

## CHAPTER IV

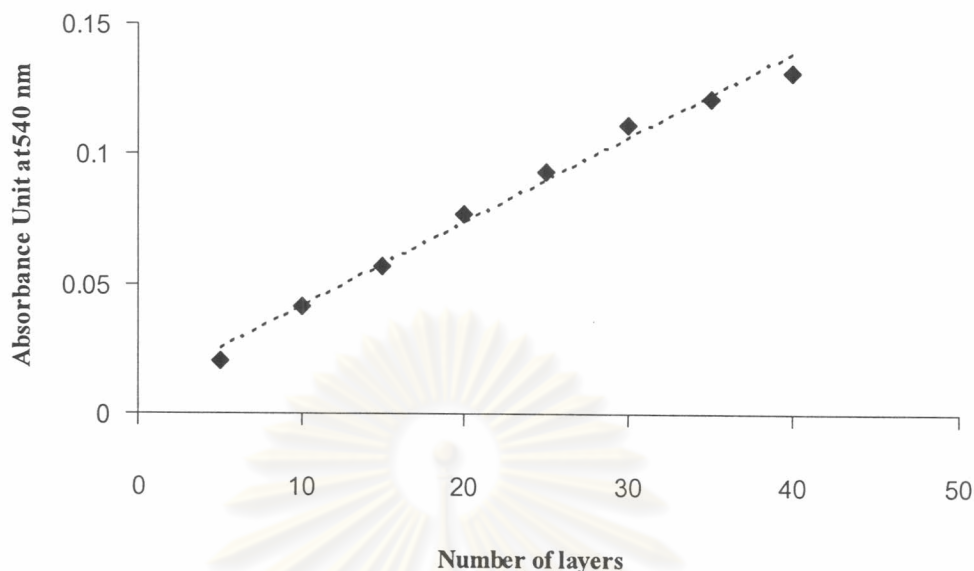
### RESULTS AND DISCUSSION

#### 4.1 Preliminary study of the construction of polyelectrolyte multilayers on glass slide using the Layer-by-Layer technique .

##### 4.1.1 Study the possibility of construction of PEM from Chitosan and Nylosan dye on glass slide

Polyelectrolyte multilayers assembled from cationic Chitosan and anionic Nylosan dye were deposited on glass slides by electrostatic attraction between ammonium groups ( $-\text{NH}_3^+$ ) of Chitosan and sulfonate groups ( $-\text{SO}_3^-$ ) of Nylosan dye in acidic condition and characterized using the UV-Vis spectroscopic technique. It is important to note that when the Nylosan dye is assembled into PEM, its characteristic absorbance is controlled by the electrostatic environment of the PEM and present an absorbance peak at 540 nm. It is therefore possible to monitor the Layer-by-Layer deposition of the PEM as a function of the number of layers. The expected linear relationship between the absorbance at 540 nm and the number of layers was confirmed with UV-Vis measurements as shown in Figure 4.1. Multilayers of up to 40 bi-layers of Chitosan and Nylosan were successfully deposited on glass slides.

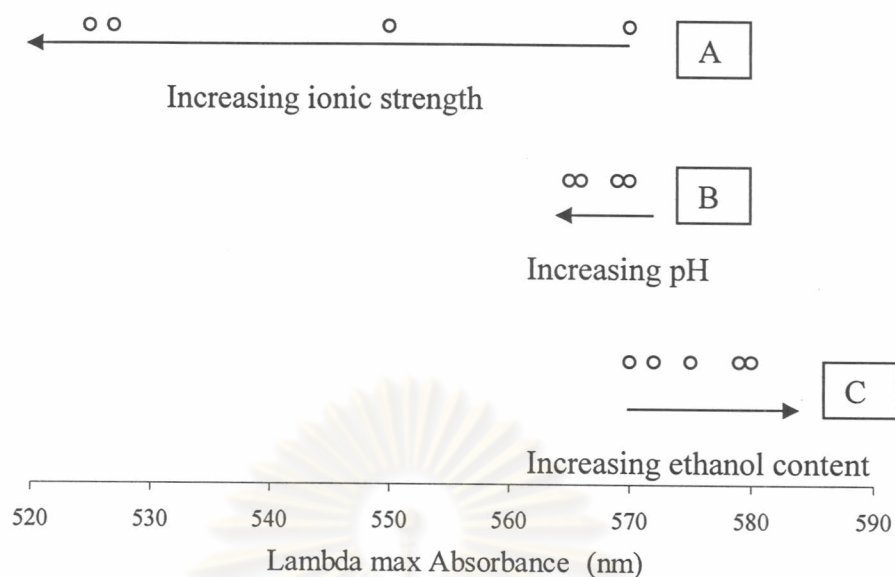
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**Figure 4.1** Absorbance value at 540 nm of a Chitosan–Nylosan thin film as a function of the number of deposited layers.(See the condition p.43)

#### 4.1.2 Study of the solvatochromic behavior of the Nylosan dye solution

Certain dye molecules are known to present solvatochromic properties depending on the ionic strength, pH or polarity of the surrounding solvent. This phenomenon is characterized by a shift of the  $\lambda_{\max}$  value of the dye's absorbance spectrum toward higher wavelength called, "Bathochromic shift or red shift" or lower wavelength called, "Hypsochromic shift or blue shift". Before the build up of the Chitosan–Nylosan PEMs, a study of the solvatochromic behavior of the Nylosan dye was conducted. The influence of the nature of the solvent on the  $\lambda_{\max}$  value of a dye, an effect referred to as solvatochromism. For example, if a dipole moments of a dye molecule is larger in the first excited state than in the ground state then the effect of a more polar solvent will be to stabilise the first excited state more than the ground state. The consequence will be a bathochromic shift of the absorption maximum as the solvent polarity is increased [11]. Sample solutions of the Nylosan dye as a function of increasing pH, ionic strength and ethanol content were prepared and measured using a UV–Vis spectrophotometer. These results are reported in Figure 4.2, and the different effects of the studied parameters on the  $\lambda_{\max}$  absorbance of the dye could be clearly seen.



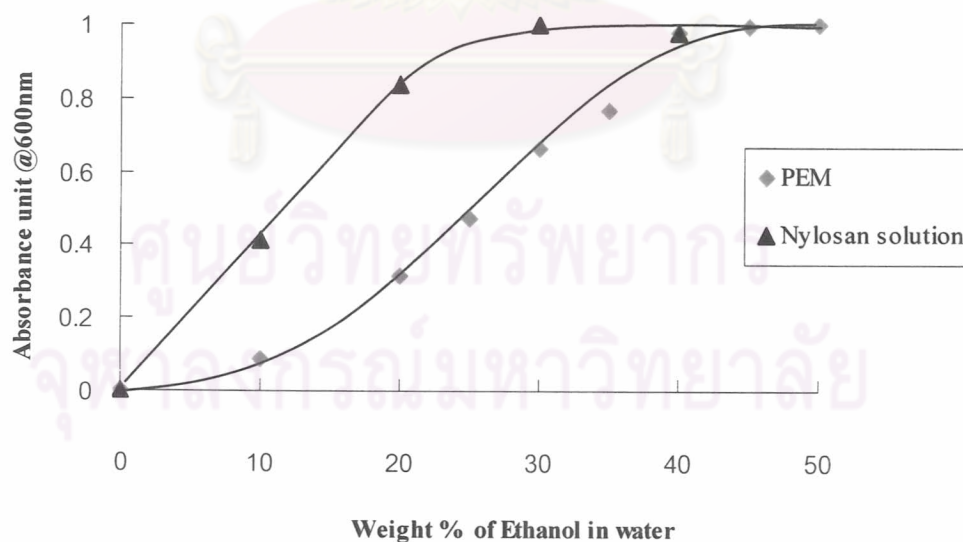
**Figure 4.2**  $\lambda_{\max}$  absorbance values of the Nylosan dye in solution of (A) increasing ionic strength: 0, 0.1, 0.5 and 1M NaCl ; (B) increasing pH: 3, 4, 5 and 7; (C) increasing ethanol content in water: 0, 10, 20, 30 and 40%. (See the condition p.43)

An increase of both pH and ionic strength of the solution led to a shift of  $\lambda_{\max}$  towards lower wavelengths respectively from 570 to 525 nm and from 570 to 565 nm. Contrarily, an increase in ethanol content resulted in a shift of the  $\lambda_{\max}$  absorbance towards higher wavelengths from 570 to 580 nm. These observations confirmed that any shift of the  $\lambda_{\max}$  absorbance toward higher wavelength should be the result of the ethanol content in water rather than the pH or ionic strength of the solution. As mentioned earlier, when Nylosan-dye molecules were assembled into PEM, the absorbance spectrum of the thin film presented a maximum at 540 nm which gave a light purple color. This characteristic color of the dye in the PEM thin film also matched the color of the dye when dispersed in aqueous solutions of ionic strength equal to 0.1 M NaCl. This expected similarity in color of the dye when assembled into PEM is due to the electrostatic interactions between the sulfonate groups of the dye and the Chitosan's ammonium groups. These electrostatic interactions were also similar to those between Nylosan dyes and  $\text{Na}^+$  counterion in solution both leading to a decrease in  $\lambda_{\max}$  absorbance from 570 to 540 nm and giving a light purple color of the thin film. The following section is a study of the effect of increasing ethanol

content in water on the absorbance response of a 40 layers Chitosan–Nylosan thin film.

#### 4.1.3 Study the potential use of Chitosan-Nylosan thin films as an alcohol sensor.

It is important to note that in the next experiment, the changes in absorbance value at 600 nm were used as a characteristic of the film response to ethanol in solution instead of monitoring the shift of  $\lambda_{\text{max}}$  absorbance. This choice is due to the fact that while  $\lambda_{\text{max}}$  varied from 540 to 580 nm, the absorbance at 600 nm increased nearly 50%, which made it a better characteristic for sensor applications. In this experiment, 40 layers of Chitosan and Nylosan were deposited on pre-cut glass slides following the procedure already described in Chapter 3. The resulting PEM thin film was then introduced into a UV–Vis cuvette and exposed to solutions of various ethanol contents. The change in absorbance of the PEM thin film as function of the ethanol content was represented by curve A in Figure 4.3.



**Figure 4.3** Increase in absorbance at 600 nm of the Nylosan dye as a function of various environments. Changes in absorbance when the dye is deposited in to PEM (diamonds). Changes in absorbance when the Nylosan dye is dissolved in a water/ethanol mixture (triangles). (See the condition p.43)

No significant effect on the thin film's absorbance could be seen for ethanol content between 0% and 10%. At ethanol contents between 10% and 45%, a constant increase in absorbance was observed with a maximum at 45%. Further increase of the ethanol concentration to 50% content did not lead to any change in absorbance. Surprisingly, the changes in absorbance of the dye as a function of the ethanol content were different when the dye was dissolved in aqueous solution as displayed by curve B in Figure 4.3. In this case, the absorbance at 600 nm reached a plateau for ethanol content above 30%, while this plateau was reached for ethanol content above 45% in the Nylosan–Chitosan PEM.

The delayed shift of the dye's absorbance is due to the electrostatic nature of the PEM was interpreted. Firstly, this delay could be attributed to a lower ethanol content inside the PEM versus outside the PEM, in the surrounding solution. The ability of the PEM to separate organic solvent from water has already been reported and for example when deposited onto porous alumina, PEM could be used to separate water from ethanol by permeation. The justification for this phenomenon lies in the highly ionic structure of the PEM, which promoted the diffusion of ions and water molecules, but limited the access to less polar solvent such as ethanol. A second argument for the delay in absorbance increased at 600 nm was the potentially competitive interaction between the ethanol-Nylosan system and the electrostatic interaction between the Nylosan-Chitosan complex. ATR-FTIR studies were currently being pursued to characterize the amount of ethanol present in the Chitosan-Nylosan PEM as a function of the solution's ethanol content while monitoring the absorbance increase at 600 nm. It was also interesting to note that when testing thin films built from various number of layer (10, 20, 30 layers) the change in absorbance as a function of ethanol content was proportional to the initial absorbance of the thin film in water. These results suggest that this phenomenon is based on a bulk sensor effect and not limited to the surface of the film.

Lastly, the stability of the Chitosan-Nylosan PEM was studied. A PEM thin film was exposed to cycles of water and 50% ethanol content and the absorbance changes were monitored using UV-Vis absorbance. After five cycles, the thin film had partially disappeared and released the Nylosan-dye back into the solution. This decomposition is mostly due to the loss of electrostatic interactions between the Chitosan and the Nylosan, which are the structural binding forces of the PEM system.

Consequently, this led to the slow release of the dye into the solution and to the decomposition of the film. Different strategies are being investigated to improve the stability of the dye in the PEM. Nevertheless, even considering the low cyclability of the Chitosan-Nylosan PEM, this system could be used as a disposable sensor tool for quick and inexpensive ethanol content measurements.

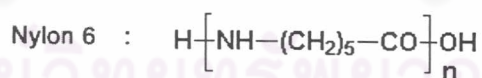
## 4.2 Study the construction of PEM and parameters controlling the growth of PEM on nylon multifilament.

### 4.2.1 Investigation of the condition of PEM formation on nylon multifilament

#### 4.2.1.1 Pre-study dye ability on nylon multifilament

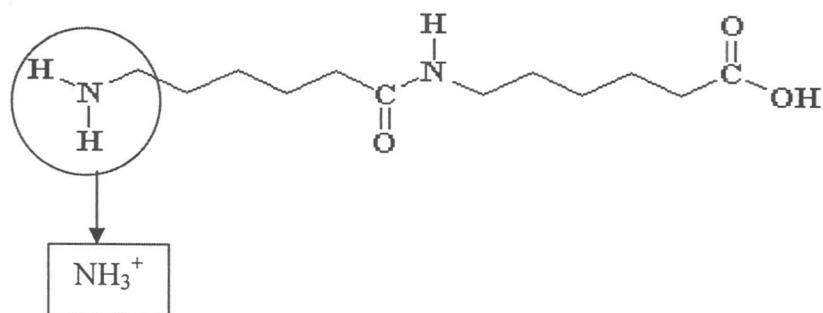
The objective of this experiment was to find non-dyeable condition of nylon multifilament. Later on, this condition will be used for PEM formation in order to unambiguously prove that the dye fixation should be attributed to PEM deposition. Nylon multifilament was selected for the substrate and dyed with Scarlet G dye solution with pH 3-12.

