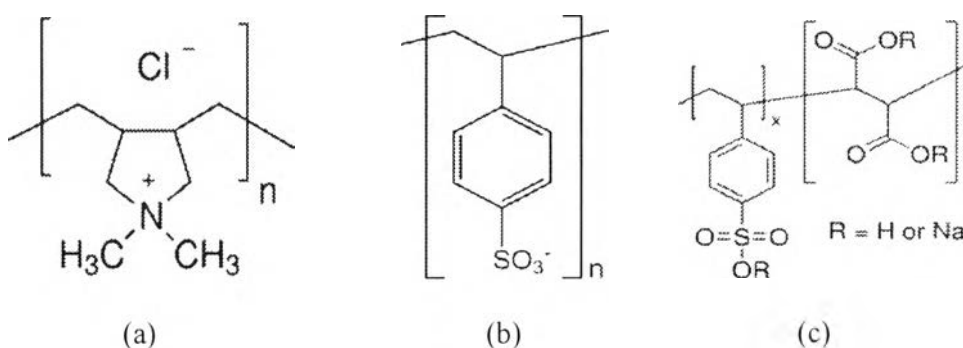


## CHAPTER VI RESULT AND DISCUSSION

### 4.1 Interfacial Polymerization Polyaniline



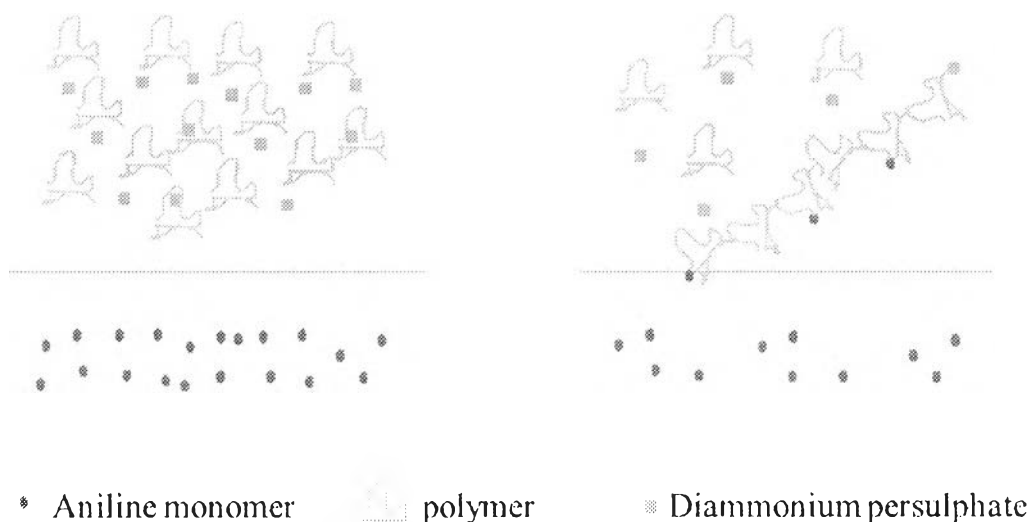
**Figure 4.1** Structure of polyelectrolyte;

- (a) Poly(diallyldimethylammonium chloride) (PDADMAC),
- (b) Poly(sodium 4-styrenesulfonate) (PSS) and
- (c) Poly(4-styrenesulfonic acid-co-maleic acid) (CoPSS).

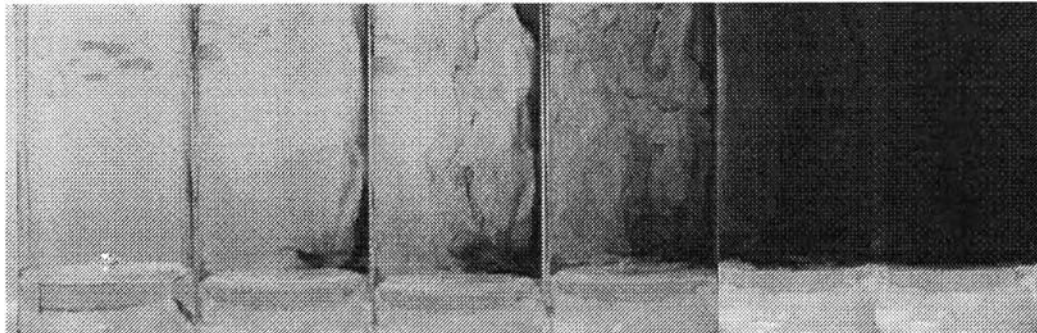
Polyelectrolytes are polymers which possess either positive or negative charge in water. There are two kinds of polyelectrolytes, weak and strong polyelectrolyte. Weak polyelectrolyte can be partially charged in solution whereas strong polyelectrolyte can dissociate completely. Polyelectrolytes shown in figure 4.1 (A and B) are strong polyelectrolytes that were used in this work to make primer before film assembly on substrate and to cap other polymers having charges by electrostatic interaction.

There are many methods available to polymerize aniline into polyaniline. In this work, the interfacial polymerization was used to overcome the limitation of polyaniline that is insoluble in water. PSS carrying negative charges, were used as an ionic dopant, template and capping agent to enhance solubility and disperse polyaniline in water, following figure 4.2. Kuo and Wen (2008) describes in chapter 2 reported that PSS helps to minimize the repulsive electrostatic interaction between the equally charged functional groups of  $-SO_3H$  in polymer backbone. Interfacial polymerization consisted of two phases which are organic and aqueous phases. Organic phase contain the aniline monomers dissolved in chloroform. Aqueous phase has diammonium peroxodisulphate (APS) as strong oxidizing agent or initiator and PSS or CoPSS 3:1 or CoPSS 1:1 as capping agent.

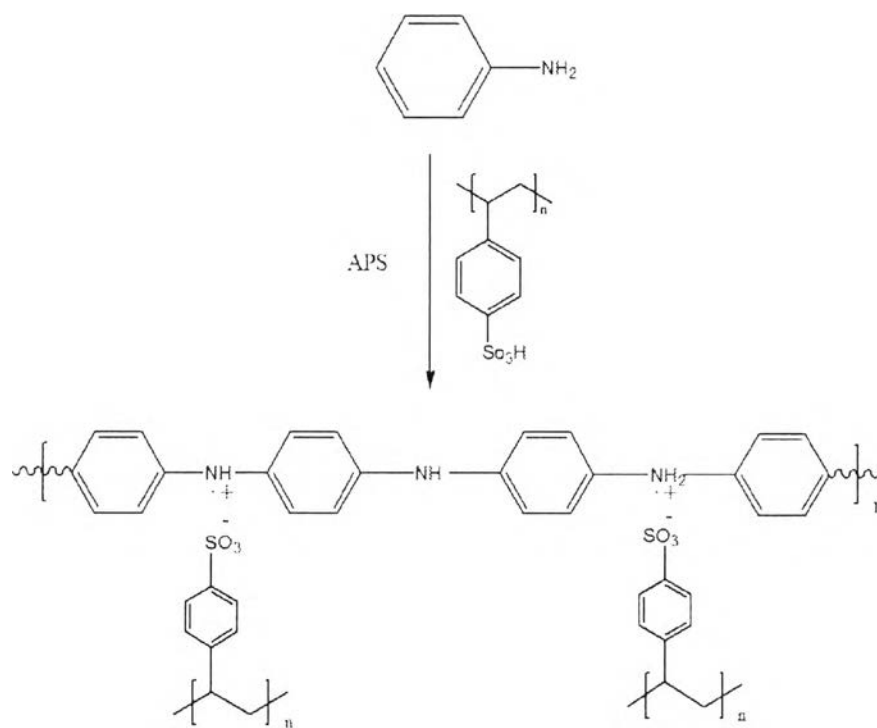
Aniline monomers are protonated at interface by PSS, CoPSS 3:1 or CoPSS 1:1, capped aniline monomer and lead to disperse in aqueous phase. Water soluble polyaniline (PANI) begins polymerization at interface where can see blue color and after 24 hours the color will disperse and change to dark green in aqueous phase shown in figure 4.3 and structure of electrostatic interaction PANI-PSS shown in figure 4.4. Moreover, it has  $\pi$ - $\pi$  interaction between benzene ring of aniline and capping agent.



**Figure 4.2** Schematic of interfacial polymerization of polyaniline.



**Figure 4.3** Interfacial polymerization polyaniline.

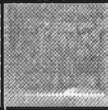
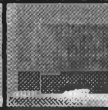
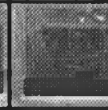
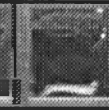
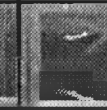
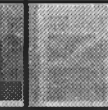
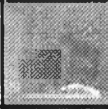
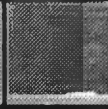
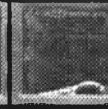
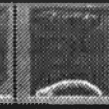
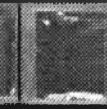
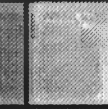


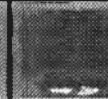

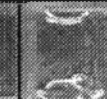
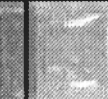


**Figure 4.4** PANI polymerization.

## 4.2 Effect of APS Concentration on PANI Polymerization

In this experiment, ratio of organic phase to aqueous phase is 30:100. First, we have to find the optimal condition which is the APS concentration that gives the highest yield PANI. We synthesized PANI with various concentrations of APS at 15 mM of each capping agent (PSS, CoPSS 3:1 and CoPSS 1:1) and 10 mM aniline monomer. They indicated that APS concentration and three capping agents have effect on PANI. Not only different concentration of APS produces different green color PANI but also different capping agent. The different color of PANI is shown in table 4.1 (dilute 15 times) and characterized with UV-vis spectrum in figure 4.5.

