

## **CHAPTER III**

### **EXPERIMENTAL**

#### **3.1 Materials**

##### **3.1.1 Substrates**

###### **3.1.1.1 Glass slide**

Glass slide was used for the PEM deposition from polyelectrolyte and dye because samples was easily be characterized using a UV-Vis spectrophotometer. In this research, glass slide substrate was used for the construction of PEM in order to confirm the growth behavior of PEM on nylon multifilament at same condition.

###### **3.1.1.2 Silicon wafer**

Silicon wafer was coated with PEM films and then immersed in soaping solution to check the stability of the PEM. Different thickness of PEM on silicon wafer can induce light interference which lead to the appearance of different colors. The approximate thickness was correlated to the color appearance of thin film on silicon wafer. When the thin film was half immersed in the solution as standard detergent or adjusted pH solution, the color changed, indicating that film became thicker or thinner. If the film was thinner, it means that the film had decomposed.

###### **3.1.1.3 Nylon multifilament**

Nylon multifilament (Nylon 6, Partially Oriented Yarn, No twist) were kindly donated from Asia Fiber Co, ltd. This substrate was used for the study of the influence of relevant parameters on the formation of polyelectrolyte multilayers. In the pre-study, the nylon multifilament could not be dyed at high pH condition. When the PEM from cationic polyelectrolyte and anionic dye was constructed at high pH condition, dye appeared on nylon. So this result unambiguously proves that the dye fixation was attributed to PEM and the growth of PEM was easily seen by the increase in color strength.

### 3.1.1.4 Silk multifilament

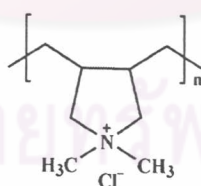
Silk multifilament (Chul 1, Degum, Denier 2.2-2.5, No twist) was used to study the efficiency of the PEM protection against the releasing of dye. Because the charged ability of silk depend on pH condition, at low pH, amine group of silk became positive charge (ammonium cation), vice versa. Therefore silk can successfully be dyed with cationic and anionic dye solution by ionic interaction. The disadvantage of dyed silk with acid dye is its low color fastness to washing. In this research, PEM from cationic and anionic polyelectrolyte are expected to decrease the dye release from dyed silk.

## 3.1.2 Chemicals

### 3.1.2.1 Polyelectrolytes

#### 3.1.2.1.1 Poly(diallyldimethylammonium chloride)

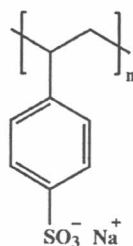
PDADMAC (medium molecular weight, 20 wt% in water, typical  $M_w$  200,000 – 350,000) was purchased from Aldrich. PDADMAC was strong cationic polyelectrolyte which was positive charges along the backbone chain and independent pH condition. The chemical structure of PDADMAC is shown in Figure 3.1



**Figure 3.1** Chemical structure of poly(diallyldimethylammonium chloride)  
: PDADMAC.

#### 3.1.2.1.2 Poly(sodium 4-styrene sulfonate)

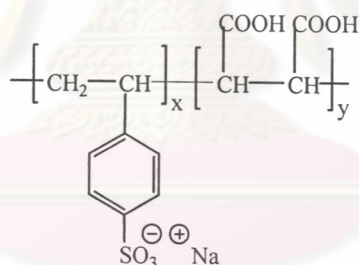
PSS (typical  $M_w$  70,000) was purchased from Aldrich. PSS was strong anionic polyelectrolyte which was negative charges along the backbone chain and independent pH condition. The chemical structure of PSS is shown in Figure 3.2



