CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of Synthesized Polyaniline

The polymerization of aniline was designed to be as simple as possible. The reaction can be summarized into a simple stoichiometric relation [63] in Figure 4.1. The polyemeraldine salt was first synthesized by the oxidation of aniline hydrochloride with ammonium peroxydisulfate in aqueous at room temperature. Then, the green precipitate of polyemeraldine salt was converted to blue powder of polyemeraldine base by ammonium hydroxide. The polyemeraldine base can be dissolved in organic solvent and blended with other polymers.

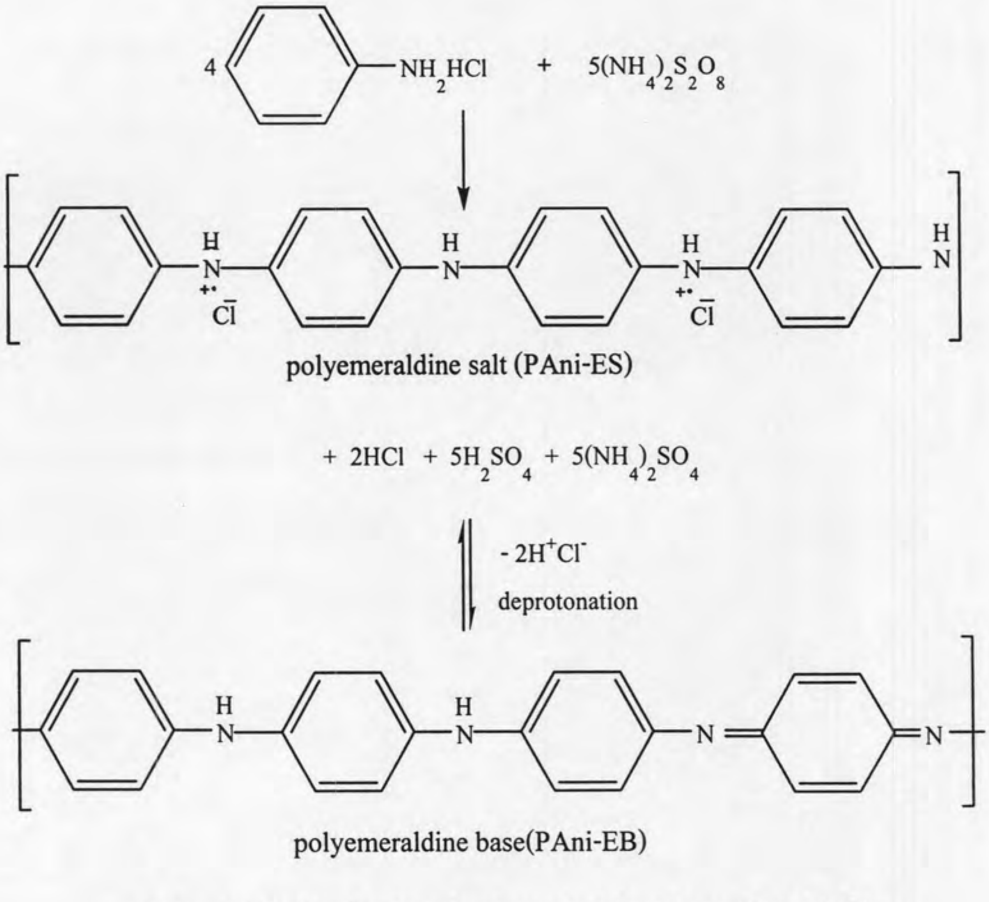

Figure 4.1 Synthesis of polyemeraldine base (PAni-EB).

The IR spectrum of synthesized PAni-EB was shown in Figure 4.2. The spectrum showed all peaks in good agreement with the characteristic peaks of PAni-EB reported by Sberveglieri [73]. All the peak locations, related to the chemical bonds, were tabulated in Table 4.1.

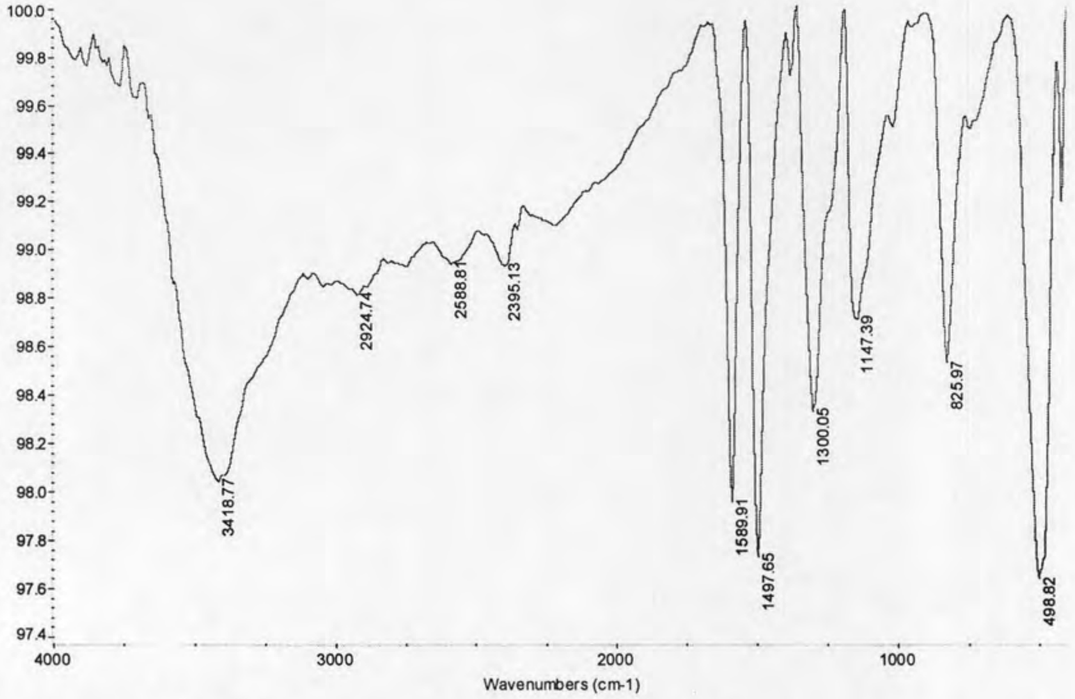

Figure 4.2 The IR spectrum of synthesized PAni-EB.

