



CHAPTER III

ELECTRICAL CONDUCTIVITY RESPONSE OF POLYPYRROLE TO ACETONE VAPOR: EFFECT OF DOPANT ANIONS AND INTERACTION MECHANISMS

Electrical Conductivity Response of Polypyrrole to Acetone Vapor: Effect of Dopant Anions and Interaction Mechanisms

Abstract

The chemically prepared undoped polypyrrole (PPy) and the PPy doped with seven dopant anions, at a dopant to monomer molar ratio of 1/12, were used as chemical sensors to detect acetone vapor. The negative changes in specific conductivity, $\Delta\sigma$, of PPys upon exposed to acetone vapor were observed. The magnitudes of $\Delta\sigma$ depend critically on the type of the dopants which induces different properties amongst doped PPys. For the sulfonate doped PPy, $\Delta\sigma$ depends exponentially on the doping level (N^+/N) and on the initial specific conductivity. It also depends linearly on the proportions of the bipolaron species and of the order aggregation of PPy. However, it depends inversely on the proportion of the imine-like nitrogen defect ($=N^-$). An environmental scanning electron microscope and an X-ray diffractometer, for instances, were used to investigate the interaction between PPy and acetone molecules. The swelling or the disordering effect, the hydrogen-bonding formation, and the reduction of charge carrier species are suggested to be the mechanisms causing the PPy conductivity changes when exposed to acetone vapor.

Keywords: polypyrrole, acetone vapor, sensor, hydrogen-bonding, swelling, disordering

1. Introduction

Conductive polymers have been developed with the aim to be an alternative gas sensor because of several advantages over other available materials [1]. The conductive polymer based sensor can be operated at room temperature. They are light, non-corrosive, and can be prepared easily. Polypyrrole, PPy is one of the most interesting amongst many conductive polymers known due to its relatively high environmental stability [2] and the ease of synthesizing and doping with various dopants [3].

Utilizing dopants with different chemical structures results in some modifications of PPy properties, i.e. the surface morphology [4], the solubility [5], the moisture content [6], and the degree of water sorption [7]. In this work, we shall report the effects of dopant anions on electrical response of PPy toward acetone vapor. Acetone is the flammable ingredient in a lacquer, the material used for interior decoration as well as in various chemical plants. When its concentration in the air is between the lower explosive limit, LEL and the upper explosive limit, UEL, 2.5-12.8 %, it can be easily ignited [8]. This is one of the main causes of fire accident on construction sites and in chemical stores. Upon an acetone exposure, the conductivity of the electrochemically deposited PPy film decreased [9]. This response was much smaller than that of alcohol, because of the lower polarity of acetone. In addition, the baseline resistance of the film drifted towards higher values [9]. Nigorikawa *et al.* [10] also found an increase in resistivity of PPy upon an acetone vapor exposure. A lower electronegativity of acetone as compared to the work function of PPy suggests the reduction of PPy caused by acetone. An exposure of Langmuir-Blodgett film of PPy to a gaseous acetone [11] caused a stable and reproducible electrical resistance increases. The resistance response increases with chemical's polarity; for acetone, the response is smaller than those of methanol and ethanol, but it is bigger than those of ethyl acetate and toluene.

2. Experiment

2.1 Materials

Pyrrrole monomer (AR grade, Fluka) was purified by distillation under the reduced pressure prior to use. Ammonium persulfate (AR grade, Aldrich) was used as the oxidant without further purification. The dopants used were: α -naphthalene sulfonic acid, sodium salt, A (AR grade, Fluka); β -naphthalene sulfonic acid, sodium salt, B (AR grade, Fluka); camphor sulfonic acid, C (AR grade, Fluka); dodecylbenzene sulfonic acid, sodium salt, D (AR grade, Fluka); ethane sulfonic acid, E (AR grade, Fluka); perchloric acid, P (AR grade, Fluka); and *p*-aminobenzoic acid, AB (AR grade, Fluka). They were used as received.

2.2 Instruments

The instruments used in this work were: a thickness gauge (Peacock, model PDN 12N) with a resolution of 0.001 mm; an environmental scanning electron microscope (ESEM, ElectroScan, E3 ESEM) with an acceleration voltage and the magnification of 20 kV and 3500 times, respectively; the water vapor pressure used was 400 – 800 Pascal; a thermohygrometer (Cole-Parmer, model P-03313-86); an X-ray photoelectron spectrometer (XPS, Perkin Elmer, model PHI 5400) with a non-monochromatic MgK α source (1253.6 eV and 15 kV x 20 mA); a Fourier transform infrared spectrometer (FT-IR, Bruker, model FRA 106/S) with a resolution of 4 cm⁻¹ and numbers of scan of 20; a thermogravimetric analyzer (TGA, Perkin-Elmer, model TGA7) with a heating rate of 10 °C/min under N₂ atmosphere; an X-ray diffractometer (XRD, Rigaku, model D/MAX-2000) with Cu K-Alpha 1 as an X-ray source and a scanning speed of 5 degree/min; an ultraviolet-visible spectroscopy (UV-Vis, Perkins-Elmer, model Lambda 16), with a scan speed of 1440 nm/min; and a custom-made four-point probe conductivity meter.