Because of amide groups present in the molecular chain and end groups of the nylon multifilament. Nylon multifilament can become charged when the pH conditions are changed.



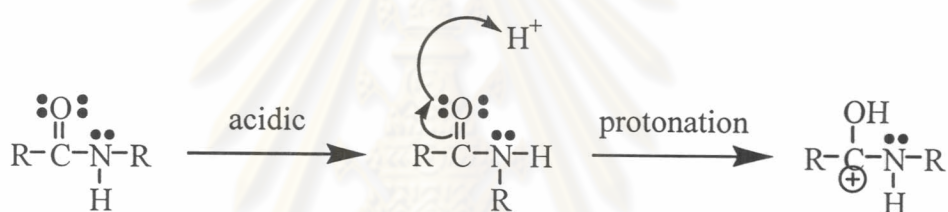
**Figure 4.4** Schematic of the chemical structure of nylon 6

In acidic condition, the amine end group is protonated and become ammonium group which was mainly interaction group, interact with sulfonate anion group of Scarlet dye as follows,



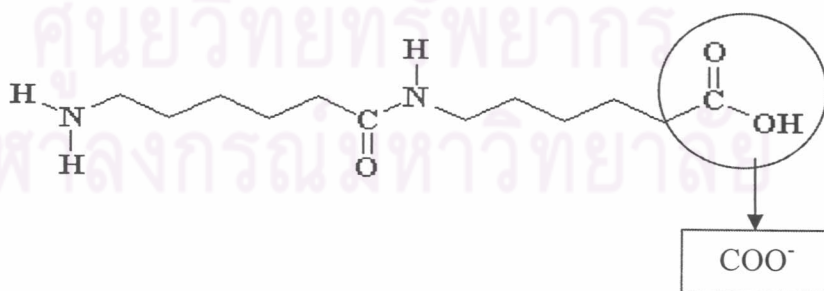
**Figure 4.5** Schematic of amine end group in acidic condition

A less probable reaction in severe acidic condition which may be shown here is amide groups were protonated and became carbocation that called “protonated amide” [26] as follows,



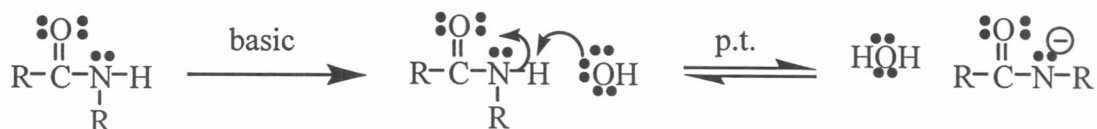
**Figure 4.6** Schematic of chemical reaction of amide group in acidic condition.

In basic condition, the carboxylic end group is attacked by hydroxide and become carboxylate group, as follow,



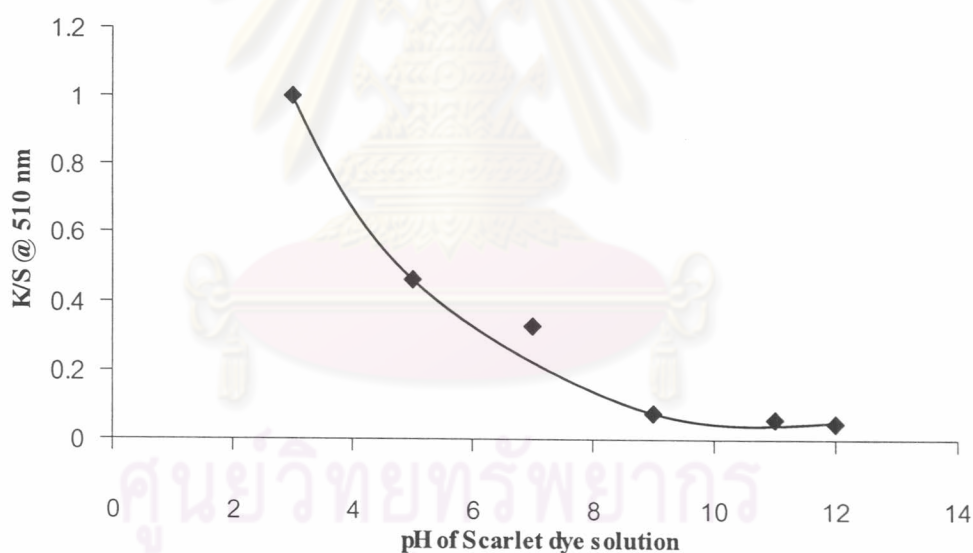
**Figure 4.7** Schematic of carboxylic end group in basic condition.

A less probable reaction in severe basic condition which may be shown are, amide group was attacked by hydroxide and an amide NH was removed to form the amidate anion, as follow,



**Figure 4.8** Schematic of chemical reaction of amide group in basic condition.

Figure 4.9 shows that with increasing pH a decrease in K/S values at 510 nm can be observed because of under acidic condition, the sulfonate groups of Scarlet G dye stick with ammonium groups of nylon multifilament by ionic interaction while the carboxylate anion groups of nylon multifilament in basic condition repelled the sulfonate groups of Scarlet G dye and the dyes could not affix onto nylon multifilament.



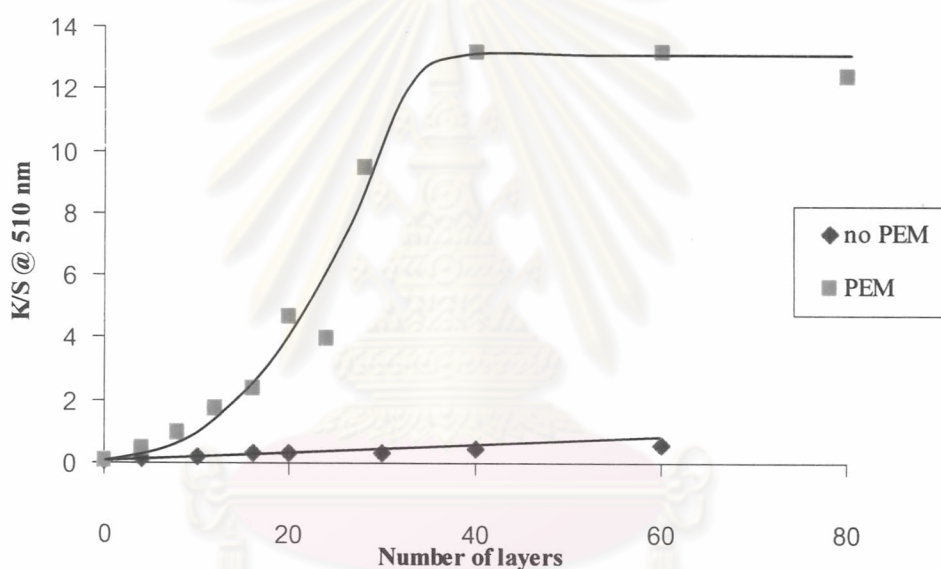
**Figure 4.9** K/S value at 510 nm of dyed nylon multifilament as a function of the pH of Scarlet G dye bath. (See the condition p.44)

Due to non-dyeable condition: pH 11, Scarlet G dye molecules could not affix into nylon multifilament. So this condition was selected to deposit PEM from cationic polyelectrolyte (PDADMAC) and Scarlet G dye on nylon multifilament in order to unambiguously prove that the dye fixation was attributed to the PEM assembly.

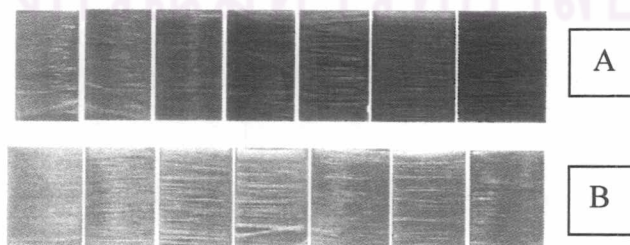


#### 4.2.1.2 Preparation of PEM on nylon multifilament at pH 11

PEM from PDADMAC and Scarlet G dye were deposited on nylon multifilament at pH 11. The growth behavior of the PEM was studied by following change in their K/S at 510 nm. It was assumed that the more PEM is deposited, the larger K/S value is obtained. K/S at 510 nm of the fiber dyed in Scarlet G solution at the same pH condition was also observed. As shown in Figure 4.10 and Figure 4.11, there is a large different between K/S of specimen coated with PEM and specimen dyed with Scarlet G dye solution.



**Figure 4.10** K/S value as a function of the number of PDADMAC-Dye layer (squares) and number of dye layers (diamonds).  
(See the condition p.45)



**Figure 4.11** Schematic of PEM from PDADMAC/Scarlet dye on nylon fiber (A) and dyed nylon with Scarlet dye solution (B) at pH 11

When the number of layers is increased, the K/S value of dyed nylon multifilament was not significantly increased because at pH 11, the carboxylate anion groups of nylon multifilament repelled the sulfonate anion groups of Scarlet G dye. Consequently, the dye molecules could not affix on nylon multifilament. While the K/S values of PEM coated on nylon multifilament increased in a non-linear relationship at the beginning of multilayer build up at the first 10 layers. The additional polyelectrolyte penetrate in substrate/multilayer interface because the thickness increment from each layer was limited. The increasing number of layers increased PEM thickness induced the penetration of the additional polyelectrolyte increased since polyelectrolyte chain was able to penetrate deeply into the multilayers. Until the critical thickness limited of PEM which polyelectrolyte was not able to penetrate deeper into the multilayers. The K/S values were proportional to the number of layers in a linear relationship up to 40 layers because the PEM thickness was above the critical thickness limited while the depth of penetration of the additional polyelectrolyte were almost constant. After 40 layers, the K/S values were almost constant because it was the maximum color strength on the specimen surface which the resolution of Macbeth spectrophotometer could not detect. This result confirmed that PEM from PDADMAC and Scarlet G dye were successfully coated on nylon multifilament.

#### **4.2.2 Parameters controlling the growth of PEM on nylon multifilament**

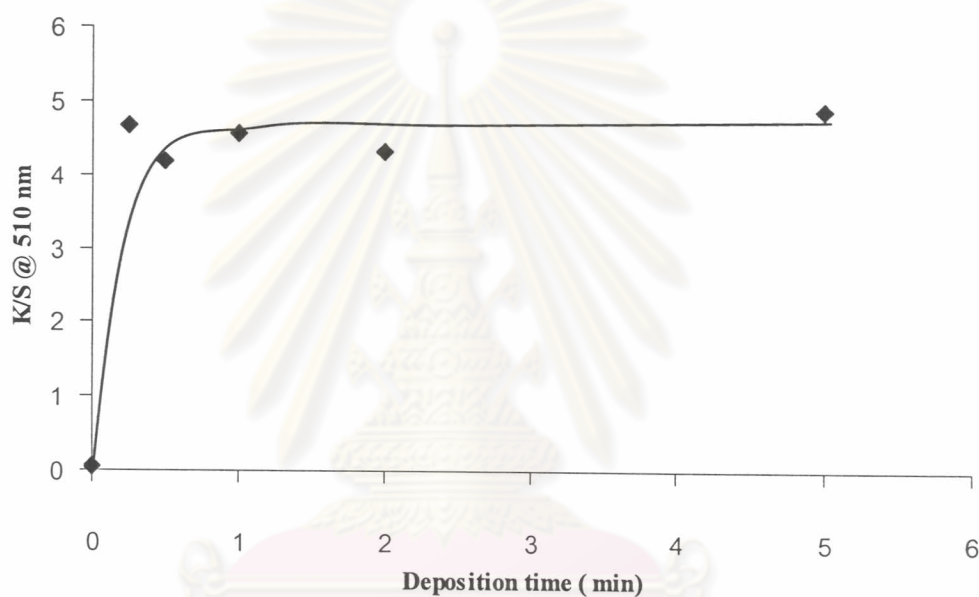
##### **4.2.2.1 Deposition time**

Deposition time is an important parameter, which indicates the adsorption behavior during multilayer formation.

The varied deposition time in this study included the fixed deposition time in both of solutions, the fixed deposition time 5 minutes in PDADMAC and varied deposition time in Scarlet G dye solution and vice versa.