**Table 4.1** PANI solutions in presence of various capping agents and APS concentrations

APS concentration Capping agent	1 mM	2 mM	3 mM	4 mM	5 mM	10 mM
PSS						
CoPSS (3:1)						
CoPSS (1:1)						

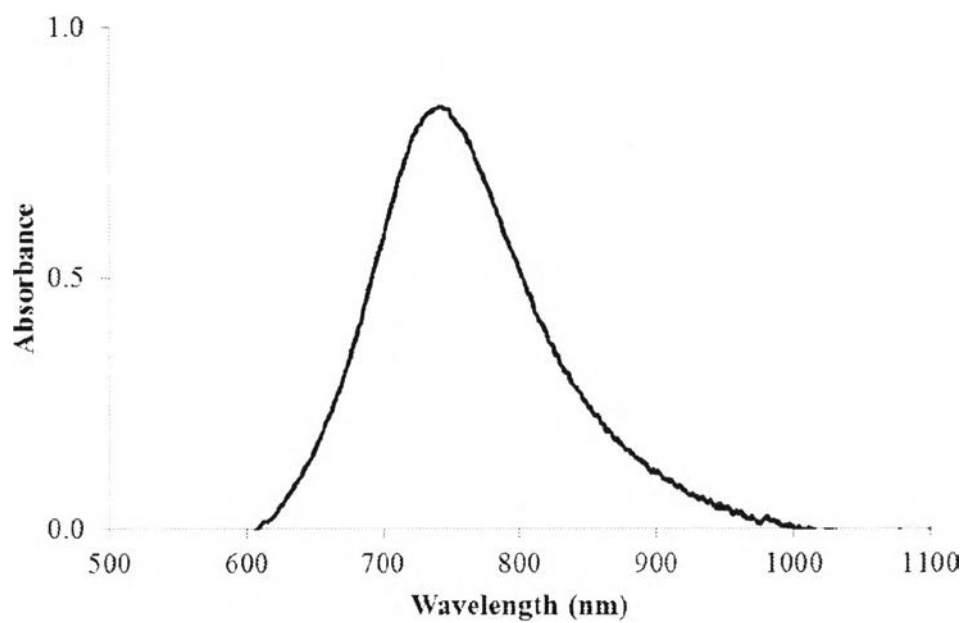


Figure 4.5 UV-vis spectra of polyaniline.

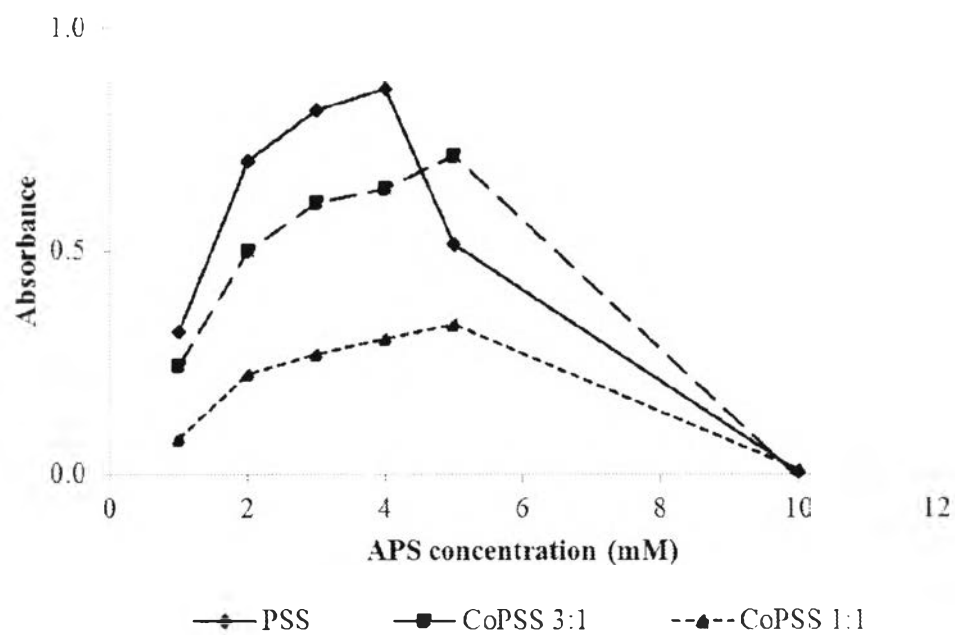


Figure 4.6 Plot of PANI absorbance with different capping agent and various APS concentrations.

We used UV-vis spectra to make the new plot shown in figure 4.6. For example, spectrum in figure 4.5 at 740 nm is the highest absorbance of peak so we made the new plot from this value with referred the highest absorbance as the yield.

At same PSS concentration (15mM), different APS concentrations gave different highest absorbance or yield of PANI. At 1-5 mM APS can produce PANI because they had green peak around 740 nm but 10 mM APS had no peak and produce PANI. Intensity of green color or yield PANI can observe at the highest absorbance of each peak from UV-vis spectrum. It showed that 1-4 mM APS had darker solution, respectively, because PSS can protonate to cap aniline monomer and allow PANI-PSS to disperse in water. Concentrations more than 4 mM APS rapidly decreased absorbance because they are more active than capping agents, PSS cannot cap aniline monomer to disperse in water. The optimal APS concentration is 4 mM because it gives the highest yield or absorbance.















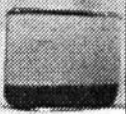
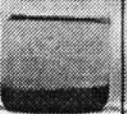
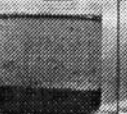
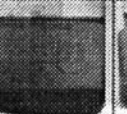
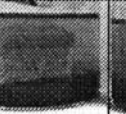


Different capping gives different yield and different optimal APS concentration indicated in figure 4.6. For CoPSS 3:1 and CoPSS 1:1, 5 mM APS is the highest yield so different capping or ratio of sulfonate to maleic group has effected on yield of PANI.

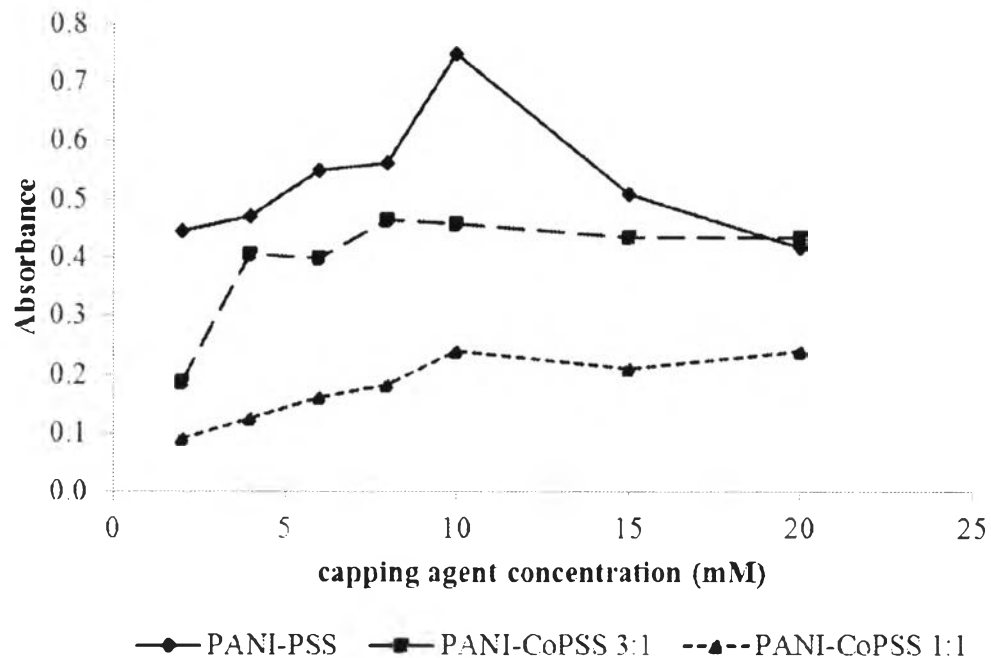
APS concentrations and three kinds of polymer with different ratio sulfonate to maleic group have effect on PANI polymerization. Figure 4.6 showed that PSS had highest absorbance or yield at 4 mM while both CoPSS 3:1 and 1:1 had at 5 mM. The 100 percent sulfonate group, PSS, can easily protonate and cap aniline monomer to polymerize and disperse in water. 75 percent and 50 percent sulfonate group, CoPSS 3:1 and 1:1 respectively, can cap aniline to polymerize also but they have to use more concentration of APS to polymerize because they have competition between sulfonate and maleic group so they have to have more APS concentration to activate sulfonate group for protonation at interface. Therefore, CoPSS had highest yield at higher concentration than PSS. At highest yield of each capping, PSS had highest absorbance and then CoPSS 3:1 and 1:1, respectively. This figure indicated that the more sulfonate group has the more yield has.

In this work, we fixed APS concentration at 3 mM because next, we wanted to study the effect of three types of capping agent on PANI polymerization. We didn't use 4 mM APS because after 4 mM APS of PANI-PSS rapidly decreased so we wanted to make sure that our solution didn't have excess APS .

### 4.3 Effect of Capping Concentration on PANI Polymerization

**Table 4.2** PANI solution at 3 mM APS with various capping concentration

capping \ Conc.	Conc.						
	2 mM	4 mM	6 mM	8 mM	10 mM	15 mM	20 mM
PSS							
CoPSS 3:1							
CoPSS 1:1							



**Figure 4.7** Plot of PANI absorbance with various capping agent concentrations at 3 mM APS.



PANI was polymerized with three kinds of capping agent at 3 mM APS as showed in table 4.2. PANI capped PSS (PANI-PSS) solution, can be dispersed and stabilized in water because of 100 percent sulfonate group of capping. From UV-vis spectrum, the new plot indicated that PANI-PSS had the highest yield at 10 mM. PSS concentration less than 10 mM has lower sulfonate group to cap aniline monomer to polymerize. For PSS concentration higher than 10 mM had lower absorbance also because of PSS viscosity.