Table 4.1 The IR characteristic peaks of the synthesized PAni-EB

Wavenumber (cm^{-1})	Functional group
3418.77	N-H stretching of aromatic amine
1589.91	C=C stretching of quinoid imine
1497.66	C=C stretching of benzenoid diamine
1300.05	C-N-C stretching of a secondary of aromatic amine for both quinoid and benzenoid segments
1147.39	Vibration mode of quinoid ring
825.97	Out of plane bending of para-substitute of aromatic benzene ring

4.2 Citric Acid Doped Polyaniline Characterization

4.2.1 Fourier-Transform Infrared Spectrometer (FT-IR)

The supporting evidence of the protonation of PAni-EB could be observed in IR spectra. The IR absorption spectra of PAni-EB, PAni-EB doped with hydrochloric acid (PAni-HCl) and PAni-EB doped with citric acid (PAni-citric acid) were shown in Figure 4.3. Red shift of 1589.91, 1497.65 and 1147.39 cm^{-1} bands of PAni-EB (consistent with quinine and benzene ring deformation) to 1559.13, 1473.23 and 1112.69 cm^{-1} in PAni-HCl had influence from protonation at amine and imine nitrogens in PAni chain [74]. Moreover, the broad and intense bands at 1112.69 cm^{-1} in PAni-HCl illustrated a high degree off PAni doping by HCl [75]. These characteristic peaks indicated the doping of PAni-EB to a conductive form of PAni-ES by HCl doped. The IR spectrum of PAni-citric acid in Figure 4.3 (c) showed all peaks in good agreement with the characteristic peaks of PAni-HCl (Figure 4.3 (b)). This can conclude that PAni-EB was doped with citric acid to PAni-ES.

Apart from this, the citric acid doped polymer showed peak at 1715.54 cm^{-1} which could be the convolution of the carbonyl (–C=O) stretching band. Besides, the formation of carboxylate anion (-COO$^-$) stretching should be observed at 1575 cm^{-1} [42] but it seemed to overlap with the band 1572.14 cm^{-1} represented the quinoid ring stretching vibrations of PAni chain. However, the increasing of intensity at this band was observed in PAni-citric acid compared to PAni-HCl. The observation of -COO$^-$ counter ion confirmed the doping of PAni-EB by citric acid.

