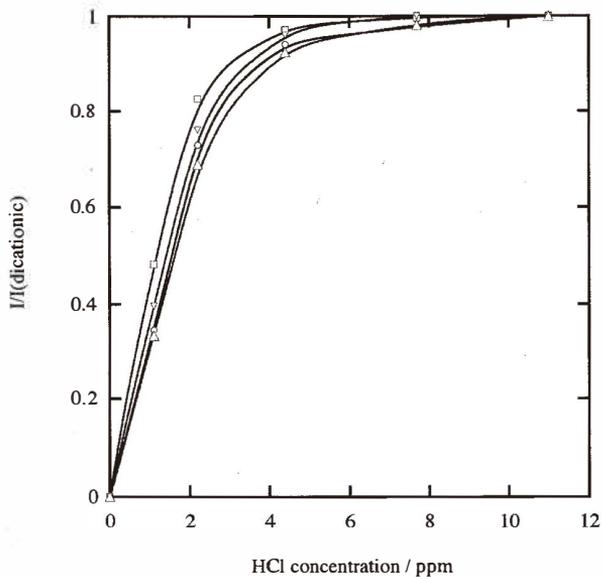


Fig. 3. Normalized absorbance changes of the dicationic forms as a function of HCl gas concentration at the Soret band. \circ TP(OCH₃)₄PH₂, \square TP(OC₄H₉)₄PH₂, ∇ TP(O-2-EH)₄PH₂, \triangle TP(OCH(CH₃)₂)₄PH₂

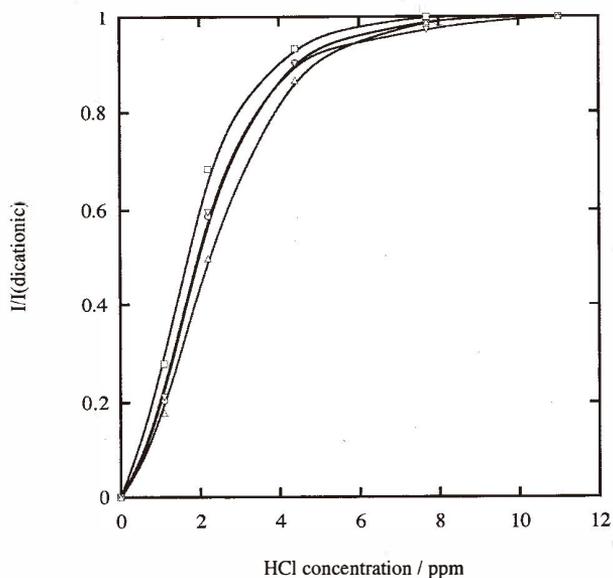


Fig. 4. Normalized absorbance changes of the dicationic forms as a function of HCl gas concentration at the Q band. \circ $\text{TP}(\text{OCH}_3)_4\text{PH}_2$, \square $\text{TP}(\text{OC}_4\text{H}_9)_4\text{PH}_2$, ∇ $\text{TP}(\text{O-2-EH})_4\text{PH}_2$, \triangle $\text{TP}(\text{OCH}(\text{CH}_3)_2)_4\text{PH}_2$.

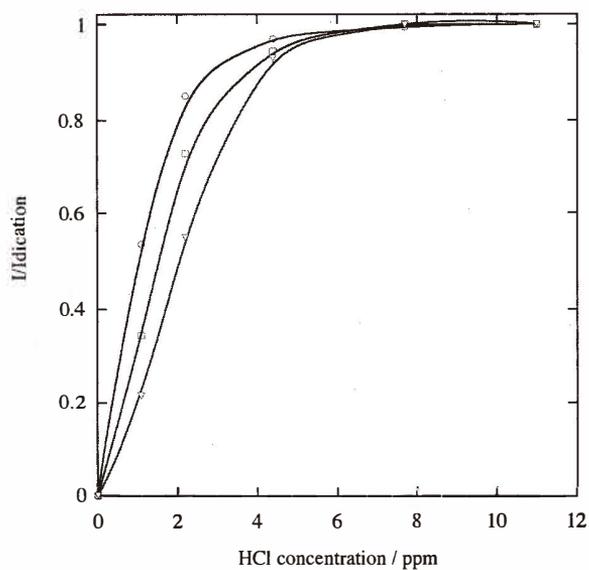
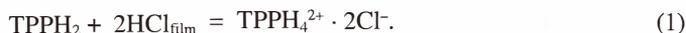