**Figure 3.2** Chemical structure of poly(sodium 4-styrene sulfonate): PSS

### 3.1.2.1.3 Poly(4-styrenesulfonic acid-co-maleic acid), sodium salt

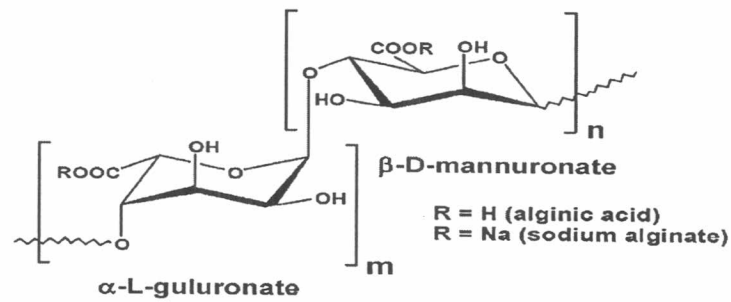
PSS-co-MA (Typical  $M_w$  20,000) was purchased from Aldrich. PSS-co-MA was the anionic polyelectrolyte which included the strong anionic group (sulfonate group) and weak anionic group (carboxylic group). PSS-co-MA is highly negatively charged at high pH because carboxylic groups of the maleic group are converted to carboxylate groups. The chemical structure of PSS-co-MA is shown in Figure 3.3



**Figure 3.3** Chemical structure of poly(4-styrenesulfonic acid-co-maleic acid), sodium salt : PSS-co-MA.

### 3.1.2.1.4 Alginic acid, sodium salt

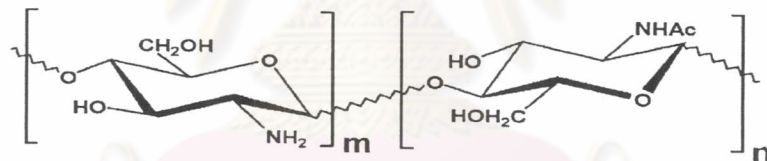
Alginic acid was purchased from Aldrich. Alginic acid is a weak anionic polyelectrolyte. The negative charges of alginate depend on pH condition. At high pH, the carboxylic group is converted to carboxylate group, then the negative charges density is increased. The chemical structure of alginic acid is shown in Figure 3.4.



**Figure 3.4** Chemical structure of alginic acid [24]

### 3.1.2.1.5 Chitosan

Chitosan (Mw 800,000, 84% deacetylation) was purchased from Fluka. Chitosan is protonated at low pH. Amine group was converted to ammonium group and the positive charges were increased. The chemical structure of chitosan is shown in Figure 3.5

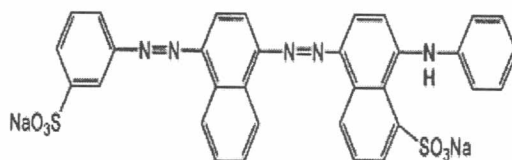


**Figure 3.5** Chemical structure of chitosan [24]

### 3.1.2.2 Dyes

#### 3.1.2.2.1 Nylosan Navy N-RBL ( C.I. Acid blue 113 )

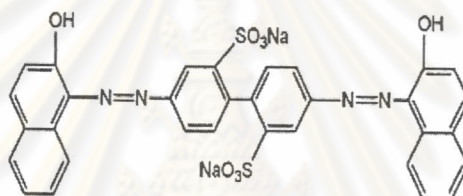
Nylosan was provided by the department of Materials Science, Chulalongkorn University. The chemical structure of Nylosan is shown in Figure 3.6.



**Figure 3.6** Chemical structure of acid dye ( phenyl amino )-5- [[4-(3-sulphonatophenyl) azo]-(1-naphthalenyl) azo]-1-naphthalenesulfonic acid disodium salt [25].

### 3.1.2.2.2 Scarlet G (C.I. Acid Red 97)

Scarlet G was provided by the department of Materials Science, Chulalongkorn University. The chemical structure of Scarlet G is shown in Figure 3.7



**Figure 3.7** Chemical structure of Scarlet G dye [25].

### 3.1.2.3 Others

#### 3.1.2.3.1 Sodium Chloride ( NaCl )

Sodium chloride was purchased from CARLO ERBA. Sodium chloride was dissolved in water and dissociated cation and anion in the solution. Salt was used for increasing the ability of PEM deposition on substrate and thickness of PEM.

#### 3.1.2.3.2 Adjusted pH chemicals

##### 3.1.2.3.2.1 Sodium hydroxide ( NaOH )

Sodium hydroxide was used to adjust the pH to value comprise between 9 - 11

##### 3.1.2.3.2.2 Sodium acetate trihydrate ( $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ )

Sodium acetate trihydrate was used to adjust the pH to value comprise between 6 - 8

### **3.1.2.3.2.3 Acetic acid glacial ( CH<sub>3</sub>COOH )**

Acetic acid was purchased from Lab-Scan Analytical Science, was used to adjust the pH to value comprise between 3 - 5

### **3.1.2.3.3 Piranha solution**

Sulphuric Acid concentrated : H<sub>2</sub>SO<sub>4</sub> and Hydrogen peroxide : H<sub>2</sub>O<sub>2</sub>, both of solutions were purchased from AnalaR®. Piranha solution was used for removed organic contaminants and made hydrophilic on surface of substrate.