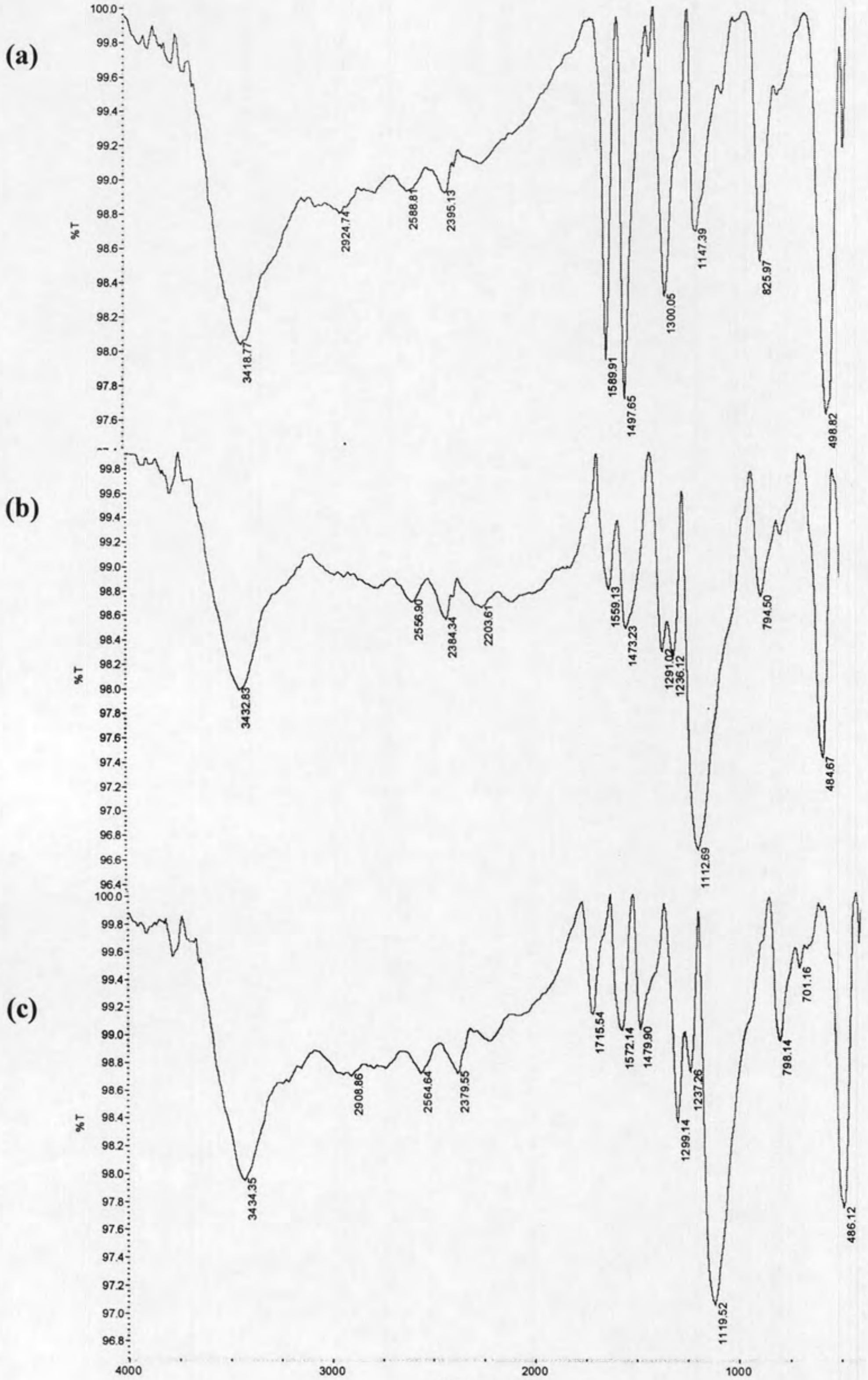

Figure 4.3 The IR spectra of (a) PAni-EB, (b) PAni-HCl, (c) PAni-citric acid.

4.2.2 Scanning Electron Microscope (SEM)

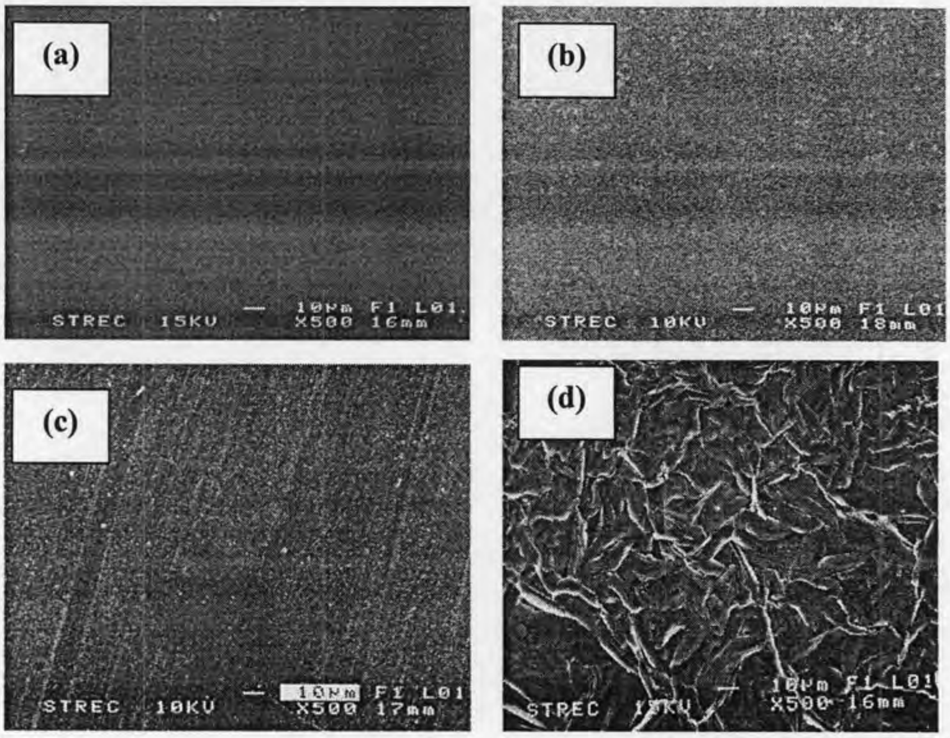

Figure 4.4 SEM of (a) PVA (b) PVA-citric acid (c) PAni-EB-PVA (d) PAni-PVA blended film.

In order to investigate the above assumption in more detail, morphology of the polymer films were characterized by SEM. The morphology of PVA film shown in Figure 4.4 (a) was smooth and homogeneous. The morphology of PVA mixed citric acid shown in Figure 4.4 (b) was quite similar to PVA film but it was more flexible. It could be caused by a cross-linked of PVA by citric acid. Figure 4.4 (c) showed the morphology of PVA mixed PAni-EB in which evenly distribution of PAni-EB particles in PVA film was observed. It indicated a good blended between PVA and PAni. Moreover, the color of film was blue, indicating the nonconductive form of PAni. Figure 4.4 (d) showed the morphology of the PAni-EB mixed PVA and citric acid. The morphology of film was different from other films and the color was green indicating the conductive form of PAni. It confirmed that citric acid was served the function of cross-linking for PVA and doping for PAni. Moreover, PAni aggregates were distributed homogeneously in the blended film. Concisely, tthe additional of PVA facilitates the fabrication of polyaniline film.

4.2.3 Conductivity of Polymer Films

In Figure 4.5, when exposed to ammonia gas, the conductance of PVA, PVA-citric acid and PVA-PAni-EB films were not changed while the conductance of PVA-PAni-EB-citric acid film (PAni- PVA blended film) was vastly increased. This indicated the change of film conductance did not depend on the adding of PVA but on citric acid dopant. The conductivity of the PAni- PVA blended film also correlated with the IR characterization of citric acid doped PAni.

