# Study of the Actions of BTEX Compounds on Polypyrrole Film as a Gas Sensor

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**ABSTRACT:** Polypyrrole (PPy) thin films were prepared electrochemically at a constant potential. Gas-sensing behaviors, including reproducibility, sensitivity, and response time to various benzene, toluene, ethylbenzene, and xylene (BTEX) compound concentrations, were investigated. BTEX compounds were found to be able to compensate for the doping level of PPy and, hence, decrease the conductivity of PPy on exposure to them. A reasonable reproducibility of the resistance change ($\Delta R$) was obtained. The sensitivity for each compound was 2.3 m$\Omega$/ppm (benzene), 0.4 m$\Omega$/ppm (toluene), 8.3 m$\Omega$/ppm (ethylbenzene), and 2.9 m$\Omega$/ppm (xylene). An adsorption model correlated well with the experimental results and was used to interpret the sensing behaviors. The parameters of this model, including the adsorption equilibrium constant and the $\Delta R$ caused by a pseudomonolayer of the detecting layer $\{[m(r_1 - r_0)]/n$, where $m$ is the number of active sites on the pseudomonolayer; $r_1$ and $r_0$ are the site resistances when the site is vacant and occupied, respectively; and $n$ is the thickness of the film$\}$, were determined. According to the parameters, toluene vapor had the most prominent effect in undoping PPy film but the poorest affinity to the active sites of the film. On the other hand, ethylbenzene showed the highest affinity to PPy film compared to the other BTEX compounds and consequently led to the highest sensitivity for such a sensor. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 954–961, 2001

**Key words:** polypyrrole; gas sensor; BTEX; adsorption model

## INTRODUCTION

It is well known that electron-conducting polymers can be used as chemical sensors by the measurement of the conductivity changes as a function of secondary doping or undoping of detected species. Polypyrrole (PPy)-impregnated filter paper was initially used to measure the response to

ammonia vapor by Nylander et al.[1] in 1983. Later, a similar device was used to measure responses to other gases[2–6] under suitable conditions; presumably, these gases reacted with PPy by oxidizing and reducing the PPy. Some authors have covered the use of PPy as the sensitive layer in ammonia sensors.[5,6] Bruschi et al.[7] proposed a method based on the chemical polymerization of pyrrole vapor onto a pattern with metal chlorine salt as an oxidizing agent. Bartlett et. al.[4] proposed a method that used electrochemical deposition of the conducting polymer in the development of gas sensor. To improve the characteristics of PPy film, several PPy-based composites as gas sensors have been studied.[8–14] Gustafsson et al.[15]
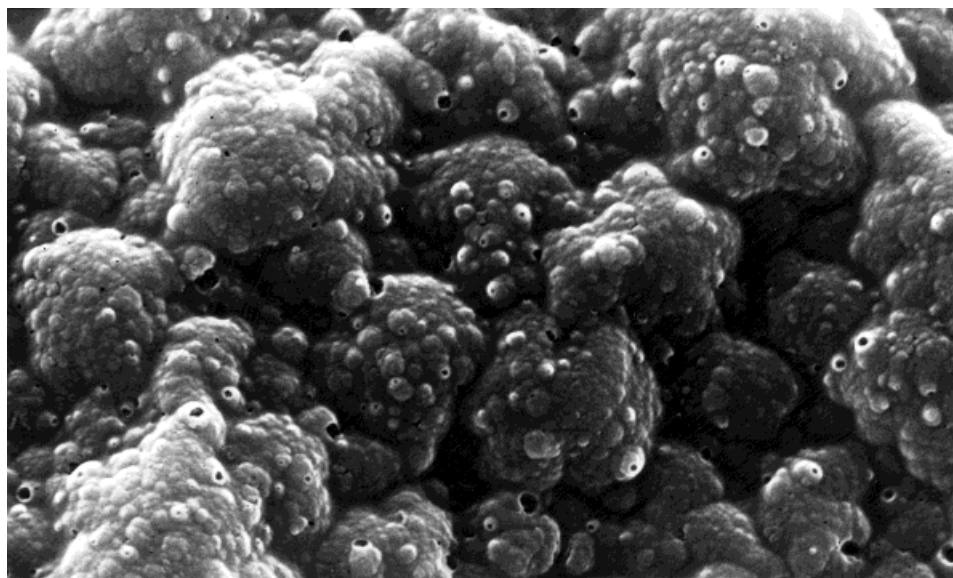
**Figure 1** Scanning electron micrograph of the surface morphology of PPy film prepared at a constant potential of 0.75 V versus SCE with an electrical charge equal to 0.05 C.

investigated the interaction between ammonia and a conducting polymer, focusing on PPy.