2.3 The Polymerization Procedure

The doped PPy were chemically synthesized by the *in situ* doped, oxidative coupling polymerization according to the method of Shen and Wan [12]. The solution of 0.6846 g (3.0 millimole) ammonium persulfate in 10.0 ml deionized water was slowly added to the mixture of 1.2 millimole of dopant anion and 1.0 ml (14.5 millimole) pyrrole in 20.0 ml deionized water. The reaction was carefully maintained at 0 ± 0.5 °C for 2 hours. The obtained PPy was precipitated by pouring the reaction mixture into a large excess amount of deionized water. The PPy powder was washed several times with deionized water and methanol before drying in a vacuum at room temperature for 2 days. The PPy doped with α -naphthalene sulfonate is notified as PPy/A, for instance. The undoped PPy was synthesized by the same procedure but in the absence of a dopant anion; it is identified as PPy/U.

2.4 Effect of Dopant Anions on the Response of PPys toward Acetone Vapor

To fabricate a stable sensor, an aging period greater than 50 days of PPys was allowed so that the specific conductivity of PPy attained its steady value. 0.05 g of PPy powder was ground and pressed by a hydraulic press at 60 kN into a pellet with the diameter of 2.5 cm and a thickness between 60 – 90 μm , measured by a thickness gauge. Their specific conductivity values, σ were measured by a custom-made four-point probe conductivity meter [13]. Si and SiO₂ sheets with known resistance values were used in the probe calibration. The suitable current used was determined for each PPy; it was set at a level so that each PPy still had its Ohmic behavior without the Joule heating effect. For instance, the currents used for PPy/U and PPy/A were $2 (\pm 0.5)$ mA and $20 (\pm 1)$ mA, respectively.

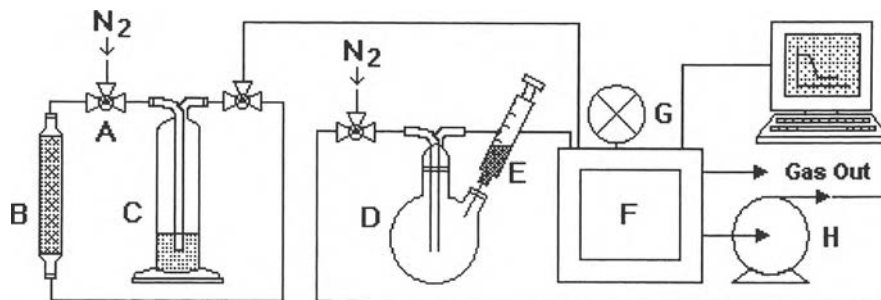


Figure 1 The schematic draw of the flow system: A) the three way value; B) the dryer column; C) the water reservoir; D) the 2-neck round bottom flask; E) the syringe for acetone injection; F) the chamber consisting of the four probe conductivity meter and the thermohygrometer; G) the pressure gauge; H) the diaphragm pump; and I) the data acquisition system.

The flow system, as shown in Figure 1, consists of a humidity-control set (A-C), an acetone container (D), and an exposure chamber (F) which contains the four-point probe (linear array) and the thermohygrometer. 4.00 ml of acetone in the container was slowly vaporized and flowed into a closed-loop system having a total volume of 7728 cm³. The acetone concentration in N₂ was 17 vol.%. The controlled temperature and humidity were 25 ± 1 °C and 50 ± 10 %RH, respectively. The change in the specific conductivity was monitored by a data acquisition system (Data Translation board, model DT2801) interfaced with a personal computer and reported in terms of $-\Delta\sigma$.

2.5 Effect of Acetone Vapor Concentrations on the Response of PPys

Only PPy/U and some of doped PPys were selected for this experiment. The volume of acetone vapor in the container was varied in order to vary the acetone vapor concentration in the system from 10% of LEL (0.25 vol.%) to the saturated concentration of acetone vapor at 25 °C (30 vol.%). The controlled temperature and relative humidity for this system were 25 ± 1 °C and 50 ± 10 %RH, respectively. The parameters obtained from this experiment were the response pattern (linear/non-linear), the sensitivity (the slope of the plot between $-\Delta\sigma$ and acetone vapor

concentration) and the maximum detectable concentration. The first two parameters are assigned only in the concentration range of LEL – UEL of acetone vapor.

2.6 Interaction between Acetone Vapor and PPy

The conditions for each experiment were designed to suit the performance and signal stability of each instrument. The change in morphology after the prolonged exposure to acetone of PPy pellet pressed at 30 kN/1.3 cm² was studied by ESEM. The water vapor pressure used was 400 – 800 Pascal. The pictures of pellet surface were taken before and after exposing to the saturated acetone vapor in N₂ for 24 hours at the magnification of 46x and 3500x. For the XPS experiment, the change in the proportions of chemical species: neutral nitrogen, polaron species, bipolaron species, and imine-like nitrogen (=N-) were monitored from the PPy sample treated under the same conditions as those in the ESEM experiment. To study the type of absorption of acetone onto PPy (physisorption or chemisorption) and bonding, the TGA thermograms and the FT-IR spectra of PPy powder before and after exposing to the saturated acetone vapor in N₂ for 24 hours were recorded. The XRD experiment was performed on the PPy/A pellet before and after immersing in acetone liquid for 30 minutes, in order to study the change in the microstructure of PPy. The changes in visible spectra of PPy/B film, cast from *m*-cresol solution on a glass slide, were monitored during an exposure to the saturate acetone vapor.