Fig. 5. Normalized absorbance changes of the dicationic forms of the $\text{TP}(\text{OCH}_3)_4\text{PH}_2$ -polymer composite as a function of HCl gas concentrations. \circ BMA, \square HMA, ∇ HA.

The spectral changes associated with exposure to HCl gas are caused by the formation of porphyrin dicationic forms. The protonation reaction taking place when HCl gas is introduced to the film can be written as follows:



The HCl concentration in the film is different from the concentration of HCl in the test gas. For simplicity, it is assumed that the HCl concentration in the film, $[\text{HCl}_{\text{film}}]$, is correlated with the HCl gas concentration in the gas phase, $[\text{HCl}_{\text{gas}}]$. By considering the Freundlich isotherm, $v = a \cdot p^n$, the correlation between $[\text{HCl}_{\text{gas}}]$ and $[\text{HCl}_{\text{film}}]$ can be expressed as follows:

$$[\text{HCl}_{\text{film}}] \rightleftharpoons a[\text{HCl}_{\text{gas}}]^n, \quad (2)$$

where a and n are constants. Qualitatively, it can be said that the n -value is a parameter which distinguishes among the types of sorption; Langmuir for $n < 1$, Henry for $n = 1$, and multilayer formation and/or clustering for $n > 1$.

The equilibrium constant can be written as follows.

$$K_{\text{eq}} = [\text{TPPH}_4^{2+} \cdot 2\text{Cl}^-] / ([\text{TPPH}_2] \cdot a^2 \cdot [\text{HCl}_{\text{gas}}]^{2n}) \quad (3)$$

$$\text{for } \text{TPPH}_2 + 2\text{HCl}_{\text{film}} \rightleftharpoons \text{TPPH}_4^{2+} \cdot 2\text{Cl}^- \quad (4)$$

The fraction of the dicationic form, α , can be expressed by absorbance A :

$$A = A_0 + \alpha(A_1 - A_0), \quad (5)$$

where A_0 and A_1 are the limiting absorbance values for $\alpha = 0$ and $\alpha = 1$, respectively. The fraction of the dicationic form can be estimated as a function of $[\text{HCl}_{\text{gas}}]$. Therefore, eq. (3) can be written as follows:

$$K_{\text{eq}} = A / ((A_1 - A) \cdot a^2 \cdot [\text{HCl}_{\text{gas}}]^{2n}). \quad (6)$$

The concentration of HCl gas is expressed as

$$[\text{HCl}_{\text{gas}}] = [A / K_{\text{eq}} \cdot a^2 \cdot (A_1 - A)]^{1/2n}. \quad (7)$$

By applying eq. (7), the $K_{\text{eq}} \cdot a^2$ and n value of each composite film can be estimated. Preliminary estimations applied to the calibration curves (correlations between absorbance and HCl gas concentration) suggest that no distinct regularities between n and the substituent species of porphyrin can be observed. It seems that the value of n is mainly attributable to the polymer species. By taking a mean value of n for each polymer, the term $K_{\text{eq}} \cdot a^2$ was re-estimated. The estimated values of $K_{\text{eq}} \cdot a^2$ for TP(OR)₄PH₂-polymer composite films are summarized in Table 3.

Table 3
The estimated values of $K_{eq} \cdot a^2$ for TP(OR)₄PH₂-polymer composite films.