The attention of various air-pollution-control agencies has been increasingly focused on the control of volatile organic compounds (VOCs). Considerable quantities of VOCs are produced from industrial sources such as printing and coating facilities, foundries, and electronics and paint manufacturing facilities. A group of VOCs, including the aromatic hydrocarbons benzene, toluene, ethylbenzene, and xylene (BTEX), is widely used in industry and poses serious adverse effects on air quality. In this article, we present the results of a study on the behaviors of PPy sensors exposed to BTEX compounds. Hwang, Yang, and Lin[14] proposed a microscopic gas-sensing model that indicated that the sensitivity of the sensor depends on the site number of a monolayer ($m$), the thickness of the sensing film ($n$), the adsorption equilibrium constant ($K_m$), and the change of site resistance ($\Delta R$). We used the microscopic sorption model to explain sensing behaviors and also endeavored to show a correlation between sensing parameters and the experimental results and give an interpretation for the different responses.

## EXPERIMENTAL

An interdigitated gold electrode screen-printed onto the surface of an alumina substrate was used. Its structure and dimensions were the same as reported in earlier articles.[12,13] Chemiresistors were fabricated by the electrical deposition of these electrodes with the PPy thin film. Polymerization was carried out by a solution that contained $0.1M$ $LiClO_4$ (99%, Janssen) and $0.1M$ pyrrole monomers (99%, Janssen) under $N_2$ atmosphere. Cyclic voltammetry measurements were carried out in a $0.1M$-$LiClO_4$ electrolyte system to
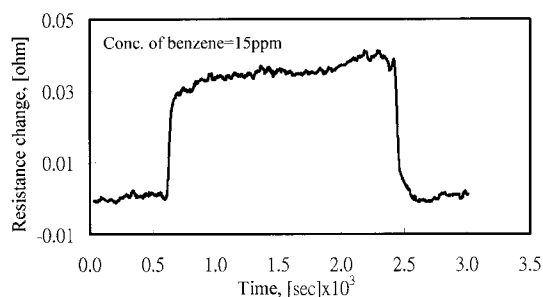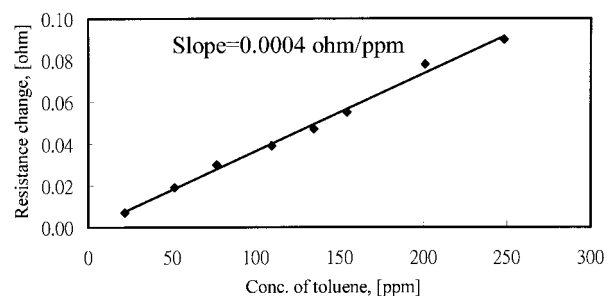


**Figure 2** $\Delta R$ of the PPy sensor exposed to benzene with a concentration of 15 ppm.
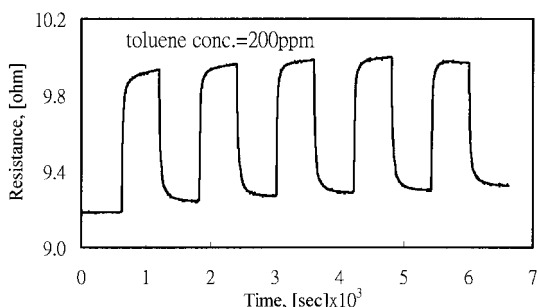
**Figure 3**   Several on–off cycles to study the reproducibility of the sensing behavior to toluene vapor at 200 ppm.