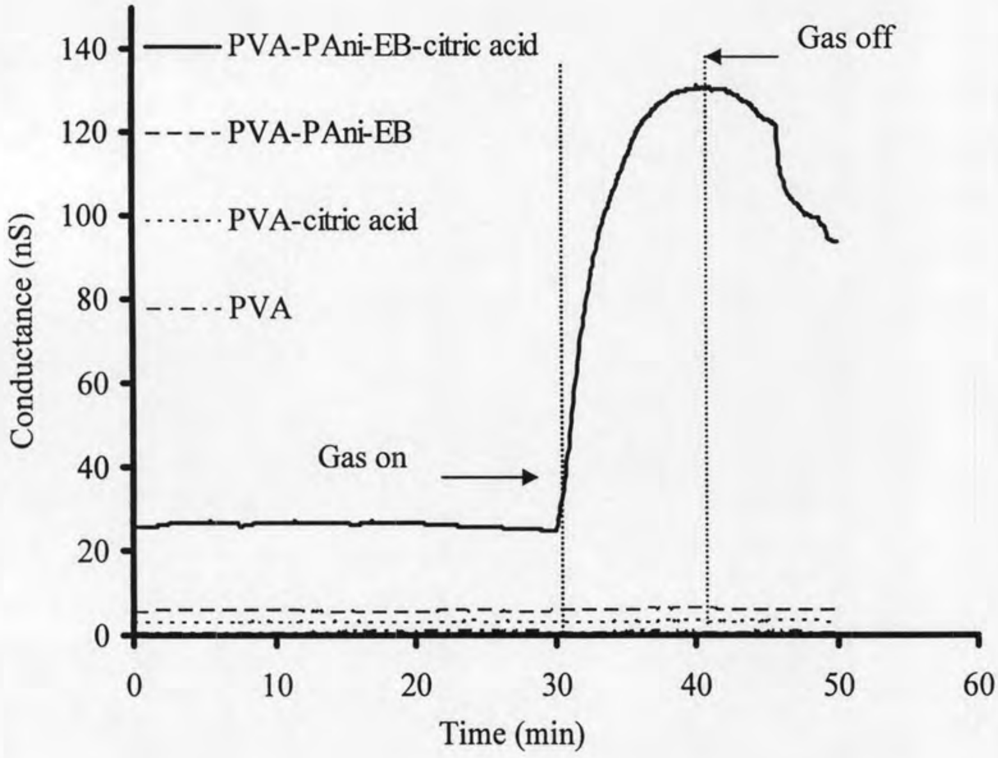

Figure 4.5 Conductance of polymer films on the exposure of 90 ppm ammonia gas.

The conductance of PAni-PVA blended film increased when it exposed to ammonia gas. This response exhibited an inverse nature comparing with other acid doped polyaniline conductance reported earlier [29]. An unusual response in magnitude and sign observed in the present case illustrated a significant role of the incorporated citric acid in sensing mechanism. In conventional PAni doped with HA type acid such as HCl, the sensing mechanism was governed by the protonation/deprotonation phenomena. The reversibility in such PAni has been explained on the basic of the formation of energetically more favorable ammonium ion (NH_4^+) at N^+-H adsorption centre leading to a rise in the resistance on exposure to ammonia [28], hence, the conductance decreased. The same ammonium ion decomposed back into ammonia leaving out the proton on the adsorption site in the air environment. As the responses observed in the present case were in contrast with that of the conventional trend. The sensing behavior was likely to involve a different process, especially interaction of ammonia with citric acid. Although, the exact mechanism of sensing was not very clear at this stage, the increasing of conductance on exposure to ammonia could be probably the interaction of NH_3 with the dopant citric acid. For citric acid doped PAni, ammonia could attack two adsorption sites. The first site was the protonated PAni chain at N^+-H. Another site was the protonated citric acid at carboxylic sites. The latter protonation created $-COO^-$ anion in the polymeric chain simultaneously leaving one site free for conduction, hence, the conductance increased. In overall, the conductance increase of PAni-PVA blended film imparted from the domination of NH_3 attraction at carboxylic site when exposed to NH_3.