TPPH derivatives	HA	HMA	BMA	EC
TP(OCH ₃) ₄ PH ₂	0.175	0.417	0.866	0.205
TP(OC ₄ H ₉) ₄ PH ₂	0.209	0.746	0.974	0.168
TP(O-2-EH) ₄ PH ₂	0.147	0.514	1.155	0.184
TP(OCH(CH ₃) ₂) ₄ PH ₂	0.642	0.366	0.911	0.210

K_{eq} is related to the pK value of the porphyrin. Meot-Ner and Adler⁽⁸⁾ reported that the visible and near ultraviolet absorption spectra of substituted *ms*-tetraphenylporphyrins, *ms*-tetraalkylporphyrins and their acid dications show increasing bathchromic shifts relative to *ms*-tetraphenylporphyrin itself as the electron donating power of the substituents increases. They concluded that the observed substituent effects on the bathchromic shifts are truly intramolecular, and the solvent-mediated transmission of substituent effects from the *para*-phenyl positions to the porphyrin ring can be ruled out. Based on the spectra of the acid dications in DMF, the relationship between frequency shifts of the Q(0-0) bands of the dications and the observed acid dissociation constants (measure of the basicity of the pyrrole ring) was examined. Experimentally, a linear relationship between the dissociation constant and $(\lambda_{max}/nm)^{-1}$ of the Q(0-0) bands for dications was confirmed, i.e., $[1000 \cdot (\lambda_{max})^{-1} = 1.5744 - 0.048832 \cdot pK]$. It is expected that the same relationship exists between the pK value of the porphyrin in the polymer matrix and the λ_{max} values for the dicationic form in the polymer. λ_{max} of the Q band of the dicationic form in the polymer composite is shown in Fig. 6. For TP(OR)₄PH₂, except for the EC composite, λ_{max} of the dicationic form in the polymer is almost same as that in DMF-HCl solution. λ_{max} for TPPH₂ was considerably lower than that for TP(OR)₄PH₂. The difference between λ_{max} of TP(OR)₄PH₂ and that of TPPH₂ suggests that K_{eq} of the former is considerably larger than that of the latter. Furthermore, K_{eq} of TP(OR)₄PH₂ in an acrylate polymer is almost uninfluenced by the R-group. A key factor for HCl sensitivity, $K_{eq} \cdot a^2$, is summarized in Fig. 7 as a function of the glass transition temperatures of the polymers. For the TP(OR)₄PH₂-acrylate polymers, λ_{max} of the Q band of the dicationic form suggests that K_{eq} is uninfluenced by the polymer matrix. The changes in $K_{eq} \cdot a^2$ with T_g of the polymer matrix suggest that the number of sorption sites depends on the polymer species. It should be noted that from $T_g = 208$ K to 293 K the sensitivity increases as T_g increases, and then decreases with further increases in T_g . The maximum sensitivity was observed for the polymer (BMA) with $T_g = 293$ K. The appearance of the maximum in sensitivity can be explained as follows. For a polymer with a lower T_g , a higher free volume is expected. For the polymers, the fraction of the free volume, f_p , can be approximated by

$$f_p = 0.025 + \alpha_p(T - T_g),$$

where α_p is a constant and depends on the components of the polymer. It seems that the value of α_p is almost the same for the series of acrylate polymers used. For the polymer with T_g higher than the working temperature (in this study, the working temperature was 318 K),