**Figure 5**   $\Delta R$s of the PPy sensor plotted against toluene concentration.

determine the polymerization voltage. With a platinum reference electrode, PPy was deposited on an alumina substrate that had an interdigitated gold circuit on it and was coated in advance by a very thin conducting PPy film through a chemical oxidation reaction as described elsewhere.[3] Electropolymerization was carried out at a constant potential of 0.75 V versus standard calomel electrode (SCE) with an electrical charge of 0.05 C. The deposited polymer layers were then washed with $CH_3CN$ several times and were dried in an oven at 90°C for 5 h. The responses to the BTEX compounds (with a $N_2$ mixture with a purity level of 99.99%) were measured by a device that mainly consisted of a current–voltage (I-V) meter and a home-designed automatic data-acquisition system. Resistance mea-

surements were taken when the maximum reading was reached. The response time and recovery time were obtained by measuring the time required to reach 95% of the plateau value.

## RESULTS AND DISCUSSION

Figure 1 shows the surface morphology of the synthesized PPy film. It is well known that a higher porosity of sensing film usually leads to a better response because of a higher diffusion rate and higher gas adsorption, but this occurs at the expense of its selectivity. The surface parameters of the sensing film, such as particle size and microroughness, are highly dependent on the electrochemical conditions of the film's preparation. In our previous work[13] on the PPy–PVA compos-
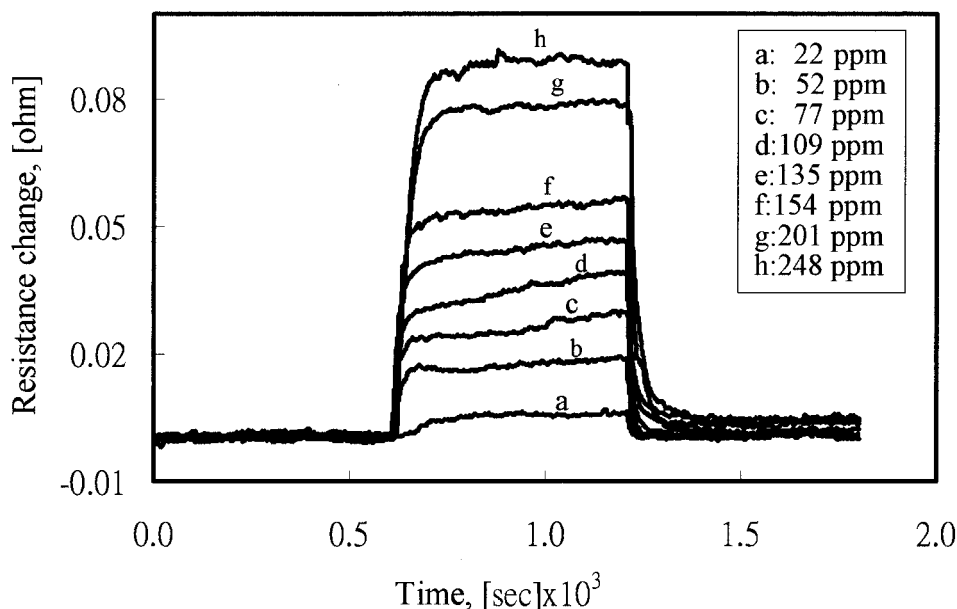


**Figure 4**   $\Delta R$s caused by increasing toluene concentration in steps from 22 to 248 ppm in $N_2$.
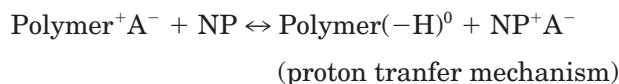
ite film prepared by the electrochemical codeposition process, we found that a higher electrical charge and the incorporation of PVA resulted in a different morphology and led to a more porous structure and, therefore, led to a different sensing behavior. However, the relationship between surface morphology or surface roughness and sensing performance is beyond the scope of this article. We, therefore, prepared the sensing PPy film at a constant potential of 0.75 V versus SCE with a constant electrical charge of 0.05C to exclude the possible effect of surface morphology of the film.