3. Results and Discussion

3.1 Effect of Dopant Anions on the Response of PPys toward Acetone Vapor

During exposures to acetone vapor at the concentration of 17 vol.% in N₂, the specific conductivity values of all PPys were found to decrease. The response of PPy/U is shown in Figure 2 as a representative one. The changes in conductivity were reversible after an evacuation overnight. The magnitudes of the equilibrium specific conductivity decrement, $-\Delta\sigma$ (see Figure 2 for its definition), depend on the

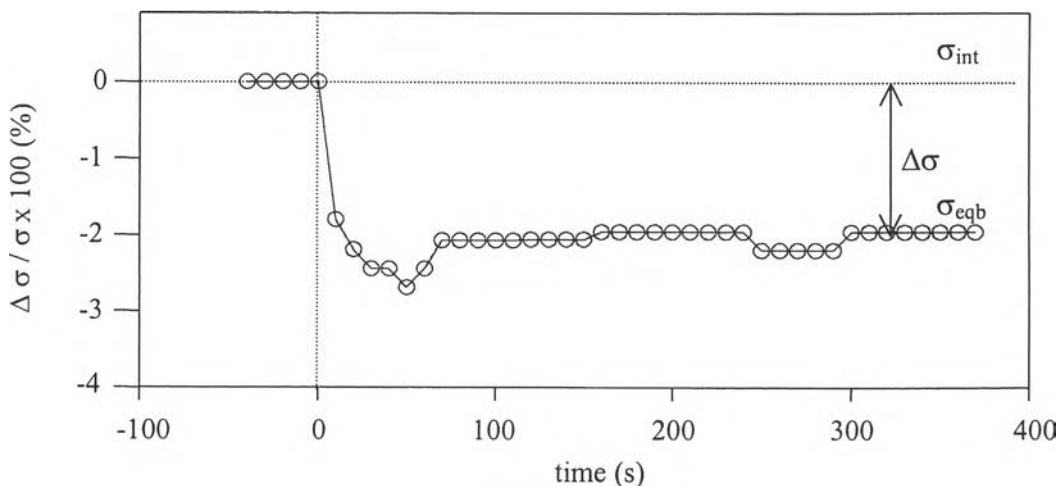


Figure 2 The response of PPy/U to acetone vapor at the concentration of 17 vol.% in N₂ at 24 °C and at 49 %RH.

type of dopants existing in PPys. Figure 3 shows a plot of the electrical responses of all PPys in terms of $-\Delta\sigma$, along with the specific conductivity of the fresh ones, and their nitrogen compositions: imine-like nitrogen defect ($=N^-$); polaron species ($-NH^{+\cdot}$); and bipolaron species ($=NH^{+\cdot}$), as characterized by XPS [14,15].

A PPy with a larger amount of N^+ (polaron and bipolaron species) and correspondingly a higher specific conductivity value has a higher response toward acetone vapor. PPy/A and PPy/B have an outstanding sensing ability. Their $\Delta\sigma$ values are -0.4 and -0.2 S/cm, respectively. On the other hand PPy/AB, which was reported as the ineffectively doped PPy [15a], has the poorest response: -1.5×10^{-4} S/cm. It has a low N^+ quantity, no bipolaron species, and a large proportion of $=N^-$. PPy/U is not environmentally stable [15a]: it has a variation in responses toward acetone. For the sulfonate doped PPys; i.e. PPy/A, PPy/B, PPy/C, PPy/D, and PPy/E, their $-\Delta\sigma$ values in response to 17 vol.% acetone vapor depend exponentially on the doping level or N^+/N and their initial specific conductivity values with the goodness of fit, R^2 of 0.80 and 0.79, respectively. In addition, these $-\Delta\sigma$ values depend linearly on the proportion of bipolaron species and the order aggregation of PPy with R^2 of 0.63 and 0.65, respectively. As characterized by XRD [15a], the proportion of the order aggregation is the proportion of the overall area of X-ray diffraction pattern, excluding the broad maxima at 2θ of 25.4 – 27.8°.