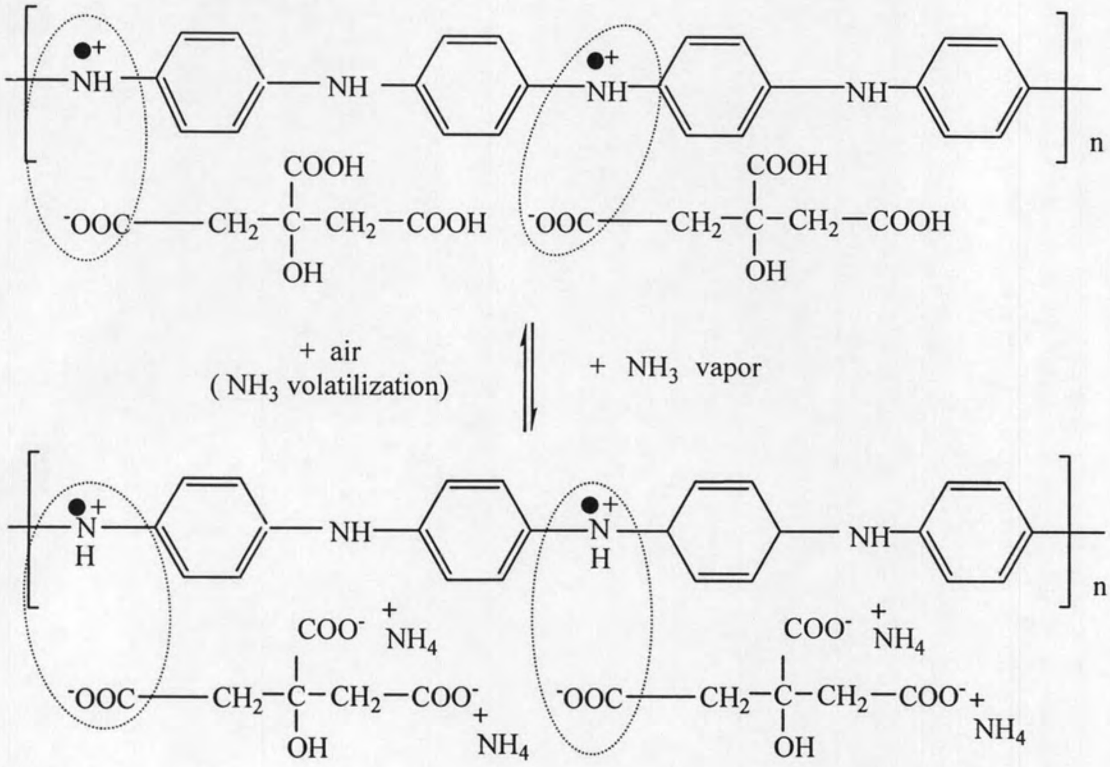

Figure 4.6 Proposed mechanism of PAni-PVA blended film for ammonia sensing

4.3 Ammonia Sensing

4.3.1 Effect of Citric Acid Dopant

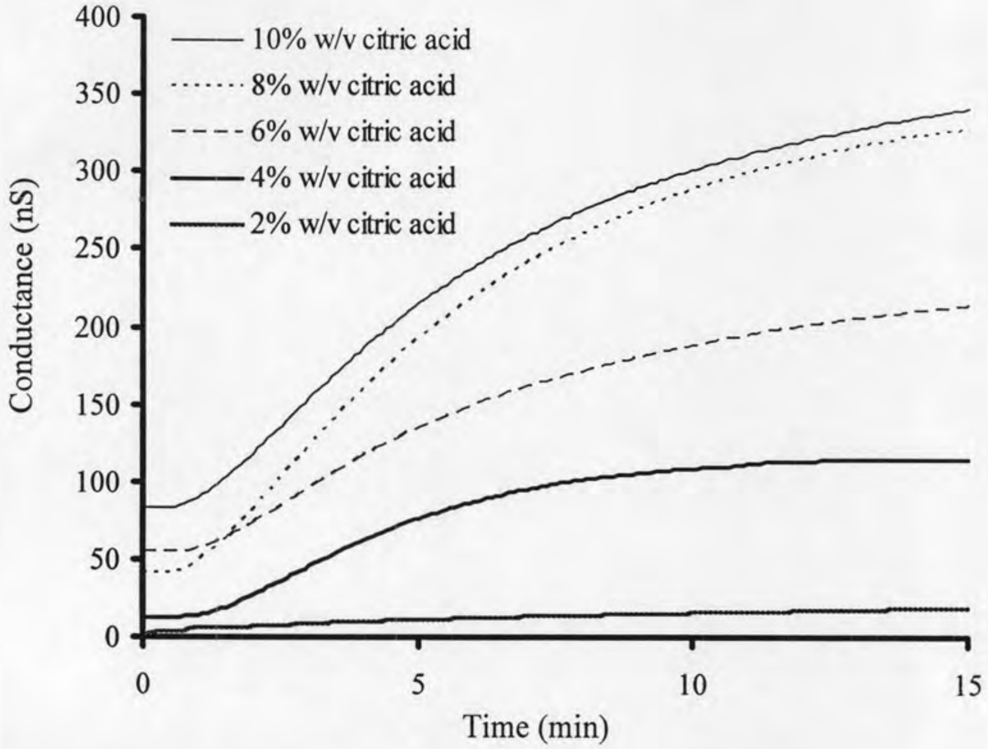

Figure 4.7 Conductance of PAni-PVA blended films with different quantities of citric acid when exposed to 90 ppm of ammonia gas.

Figure 4.7 showed the conductance of PAni-PVA blended films on exposure to 90 ppm ammonia gas at 2%, 4%, 6%, 8% and 10% w/v of citric acid doped. The change of conductance was proportional to the ratio of citric acid dopant. The film with 2% w/v of citric acid doped was presented a slight change of conductance. Therefore, this film was not sensitive enough for ammonia sensing. The films with 8% and 10% w/v of citric acid doped were resulted a great change of conductance. Although high sensitivity for ammonia sensing was observed, it could not be measured reliably with the set-up because the digital multimeter has a limitation of conductance detection. Moreover, the equilibration time was long and unsuitable for continuous sensing. Therefore, lower percent of citric acid was chosen. The result of 4% and 6% w/v of citric acid were shown a satisfactory change of conductance.

However, equilibration time of 4% w/v was shorter than 6% w/v of citric acid. Therefore, the optimized doping was 4% w/v of citric acid for good sensitivity and fast ammonia sensing.