### Action of Benzene

Because the saturated vapor pressure of benzene is much higher than any other of the BTEX gases and because of the limitation of the mass flow controller, only a lower concentration was studied for benzene detection. It is well known that PPy is a $P$-type (electron-acceptor) semiconductor. Therefore, exposure of electron-donating gases, such as ammonia and alcohol, to PPy causes a decrease in conductance, that is, an increase in resistance. The recovery of the conducting polymer to its initial oxidized state is ascribed to desorption, by flushing with $N_2$, of the nucleophiles (NPs). The possible interaction mechanisms are discussed elsewhere.[15] The interaction between PPy and an electron-donating compound is generally considered to be a compensation effect. Thus, $n$-type (electron-donor) dopants can decrease the doping level of the polymer chain by compensating for the effect of the original dopant. The nucleophilic interaction may be regarded as:

$$Polymer^+A^- + NP \leftrightarrow Polymer^0 + NP^+,A^-$$

(electron transfer mechanism)

or

$$Polymer^+A^- + NP \leftrightarrow Polymer(-H)^0 + NP^+A^-$$

(proton tranfer mechanism)

Both interaction mechanisms make the polymer more neutral and less conducting.

Figure 2 shows the $\Delta R$s of the sensors, pristine PPy exposed to benzene with a concentration of 15 ppm. As shown, the resistance changed immediately as benzene vapor was exposed to the PPy sensor. $\Delta R$ was approximately equal to 0.038 $\Omega$. An equivalent sensitivity was equal to 2.30 m$\Omega$/
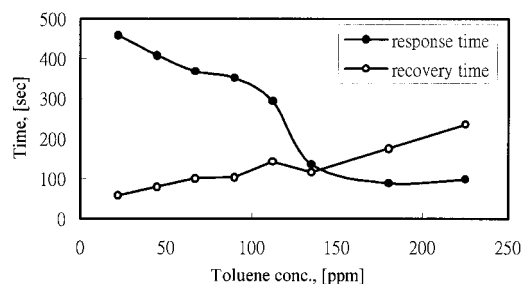


**Figure 6** ($\bullet$) Response time and ($\circ$) recovery time plotted against toluene concentration.

ppm if a linear relationship between $\Delta R$ and concentration could be kept in interested concentrations. Hereafter, we separate the discussion of benzene from the other BTEX compounds because of technical and laboratory-safety reasons.
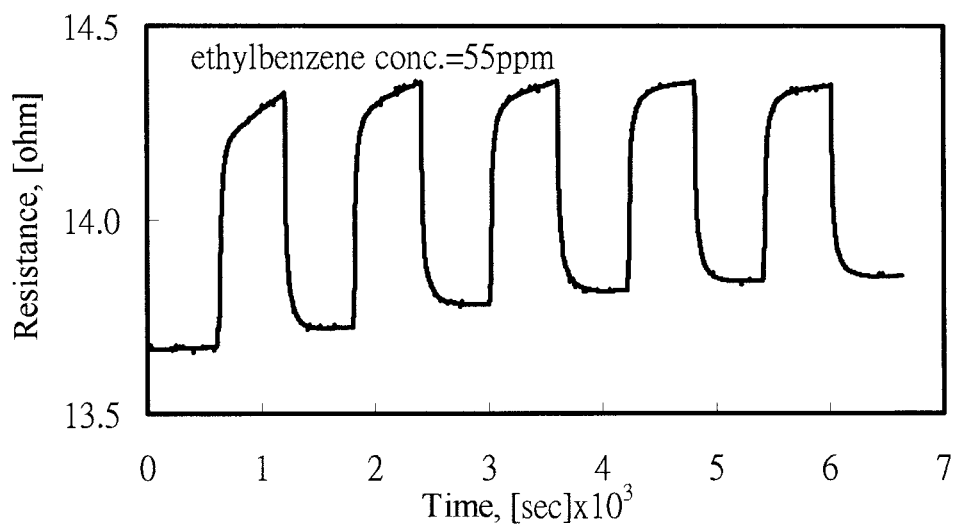
### Actions of Toluene, Ethylbenzene, and *o*-Xylene

Toluene is another electron-donating compound that causes a decrease in the conductivity of the PPy sensor. As a gas-sensing test, we used on–off cycles at 180 ppm to study the reproducibility of the sensing behavior. As shown in Figure 3, a good result was obtained in this regard. However, a drift of baseline was observed. When the concentration was increased in steps from 22 to 225 ppm in $N_2$, $\Delta R$ became greater as the toluene concentration increased, as shown in Figure 4. $\Delta R$s of pristine PPy sensor plotted against toluene concentrations are shown in Figure 5, and $\Delta R$ was linearly proportional to the toluene concentration. The slope of the linearity represents the sensitivity of the sensor characterized as the $\Delta R$ per unit toluene concentration. The sensitivity of the pristine PPy sensor to toluene vapor was thus 0.4 m$\Omega$/ppm. The response time and the recovery time for toluene vapor are shown in Figure 6 for comparison. As shown, with toluene at concentrations greater than 150 ppm, the sensor responded as quickly as in about 100 s. The response times were about 300 to 450 s for concentrations lower than 150 ppm. In contrast, vapors with higher concentrations took longer time to recover from the oxidized state.