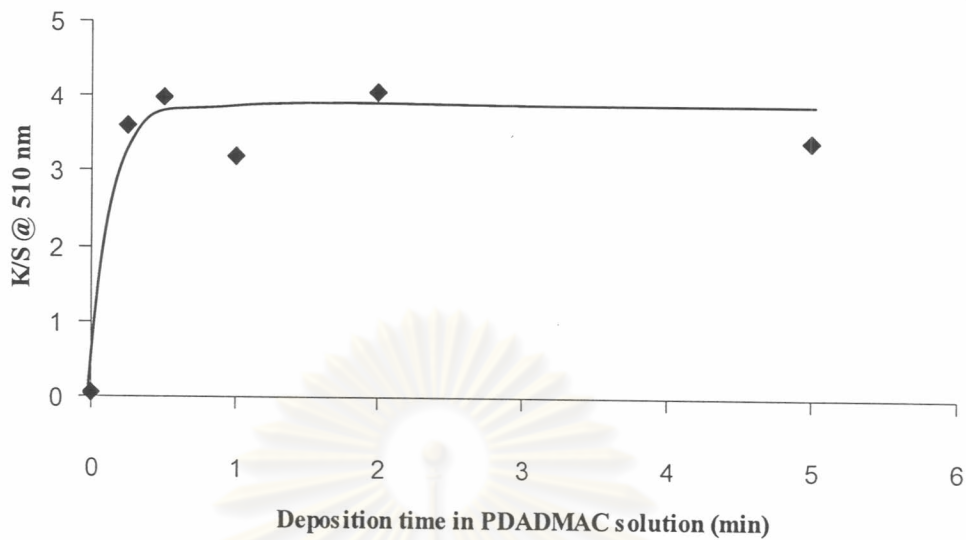
If the deposition time in PDADMAC and Scarlet G dye was kept equal for each specimen, Figure 4.12 is shown that deposition times as short as 15 sec are sufficient to obtain a maximum deposition of the PEM thin film. Further increase in the deposition time did not lead to any increase in the overall K/S value suggesting

that the deposition process was complete. The fast deposition is expected that the dye molecules size was rather small, so they moved easily within their system and stucked with positive charges of PDADMAC very fast. The salt added in the solution decreased the repulsion force between the already affixed molecules and the freely moving dye molecules and promoted the additional penetration of polyelectrolyte. The results show that at 15 second of deposition time, the adsorption of dyed on PEM surface is almost saturated. The constant in K/S value was found after 15 seconds.

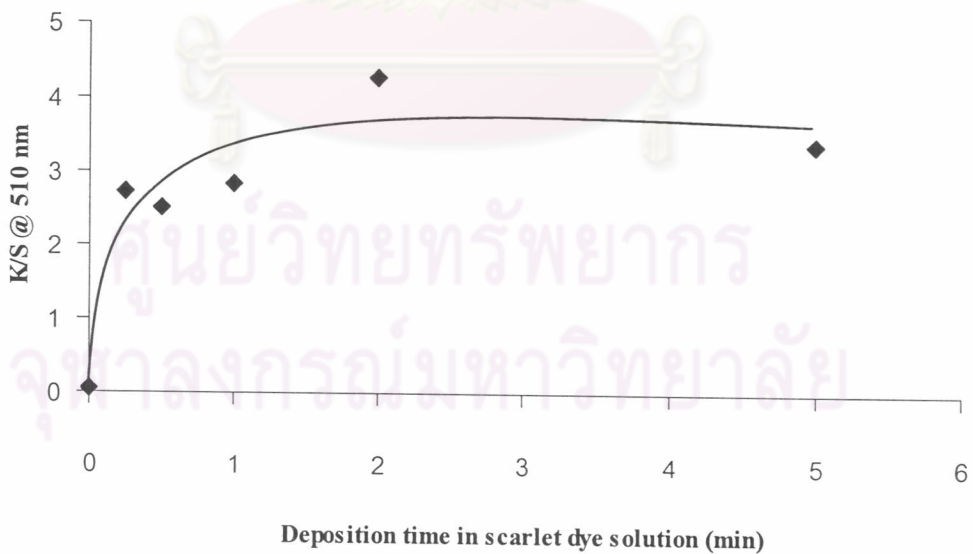


**Figure 4.12** K/S value of the nylon multifilament as a function of the deposition time of the multifilament in the PDADMAC and Scarlet G dye solutions. (See the condition p.46)

In another experiment, the deposition time in Scarlet G was fixed for 5 minutes and the deposition time in PDADMAC solution was varied from 15 seconds to 5 minutes and vice versa, K/S values of these specimens were shown in Figure 4.13 and 4.14. The curve in both Figure 4.13 and 4.14 presents the same trend as in Figure 4.12



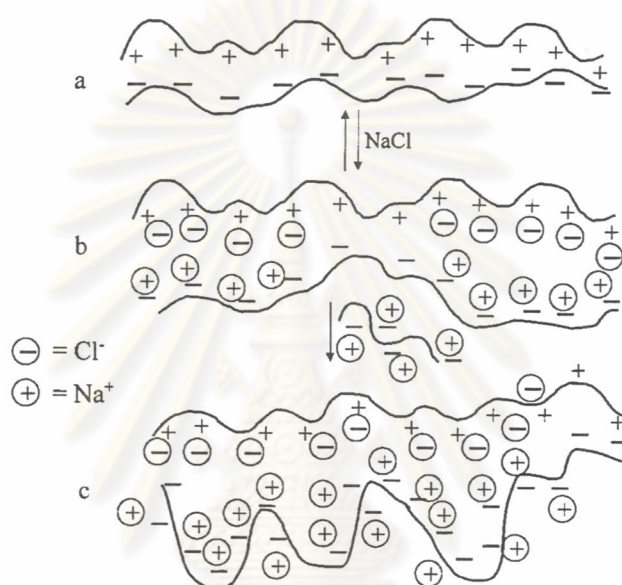
**Figure 4.13** K/S value of the nylon multifilament as a function of the fixed deposition time of the multifilament 5 minutes in Scarlet G dye solution. (See the condition p.46)



**Figure 4.14** K/S value of the nylon multifilament as a function of the fixed deposition time of the multifilament 5 minutes in PDADMAC solution. (See the condition p.46)

#### 4.2.2.2 Salt concentration

This parameter is believed to have the greatest influence on the amount deposited. How does additional salt permit overcompensation further into the multilayer? Figure 4.15 is an aid to understanding our current hypothesis: in the presence of salt, compensation of polyelectrolyte charge within the as-made multilayer transforms from intrinsic to extrinsic [27].



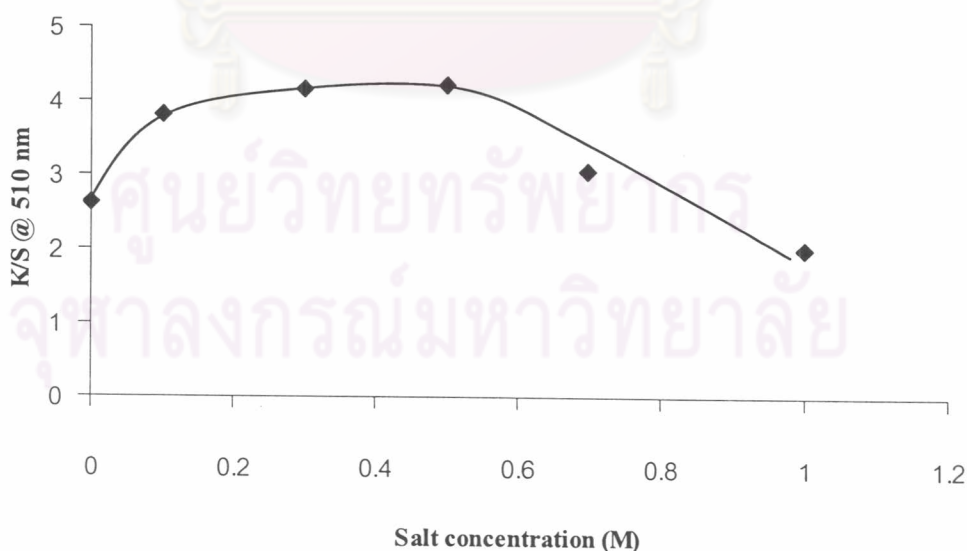
**Figure 4.15** Schematic of interior of a multilayer. Represent by two oppositely charged polymer strand (a), is intrinsically compensated as-made; with the addition of salt, extrinsic compensation occurs (b), as ions swell the multilayer, competing for polymer charge; In the presence of additional polyelectrolyte, (c), overcompensation from the surface into the film is seen.

The polymer in Figure 4.15 is actually highly swollen with salt ions and also contains more water, which is brought in with the salt. In the presence of one of the polyelectrolytes (the negative one in this example), more polymer can add, and the overcompensation extends further into the multilayer due to the effective decrease in segment-segment repulsion (the multilayer polymer is diluted by water and salt ions). Figure 4.15 depicts the swelling and addition of polymer as two distinct steps, whereas they are, in reality, simultaneous. The swelling of multilayer by salt is shown as reversible, while the polyelectrolyte addition is irreversible.

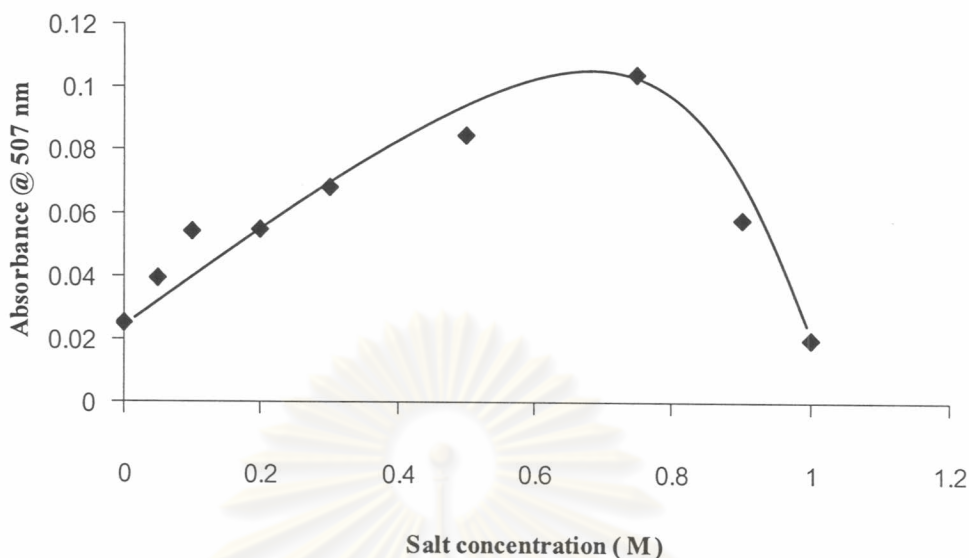
Figure 4.16 shows the increase in salt concentration up to 0.5 M lead to an increase in K/S values at 510 nm. This is due to the fact that with the presence of sufficient salt concentration, a substantial amount of Scarlet G dye or PDADMAC could add to the surface (much more than an equivalent monolayer of polymer repeat units) since salt ions carry a hydration shell with them, more water is included inside the film leading to swelling, decreased repulsive force between polymer segments and permitting a longer range for the distribution of excess charge. Therefore a greater thickness increment per layer was observed.

When the salt concentrations was increased above 0.5 M, the K/S values at 510 nm decreased due to the appearance of the precipitation of Scarlet G dye. On the other hand, excess salt concentration might induce more extrinsically compensated surface charge as compare to intrinsically compensated charges (inside the multilayers). A combination of weaker interaction and faster dye molecular motions associate to facilitate detachment of polyelectrolyte from the surface of a growing PEM.

This result was confirmed by UV-Vis measurements of the PEM which was constructed under the same condition, on glass slide substrate as shown in Figure 4.17.



**Figure 4.16** K/S value on the nylon multifilament as a function of the salt concentration in the PDADMAC and Scarlet dye solution.  
(See the condition p.46)



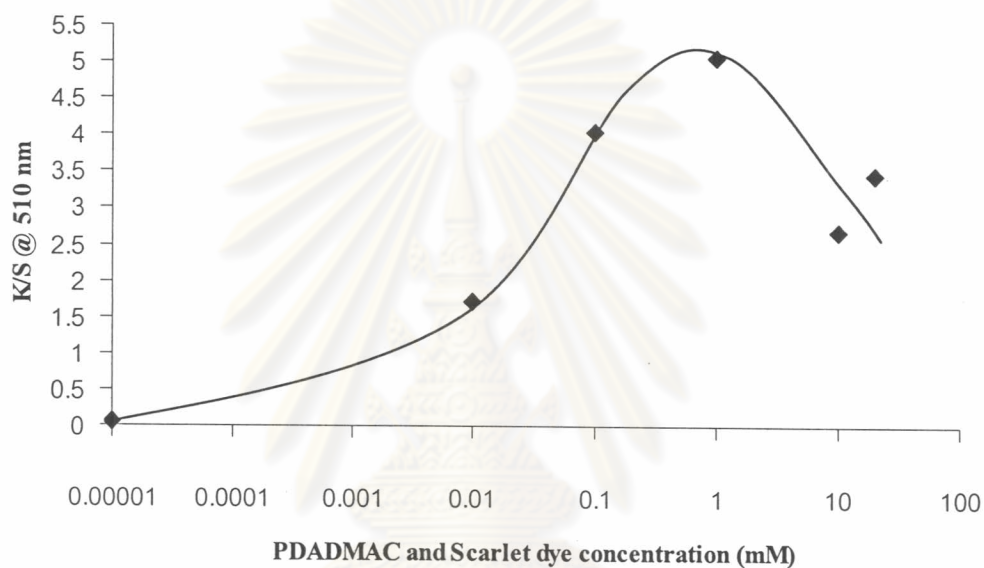
**Figure 4.17** Absorbance value on the glass slide as a function of the salt concentration in the PDADMAC and Scarlet dye solution. (See the condition p.46)

#### 4.2.2.3 Polyelectrolyte and dye concentration

Polyelectrolyte and dye concentrations were studied because generally, dilute polyelectrolyte solution are used. It is interesting to study the growth behavior of PEM when the concentration of polyelectrolyte was changed from lower to higher concentration than the normal concentration of polyelectrolyte in order to verify that the growth on the fiber present the same characteristics than on flat substrates. The concentration included the same concentration of PDADMAC and Scarlet G dye, the fixed concentration of PDADMAC 1 mM and varied dye concentration, and the fixed concentration of Scarlet G dye 0.5 mM and varied PDADMAC concentration.