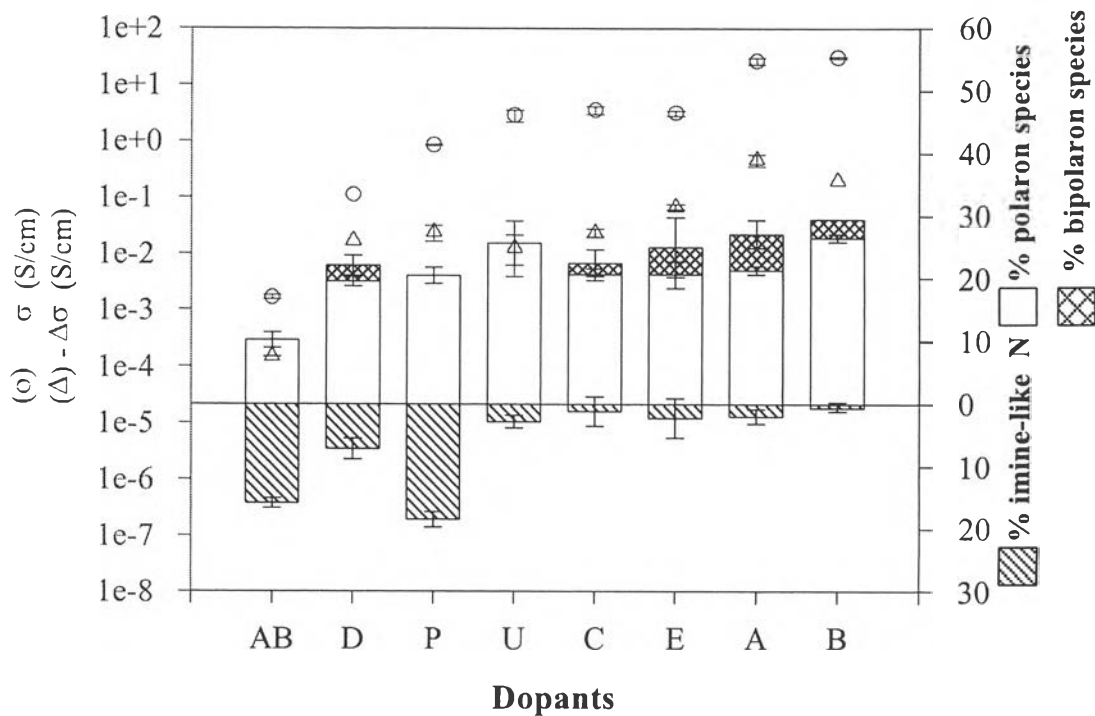


Figure 3 The electrical responses of PPys to acetone vapor at the concentration of 17 vol.% in N_2 in terms of $-\Delta\sigma$, at 25 ± 1 °C and at 50 ± 10 %RH, plotted with the specific conductivity of the fresh PPys and their nitrogen compositions: imine-like nitrogen ($=N^-$); polaron ($-NH^+$); and bipolaron ($=NH^+$) species.

In summary, PPy/A and PPy/B are found to be the most promising materials for sensing acetone whereas PPy/AB has the lowest response toward acetone vapor. They were selected for the next experiment along with PPy/U.

3.2 Effect of Acetone Vapor Concentrations on the Response of PPys

Figure 4 shows $-\Delta\sigma$ of PPy/U, PPy/A, PPy/B, and PPy/AB when exposed to different acetone vapor concentrations. Due to the small responses of PPy/U and PPy/AB, their signals shown in this figure were multiplied by factors of 10 and 100, respectively. Some parameters, the response pattern and the sensitivity (slope) in the region of LEL to UEL of acetone and the maximum detectable concentration, are tabulated in Table 1.

PPy/U, PPy/A, and PPy/B have approximate linear electrical responses toward acetone vapor in the range of its LEL – UEL. PPy/AB has a non-linear one; it has a logarithmic response. The sensitivity values, which are the slope of the plots, of these four PPys are in the order of PPy/A > PPy/B > PPy/U >> PPy/AB. Beyond the UEL of acetone, the first three PPys still have the linear responses until they reach their maximum detectable concentrations which are as high as ~25 vol.%. The maximum detectable concentration of PPy/AB is only 3 vol.%, this value can be clearly observed in the logarithm plot.

The linear responses of PPy/A, PPy/B, and PPy/U suggest that they can be used as linear sensors for acetone. The highest sensitivity toward acetone vapor of PPy/A correlates with the high proportion of bipolaron species present. The lowest sensitivity toward acetone vapor of PPy/AB correlates with its high proportion of =N-. The high acetone vapor susceptibility of PPy/A, PPy/B, and PPy/U conforms with their relatively high concentrations of charge carrier species (both polaron and bipolaron, see Figure 3). On the other hand, PPy/AB has the lowest maximum detectable concentration: it has the lowest amount of charge carrier species and very high concentration of =N- defect. The defect possibly hinders both conductivity and response toward acetone vapor. These correlations are further clarified in the next section.