Although percent sulfonate group decreases, PANI can be polymerized but they gave different absorbance or yield compared with PANI-PSS at same wavelength. It meant that PANI polymerization depends on percent sulfonate group of capping agent. PANI-CoPSS 3:1, 75 percent sulfonate, can disperse in water but lowest concentration, 2 mM. It is not enough charge to cap aniline monomer to polymerize and disperse in water so it was precipitate. The highest yield of PANI-CoPSS 3:1 is 8 mM.

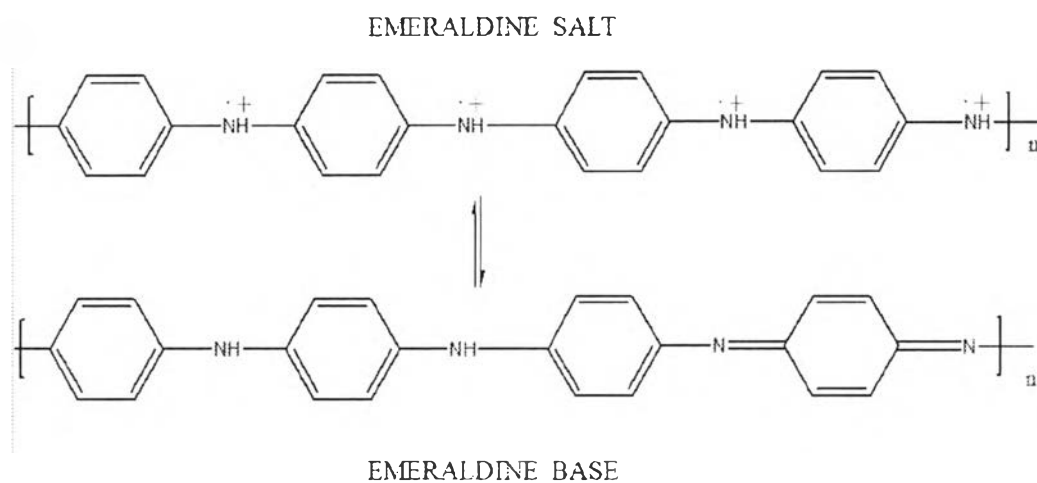
CoPSS 1:1, 50 percent sulfonate, can polymerize PANI also but all solutions that show in table 2 cannot disperse in water and become precipitate. The highest yield of PANI-CoPSS 1:1 was 10 mM. So these experiments indicated that yield, dispersion and stabilization of PANI decrease when percent sulfonate and concentration of capping agent decrease. In figure 4.7 showed that PANI-PSS had the highest absorbance and then PANI-CoPSS 3:1 and CoPSS 1:1, respectively, because of percent sulfonate of capping agent. It could imply that PSS is the best condition to synthesize PANI.

#### 4.4 Effect of pH on PANI Color

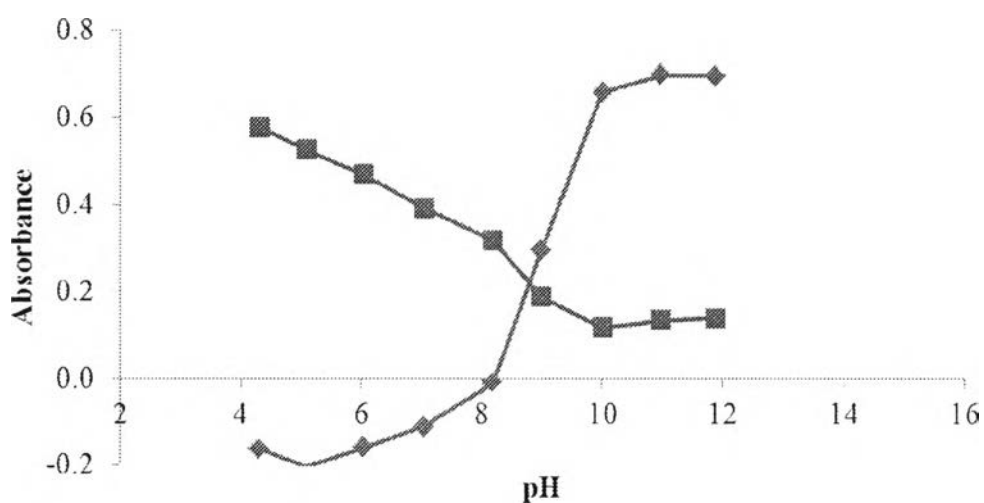
**Table 4.3** PANI in different pH

PANI \ pH	4.3	5.08	6.03	7.03	8.19	8.99	10.01	10.89	11.88
PSS									
CoPSS 3:1									
CoPSS 1:1									

PANI prepared from interfacial polymerization in this work was in its acidic form. We adjusted PANI to pH 7 before mixing in different pH of phosphate buffer because we wanted to have same dilution of PANI. PANI can change color with pH shown in table 4.3. It indicated that PANI sensitive to pH so it can use as an optical sensor either to detect acidic or basic environments. Several papers have reported the wavelength shift of PANI. PANI in form of conducting polymer or emeraldine salt becomes emeraldine base or non-conducting following figure 4.8. When pH increases, peak shifts to lower wavelength or blue shift that relates to benzenoid and quinoid rems around 350 and 550 nm, respectively. It is believed that high pH is lower conductive polymer or non-conducting because conjugate double bond or  $\pi$ - $\pi^*$  transition is shorter.



**Figure 4.8** PANI in form of emeraldine salt and base.



**Figure 4.9** Plot of PANI-PSS absorbance at difference pH.

The highest absorbance of each pH PANI-PSS spectrum at 534.294 and 795.550 nm plot with pH shown in figure 4.9. Figure 4.9-4.11 indicated that pKa of PANI-PSS, PANI-CoPSS 3:1 and 1:1 was 8.8, 8.6 and 8.2, respectively, shown in figure 4.9-4.11. pKa decreases when sulfanoate group decreases so PANI-CoPSS 1:1 has the fastest sensitivity because of the lowest pKa

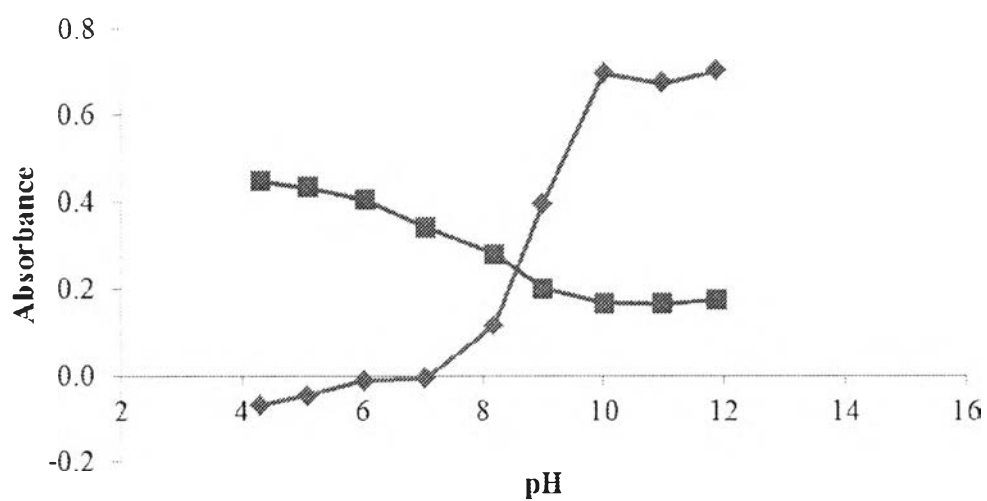


Figure 4.10 Plot of PANI-CoPSS 3:1 absorbance at difference pH.