Figure 4.18 and Figure 4.19 show the change in K/S value with increasing PDADMAC and Scarlet G dye concentrations and increasing only PDADMAC concentration up to 1 mM increased K/S values at 510 nm because the increasing concentration of both increased the amount deposition of the additional PDADMAC or Scarlet G dye molecules into PEM. After 1 mM, PDADMAC and Scarlet G dye concentration, the K/S values were decreased because at high PDADMAC concentration, the excess polyelectrolyte charges in PDADMAC solution could remove some of the dye molecules on the surface and formed complex with

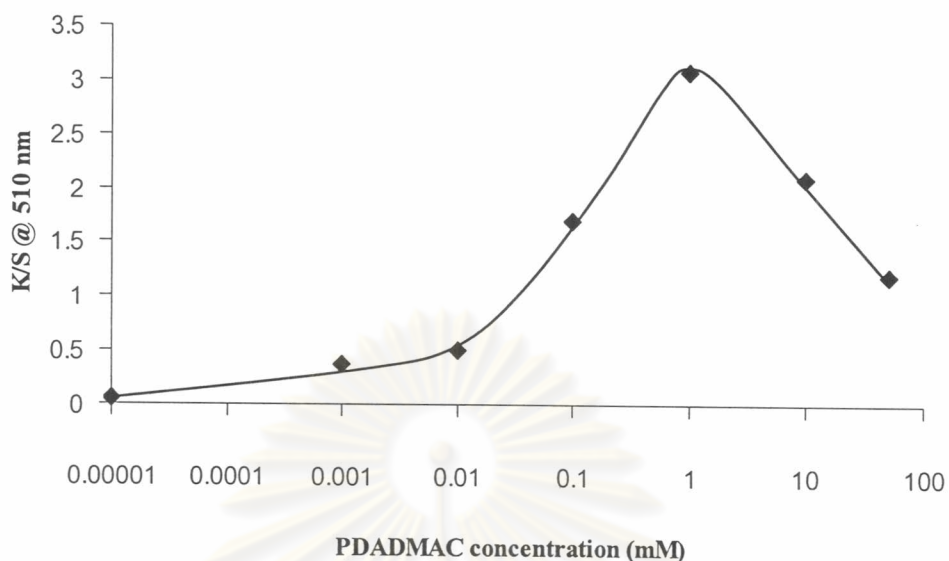
PDADMAC in the solution but did not erode the rest of the multilayer because stripping must occur absorbing polymer has had a chance to interpenetrate. Similarly, the existing surface dye molecules was minimally interpenetrated because the low molecular weight. A solution of dye did not remove PDADMAC on the surface as shown in Figure 4.20, because PDADMAC has already interpenetrated into the surface. Stripping it off the surface induced the increasing film thickness.



**Figure 4.18** K/S value of the nylon multifilament as a function of PDADMAC and Scarlet G dye at same concentration. (See the condition p.46)

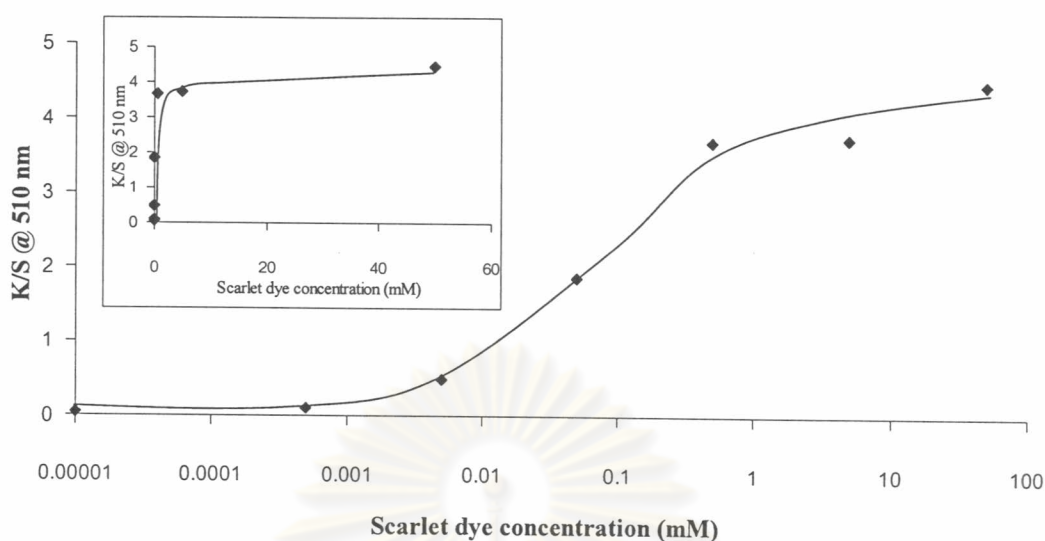
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**Figure 4.19** K/S value of the nylon multifilament for increasing PDADMAC concentration with fixed Scarlet dye concentration 0.5 mM. (See the condition p.46)

Figure 4.20 shows the increasing Scarlet G dye concentration in range 0.0005 – 0.5 mM increased the K/S values at 510 nm immediately because of the increasing amount of deposition dye inside PEM. After 0.5 mM Scarlet G dye concentration, K/S value increased slowly because the adsorption step was saturated. A solution of Scarlet dye did not remove PDADMAC on surface because PDADMAC has already interpenetrated into the surface. 1 mM PDADMAC concentration which was build up PEM in this experiment, was found suitable condition to construct PEM with Scarlet dye because of data from Figure 4.18.



**Figure 4.20** Log scale of K/S value of the nylon multifilament for increasing dye concentration with fixed PDADMAC 1 mM.

Inset : Normal scale of K/S value of the nylon multifilament for increasing dye concentration with fixed PDADMAC 1 mM.

(See the condition p.46)

This experiment demonstrated that the PDADMAC concentration had a greater influence on the stripping of PEM than the dye concentration. So the PDADMAC concentration should be controlled in order to construct PEM efficiently. The optimum concentration of PDADMAC in this system was 1 mM.

The study of the construction and factor controlling the growth of polyelectrolyte multilayers on nylon multifilament for the suitable condition to construct PEM as follows,

Number of layers : up to 40 layers

Deposition time : at least 15 second

Salt concentration : 0-0.5 M

Polyelectrolyte concentration : 1 mM

Scarlet dye concentration : 0.5 mM

pH condition depends on the type of polyelectrolyte. If polyelectrolyte pairs are composed of strong polyelectrolyte their system is independent from pH condition while weak polyelectrolyte depends on pH solution.

In this case, non-dyeable condition: pH 11 was optimum for measuring PEM from PDADMAC/Scarlet G dye on nylon multifilament in order to prove that dye fixation was attributed to PEM.

### 4.3 Dye loading and release behavior of silk multifilament

The objective of this study is to understand the dye loading and release behavior of silk. Because silk has a low color fastness to washing and can easily stain on other fibers. The basic knowledge from these experiments is an advantage prior to the PEM deposition on dyed-silk in order to improve color fastness to washing of silk.

#### 4.3.1 Dye loading behavior

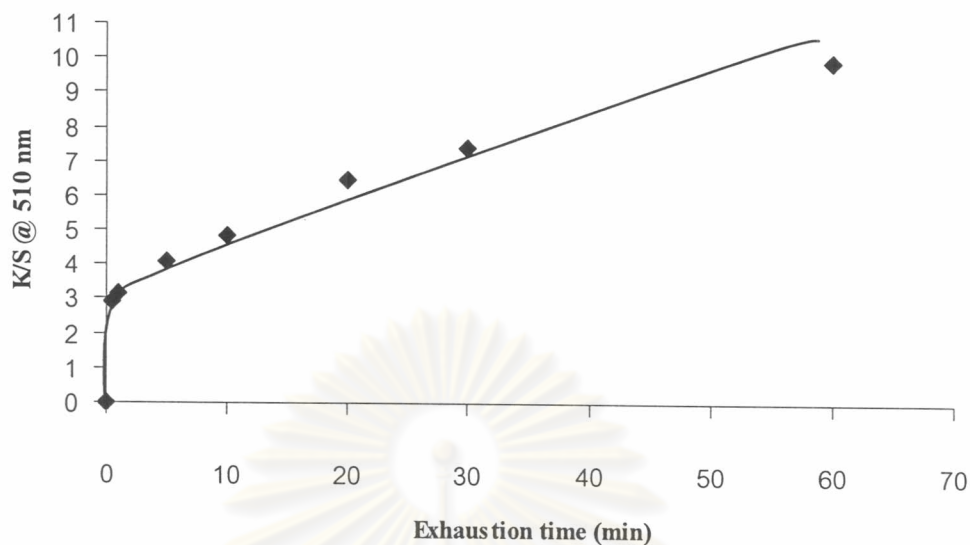
Parameters controlling the dye loading on silk which were studied, are exhaustion time, speed of the spinner, salt concentration, and pH of dye solution.

##### Exhaustion time

2 meters long silk multifilament was exhausted in Scarlet dye with a concentration of 0.5 mM and a pH = 3 and the varied exhaustion time was 30 sec, 1, 2, 5, 10, 20, 30, 60 min.

The K/S value of dyed silk from these experiment increased continuously when the exhaustion time increased (Figure 4.21) because at pH 3, The chemical structure of silk present ammonium group ( $\text{NH}_3^+$ ) interact with sulfonate group ( $\text{SO}_3^-$ ) of Scarlet dye. Because silk multifilament are natural fibers, they present a complicated structure which mainly contain several amino acid types. Therefore a large number of  $\text{NH}_3^+$  groups are presented in acidic condition.

If the Scarlet dye has a long exhaustion time, the possibility to stick on silk is increased. For deposition time from 30 seconds to 2 minutes, the dye molecules can stick on silk very fast. After the dye molecules can stick on silk slowly because the repulsion of like-charged between additional dye and the dye which stick already on silk. The advantage of added salt in the dye solution are decreased the repulsion of them and increased the dye deposition.

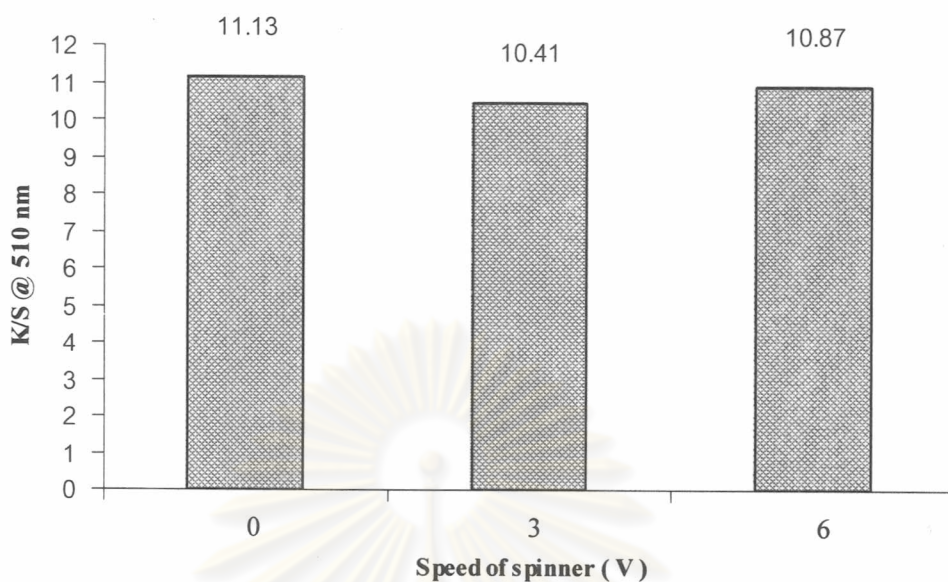


**Figure 4.21** K/S values of dyed silk as a function of the exhaustion time.  
(See the condition p.47)

#### Speed of spinner

Figure 4.22 shows the effect of the speed of spinner on the dye loading. The K/S value was found to be almost constant although the voltage of the control the speed was increased. This means that there are insignificant effect of the spinning rate on dye loading. Therefore silk were immersed in dye solution directly in order to prepare dyed silk substrate for coating with PEM to study improving color fastness.

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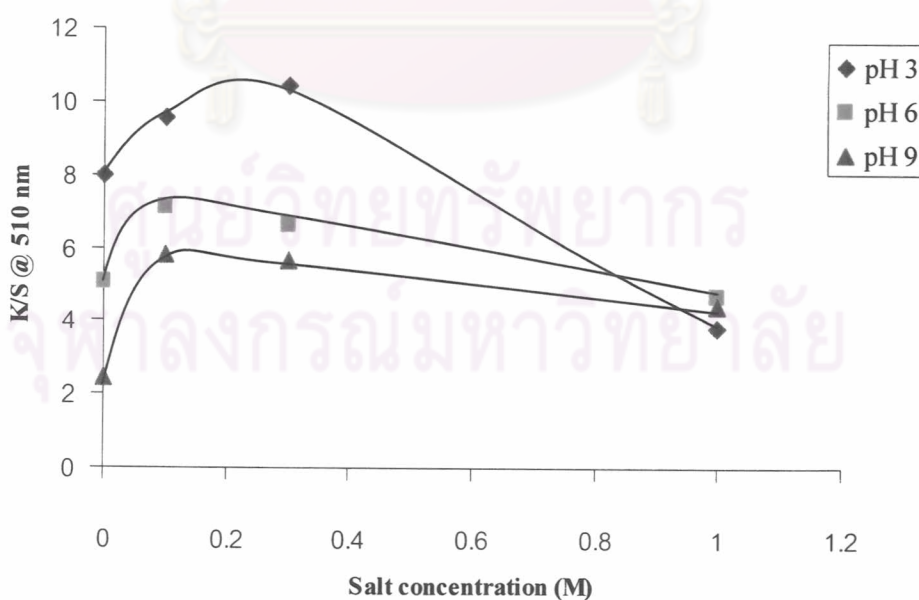


**Figure 4.22** K/S values of dyed silk in varied speed of spinner.

(See the condition p.47)

#### Salt concentration and pH condition

The effect of salt concentration and pH condition of dye solution on dye loading on silk is shown in Figure 4.23



**Figure 4.23** Effect of salt concentration and pH condition of dye solution on dye loading on silk. (See the condition p.47)

### **Salt concentration**

When the salt concentration is increase, the K/S value increased up to 0.1 M and decreased after. Because the ions from salt decreased the repulsion of like-charged between additional dye and the dye which stick on silk already led to an increase in adsorbed amount of dye. For higher salt concentration to 0.1 M, the K/S decreased because dye molecules precipitated with excess salt ions and inhibit the adsorbed amount of dye.