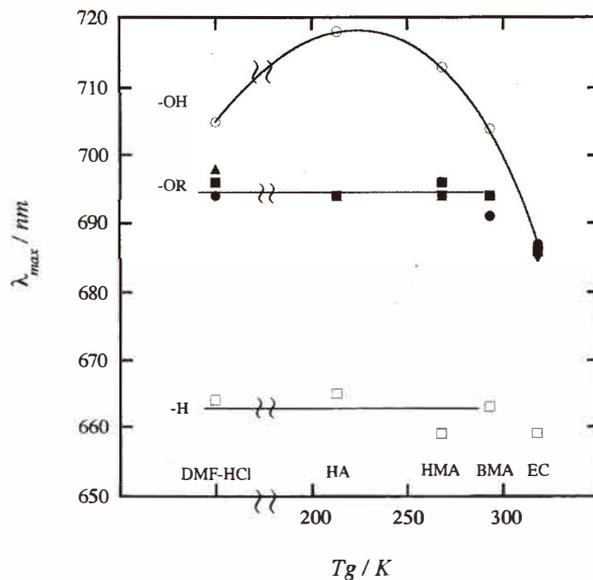


Fig. 6. Correlation between the wavelength of the maximum absorption, λ_{max} , of the Q bands of the dicationic forms of TP(OR)₄PH₂-polymer composite films with the glass transition temperature of the polymer (T_g).

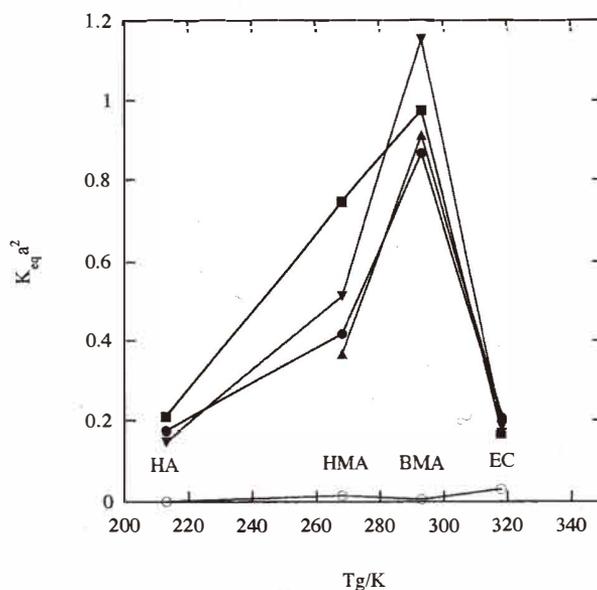


Fig. 7. Correlation between $K_{eq} \cdot a^2$ values and glass transition temperatures of the polymer matrices. ● TP(OCH₃)₄PH₂, ■ TP(OC₄H₉)₄PH₂, ▼ TP(O-2-EH)₄PH₂, ▲ TP(OCH(CH₃)₂)₄PH₂, ○ TPPH₂.

the fraction of free volume is 0.025, and the micro-Brownian motion and inner rotation of the molecular chains are depressed. With a decrease in T_g , the free volume increases and the inner rotation of the molecular chains and micro-Brownian motion successively become active. The increase in the free volume results in an increase in the spaces/cavities acting as the sorption sites for HCl, and the increase in the Brownian motion and inner rotation of the molecular chains results in a decrease in the solubility of HCl. As a result, the former causes an increase in the HCl sensitivity and the latter, a decrease in the sensitivity. Since λ_{\max} of the Q band of the dicationic form is almost uninfluenced by the polymer matrix for the acrylate polymers, it is expected that the changes in sensitivity for HCl gas with T_g contribute to the free volume and molecular motion of the polymer matrix. For the composite of 1×10^{-5} mol/g(polymer), the values of (I_0/I) were influenced by the polymer matrix. The HCl concentration dependence of $\log(I_0/I)$ for $\text{TP}(\text{OCH}_3)_4\text{PH}_2$ is shown in Fig. 8. The sensitivity is of the order of $\text{BMA} > \text{HMA} > \text{HA} > \text{EC}$. A similar dependency was also observed for the other alkoxyphenylporphyrins. For the composite with acrylate polymers, it seems that all of the porphyrins take the dicationic form in the range of 5 ppm HCl and higher. By assuming that K_{eq} is uninfluenced by the polymer species, it is expected that, at a high concentration of HCl, $\log(I_0/I)$ takes the same value. Unexpectedly, the saturated value depends on the polymer species. As mentioned above, the factor n depends on the polymer and is of the order of $\text{BMA} > \text{HMA} > \text{HA}$. If an HCl molecule in the gas interacts directly with the porphyrin, the saturated/steady value may be unchanged as a function of the polymer.