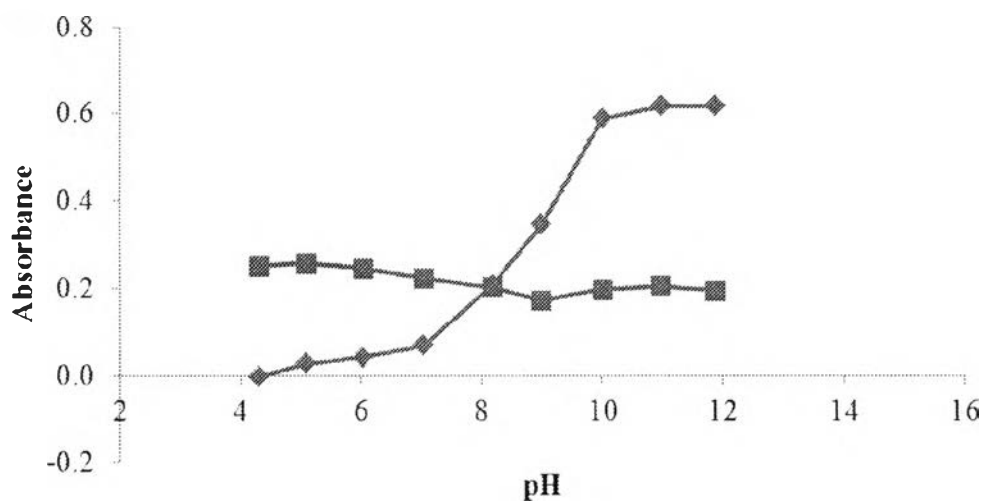
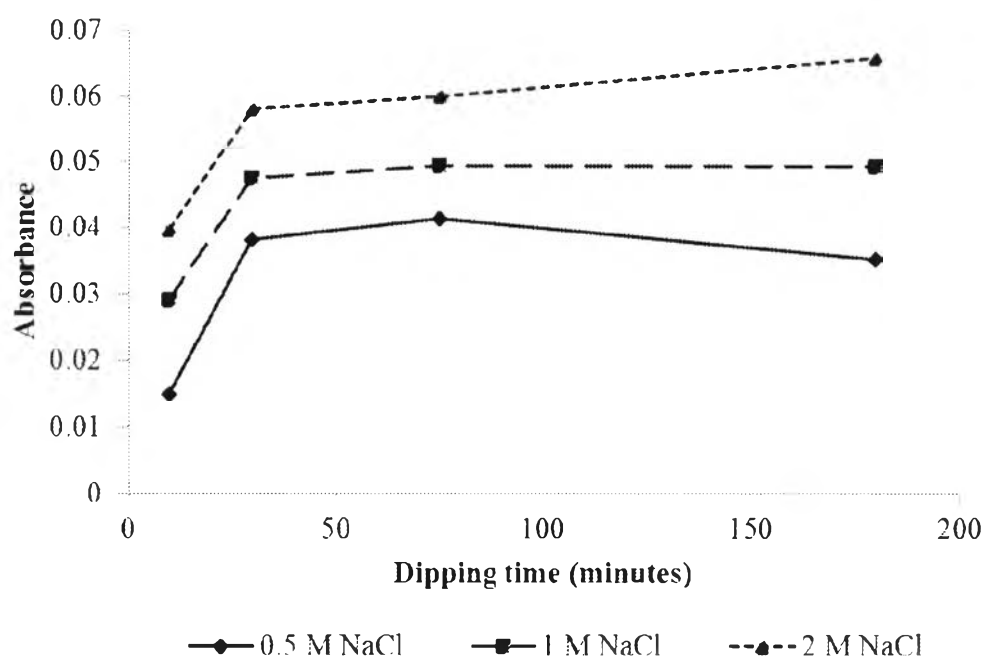


Figure 4.11 Plot of PANI-CoPSS 1:1 absorbance at difference pH.

#### 4.5 Effect of pH, Salt and Dipping Time on PANI Monolayer

We studied effect of pH, dipping time and salt on PANI monolayer to investigate the absorbance that PANI can stick on the substrate. All substrates are cleaned with HOT AMMONIA to provide charge on it and fabricated primer which is PDAD and PSS 5 layer by layer to make sure and provide hydrophilic that PANI solution can stick on substrate.



**Figure 4.12** Monolayer of PANI-PSS at pH 4.

At pH 4, figure 4.12, PANI-PSS rapidly adsorbed to high absorbance at 30 minutes and then increased a little bit. It is believed that monolayer was saturated with PANI at 75 minutes because it had steady absorbance from 30 to 75 minutes. In this figure showed that absorbance increased with NaCl concentration because NaCl can make film growth and screen repulsion of charge.

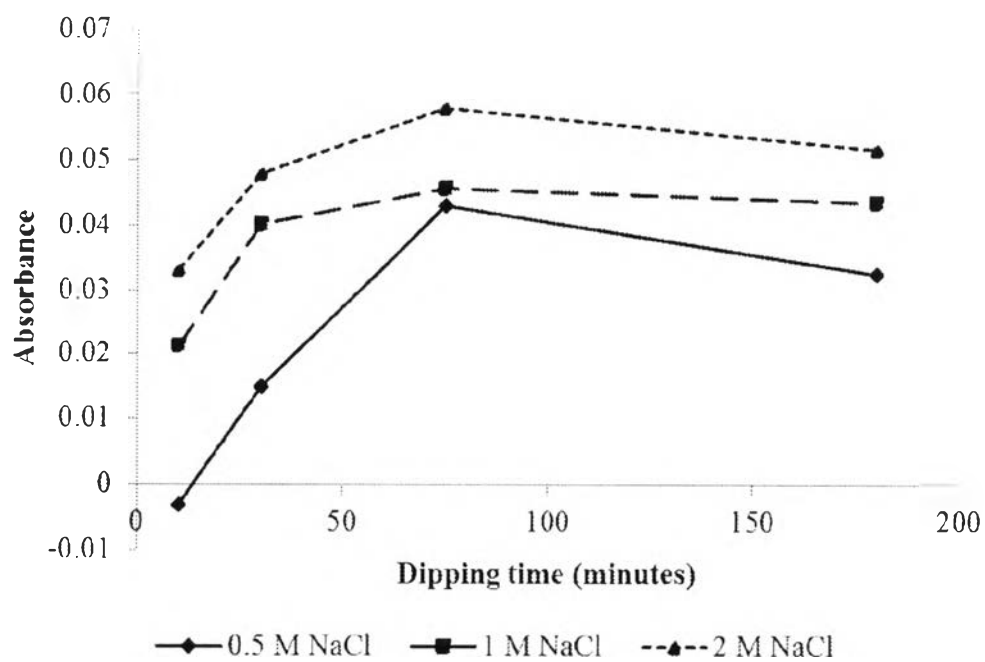


Figure 4.13 Monolayer of PANI-PSS at pH 7

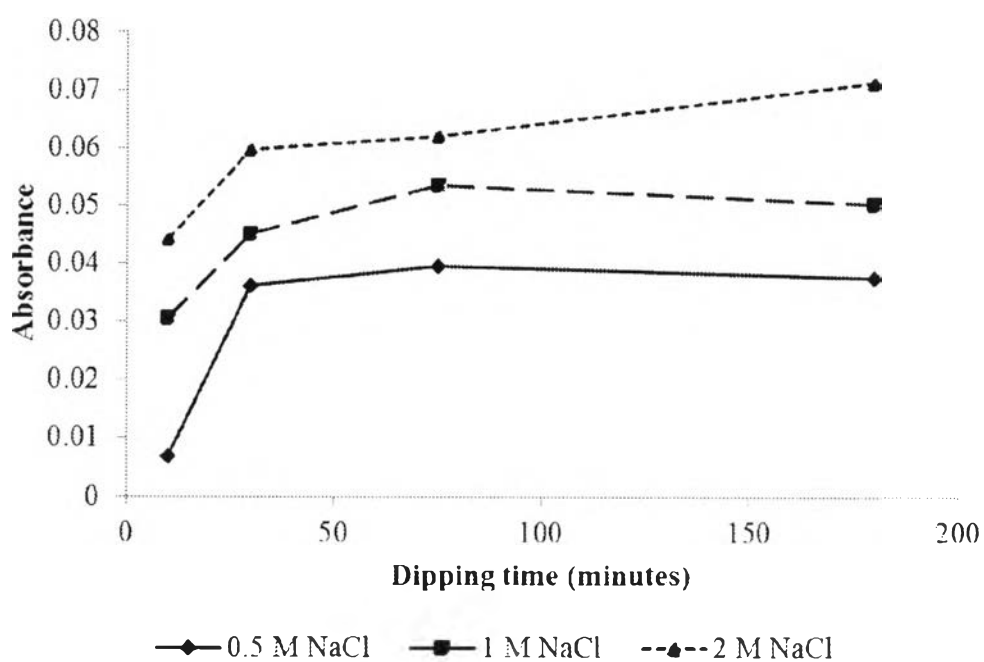
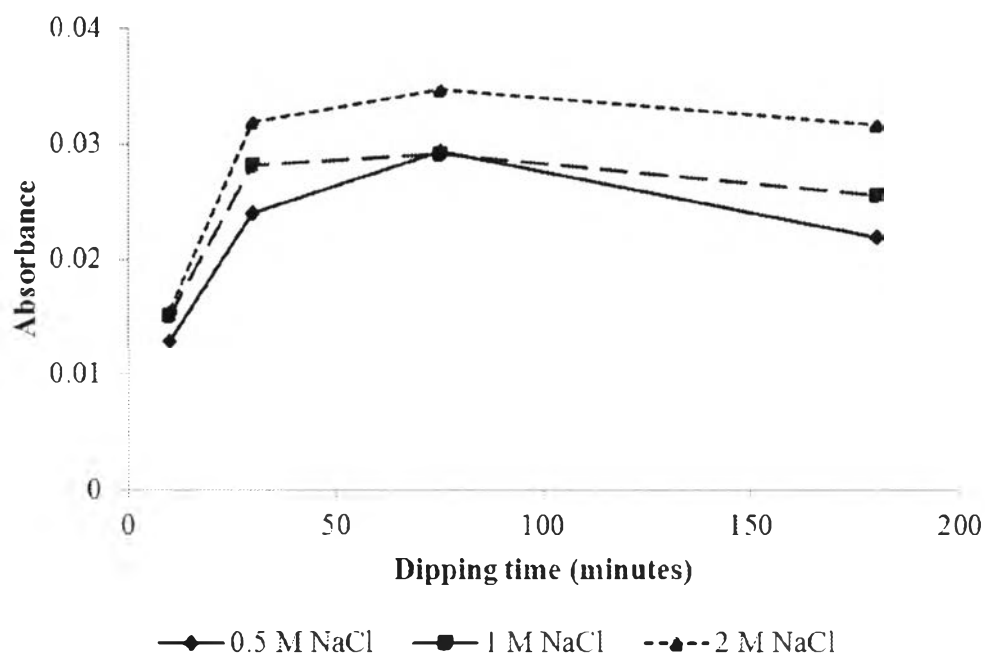
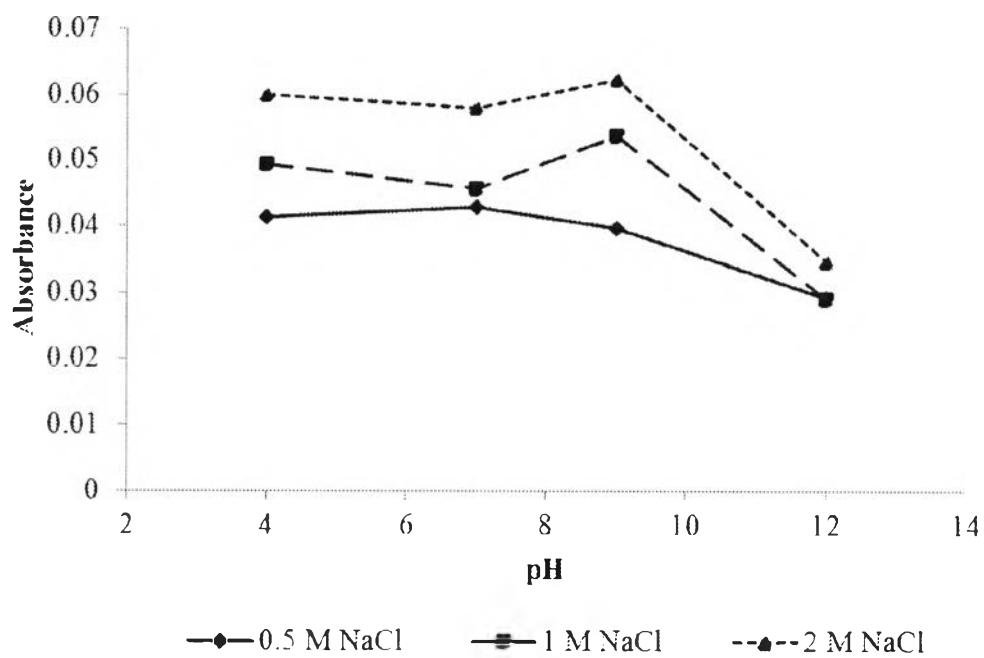