### **pH condition**

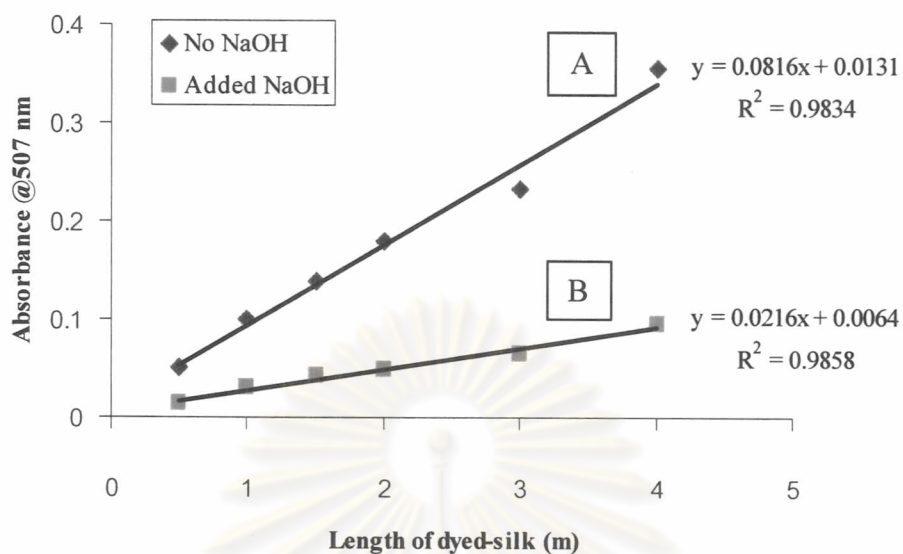
When pH is increased, K/S value decreased because at low pH, the amine groups of amino acid in the chemical structure of silk were protonated to form ammonium ion groups which interact with the sulfonate groups of dye. On the other hand at high pH, the carboxylic groups of amino acid were attacked by hydroxide to form the carboxylate anion and repel the sulfonate anion of the Scarlet dye.

### **4.3.2 Dye release behavior**

Because of silk has a low color fastness to wash, the dye release behavior was studied as follows, dye release from different length of dyed silk, kinetic of dye release in soaping solution, and the dye release in several pH of soaping solution.

#### Dye release behavior at different length dyed silk

Different lengths of silk were dyed in Scarlet dye solution together at same condition. Dyed silk were washed in soaping solution in order to study dye release behavior of different length, The result shows as Figure 4.24



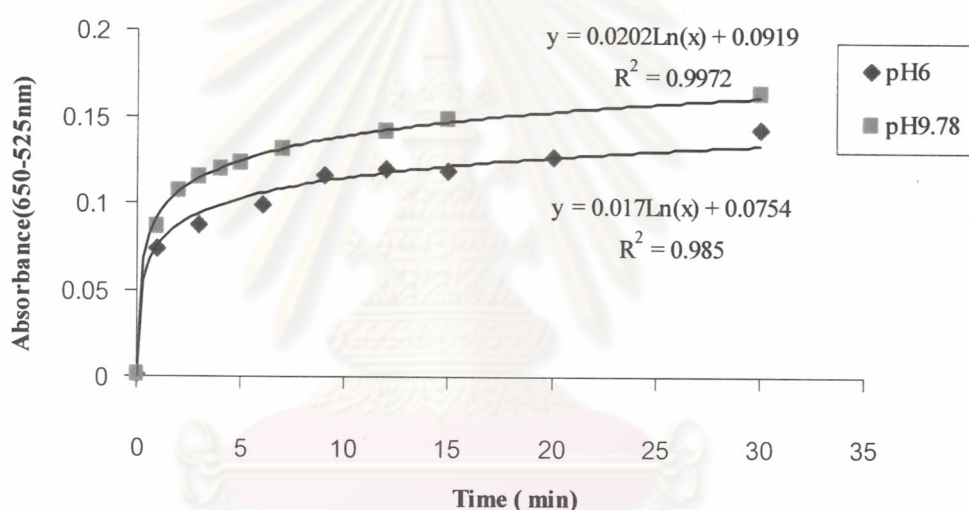
**Figure 4.24** Dye release behavior of different length of dyed silk in soaping solution. (See the condition p.48)

The increasing length of dyed silk lead to an increase in the absorbance because at high pH soaping solution, the ammonium groups ( $\text{NH}_3^+$ ) of silk became neutral amine groups so the sulfonate groups ( $\text{SO}_3^-$ ) of Scarlet dye and the carboxylic groups of silk reversed to negative charge as carboxylate groups which could repel the anionic dye molecules. Finally, the Scarlet dye release from silk. If the length of dyed silk is long, it means that the amount of dye in silk is higher than for shorter fibers. So the dye is released more. The soaping solution after wash is slightly turbid so the absorbances of this solution are higher. By adding sodium hydroxide into this standard detergent the solution were made more clear in order to measure the amount of dye in standard soap accurately. The absorbance values from curve A are higher than curve B because the absorbance of curve B received from soaping solution which was added sodium hydroxide was more clear.

#### Kinetic of dye release

Figure 4.25 shows the kinetic of absorbance of the dye as a function of increasing time. For the first five minutes, the absorbance values were increased quickly then after 5 minutes the absorbance values were increased slowly. Because of at the beginning, the excess dye molecules on dyed silk were released very fast so the

absorbance was increased immediately then slowly because of the following release of dye molecules which stick on silk. This results show that pH of soaping solution depend on kinetic of dye release. The comparison of time when the absorbance value was fixed at 0.125 between pH 6 and pH 9.78 of standard detergent solution were found that the dye release in soaping solution pH 9.78 for 5 minutes while in soaping solution pH 6 for 30 minutes. These mean that the kinetic of dye release in soaping solution pH 6 was slower than soaping solution pH 9.78 because at pH 6, the silk structure maintained the amount of ammonium groups ( $\text{NH}_3^+$ ) which stick with anionic dyes more than pH 9.78.



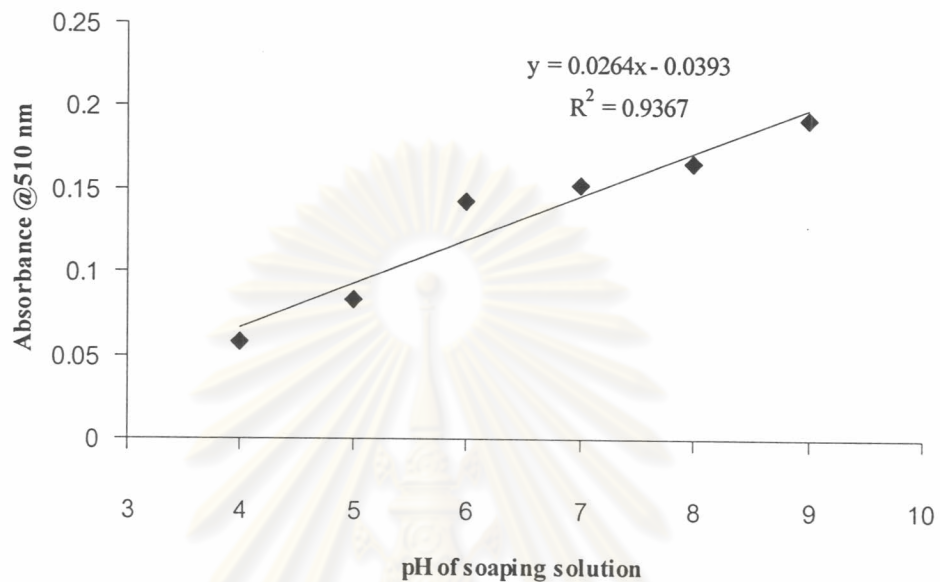
**Figure 4.25** The kinetic of dye release from silk in soaping solution pH 9.78(squares) and pH 6 (diamonds). (See the condition p.48)

#### Dye release behavior of silk in different pH of standard detergent

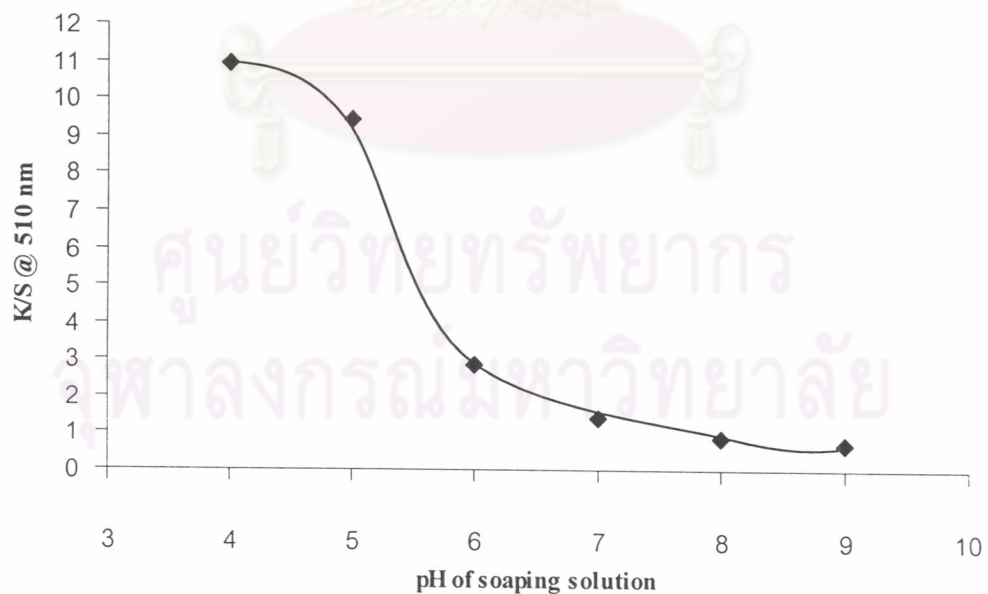
The increasing pH lead to an increase in absorbance values as it can be seen in Figure 4.26 while the K/S value in Figure 4.27 decreased. At low pH, the ammonium groups ( $\text{NH}_3^+$ ) of silk were maintained and could stick with anionic dye molecules. So the dye molecules were released slightly in low pH of soaping solution compare to high pH of soaping solution because the ammonium groups ( $\text{NH}_3^+$ ) of silk reversed to amine groups while the carboxylic groups became carboxylate anions. So the anionic dye molecules were repelled by like-charge carboxylate and release into high pH of soaping solution easier.



After washing dyed silk in different pH of soaping solution, the color strength of dyed silk after wash was measured and shows lower K/S values because the increasing pH of soaping solution increased the amount of dye release.



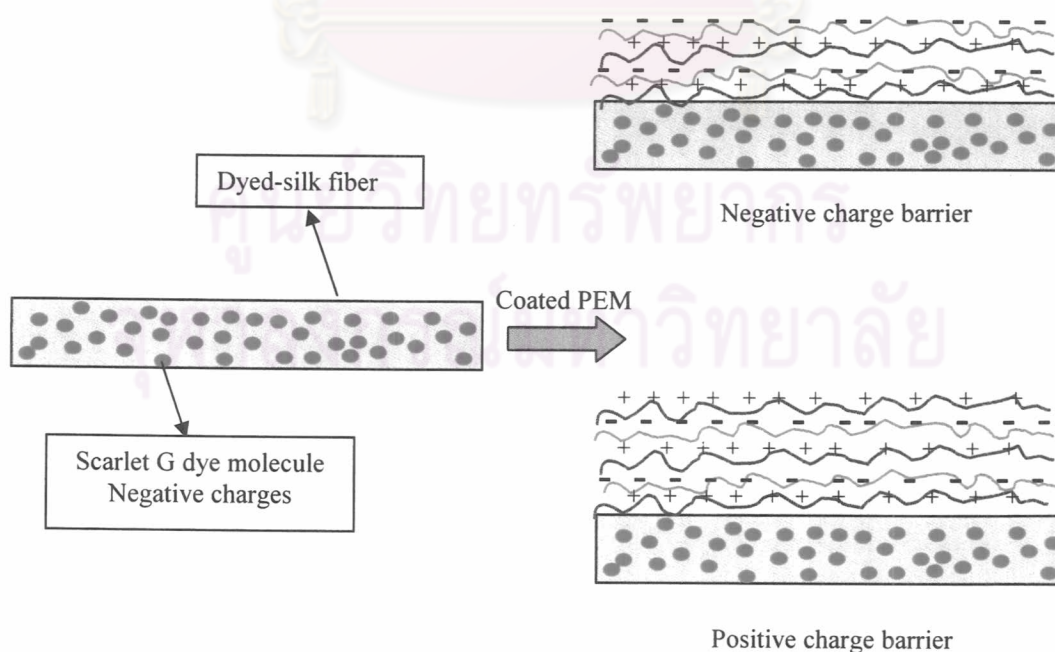
**Figure 4.26** Absorbance as a function of pH of soaping solution.  
(See the condition p.48)