4.3.2 Effect of Film Thickness

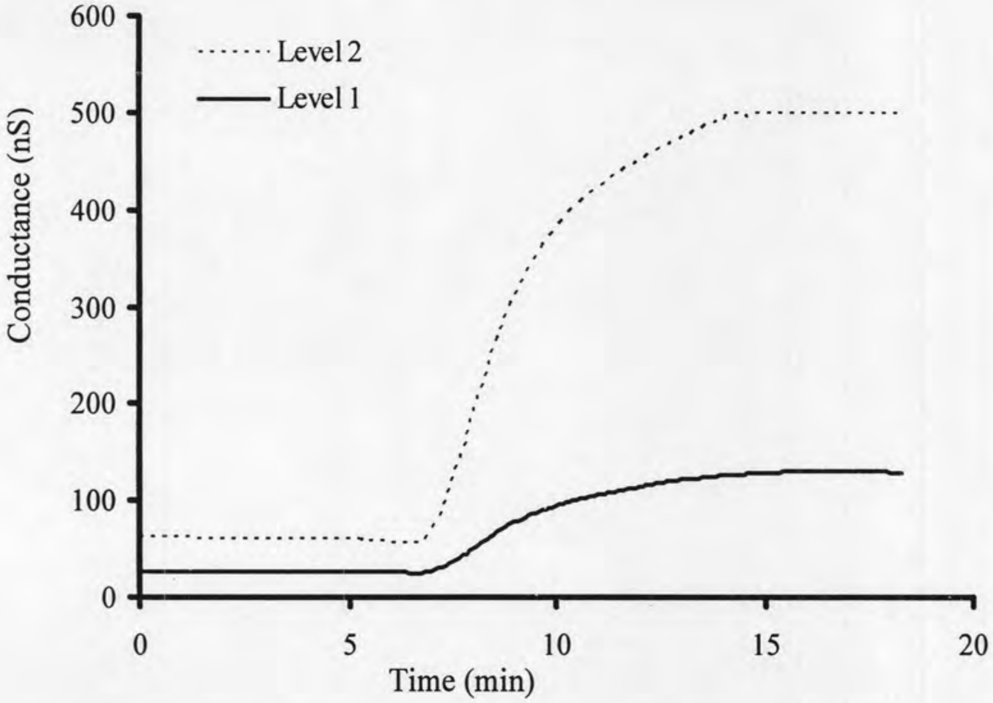

Figure 4.8 Effect of film thickness on ammonia sensing.

The thickness of the film was adjusted by the change of gate height in casting unit. The level 1 of gate height gave the film thickness of 0.15-0.20 mm and level 2 gave the film thickness of 0.25-0.30 mm. Figure 4.8 showed the conductance of PAni-PVA blended films on exposure to 90 ppm of ammonia gas at different film thickness. As expected, the conductance of film was increased with increasing of film thickness because of more sites for conduction, hence, the conductance increased. Although the level 2 resulted a great change of conductance, hence, high sensitivity for ammonia sensing, it could not be measured reliably with the set-up and the equilibration time was more than 15 minutes which is too long and unfavorable for reversible sensing system. The level 1 showed a change of conductance at satisfy sensitivity and responding time. Therefore, the level 1 of film thickness was selected for good sensitivity and fast response. Although there is a variation of film thickness in level 1, it did not significantly affect the conductance change of the film. The response of various film thicknesses were resulted a good precision as shown in Table 4.2. %RSD of the response was less than 5.1% at 10 ppm and 3.3% at 100 ppm which is in an acceptable range of AOAC peer verified methods (7.3% at 10 ppm and 5.3% at 100 ppm).

Table 4.2 Conductance of PAni-PVA blended films at level 1 of film thickness.

Thickness (mm)	**%RSD of Conductance, ΔC (nS)**	
	NH_3 10 ppm (n=3)	**NH_3 100 ppm (n=3)**
0.15 ± 0.01	5.04	3.29
0.17 ± 0.01	1.91	0.71
0.19 ± 0.01	5.07	1.37

4.3.3 Effect of Temperature and Humidity

The response of PAni-PVA blended films at different temperature and humidity were shown in Figure 4.9. The change of conductance at low temperature and high humidity was higher than that at high temperature and low humidity. The enhancement of conductivity would be resulted from the sorption of water molecule to PAni backbone, PVA backbone or donor molecules [71] and kinetic energy of ammonia molecule in the system. The water molecule favored the absorption of ammonia gas into the polymer films and the ammonia molecules have low kinetic energy at low temperature, hence unflavored ammonia molecule in gas phase. Therefore, more ammonia molecules adsorbed on the films at low temperature and high humidity, hence, increase the sensing response of the blended film.

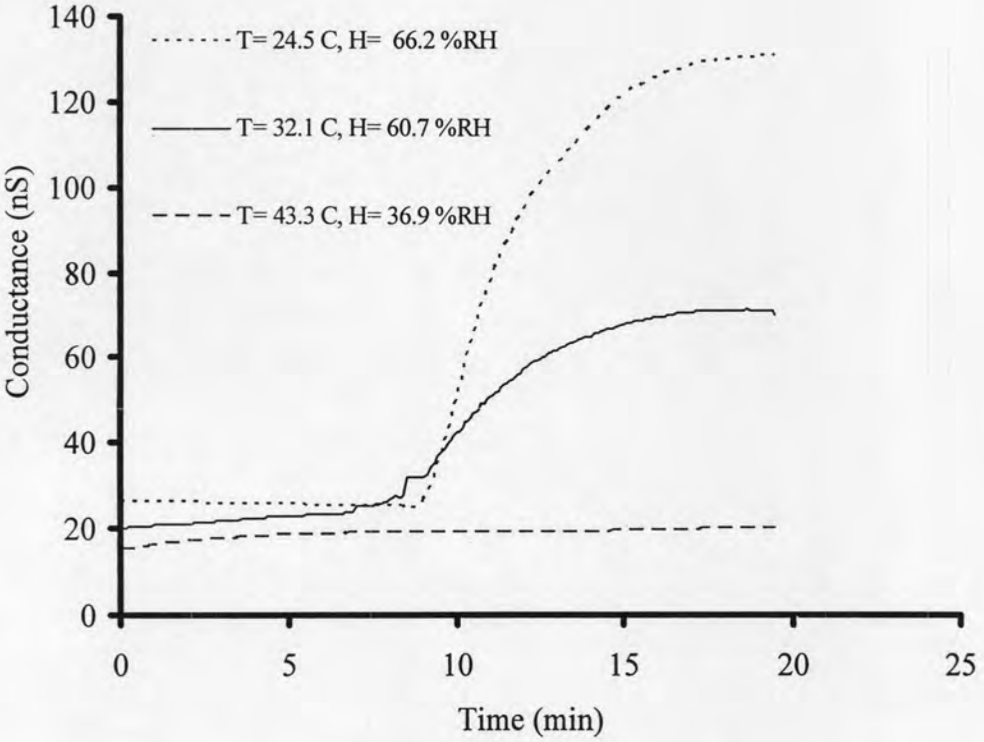

Figure 4.9 Effect of temperature and humidity on conductivity response to ammonia.