Figure 4.14 Monolayer of PANI-PSS at pH 9.



**Figure 4.15** Monolayer of PANI-PSS at pH 12.

Figure 4.12-4.15 showed that all of pH has the same behavior which the best time and NaCl concentration were 75 minutes and 2 M, respectively. But absorbance of each pH was different shown in figure 4.16. It indicated that pH 9 in 2 M NaCl was the best condition to make monolayer. It is believed that at pH 9 had that lowest charge repulsion between positive charge of anilinium and PDAD so negative charge of PSS can stick on positive charge of PDAD easily.



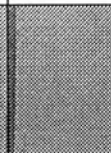
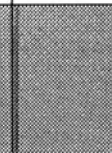
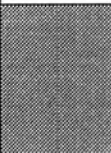
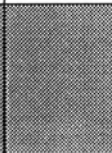



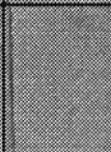
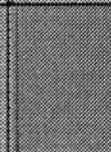
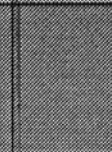
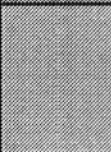
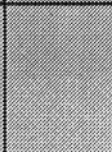


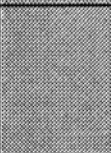

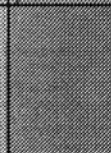

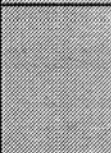
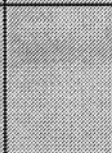


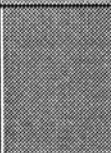



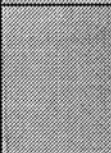



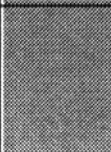



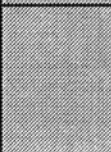
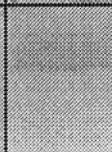

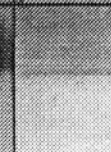


**Figure 4.16** Monolayer of PANI-PSS at 75 minutes .



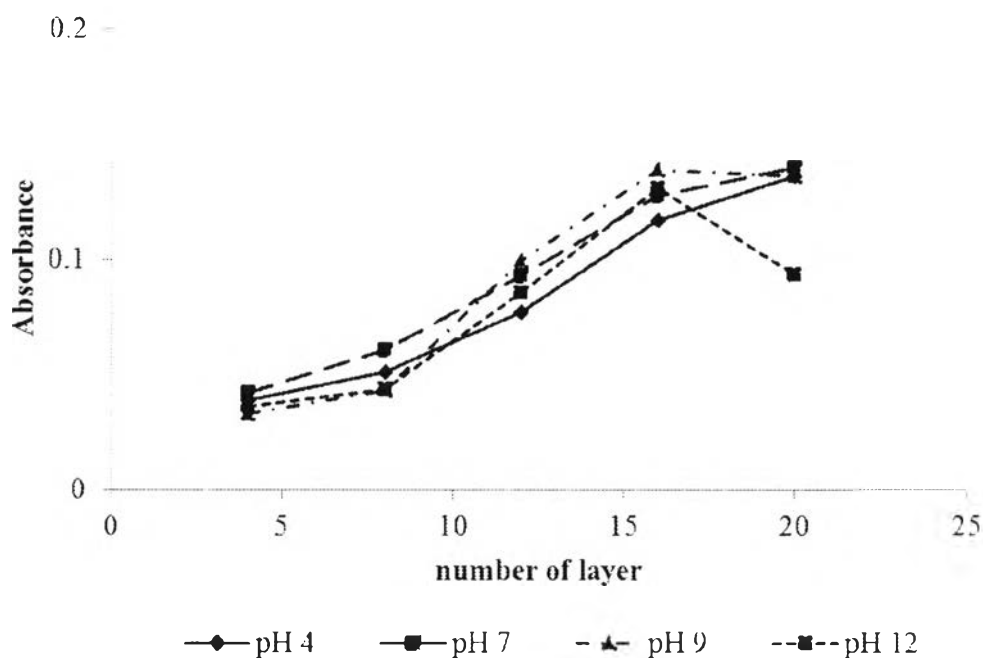
#### 4.6 Effect of pH and Number of Layer on PANI Multilayer

**Table 4.4** PANI films with various pH and layers

Number of layer	PANI-PSS				PANI-CoPSS 3:1			
	pH 4	pH 7	pH 9	pH 12	pH 4	pH 7	pH 9	pH 12
4								
8								
12								
16								
20								

We studied the effect of pH and number of layer on PANI solution on the film growth as shown in table 4.4. PANI-PSS solution appeared clear in all pH and salt to make monolayer described in topic 4.5. PANI-CoPSS 3:1 and is less stable than PANI-PSS and when the pH is increase due to the presence of maleic group. PANI-CoPSS 1:1 is the worst because it precipitated in all pH and salt hence it cannot use to make PANI films with the layer-by-layer self-assembly technique. In this experiment PANI ionic strength was adjusted to 1 M NaCl to make multilayer and film growth because PANI-CoPSS 3:1 can stabilize in this highest NaCl

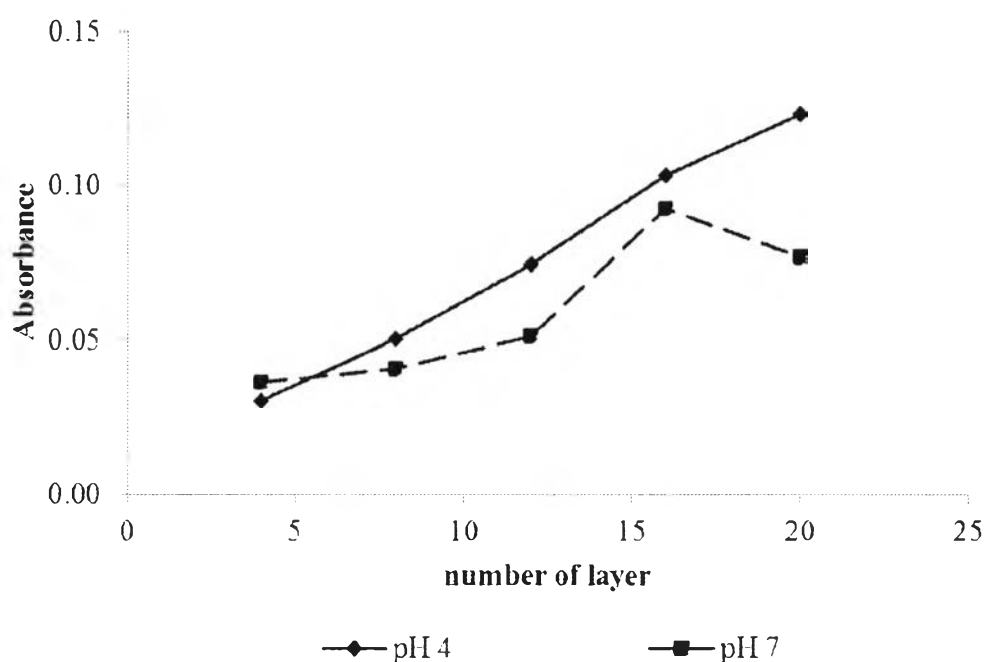
concentration. PANI multilayer films on table 4.4 dipped 5 minutes of each layer indicated that PANI-PSS of all pH can stick well on the substrate and color darker with number of layer. Unlike, PANI-CoPSS 3:1 can stick well at pH 4 because solution was quite stable and others solution cannot stabilize so they precipitated and cannot stick. Moreover, PANI-CoPSS films can investigate that pH higher than 4 had dark color at the upper edge of primer because PANI didn't disperse in water so it became hydrophobic and area of substrate without primer is hydrophobic hence it is principle of like dissolved like.



**Figure 4.17** Multilayer PANI-PSS with different pH.

PANI-PSS multilayer in different pH shown in figure 4.17 indicated that 8-16 layer-by-layer PANI-PSS all of pH increased rapidly and linearly. It is believed that at pH 9 was the best to make monolayer discussed in topic 4.5 and multilayer because it had the highest absorbance. Multilayer PANI-PSS had higher absorbance compared to monolayer so multilayer is better to make the films. PSS is the best not only to synthesize PANI solutions but also PANI films.