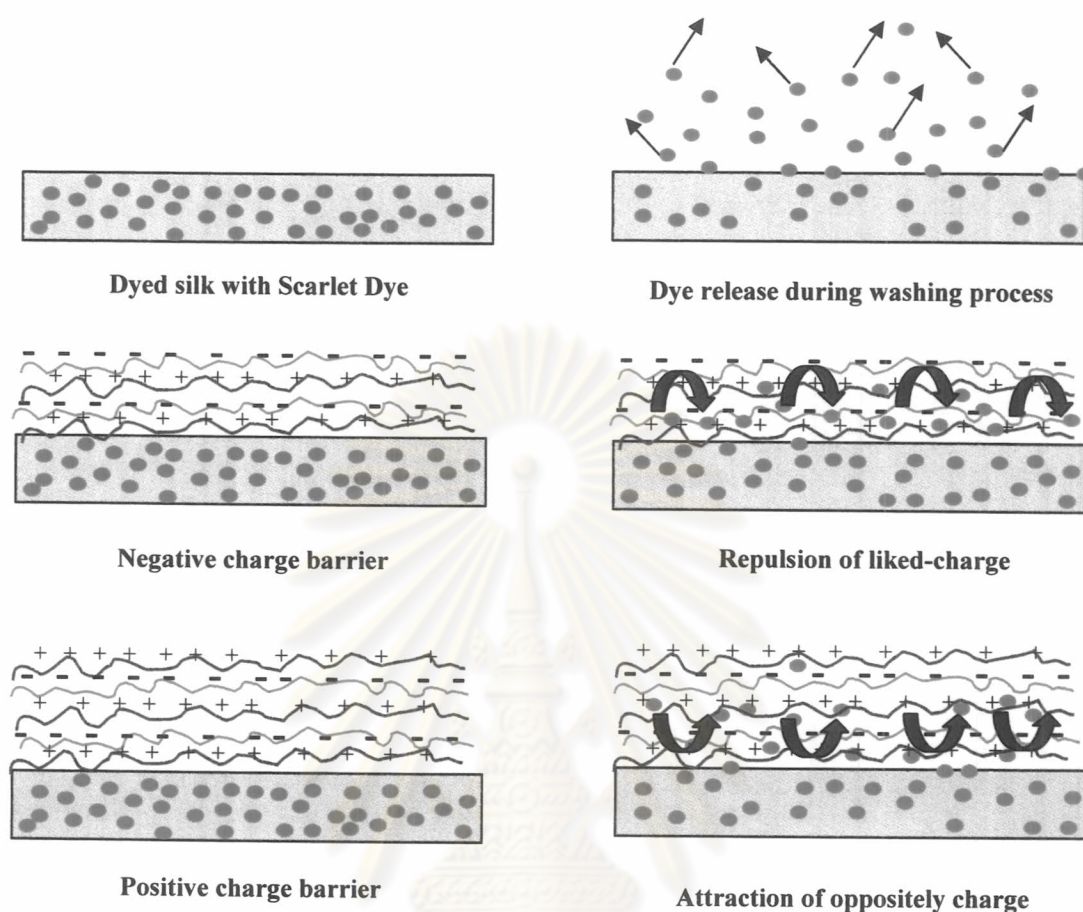
**Figure 4.27** K/S of dyed silk after wash as a function of pH of soaping solution.

#### 4.4 The stability of PEM on silicon wafer.

The low color fastness to washing of dyed-silk is generally a problem. Because of the complicated chemical structure of silk which are mainly contain both of amine and carboxylic groups from many type of amino acid in silk composition, when silk were dyed with acid dye in acidic condition, amine groups in silk were protonated and become ammonium cation ( $-\text{NH}_3^+$ ) followed by attraction with sulfonate anion groups ( $-\text{SO}_3^-$ ) of acid dye by ionic interaction so silk will be dyed with acid dye easily. When dyed-silk are washed in standard soap solution which are high pH condition, the carboxylic groups ( $-\text{COOH}$ ) inside silk become carboxylate ( $-\text{COO}^-$ ) while the ammonium cation reverse to amine group. Unless the sulfonate groups of acid dye cannot combine with amine groups but carboxylate anion groups also repel the sulfonate anion groups of acid dye. These phenomenon cause acid dye molecules release from silk easily during washing process. The idea which expected to improve color fastness to washing of dyed silk is coating PEM on the dyed silk. The concept of the coated PEM on dyed-silk in order to protect dye release is controlled charge density of PEM as follow Figure 4.28, 4.29.



**Figure 4.28** The idea which expect to improve color fastness to washing of dyed silk.



**Figure 4.29** The expected mechanism of dye release during washing process

**Negative charge barrier:** The negative charge density on PEM surface can be manipulated in order to protect anionic dye release from silk fiber by the like-charge repulsion force.

**Positive charge barrier:** The positive charge density on PEM surface can be manipulated in order to protect anionic dye release from silk fiber by attraction force between positive charge of PEM and negative charge of dye molecules induced dye fixation inside PEM.

Before coating the PEM on dyed silk, the suitable type of polyelectrolyte pairs, approximately thickness, and the stability of PEM were investigated in order to choose the condition for PEM coating on dyed-silk. This was done by coating PEM on silicon wafer substrate. Because the different thickness of PEM on silicon wafer induced the different light interference, thus different

interference color appeared. The approximately thickness was correlated to its color appearance of thin film on silicon wafer as show in Table 4.1.

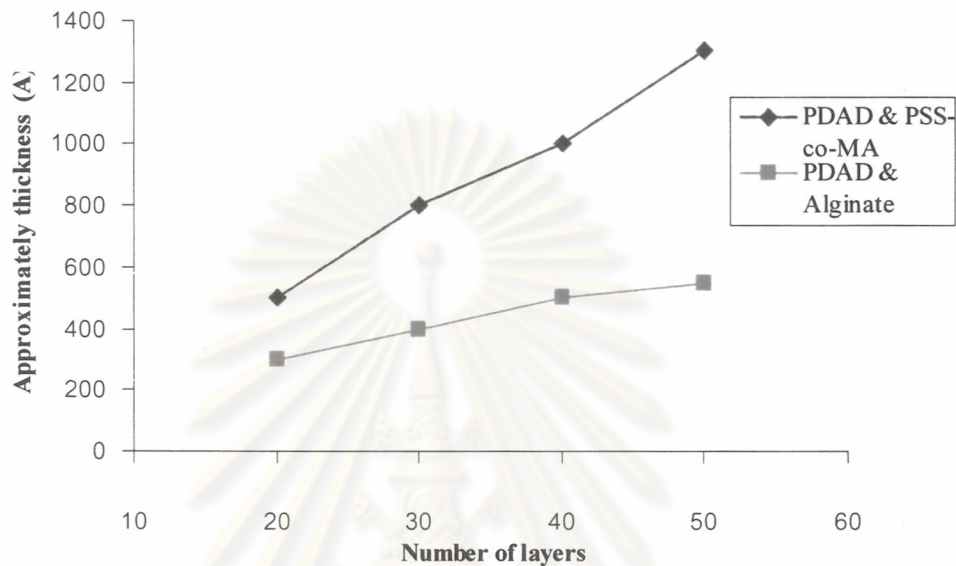
**Table 4.1** Approximately thickness vs. color of PEM on silicon wafer.

Thickness (Å)	Color
500	Brown
1000	Dark Blue
1500	Light Blue
2000	Yellow
2500	Purple
3000-3500	Green

The changes in thickness of film can be observed easily by color appearance. The advantage of this technique is that the stability of PEM can be easily investigated by observation. Nevertheless this method is only approximative and doesn't represent analytical datas.

Different types of polyelectrolyte pairs were chosen to coat PEM on silicon wafer in order to compare the potential growth of PEM at low pH condition because ionic interaction between acid dye and silk must be maintained during coating PEM on dyed silk. The selected polyelectrolyte pairs were PDADMAC/Alginate and PDADMAC/PSS-co-MA. Cationic as PDADMAC and anionic polyelectrolyte as Alginate and PSS-co-MA were chosen to construct PEM on dyed silk because PDADMAC is strong cationic polyelectrolyte and independent pH condition so it can be used for constructing PEM easily at all pH condition. While Alginate and PSS-co-MA anionic polyelectrolytes depend on pH condition. At low pH, Alginate contains carboxylic groups (-COOH) while PSS-co-MA contains strong anionic groups as sulfonate anion ( $-\text{SO}_3^-$ ) which independent condition pH condition, and carboxylic groups, in basic condition, carboxylic groups of both become carboxylate anions induce higher negative charge density. So both of Alginate and PSS-co-MA were constructed with PDADMAC at same condition except pH condition that pH 4.5 for PDADMAC/Alginate and pH 3 for PDADMAC/PSS-co-

MA to investigate the potential growth at low pH and receive higher negative charge density during washing process. The result was shown in Figure 4.30



**Figure 4.30** The approximately thickness as a function of the number of layers for a PDADMAC/Alginate and PDADMAC/PSS-co-MA multilayers deposited on silicon wafer. (See the condition p.50)

Figure 4.30 shows that there is a large difference in growth between PDADMAC/alginate and PDADMAC/PSS-co-MA caused by steric hindrance of polyelectrolyte structure and effect of pH and salt concentration in their system.

#### **Steric hindrance**

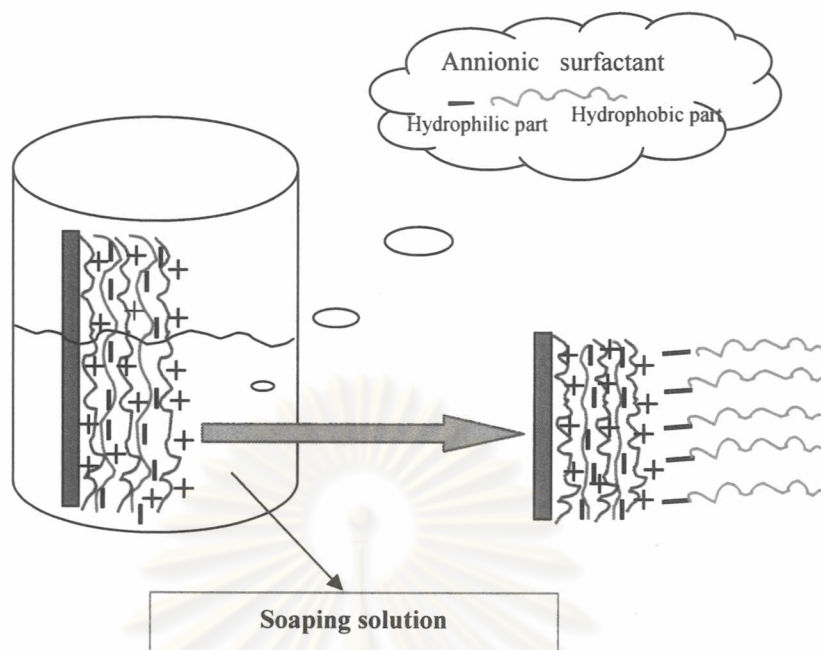
Steric hindrance of Alginate is higher than PSS-co-MA because the native chemical structure of Alginate contains two large aromatic structure as  $\alpha$ -L-gulonate and  $\beta$ -D-mannuronate in its main chain. While the chemical structure of PSS-co-MA are aliphatic main chain and contains aromatic ring pendant side chain. When PEM from PDADMAC/Alginate were coated on silicon wafer, steric hindrance of Alginate hindered the penetration of the additional Alginate in to the already formed PEM. So thickness of PEM from PDADMAC/Alginate increased slowly. While thickness of PEM from PDADMAC/PSS-co-MA increased faster because

PSS-co-MA chain could penetrate into the already formed PEM easily because of small size chain and lower steric hindrance compare to Alginate.

### **Effect of pH condition and salt concentration**

In this experiment, PEM were constructed at low pH condition in order to maintain the ionic interaction between sulfonate groups of acid dye and ammonium groups of silk as describe above. So at low pH, charge density of Alginate and PSS-co-MA were controlled while charge density of PDADMAC did not change because of strong polyelectrolyte. PEM from PDADMAC/Alginate were constructed at pH 4.5, the amount of carboxylic groups more than carboxylate groups slightly and added 1M salt concentration induced the decreasing ionic strength of PDADMAC/Alginate. So PEM from PDADMAC/Alginate demonstrated insignificantly growth. While PEM from PDADMAC/PSS-co-MA were constructed at pH 3, the amount of sulfonate groups were constant but carboxylic groups became carboxylate groups slightly. So the strong anionic groups as sulfonate could affix with cationic groups of PDADMAC easily. Added 1M salt concentration governed on carboxylate groups more than sulfonate anion,  $\text{Na}^+$  could competed PDADMAC to stick on carboxylate groups induced the attraction force between PDADMAC/Alginate were decreased. In the case of PEM from PDADMAC/PSS-co-MA, 1 M salt concentration changed the solution structure, making the chain more flexible by screening intra-chain charge interaction and thus facilitates the kinetics of the adsorption process leading to an increase in adsorbed amounts. So thickness of PEM from PDADMAC/PSS-co-MA was increased faster than PEM from PDADMAC/Alginate.

As a result of this experiment, PEM from PDADMAC/PSS-co-MA were chosen to coat PEM on dyed silk. The samples from this experiment were immersed in soaping solution half part and kept them overnight. The half part of PEM which were immersed in soaping solution was thicker and more hydrophobic as shown in Figure 4.31. Because soaping solution include anionic surfactant which are possible to penetrate inside PEM and form thicker film as follows,



**Figure 4.31** Schematic of the interference of anionic surfactant on PEM

This phenomenon interfere the evaluation of film thickness. The problem was solved by preparing a solution at pH 10 to simulate the soaping solution condition in order to avoid the interference of anionic surfactant.

The next experiment was to study the most important parameters i.e. salt concentration and pH condition which were affected to the growth behavior of PEM from PDADMAC/PSS-co-MA.

The approximately thickness of PEM from PDADMAC and PSS-co-MA 20 and 40 layers which were deposited on silicon wafer at different salt concentrations and pH condition and PEM 40 layers were immersed solution pH 10 were shown in Table 4.2.