Ethylbenzene and xylene are also electron-donating compounds. Similar to toluene, ethylbenzene and xylene caused increases in the resistance of the PPy sensor. As a gas-sensing test, we used on–off cycles at specific concentrations to study the reproducibility of the sensing behaviors. As shown in Figure 7(a, b), a reasonable
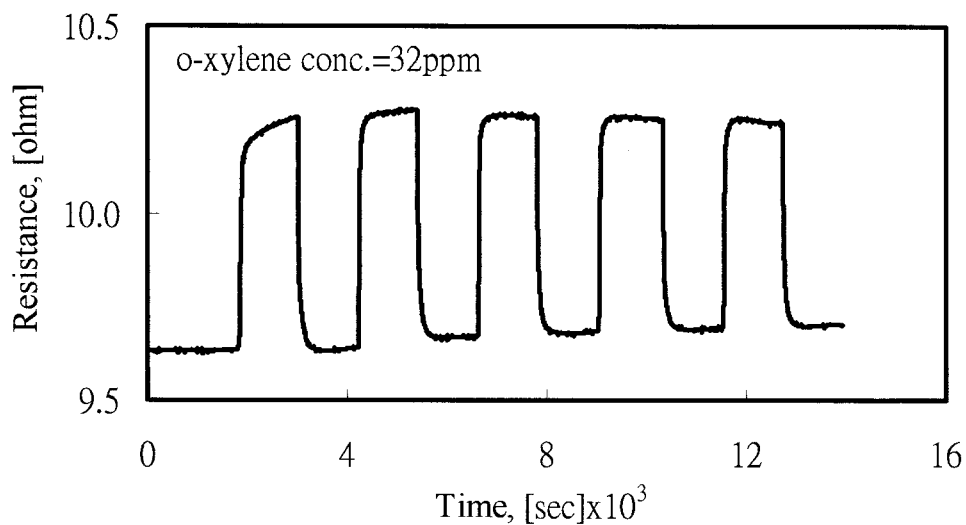
(a)



(b)

**Figure 7**  Reproducibility of several on–off cycles at constant concentrations of (a) *o*-xylene and (b) ethylbenzene to the PPy sensor.

reproducibility was obtained from *o*-xylene rather than from ethylbenzene. An irreversible interaction between ethylbenzene and PPy obviously existed. When the concentration was increased in steps from 9 to 92 ppm in $N_2$, the signal of $\Delta R$ became greater as the ethylbenzene concentration increased, as shown in Figure 8. $\Delta R$s of the pristine PPy sensor plotted against ethylbenzene concentration are shown in Figure 9; $\Delta R$ was lin-

early proportional to the ethylbenzene concentration. The sensitivity of the pristine PPy sensor to ethylbenzene vapor was thus 8.3 m$\Omega$/ppm. Similar procedures were carried out for the detection of the *o*-xylene vapor with concentrations ranging from 13 to 65 ppm. The sensitivity of the pristine PPy sensor to *o*-xylene vapor, as shown in Figure 9, was thus 2.9 m$\Omega$/ppm. The response times for ethylbenzene, as shown in Figure 10, ranged from
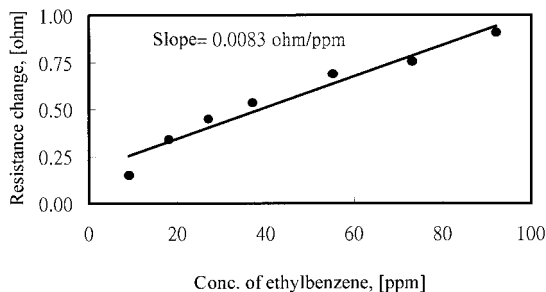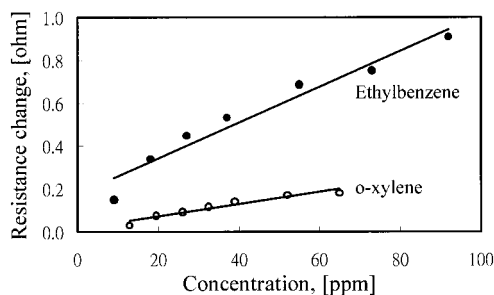
**Figure 8**  $\Delta R$s of the PPy sensor caused by increasing the ethylbenzene concentration in steps from 9 to 92 ppm in $N_2$.