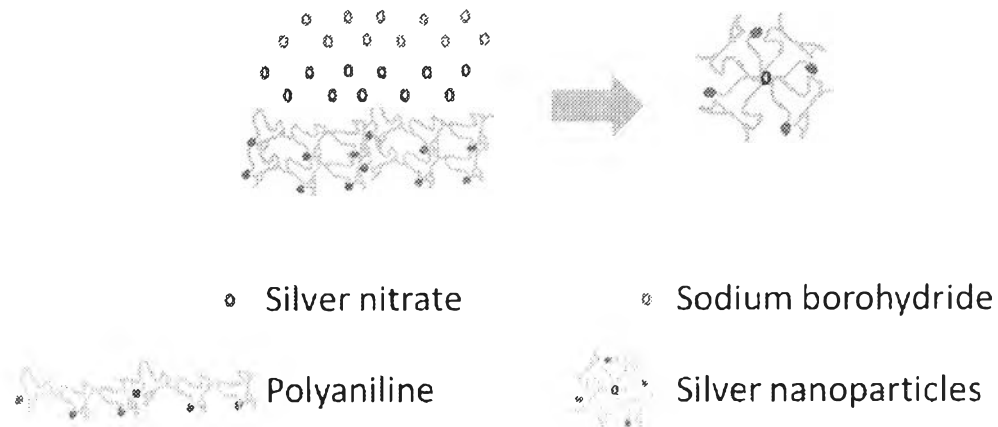
Unlike, PANI-CoPSS 3:1 shown in figure 4.18 indicated that pH 4 was the best condition to make multilayer because absorbance increased linearly and it is the most stable and hydrophilic solution. At pH 7, it can stabilize solution but added salt. pH 7 can stick on substrate at first before solution precipitate. pH 9 and 12 solution was precipitate already even without salt so solution was not stable and cannot make films. It is believed that maleic group and salt are not suitable for interfacial PANI polymerization and making films.



**Figure 4.18** Multilayer PANI-CoPSS 3:1 with different pH.

For PANI-CoPSS 1:1 was precipitate all of pH without salt so it cannot stick on the substrate and make PANI films. It is clear that stability, potential polymerization PANI solution and absorbance films are increase with percent sulfonate so PSS is good template, capping and stabilizing agent to synthesize PANI. Although PANI-CoPSS 1:1 is the worst in this part, it is believed that it is the best to synthesize silver nanoparticles.

#### 4.7 Synthesis silver nanoparticles



**Figure 4.19** Synthesis silver nanoparticles.

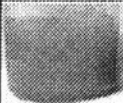
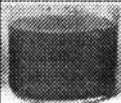
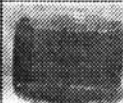

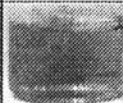
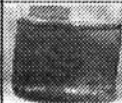

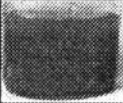
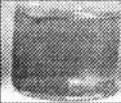
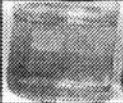
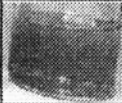
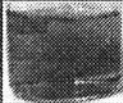
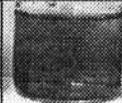
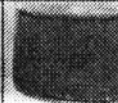
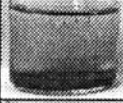
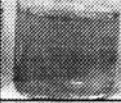
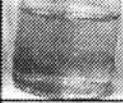

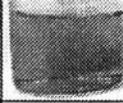
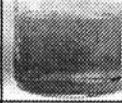
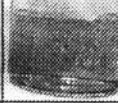





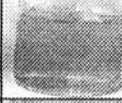


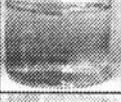


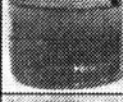

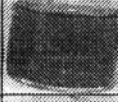
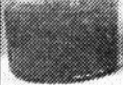
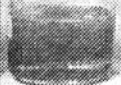
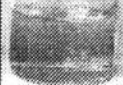


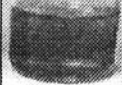

Typically PANI is prepared by oxidative polymerization of aniline with hydrochloric acid but in this work polymerize PANI with sulfuric acid because we wanted to use PANI synthesis silver nanoparticles or chloride from hydrochloric acid cannot synthesize silver nanoparticles because of precipitation into AgCl.

Silver nanoparticles normally use as antibacterial so in this work we wanted to develop not only sensitivity PANI faster but also antibacterial or food spoiled slower.

Silver nanoparticles are synthesized by reduction of silver nitrate in the presence of PANI as capping agent and using sodium borohydride to reduce silver ion to become silver nanoparticles ( $\text{Ag}^0$  or Ag). All PANI solutions used to synthesize  $\text{Ag}^0$  were 10 mM because of the highest yield so PSS, CoPSS 3:1 and CoPSS 1:1 were used 10 mM also.

In table 4.5 indicated that not only PSS, CoPSS 3:1 and CoPSS 1:1 can use to synthesize  $\text{Ag}^0$ , but also PANI. We varied capping volume to synthesize  $\text{Ag}^0$  to investigate stability, yield and optimal condition for making films. Different capping agents gave different yield, color and plasmon band which can observe on UV spectrum around 400 nm.

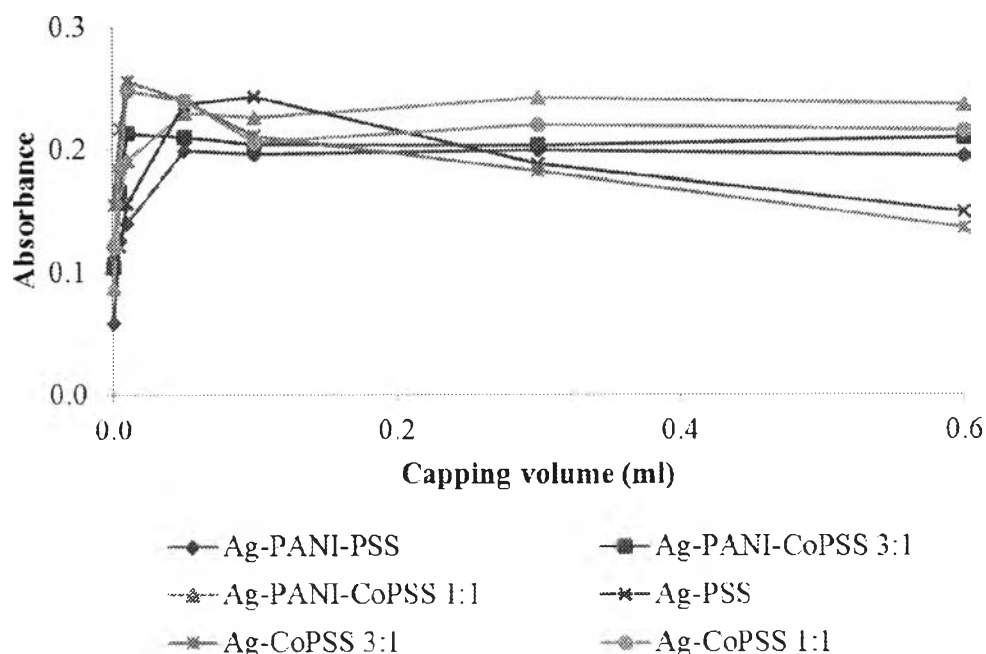
**Table 4.5** Silver nanoparticles solutions with different capping and volume

Volume capping / capping	0.001 ml	0.005 ml	0.01 ml	0.05 ml	0.1 ml	0.3 ml	0.6 ml
PANI-PSS							
PANI-CoPSS 3:1							
PANI-CoPSS 1:1							
PSS							
CoPSS 3:1							
CoPSS 1:1							

We synthesized silver nanoparticles using with and without PANI to observe stability and dispersion in water because normally silver nanoparticles without capping agent could not stabilize in water and then precipitate so they cannot be made films with layer-by-layer assembly technique.

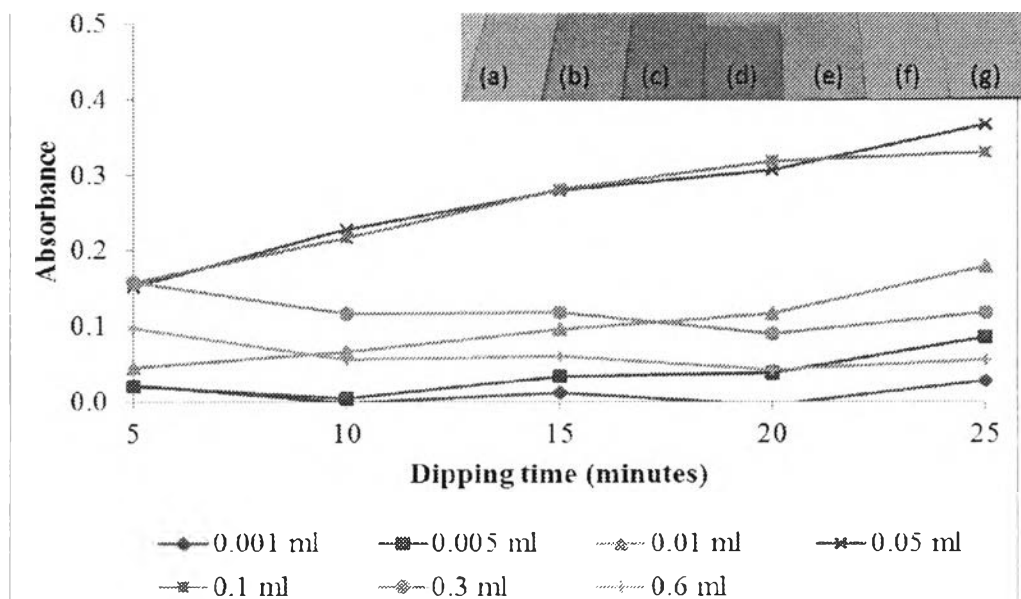
All of PANI solutions had to be adjusted pH to 7 before synthesis  $\text{Ag}^0$  due to the high acidic of the reaction 0.1 M acid. All of  $\text{Ag}^0$  solutions were pH 8-9 because sodium borohydride is strong reducing agent. All of  $\text{Ag}^0$ -PANI-PSS and  $\text{Ag}^0$ -PSS solutions didn't have any particles aggregate and precipitate at the bottom of glass that mean sulfonate group can stabilize or cap particles to disperse in solution. Unlike,  $\text{Ag}^0$ -PANI-CoPSS 3:1 and  $\text{Ag}^0$ -PANI-CoPSS 1:1 can synthesize  $\text{Ag}^0$  but they had some particles aggregate.  $\text{Ag}^0$ -PANI-CoPSS 3:1 solutions were more stable than  $\text{Ag}^0$ -PANI-CoPSS 1:1 because PANI-CoPSS 3:1 at pH 9 are more stable than PANI-CoPSS 1:1. PSS, CoPSS 3:1 and CoPSS 1:1 without PANI had