**Table 4.2** Approximately thickness as a function of salt concentration and pH condition of PEM from PDADMAC/PSS-co-MA 20 and 40 layers.

pH	Thickness (A°) at different salt concentration (M)								
	0.1	0.2	0.3	0.5		1		1.5	2
3	-	-	-	-		1000 Dark blue		800 Brown	700 Brown
4.5	500 Brown	700 Dark Brown	1000 Dark Blue	1300 Blue	>3500 grey	1800 Light Blue	>3500 grey	-	-
6	-	800 Dark Brown	-	1100 Blue	2500 Purple	1300 Blue	3000 Green	-	-
9	-	800 Dark Brown	-	1000 Dark Blue	3100 Green	1500 Light Blue	2000 Yellow	-	200 Slightly Brown

PEM 20 layers

PEM 40 layers

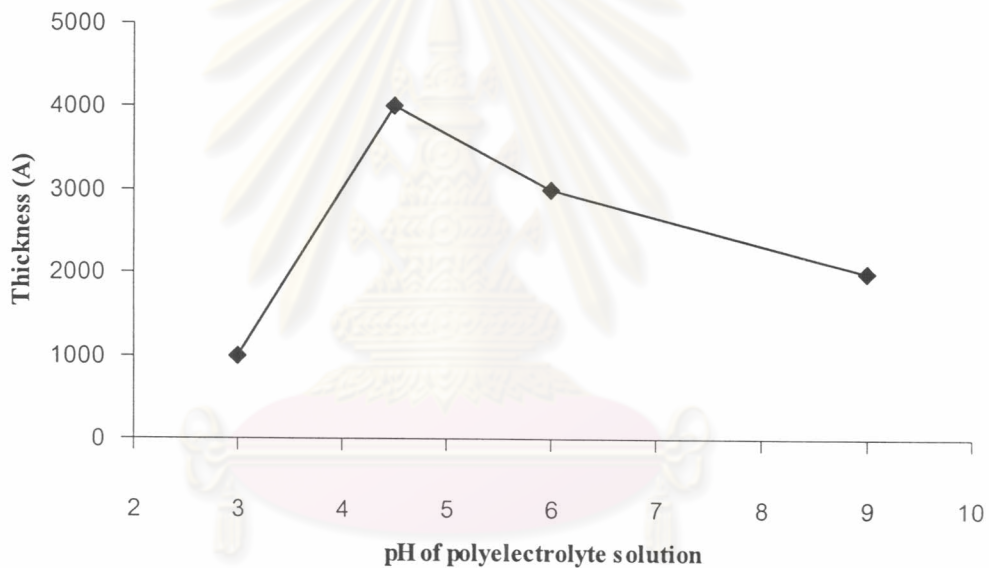
Table 4.2 shows the approximately thickness of PEM from PDADMAC/PSS-co-MA 20 and 40 layers. The increasing PEM thickness built from 20 layers was more unambiguously changed the color appearance than 40 layers because PEM 40 layers was very thick thus limited observation. So the effect of salt concentration on the growth of PEM from PDADMAC/PSS-co-MA was considered. The increasing salt concentration at pH 4.5, 6, and 9 increased the thickness because polyelectrolyte was highly swollen with salt ions and also contained more water, which is brought in with the salt so more polyelectrolyte could add, and the overcompensation extended further into the multilayer due to the effective decrease in segment-segment repulsion.



The excess salt concentration as 2M at pH 9 of PEM 40 layers was very thin because salt ions were complexed with carboxylate anion of PSS-co-MA.

Excess salt concentration did not significantly affect the growth of PEM at too low pH has pH 3 because the reduced charge density was insufficient to form stable multilayers.

The increasing pH condition decreased PEM thickness because PSS-co-MA charge density was increased due to the increasing amount of carboxylate groups ( $\text{COO}^-$ ). So the repulsion force along the chain was increased inducing that the stretched chain were received and making PEM thinner as shown in Figure 4.32



**Figure 4.32** Effect of pH of polyelectrolyte solution on 40 layers PEM from PDADMAC/PSS-co-MA growth at salt concentration 1 M.

(See the condition p.50)

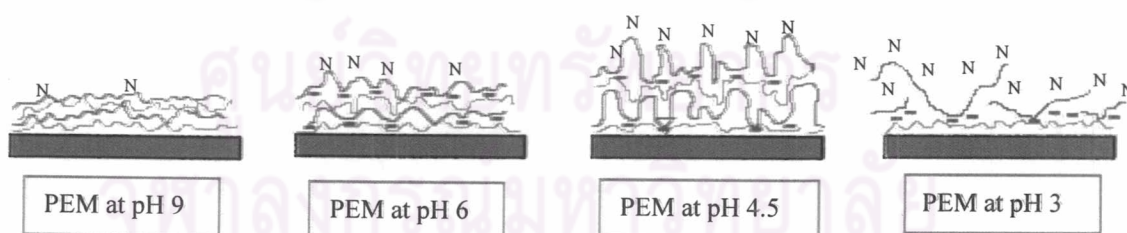
The demonstration of the growth of PEM at 1M salt concentration in different pH condition was shown in Figure 4.33. In this condition, PEM from PDADMAC/PSS-co-MA were constructed on silicon wafer at pH 3, 4.5, 6, and 9 at 1M salt concentration and found that at pH 9, the carboxylic groups of PSS-co-MA were completely ionized and became carboxylate groups because the amount of hydroxide groups were enough to attacked H of carboxylic groups and became

carboxylate groups. So the stretched chain was received, PEM on PDADMAC/PSS-co-MA at this pH were flat and thin due to the chain conformation.

At pH 6, the neutral groups as carboxylic groups of PSS-co-MA increased while the carboxylate groups decreased because of the decreasing amount of hydroxide present at lower pH. The increasing neutral groups decreased the repulsion force between like-charges of intra-chain and making small loops inside the chain caused the increasing of polyelectrolyte penetration. So PEM thickness in this pH condition was thicker than PEM at pH 9.

At pH 4.5, the neutral groups as carboxylic groups of PSS-co-MA were increased more than pH 6 due to the decreasing amount of hydroxide in acidic condition. So the increasing neutral groups were received and induced the large amount of big loops due to the more decreasing repulsion force and encouraged the penetration of the additional polyelectrolyte then the PEM at this pH were thicker more than PEM at pH 6.

At pH 3, PSS-co-MA almost had the amount of carboxylic groups led to PSS-co-MA was very low charge density because the electrostatic attraction in this condition was received from sulfonate groups. When the charge density was too low, the polyelectrolyte chain which adsorbed on the surface were insufficient to overcompensate the surface charge. This meant that the surface charges were not reversed and thus adsorption of the next layer was not possible.



**Figure 4.33** Schematic of PEM from PDADMAC/PSS-co-MA on silicon wafer at different pH conditions.

**Table 4.3** Approximately thickness of PEM from PDADMAC/PSS-co-MA 40 layers after immersed overnight in solution pH 10.

pH	Approximately thickness (Å) at different salt concentration (M)			
	0.5	1	1.5	2
3	-	1000: Dark blue	800: Brown	700: Brown
		1000: Dark blue	600: Brown	700: Brown
4.5	>3500 : Grey	>3500 : Grey	-	-
	1500: Light blue	2500: Purple		
6	2500: Purple	3000 : Green	-	-
	2500: Purple	2500: Purple		
9	3100: Green /Purple	2000: Yellow /Light blue	-	-
	3100: Green /Purple	2000: Yellow /Light blue		

Thickness before immersed

Thickness after immersed

Then PEM samples 20 layers were constructed from PDADMAC and PSS-co-MA in pH 4.5, 6, 9. The results were found that

PEM from pH 4.5 were prepared 3 samples as

Sample 1 was immersed in solution pH 10 immediately and kept overnight. It was found that sample was slightly decomposed .

Sample 2 was kept for 1 day, then immersed in solution pH 10 and kept overnight. It was found that sample was decomposed slightly.

Sample 3 was kept for 3 days, then immersed in solution pH 10 and kept overnight. It was found that sample was stable.

PEM from pH 6 and 9 were immersed in solution pH 10 immediately and keep overnight. It was found that sample was decomposed a little bit and stable respectively. So the suitable condition for coating PEM on dyed silk is as follows,

PDADMAC and PSS-co-MA concentration 1 mM, both of solutions were adjusted pH 4.5 in order to maintain  $\text{NH}_3^+ \dots \text{SO}_3^-$  and COOH was reversed to  $\text{COO}^-$  in order to give the excess negative charged surface to repel the anionic dye during washing process.

#### **4.5 Improving color fastness to wash of dyed silk multifilament by coating with PEM.**

Because of the low color fastness to washing of dyed silk, PEM was used to coat on dyed silk in order to protect dye release with charges in their morphology. In this case, PEM was constructed at low pH condition in order to maintain the ionic interaction between the ammonium groups of silk and the sulfonate groups of Scarlet G dye. Polyelectrolyte pairs which were used in this study, were PDADMAC, PSS-co-MA, and PSS, all of them could be constructed PEM at low pH. Hypothesis of construction of PEM to protect dye release from dyed silk as follows excess negative charge and loosen morphology, and dense morphology and top layers had been high negative charge or positive charge density.

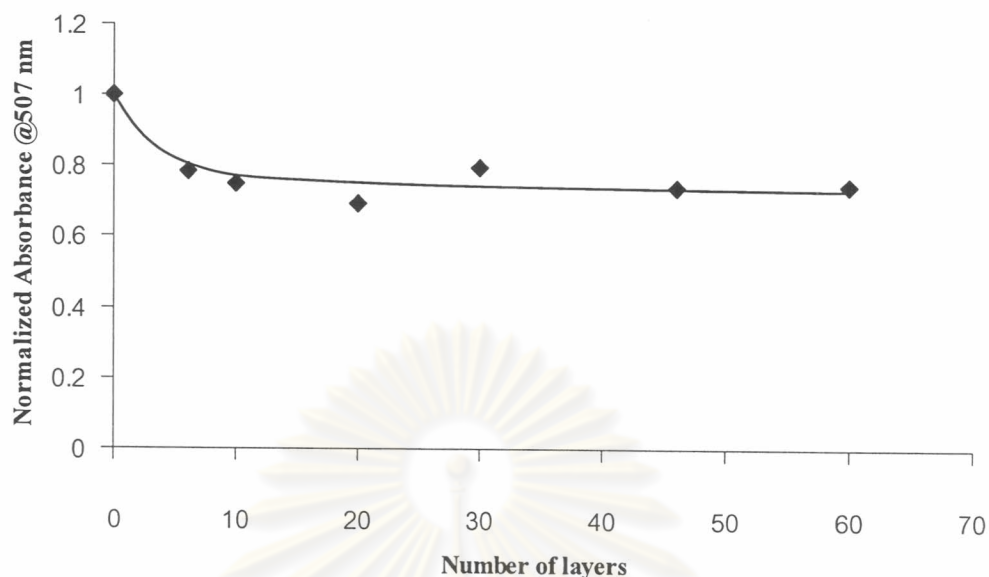
Coated dyed silk was then washed in a standard soap using applied condition from ISO 105-C01 in order to investigate the color fastness to wash. The color fastness was measured as the amount of dye released into the standard soap solution after washing by using UV-Vis spectroscopy technique.

##### **4.5.1 Efficiency of PEM from PDADMAC/PSS-co-MA on dye release protection**

###### **4.5.1.1 Effect of the number of layers**

The number of layers of PEM was varied in order to investigate the effect of thickness of the PEM on dye release behavior. The results are shown in Figure 4.34.

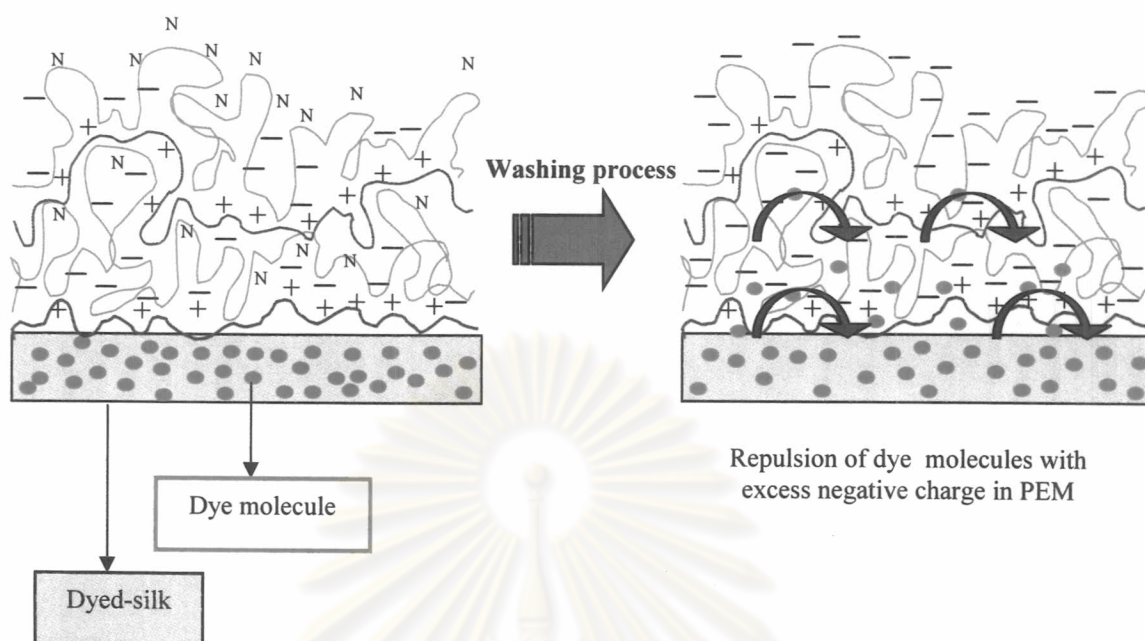
Figure 4.34 shows the absorbance of solution after the washing of the uncoated dyed silk was higher than that of coated dyed silk. The absorbance was found to be constant regardless the increasing number of layers. This result indicated that the dye release behavior independent from the thickness of PEM from PDADMAC/PSS-co-MA. It was also indicated that PEM can protect dye release by 20% ca.