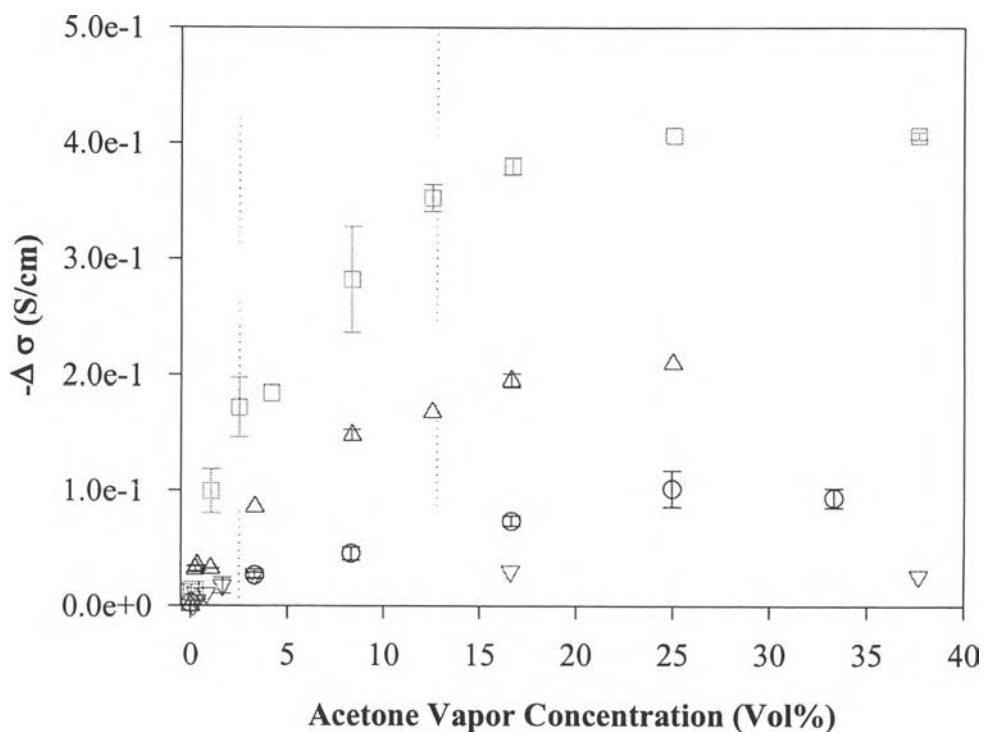


Figure 4 The electrical responses of: (□) PPy/A; (△) PPy/B; (○) PPy/U (x 10); and (▽) PPy/AB (x 100) to acetone vapor at various concentrations in N₂ at 25 ± 1 °C and at 50 ± 10 %RH.

Table 1 The type of response, the sensitivity, and the maximum detectable concentration of selected PPy's toward acetone vapor in N₂

Material	Type of response	Sensitivity in the range of LEL-UEL			Maximum detectable concentration (vol.% of acetone vapor)
		Slope (S/cm)/(vol.% of acetone vapor)	Intercept (S/cm)	R ² of linear fits	
PPy/U	Linear	-3.0E-04	-1.7E-03	0.90	~25 %
PPy/A	Linear	-1.8E-02	-1.2E-01	0.93	~25 %
PPy/B	Linear	-9.1E-03	-6.3E-02	0.91	~25 %
PPy/AB	Non-linear	-2.0E-06	-3.0E-04	0.25	~3 %

3.4 Investigation of Interaction between Acetone Vapor and PPy

Figure 5 shows the ESEM pictures of pellet surface of PPy/B before and after exposure to the saturated acetone vapor in N₂ for 24 hours. At the magnification of 46x, the overall surface of the pellet increased in irregularity upon the acetone exposure. At the magnification of 3500x, it was evident that the globular structure got some swelling after a prolonged acetone exposure.

The XPS results reveal no significant change in the chemical species of PPy upon a prolonged exposure to acetone vapor (figure is not shown). This is due to a very high vacuum system and the nature of XPS for being a very high surface sensitive technique. This confirms the *reversibility* of interaction between acetone and PPy.

The X-ray diffraction patterns of the PPy/A before and after immersing in acetone liquid for 30 minutes are shown in Figure 6 along with their deconvoluted results underneath. The most significant change after the exposure is the decrease in the proportion of the peak at 2θ of 17.0° (SD = 0.7° ; d-spacing = 5.4 \AA) which corresponds to the distance between two hard segments in PPy backbone which are separated by the counterion molecules [16]. This change is accompanied by the increase of the peak at 2θ of 20.6° (SD = 0.2° ; d-spacing = 4.3 \AA) which can be identified as the distance between neighboring pyrrole rings on the same chain [17,18] when α - α' linkages are single bonds. The second most significant change in X-ray diffractograms can be clearly seen only from the deconvoluted results. It is the proportions of two diffraction peaks at the 2θ around 25.5° (d-spacing = 3.5 \AA). These two peaks can be defined as the interplanar spacing between aromatic pyrrole units from two different chains or segments [19]. The sharper peak indicates the presence of the extent of crystalline domains as large as 32 \AA , whereas the broader one corresponds to the disorder proportion in PPy. The area ratio of the sharper peak to the broader one is 1.3 (SD = 0.1) for the fresh PPy/A. It decreases to be 0.6 (SD = 0.1) after immersing in acetone liquid for 30 min. This change indicates that acetone destroys the dispersion force between aromatic pyrrole units and increases the

disorder section in PPy which hinders the electron mobility and hence decreases the specific conductivity of PPy. This result agrees with the conclusions given above that a PPy with a higher proportion of order aggregation has a higher response to acetone.