wide range of pH so  $\text{Ag}^0$  capped with these polymers can stabilize solutions. Yield of all solutions indicated in figure 4.20.

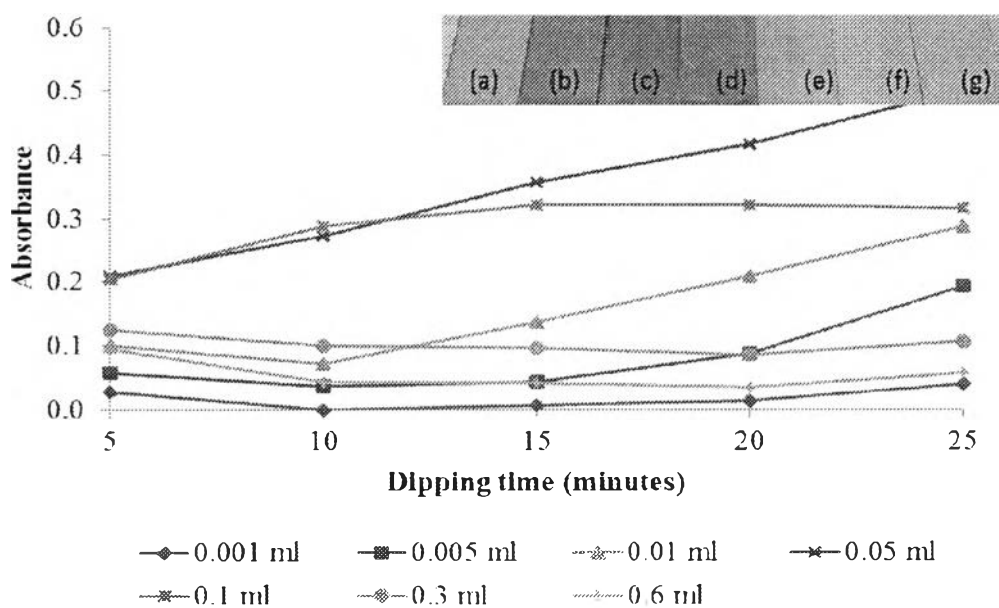


**Figure 4.20** Plot of silver nanoparticles solution absorbance with various types of capping agents.

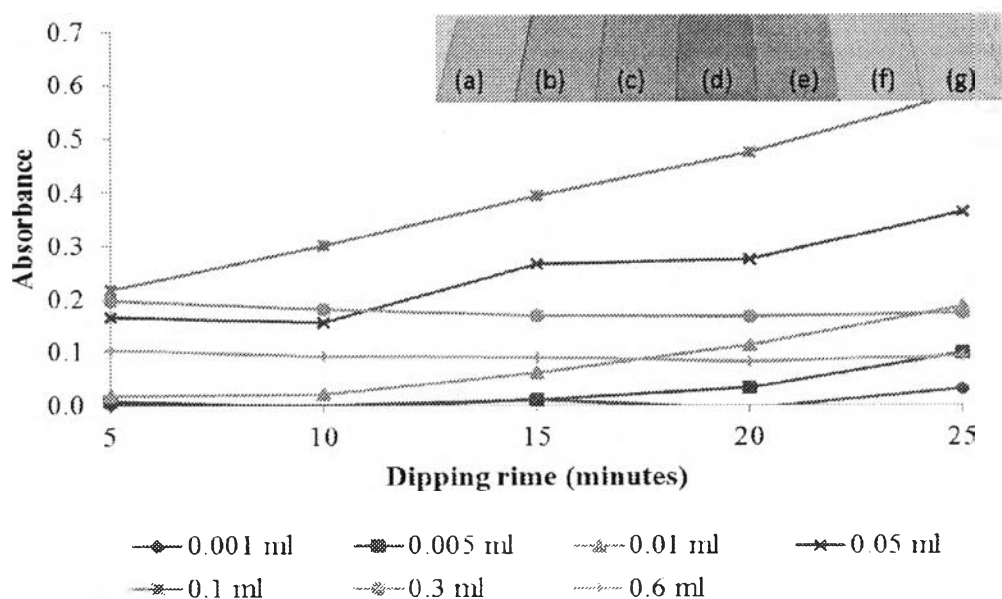
This figure showed the highest yield of each solution that Ag-PANI-CoPSS 3:1, Ag-CoPSS 3:1 and Ag-CoPSS 1:1 had the highest yield at 0.01 ml, and others at 0.05 ml. Then we made monolayer film from all of these solutions to investigate optimal condition shown in figure 4.21-4.26. Before making monolayer film, we made primer PDAD/PSS 5 layer by layer to make sure that  $\text{Ag}^0$  can stick on the substrate. Ag-PANI-CoPSS 1:1 was 0.1 ml and Ag-PSS 1:1 was 0.01 ml. The yield decreased when increasing the capping volume because competition of Ag-PANI-capping and PANI-capping or capping and yield before the highest yield is not enough capping that make Ag particles aggregated.



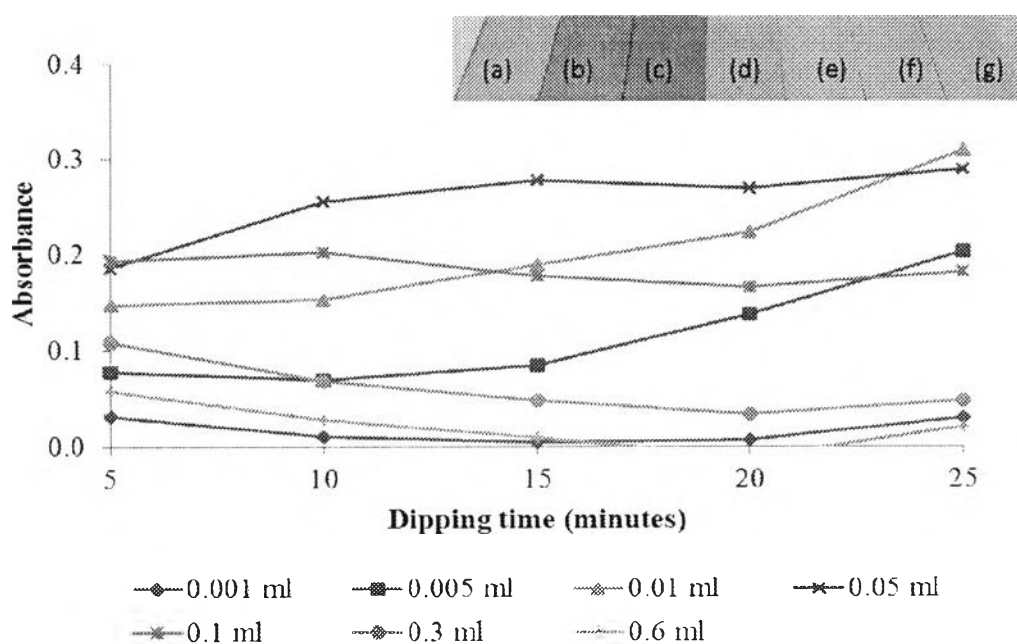
**Figure 4.21** Plot of  $\text{Ag}^0$ -PANI-PSS monolayer absorbance with dipping time and films (a) 0.001, (b) 0.005, (c) 0.01, (d) 0.05, (e) 0.1, (f) 0.3 and (g) 0.6 ml for 25 minutes.



**Figure 4.22** Plot of  $\text{Ag}^0$ -PANI-CoPSS 3:1 monolayer absorbance with dipping time and films (a) 0.001, (b) 0.005, (c) 0.01, (d) 0.05, (e) 0.1, (f) 0.3 and (g) 0.6 ml for 25 minutes.