**Figure 4.34** Effect of the number of layers on dye release behavior.  
(See the condition p.51)

**Hypothesis A:** Excess negative charge but loose morphology:  
PDADMAC/PSS-co-MA

In this case, PEM from PDADMAC/PSS-co-MA were constructed at low pH. PSS-co-MA had the large amount of neutral groups as carboxylic which decreased the repulsion force of like-charge along the chain and the loops were received. So PEM were thick but had a loose morphology. When PEM from PDADMAC/PSS-co-MA which were coated on dyed silk, were washed in standard soap solution, the carboxylic groups inside PEM became carboxylic anion groups and led to excess negative charges inside PEM. The results were expected that excess negative charges could be enough repel the anionic dye molecules and protect dye molecules release into the standard soap solution. Model in this case as shown in Figure 4.35.



**Figure 4.35** Schematic of Hypothesis A

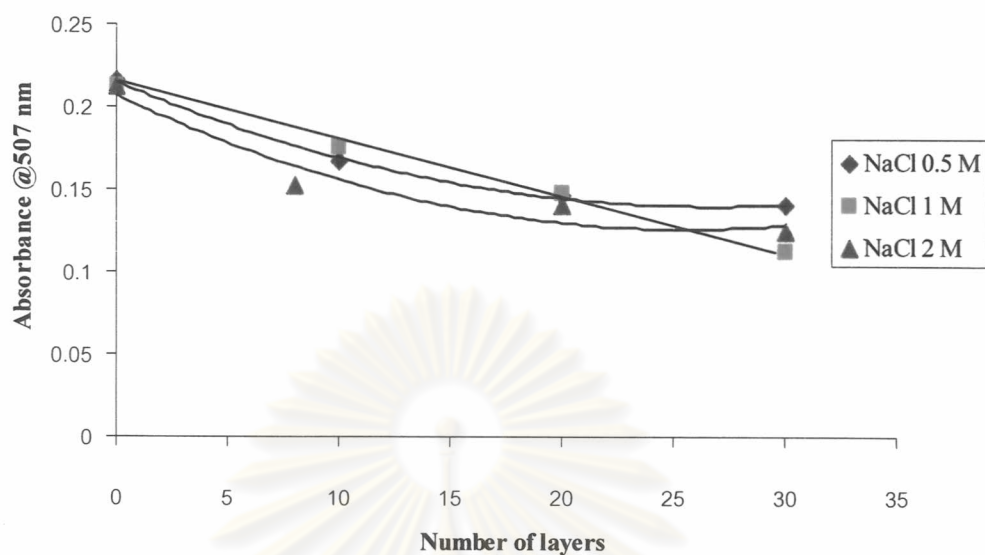
#### 4.5.2 Efficiency of PEM from PDADMAC/PSS on dye release protection

##### 4.5.2.1 Dye release from dyed silk coated with PDADMAC and

##### PSS

In 4.5.1.1, PEM from PDADMAC/PSS-co-MA were coated on dyed silk in order to make the excess negative charged density on the surface during washing process to suppress the anionic dye from discharging into standard soap. In this experiment, PEM from PDADMAC/PSS were coated on dyed silk for the same purpose. However, it was expected that the structure of PEM from PDADMAC/PSS would be denser than that from PDADMAC/PSS-co-MA due to the absence of neutral block.

Figure 4.36 shows that the absorbance was decreased when the number of layers increased as the PEM became thicker so it was more difficult for the dye molecule to be released. Generally, as the concentration of salt increases, the thickness of PEM is also increased but the structure is looser. As a consequent, when the concentration of salt increased, the absorbance was almost constant.

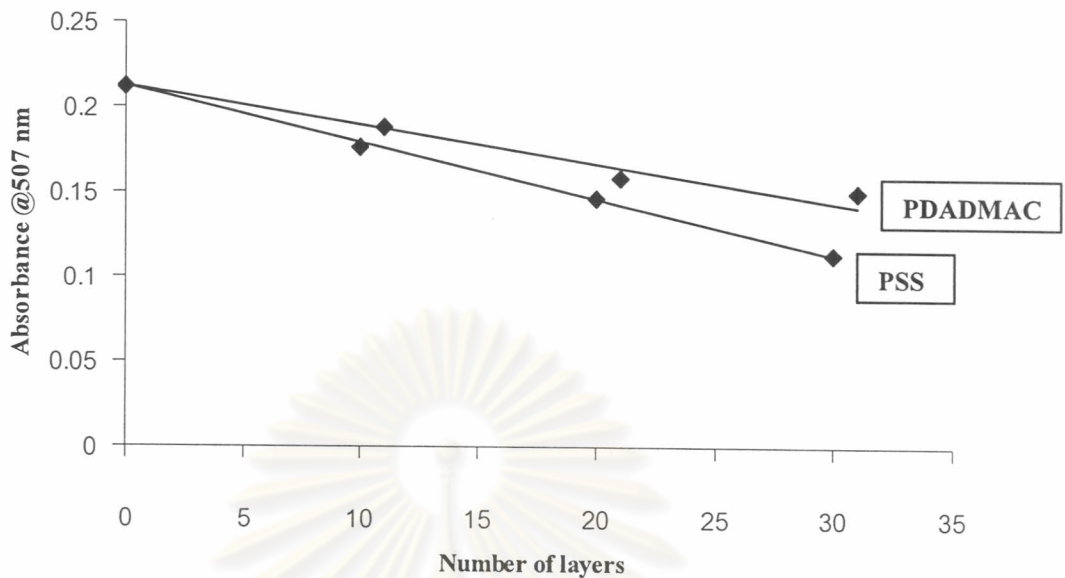


**Figure 4.36** Effects of the number of layers at varied salt concentration on dye release behavior. (See the condition p.52)

#### 4.5.2.2 Effects of type and charged density on the top layer

From 4.5.2.2.1, the top layer of the PEM contains anionic polyelectrolyte (PSS) which had good efficiency to protect dye release. In this experiment, the top layer was compared between positive charge of PDADMAC and negative charge of PSS in order to investigate the efficiency to protect dye release as shown in Figure 4.35

Figure 4.37 shows that PEM with PDADMAC on top had lower efficiency to protect dye release than PEM with PSS on top layer. It was expected that the positive charged surface attracted small anionic dye molecules in the PEM to come out to the surface during washing process. Consequently, the dye molecules were easy to release in the standard soap.

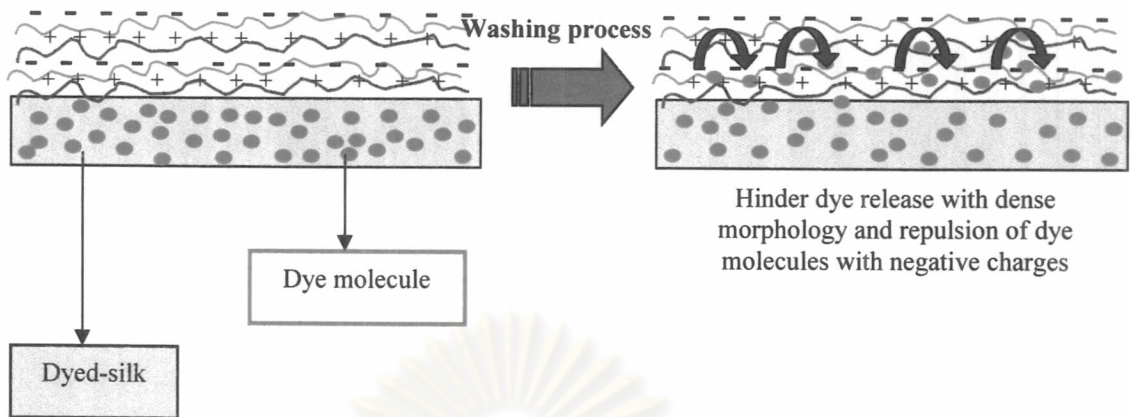


**Figure 4.37** Dye release from coated silk with PEM from PDADMAC/PSS which was PDADMAC and PSS on top layer.  
(See the condition p.52)

**Hypothesis B:** Top layer had high negative charge density but dense morphology: PDADMAC/PSS; The top layer was PSS.

In this case, PEM from PDADMAC/PSS were constructed at low pH. Both of polyelectrolyte pairs were strong polyelectrolytes which are independent from pH condition. So the repulsion force along the chain due to like-charge led to almost stretched chain. PEM from PDADMAC/PSS were flat and dense morphology. The results were expected that dense morphology of PEM and high negative charge density on PEM surface could protect dye molecules release into standard soap by hindered the mobility of small dye molecules and repelled sulfonate groups of Scarlet dye by high negative charge density on PEM surface. Model in this case as shown in Figure 4.38.

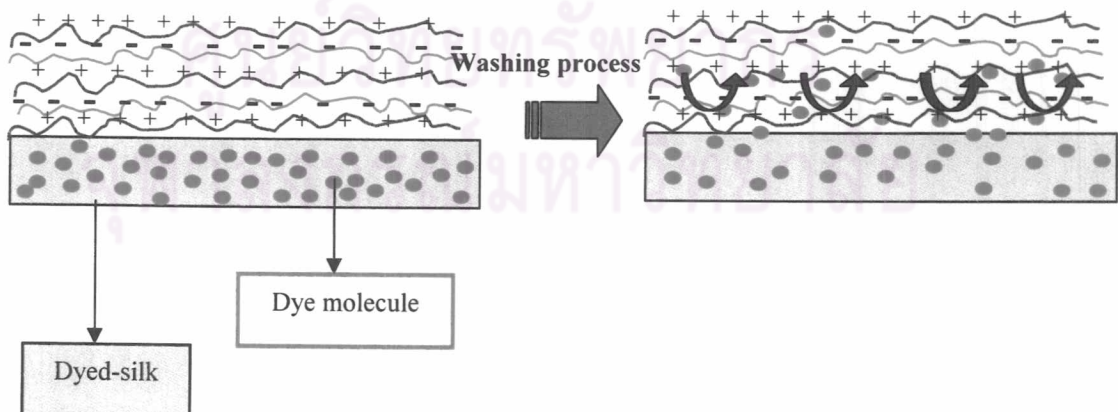




**Figure 4.38** Schematic of Hypothesis B

**Hypothesis C:** Top layer had high positive charge density but dense morphology : PDADMAC/PSS; The top layer was PDADMAC

In this case, PEM from PDADMAC/PSS had high negative charge on PEM surface led to fixation of dye molecules inside PEM by attraction between anionic groups of dye and cationic groups of PDADMAC. Dense morphology of PEM hindered the motivation of small dye molecules release into standard soap solution. Model in this case as shown in Figure 4.39.

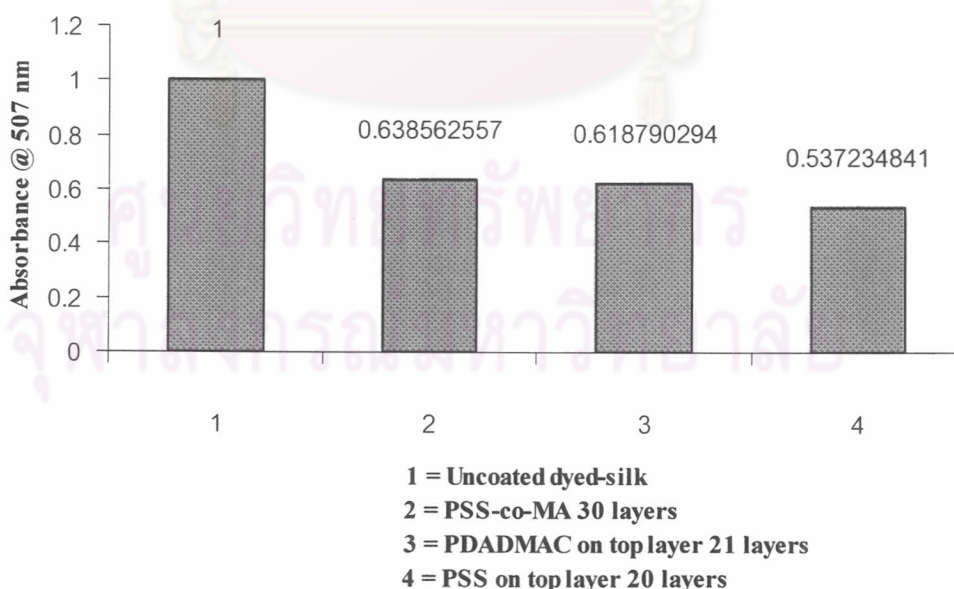


**Figure 4.39** Schematic of Hypothesis C

#### 4.5.3 Comparison the efficiency to protect dye release between uncoated dyed silk, PDADMAC/PSS-co-MA coated dyed silk and PDADMAC/PSS coated dyed silk.

Before coating on dyed silk, PEM from PDADMAC/PSS-co-MA and PDADMAC/PSS were constructed on silicon wafer in order to find the condition which both PEM had the same thickness. Then PEM were coated on dyed silk multifilament and wash in the standard soap. The absorbance at 507 nm of standard soap solution after wash for uncoated dyed silk, PDADMAC/PSS-co-MA coated dyed silk and PDADMAC/PSS coated dyed silk is shown in Figure 4.40.

PEM from PDADMAC/PSS-co-MA had low efficiency to protect dye release because the film was swollen thus possessed more free space to encourage the small dye molecules to come out while dense structure of PEM from PDADMAC/PSS had better efficiency. In the case of PDADMAC/PSS, when PDADMAC was on the top layer, PDADMAC can induced small dye molecule in PEM to migrate to the surface, so dye could be released easier than PEM with PSS on the top layer. PSS was assumed to repel the dye so that it can not come out. This results show that PEM with PSS on top layer had the efficient dye release for about 47 % of the uncoated dyed silk less than conventional coated dyed silk.



**Figure 4.40** Comparison of dye release between uncoated dyed silk, PDADMAC/PSS-co-MA coated dyed silk and PDADMAC/PSS coated dyed silk. (See the condition p.53)