The TGA thermogram of the PPy/B after an exposure to the saturated acetone vapor for 24 h (Figure 7) shows a desorption of chemicals when the temperature was increased to 180 - 240 °C. This temperature is well above the boiling point of acetone (56.1 °C). The result suggests the chemisorption of acetone in the PPy matrix during the prolonged exposure.

The FT-IR spectrum of the PPy/D after exposure to the saturated acetone vapor for 24 h (Figure 8) confirms the above statement. The stretching vibration of C=O group in acetone adsorbed onto PPy (Figure 8b) has a frequency of 1709 cm^{-1} , lower than that of C=O group in acetone vapor: 1738 cm^{-1} (Figure 8c). This was probably caused by the hydrogen-bonding formation between C=O group of acetone and N-H group of pyrrole repeating unit. This hydrogen-bonding weakened the C=O bond by forming a new O \cdots H bond using the lonepair electrons of O in carbonyl group. This finding explains the inverse correlation between acetone response and the presence of =N- which is a non-donor for hydrogen-bonding. From the experimental study to determine the effect of dopant to monomer molar ratio of PPy/A on the response toward acetone vapor [15b], as the ratio increases, the moisture content is lower due to the presence of hydrophobic dopant whereas the electrical response toward acetone vapor is enhanced. This is because the existing water molecules decrease the amount of active sites for acetone (neutral and charged -NH-) and increase the amount of =N- in PPy, as evidenced by XPS [15c,15d,20].

Upon exposure to the saturated acetone vapor, the absorbance peaks in visible spectrum of PPy/B film evidently decreased, as shown in Figure 9. The peak reduction agrees with the change observed by Blackwood and Josowicz [21] upon an exposure to methanol vapor of the PPy/TCNQ film. It was claimed from the reduction in polaron and bipolaron species that methanol acts as a reducing agent toward PPy. The same reason should also be applicable for the acetone exposure.

Acetone as a reducing agent conforms to the finding that acetone reduces the conductivity of PPy. The decreases in bipolaron were found to be more dominant than those of polaron (-89 %, SD = 9 % and -33 %, SD = 9 %, respectively). This explains the best sensitivity of PPy/A which possesses the highest proportion of bipolaron. Note that there was no significant change in the transition energies from the UV-Vis technique observed.

4. Conclusions

The electrical sensitivity to acetone vapor of conductive PPys can be modified by utilizing various types of dopant. The dopants which provided PPy with higher specific conductivity, higher order aggregation, higher proportions of N^+ , especially bipolaron and lower proportion of imine-like nitrogen defect can improve the sensitivity to the acetone vapor. The PPy/A and PPy/B are ones of the most promising candidates amongst PPys investigated as a polymeric sensor for acetone vapor. Acetone molecules mostly diffused into the intersegmental spaces in the PPy matrices, which were previously separated by the dopant molecules. Some of them also destroyed the dispersing forces between aromatic pyrrole rings. Acetone molecules generally absorbed into a PPy matrix *via* a hydrogen-bonding. These interactions hindered the electron jumping and hence decreased the specific conductivity of PPy. The changes in visible spectra of PPy during an acetone exposure indicate the reduction of charge carrier species, especially bipolaron. This explains the superior sensitivity of PPy/A and PPy/B which have relatively high proportion of charge carries species, especially bipolaron in PPy/A. The improvement of PPy specificity toward acetone over moisture and other components in lacquer will be reported elsewhere.