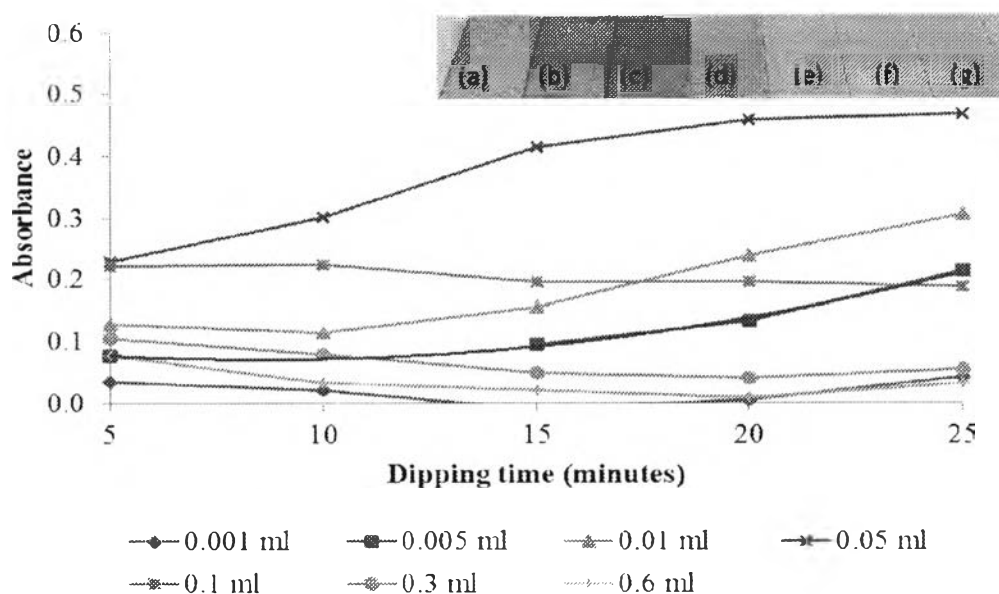


**Figure 4.23** Plot of  $\text{Ag}^0$ -PANI-CoPSS 1:1 monolayer absorbance with dipping time and films (a) 0.001, (b) 0.005, (c) 0.01, (d) 0.05, (e) 0.1, (f) 0.3 and (g) 0.6 ml for 25 minutes.

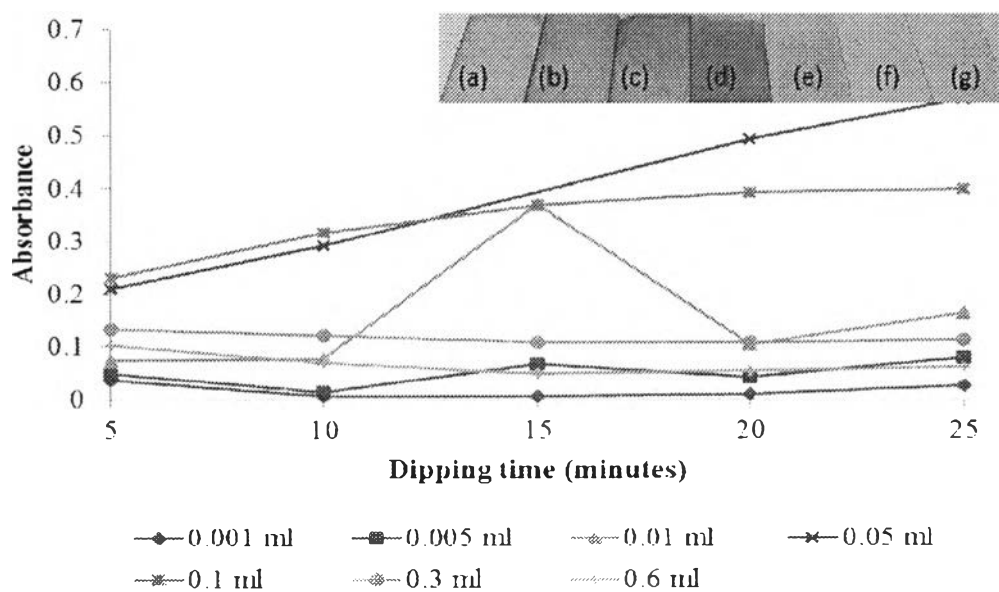


**Figure 4.24** Plot of  $\text{Ag}^0$ -PSS monolayer absorbance with dipping time and films (a) 0.001, (b) 0.005, (c) 0.01, (d) 0.05, (e) 0.1, (f) 0.3 and (g) 0.6 ml for 25 minutes.

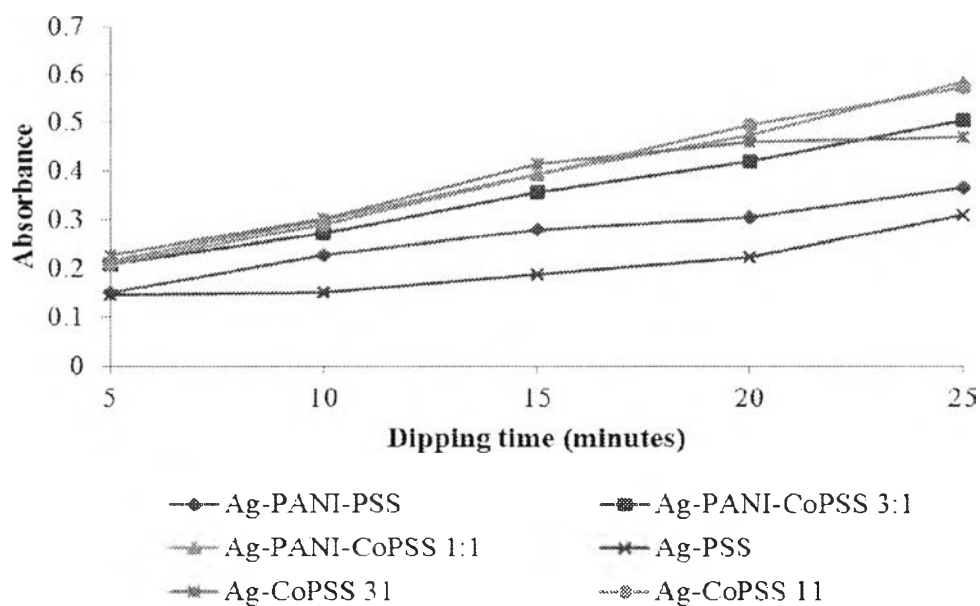




**Figure 4.25** Plot of Ag<sup>0</sup>-CoPSS 3:1 monolayer absorbance with dipping time and films (a) 0.001, (b) 0.005, (c) 0.01, (d) 0.05, (e) 0.1, (f) 0.3 and (g) 0.6 ml for 25 minutes.

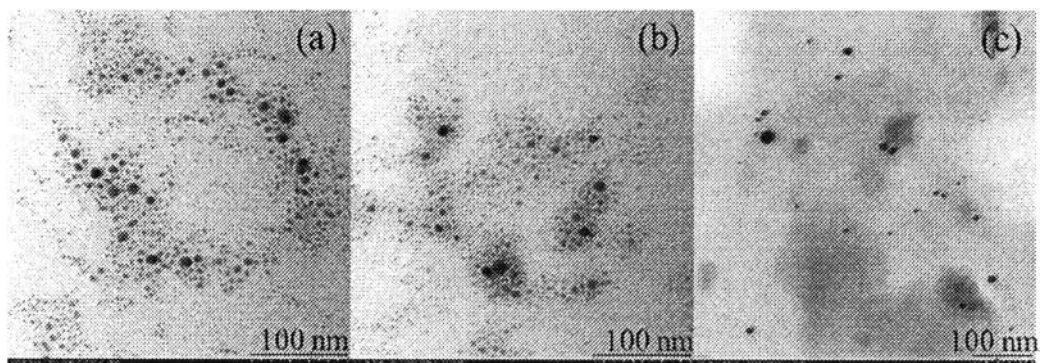


**Figure 4.26** Plot of Ag<sup>0</sup>-CoPSS 1:1 monolayer absorbance with dipping time and films (a) 0.001, (b) 0.005, (c) 0.01, (d) 0.05, (e) 0.1, (f) 0.3 and (g) 0.6 ml for 25 minutes.



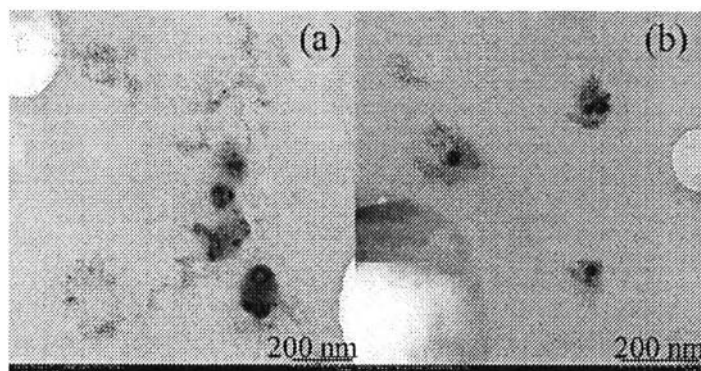
**Figure 4.27** Plot of  $\text{Ag}^0$  monolayer of each highest yield absorbance with dipping time.

In this figure 4.27, Ag-PANI-CoPSS 1:1 and Ag-CoPSS 1:1 had highest absorbance and then Ag had CoPSS 3:1 and PSS, respectively. It indicated that percent sulfonate group and PANI have effected on films. The absorbance increased when percent sulfonate group decreased. Moreover, this figure indicated that Ag with PANI had a higher absorbance than without PANI and the best condition to make silver nanoparticles monolayer is PANI-CoPSS 1:1.



**Figure 4.28** TEM image of silver nanoparticles capped with (a) PANI-PSS, (b) PANI-CoPSS 3:1 and (c) PANI-CoPSS 1:1.

Silver nanoparticles could be characterized by transmission electron microscope or TEM shown in figure 4.28 which confirmed that we can synthesize silver nanoparticles capped with PANI in various capping agents in nanoscale acutally. But PANI-PSS and PANI-CoPSS 3:1 had some particles aggregation and became large particles shown in figure 4.29. It confirmed that PANI-CoPSS 1:1 is the best to use as capping agent for synthesis silver nanoparticels that can disperse in water.



**Figure 4.29** TEM image of silver nanoparticles capped with (a) PANI-PSS and (b) PANI-CoPSS 3:1.