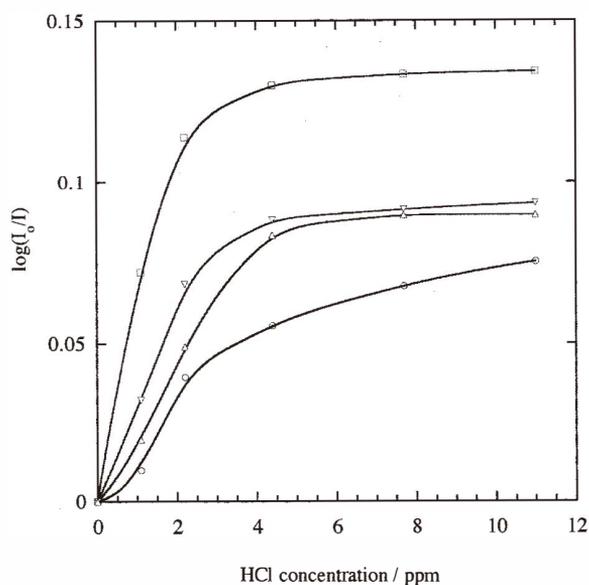


Fig. 8. HCl concentration dependence of $\log(I_0/I)$ at the Soret band for $\text{TP}(\text{OCH}_3)_4\text{PH}_2$ -polymer composite films. ○ BMA, □ HMA, ▽ HA, △ EC.

Furthermore, it is expected that the sorption rate of HCl in the polymer matrix becomes faster as the glass transition temperature decreases. The sorption rate is closely related to the response. The response to HCl is an important factor for the HCl gas sensor. The response and recovery of the acrylate polymer composites, when HCl gas flowed into the chamber, are shown in Figs. 9 to 11. The reversibility of the sensor is observed for all composite films studied, even some of them show slow recovery behaviors. A faster response to changes in HCl concentration was observed for the composite of the polymer having the lowest glass transition temperature (HA).

4. Conclusion

Optochemical HCl sensors using alkoxy-substituted tetraphenylporphyrins dispersed in acrylate polymer matrices were characterized. The sensors composed of BMA show a high sensitivity even at 1 ppm, suggesting that these sensors can be used to detect sub-ppm levels of HCl gas.

The sensing process was characterized by the following steps: the sorption of HCl to the polymer matrix ($\text{HCl}_{\text{gas}} \rightleftharpoons \text{HCl}_{\text{film}}$), and the diprotonation of the porphyrin ($\text{TPPH}_2 + 2\text{HCl}_{\text{film}} \rightleftharpoons \text{TPPH}_4^{2+} \cdot 2\text{Cl}^-$). It is expected that the equilibrium constants of the

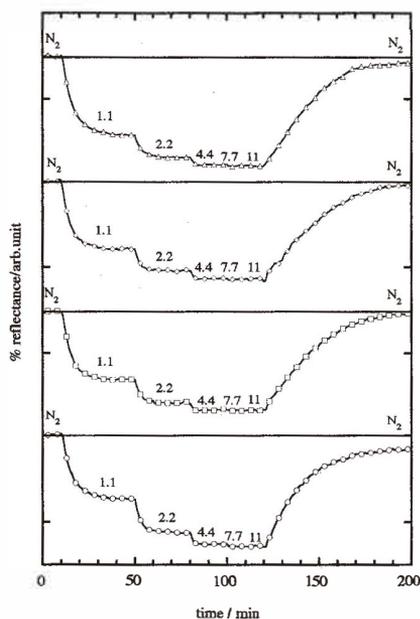


Fig. 9. Response and recovery of $\text{TP}(\text{OR})_4\text{PH}_2$ -BMA composites at the Soret band. HCl concentrations in ppm are shown in the figure. \circ $\text{TP}(\text{OCH}_3)_4\text{PH}_2$, \square $\text{TP}(\text{OC}_4\text{H}_9)_4\text{PH}_2$, \diamond $\text{TP}(\text{O}-2\text{-EH})_4\text{PH}_2$, \triangle $\text{TP}(\text{OCH}(\text{CH}_3)_2)_4\text{PH}_2$.