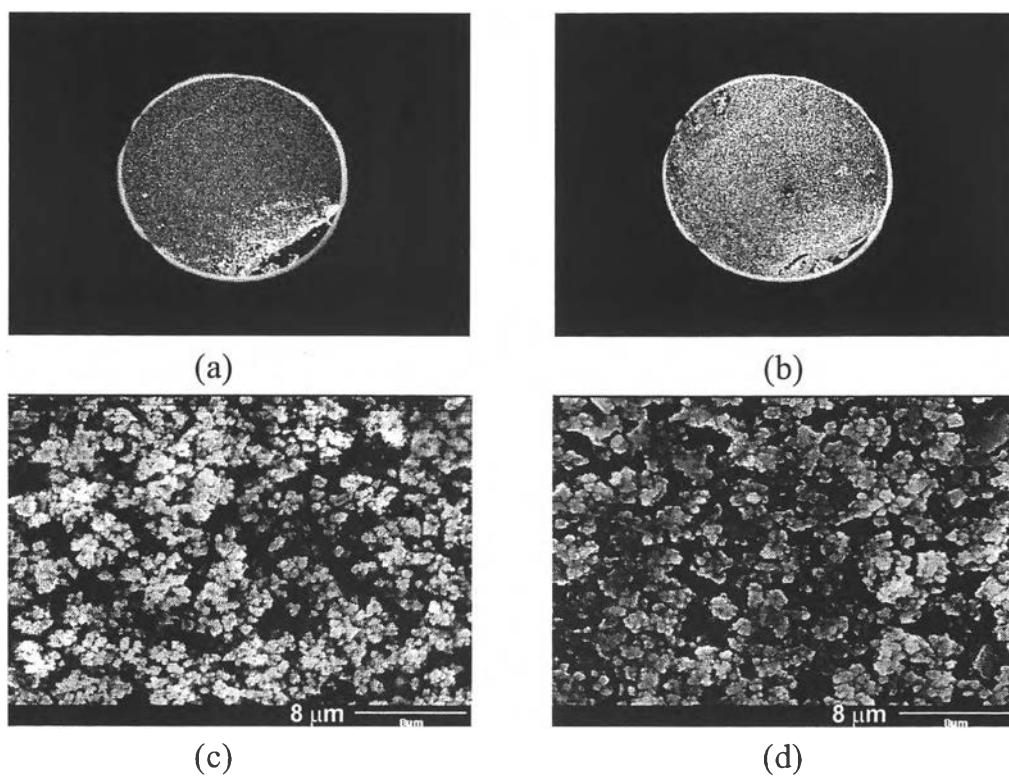


Figure 5 The morphology of PPy/B pellets: a) before and b) after exposure to the saturated acetone vapor in N₂ for 24 hours at the magnification of 40x: c) before and d) after exposure to the saturated acetone vapor for 24 hours at the magnification of 3500x.

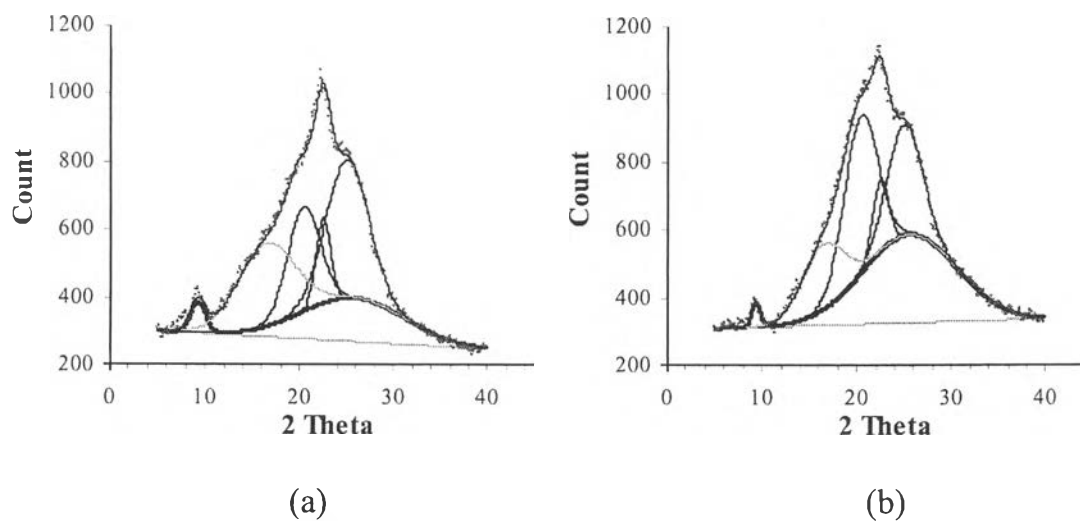


Figure 6 The X-ray diffractograms of: a) fresh PPy/A pellet; and b) the same PPy/A pellet after immersing in the acetone liquid for 30 min, with their deconvoluted results underneath.

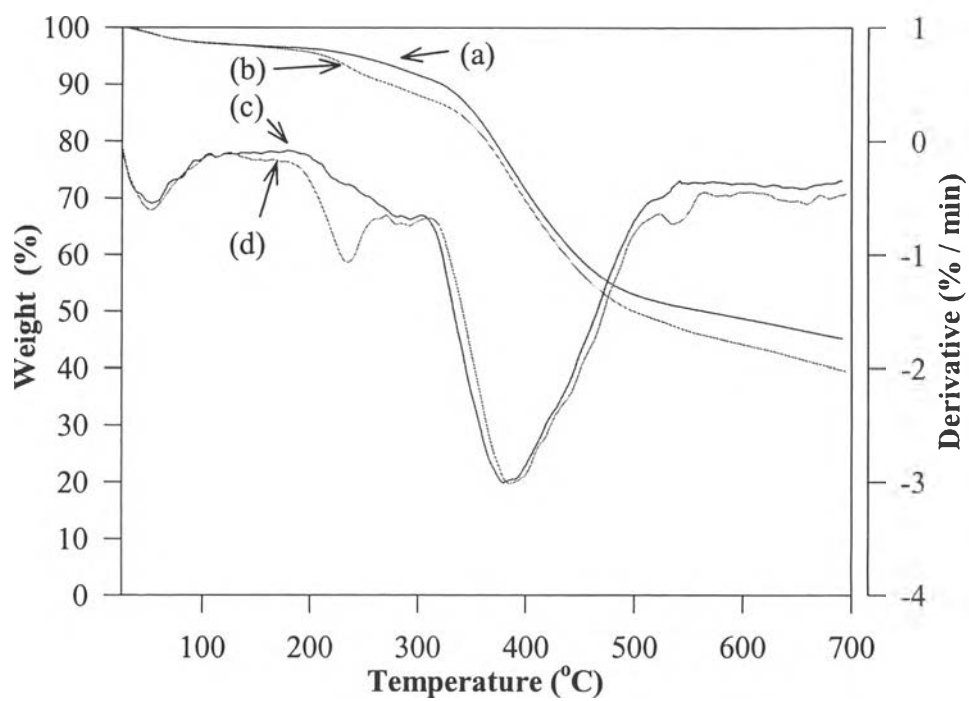


Figure 7 The TGA thermograms of: a) fresh PPy/B; and PPy/B after the exposure to the saturated acetone vapor in N₂ for 24 hours; and their derivatives c) and d), respectively.