**Figure 10**  (■) Response time and (□) recovery time plotted against the concentration of ethylbenzene.
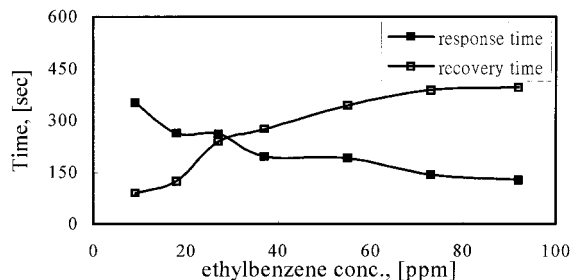
130 to 350 s for high concentration (90 ppm) to low concentration (9 ppm). Compared to toluene, the response speed from ethylbenzene was much faster. The recovery time ranged from 400 s (90 ppm) to 100 s (9 ppm). Compared with the recovery speeds of toluene, the desorption of ethylbenzene from PPy was much slower, which showed that the interaction of the PPy film with ethylbenzene was stronger than with toluene. This may imply that ethylbenzene had a better affinity to PPy. The response time of *o*-xylene was much longer than that of toluene or ethylbenzene. The hysteresis from response time and recovery time is plotted against gas concentration in Figure 11, in which hysteresis decreased with gas concentration for each of the concerned vapor compounds. The hysteresis might have been caused by the interaction of the detected gas with the sensing material and, hence, resulted in the physical change of the sensing material. However, we could not find a regular trend for the response time and recovery time for better interpretation.

## Calculation of the Parameters for the Gas-Sensing Model

Hwang, Yang, and Lin previously proposed a microscopic gas-sensing model[14] to explain the be-



**Figure 9**  $\Delta R$s of the PPy sensor plotted against the concentration of (●) ethylbenzene and (○) *o*-xylene.

haviors of PPy-based sensors to electron-donating compounds. The overall resistance of the composite film can be regarded as the paralleling of several pseudomonolayers, and each layer is composed of several resistors in series. In this model, $R$, $r$, $n$, and $m$ represent the resistance of the monolayer, the resistance of the active site, the thickness of the thin film, and the number of active sites on the pseudomonolayer, respectively. It shows that the plot of reciprocal of $\Delta R$ against the reciprocal of gas concentration is a linear relationship according to the following equation based on the proposed model:

$$1/\Delta R_t = n/[m(r_1 - r_0)]$$
$$+ \{n/[m(r_1 - r_0)K_m]\}(1/C_{A0})$$

where, $\Delta R_t$ is the resistance difference after and before gas sorption, $C_{A0}$ is the concentration of the detected gas, and $r_1$ and $r_0$ are the site resistances when the site is vacant and occupied, respectively. The value of $[m(r_1 - r_0)]/n$ can be determined from the reciprocal of the intercept, and $K_m$ can be obtained by dividing the intercept by the slope. It was previously reported that this model interpreted well the behaviors of PPy–poly(ethylene oxide)[12] and PPy–poly(vinyl alcohol)[13] composite sensors exposed to ethanol vapors as shown by the comparison of experimental results. An increase in the polymerization charge usually led to a thicker sensing film, that is, a greater $n$ value, and therefore decreased $[m(r_1 - r_0)]/n$ values. However, the thickness (determined by the total electrical charge) was kept constant in this investigation. Figure 12 shows the plot of $1/\Delta R_t$ versus $1/C_{A0}$ for the PPy thin film exposed to toluene, ethylbenzene, and *o*-xylene vapors, respectively. The values of $[m(r_1 - r_0)]/n$ and $K_m$ are shown in Table I. As shown, the values of the parameter $[m(r_1 - r_0)]/n$ exhibited the order: tol-
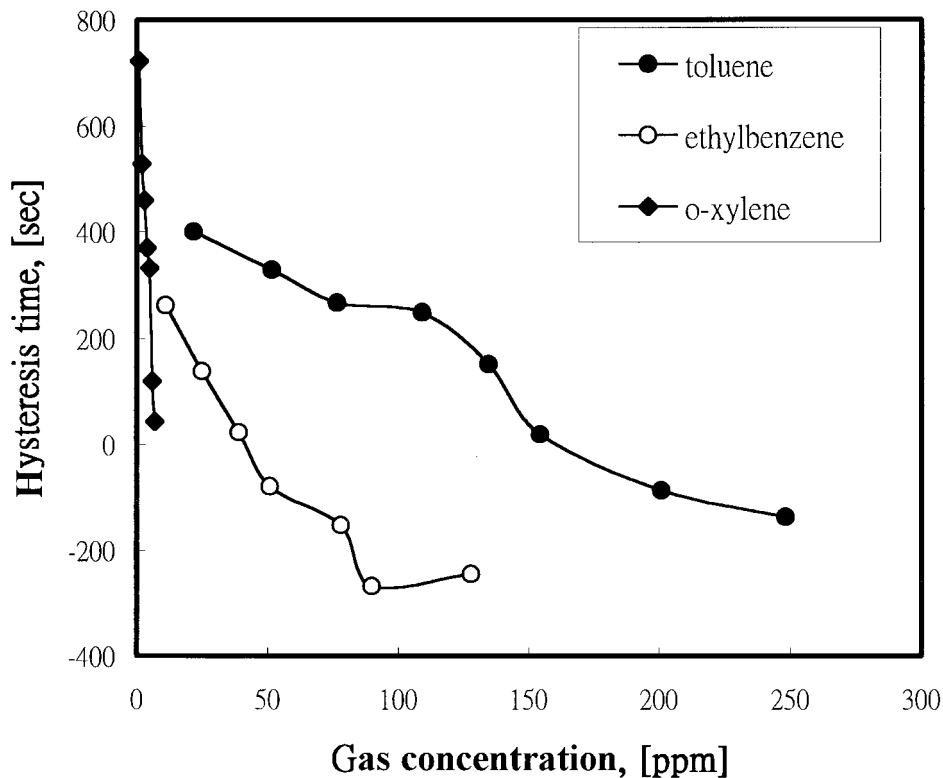
**Figure 11**   Hysteresis of the response time for (●) toluene, (○) ethylbenzene, and (♦) *o*-xylene.

uene (2.87) > ethylbenzene (1.36) > *o*-xylene (0.56). This means that toluene was the compound that caused the most significant $\Delta R$s of one

active site of PPy and that manifested itself as the most effective undoping compound to compensate for the original doping level of PPy. This can be
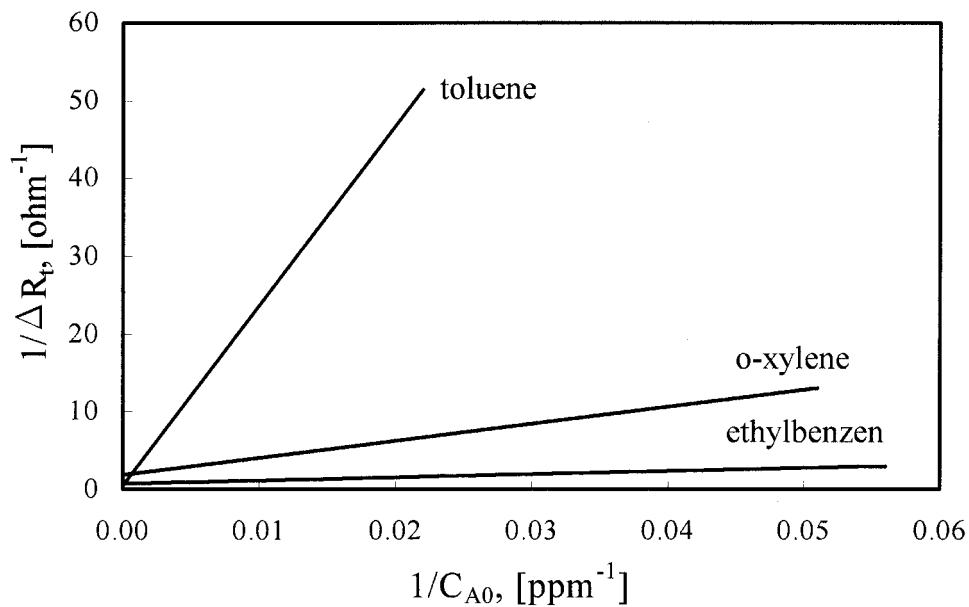