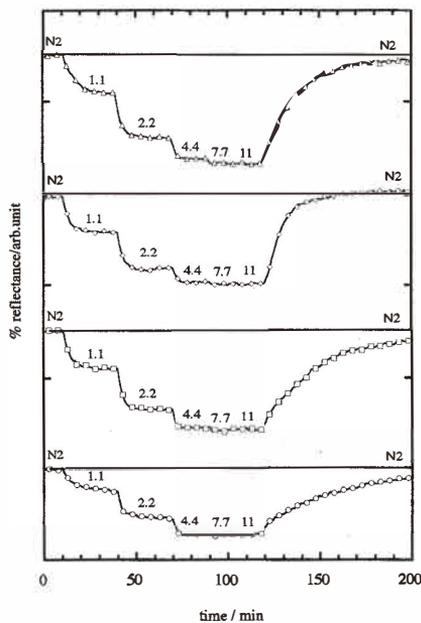


Fig. 10. Response and recovery of TP(OR)₄PH₂-HMA composites at the Soret band. HCl concentrations in ppm are shown in the figure. ○ TP(OCH₃)₄PH₂, □ TP(OC₄H₉)₄PH₂, ◇ TP(O-2-EH)₄PH₂, △ TP(OCH(CH₃)₂)₄PH₂.

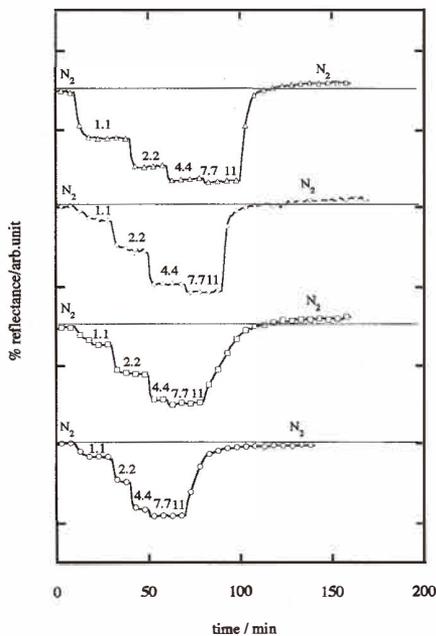


Fig. 11. Response and recovery of TP(OR)₄PH₂-HA composites at the Soret band. HCl concentrations in ppm are shown in the figure. ○ TP(OCH₃)₄PH₂, □ TP(OC₄H₉)₄PH₂, ◇ TP(O-2-EH)₄PH₂, △ TP(OCH(CH₃)₂)₄PH₂.

diprotonation for all tetraalkoxyphenylporphyrins used are almost the same, i.e., the effect of the alkyl chain of the substituent is not observed, and those values are larger than that of tetraphenylporphyrin. The sensitivity is influenced by the polymer matrix and is of the order of BMA>HMA>HA; it is related to the number of sorption sites in the polymer. A faster response to the HCl increase was observed for the composite made from a polymer with a lower glass transition temperature, but the sensitivity decreased.

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About the Authors

Heru Supriyatno received his M.S. and Ph.D. in Engineering from Ehime University in 1995 and 2001, respectively. He is presently a foreign researcher at Ehime University.

Katsuhiko Nakagawa received his M.S. in Engineering in Industrial Chemistry from Ehime University in 1971 and Ph.D. in Science from Kyoto University in 1991. He has been working at Niihama National College of Technology since 1981.

Yoshihiko Sadaoka received his M.S. in Engineering in Industrial Chemistry from Ehime University in 1971 and Ph.D. in Engineering from Kyushu University in 1979. He has been working in the Faculty of Engineering, Ehime University since 1971.