4.3.4 Response Time and Recovery Time

From Figure 4.7 in section 4.3.1, the equilibration time of PAni-PVA blended film when exposed to ammonia was approximately 10 minutes, therefore, the response time was set to 10 minutes for ammonia sensing. Figure 4.10 showed the conductance of PAni-PVA blended film for ammonia gas exposure at 10 ppm and 90 ppm. Both responses of film reached the equilibrium within 10 minutes. Therefore, the response time was set at 10 minutes. When the ammonia was turned off for film recovery, the conductance was decreased almost to the baseline after 20 minutes. The mechanism in this case was explained by Nicolas-Debarnot [29]. This mechanism indicated PAni-PVA blended film for ammonia sensing would be reversible and the recovery time was set at 20 minutes. In comparison to other sensors, PAni-PVA blended film was beneficial the regeneration of the sensor which is better than polypyrrole [33] and polyaniline sensors based on surface plasmon resonance [76] which cannot be regenerated after exposing over 10 ppm of ammonia gas. Moreover, this PAni-PVA blended sensor was in film configuration which can prepare easier than pellet form as reported by Prasad et.al [77]. In addition, instrumental design was simple and easily operated.

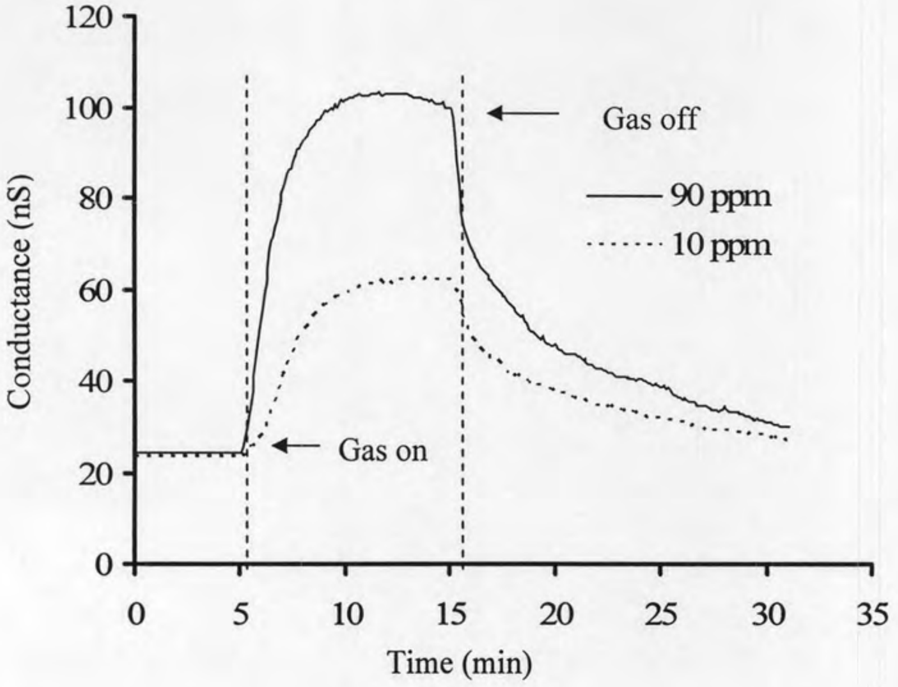

Figure 4.10 Response time and recovery time of PAni-PVA blended films.

However, the recovery of film was not completely to an initial state due to chemisorbed ammonia in PAni-PVA blended film. Increasing concentrations leaded to increased competition for sensing sites and some amount of irreversibility in desorption. The optimized response time of 10 minutes and recovery time of 20 minutes were chosen to cover the range of working ammonia concentration and for shortly and effectively repeating ammonia sensing.

4.3.5 Repeatability

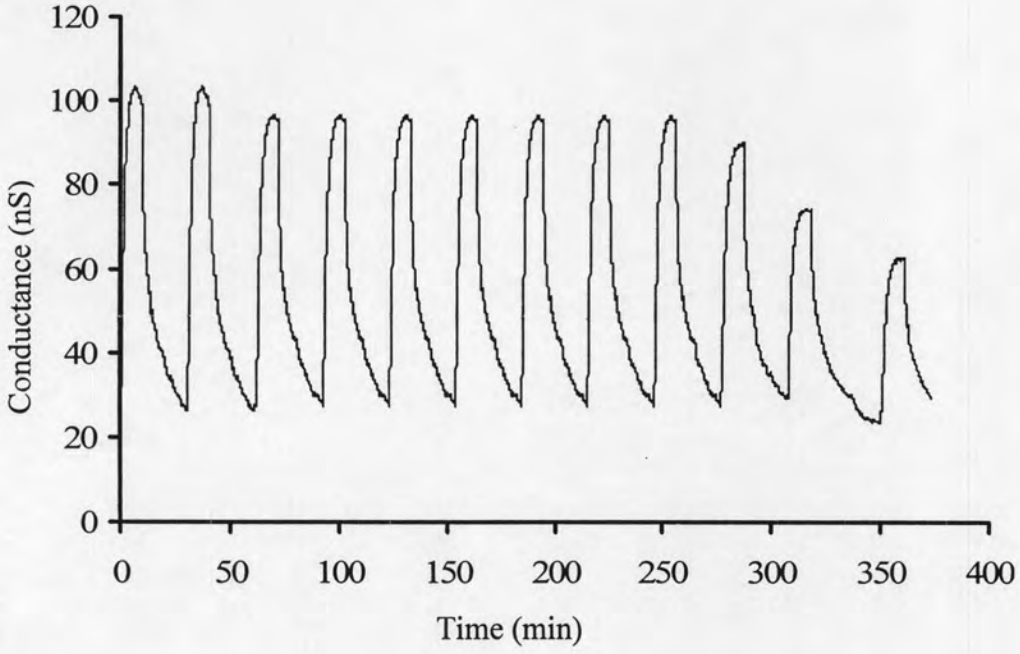

Figure 4.11 Response of PAni-PVA blended film when repeatedly exposed to ammonia gas.