**Figure 12**   $1/\Delta R_t$ versus $1/C_{A0}$ for the PPy thin film exposed to toluene, ethylbenzene, and *o*-xylene vapors.

**Table I   Parameters of $[m(r_1 - r_0)]/n$ and $K_m$ Based on the Microscopic Sorption Model and Figure 10**

|  | Toluene | Ethyl-benzene | $o$-Xylene |
|---|---|---|---|
| $m(r_1 - r_0)/n$ | 2.87 | 1.36 | 0.56 |
| $K_m$ | $1.50 \times 10^{-4}$ | $1.83 \times 10^{-2}$ | $8.08 \times 10^{-3}$ |

explained by the fact that the ionization potential of the methyl group is greater than the ethyl group. Meanwhile, $K_m$ was dependent on the affinity of the detected compound to the sensing material (PPy) and was found have the order: ethylbenzene $(1.83 \times 10^{-2})$ > $o$-xylene $(8.08 \times 10^{-3})$ > toluene $(1.50 \times 10^{-4})$. Because the values of $m$ and $n$ were regarded to be identical (i.e., polymerization conditions and polymerization period), therefore, the affinity of vapor to the conducting material film determined the value of the sorption equilibrium constant, $K_m$. Accordingly, ethylbenzene was the compound among the investigated BTEX compounds that had the highest affinity (two orders of magnitude greater than that of toluene) for conducting PPy. The results of response speed and recovery speed discussed in the last section also complied with the affinity hypothesis; that is, ethylbenzene had a higher affinity to PPy and exhibited a quick response but had slower desorption from the active sites of the film. On the other hand, although toluene had the highest effect in undoping the oxidized PPy, it had the poorest coverage of the active sites on PPy. Accordingly, this implies that the sensing ability of the conducting polymer film depended not only the secondary doping (or undoping) level by the detected compound but also on the affinity of the compound to the sensing film. However, the affinity of the compound to the sensing material dominated the sensitivity of the sensor in this investigation.

## CONCLUSIONS

The sensing behaviors of the PPy gas sensors to BTEX compounds were investigated. The conducting PPy thin film deposited on a suitable interdigitated circuit could be used to detect BTEX vapors with reasonable sensitivity. According to the plot of $\Delta R$ versus gas concentration, the sensitivity for each gas was measured as follows: toluene = 0.4 mΩ/ppm, ethylbenzene = 8.3 mΩ/

ppm, and $o$-xylene = 2.9 mΩ/ppm, respectively. A microscopic sorption model was used to interpret the results. A linear relationship of $1/\Delta R_t$ plotted against $1/C_{A0}$ was obtained from the theoretical considerations and correlated well with the experimental results. The parameters $K_m$ and $[m(r_1 - r_0)]/n$ for this model were determined from such a plot. For $[m(r_1 - r_0)]/n$, the values exhibited the following order: toluene (2.87) > ethylbenzene (1.36) > $o$-xylene (0.56), which shows that toluene, with a single methyl group on a benzene ring, had the most prominent effect in undoping the original doped PPy film. For $K_m$, an order of ethylbenzene $(1.83 \times 10^{-2})$ > $o$-xylene $(8.08 \times 10^{-3})$ > toluene $(1.50 \times 10^{-4})$ was found, which shows that ethylbenzene had the highest affinity for conducting PPy. Consequently, ethylbenzene exhibited the best sensitivity to the PPy sensor, which shows that the affinity (i.e., the coverage) of the detected vapor to the sensing material dominated the sensitivity of the gas sensor.

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