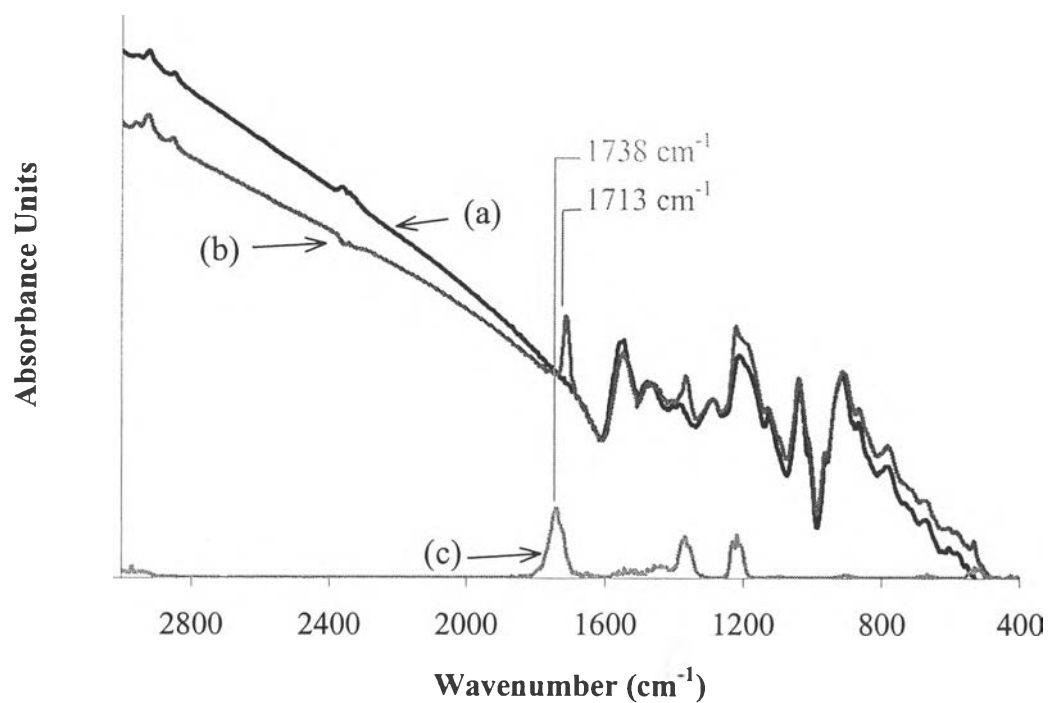


Figure 8 The FT-IR spectra of: a) fresh PPy/D; b) PPy/D after the exposure to the saturated acetone vapor in N₂ for 24 hours; and c) acetone vapor.

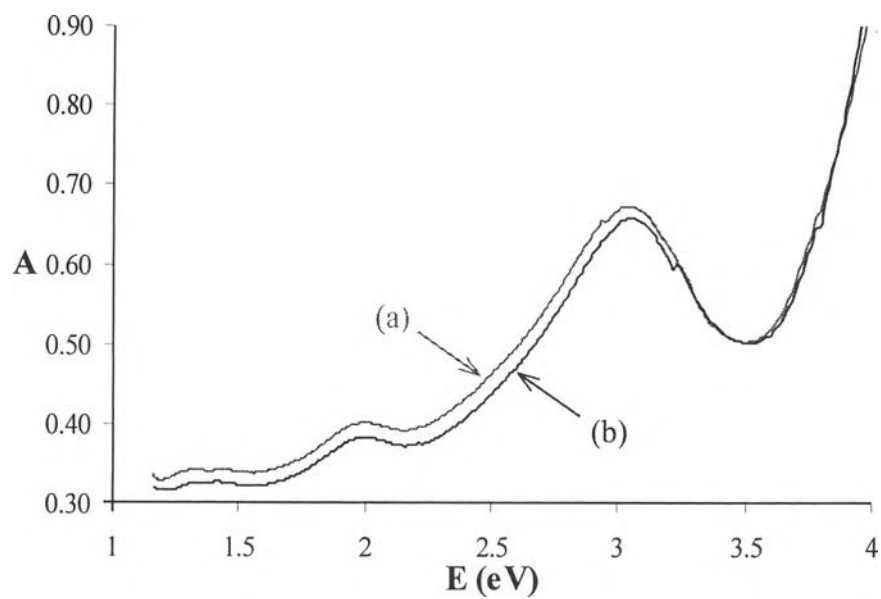


Figure 9 The visible spectra of a) the fresh PPy/B film, and b) the same film upon exposure to saturated acetone vapor.

5. Acknowledgements

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