Figure 4.11 showed the response of PAni-PVA blended film when repeatedly exposed to ammonia gas. The response of the film was resulted a similar value for 9 cycles. After 9 cycles, the conductances were decreased. This might caused by the increasing of protonation of ammonia at N^+-H of polymer chain rather than at carboxylic group of citric acid. Since the proposed mechanism of the PAni-PVA blended film was dominated by the deprotonation at carboxylic group of citric acid, the raising of deprotonation at N^+-H of polymer chain would lead to a decrease of overall conductance.

Table 4.3 Repeatability of PAni-PVA blended film when exposed to various ammonia concentrations

Cycle	**Change of conductance, ΔC (nS)**			
	10 ppm	**30 ppm**	**60 ppm**	**90 ppm**
cycle 1	15.40	53.20	128.00	187.00
cycle 2	16.10	53.20	127.00	185.00
cycle 3	15.20	53.50	126.00	182.00
cycle 4	15.20	52.90	127.50	181.00
cycle 5	15.30	53.20	124.00	183.00
cycle 6	15.90	53.50	125.00	179.00
cycle 7	15.70	55.30	125.50	176.00
cycle 8	16.20	53.60	125.00	177.00
cycle 9	14.90	54.30	124.00	173.00
average	15.54±0.45	53.63±1.38	125.78±1.16	180.33±2.50
%RSD	2.90	1.38	1.16	2.50

Table 4.3 summarized the repeatability of PAni-PVA blended film when continuously exposed to ammonia gas in the range of 10 – 100 ppm. %RSD of the conductivity response was ranged from 1.16% to 2.90%. It indicated a good precision of this sensor recommended by AOAC Peer Verified Methods (5.3% at 100 ppm and 7.3% at 10 ppm).

4.3.6 Linearity

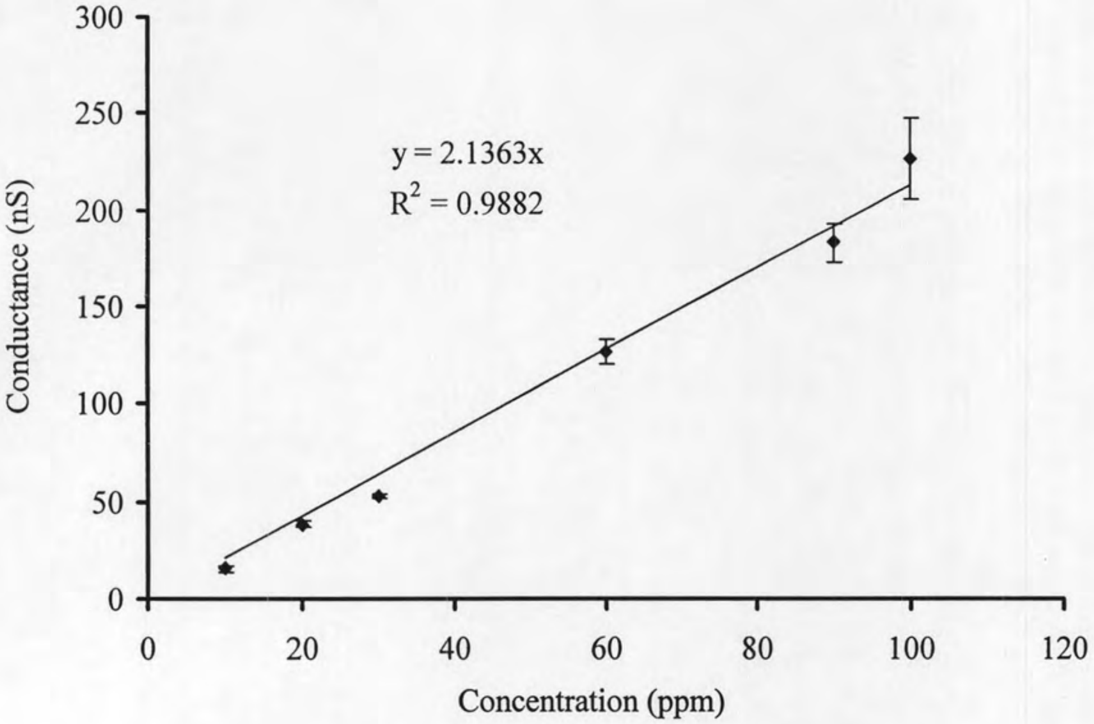

Figure 4.12 Conductance of PAni-PVA blended film with 4% citric acid when exposed to ammonia gas.

The linearity of the PAni-PVA blended sensor was studied in the concentration range covered the recommended threshold limit value for human exposure [78]. Figure 4.10 showed the change of the conductance of PAni-PVA blended films on exposure to ammonia gas in range of 10 to 100 ppm. The linear fit showed a correlation coefficient of 0.9882. This suggested that the PAni-PVA blended film sensor can be reliably used to detect ammonia concentrations in this range.