### **3.1.2.3.4 Ethanol ( C<sub>2</sub>H<sub>5</sub>OH )**

Ethanol was used for solvatochromism test of PEM on glass slide.

### **3.1.2.3.5 Deionized water**

### **3.1.2.3.6 Standard soap without optical brightening agent**

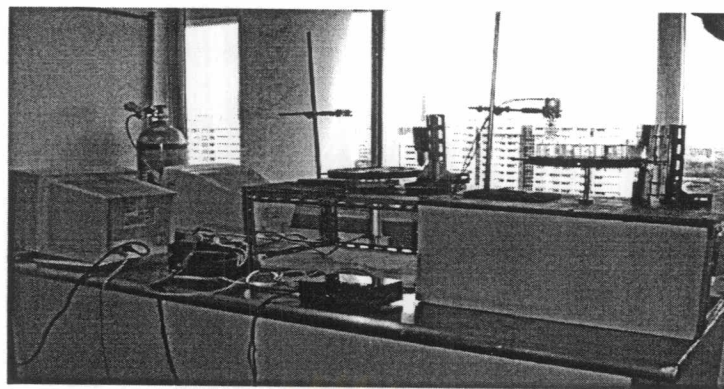
Standard soap was purchased from SDC ENTERPRISES LIMITED. This soap was suitable for use in procedures specified in ISO 105:1989:C01 to C05.

## **3.2 Equipments**

### **3.2.1 Experimental equipments**

#### **3.2.1.1 Automatic dipping machine**

Automatic dipping machine was an important equipment. The number of layers and dipping time in each solution were determined and controlled by computer program. This machine made it convenient for the user to control the dipping time in each solution accurately in order to receive the completely thin film. The automatic dipping machine is shown in Figure 3.8

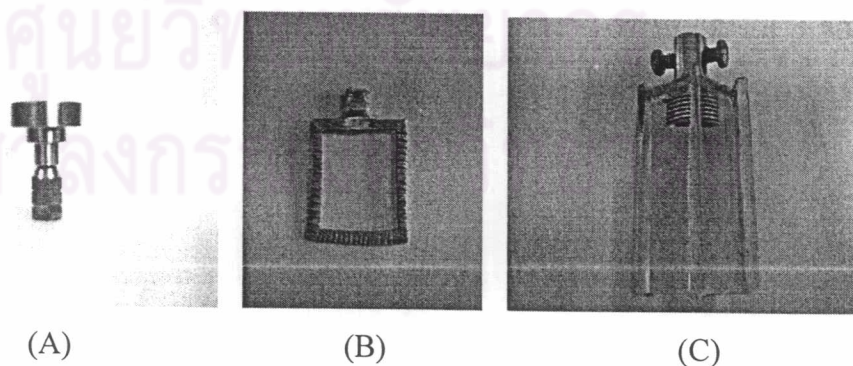


**Figure 3.8** Automatic dipping machine.

### 3.2.1.2 Holder supports

The holder was an important equipment because it supported the substrate to be immerse in the solution. The holder was affixed to the small motor to stir the substrate in the solution in order to mix solution homogeneous and promote even PEM deposition on substrate.

In early experiment, a stainless steel shaft was used for support the planar substrate while for the multifilament, aluminium holder was used but the inconvenient of this holder were, at high pH, holder was oxidized and became black, and could not wrap long length of multifilament. A new holder which was a resin holder, was designed, and was easier to wrap and resisted the severe condition. This type of holders are shown in Figure 3.9



**Figure 3.9** Holder supports : Holder for planar substrate (A), Holder for multifilament substrate ; aluminium holder (B) and transparent resin holder (C).

### 3.2.1.3 pH/ion meter

(Model 25 from Denver Instrument) was used for measure pH in the solutions.



Figure 3.10 pH/ion meter : Model 25

### 3.2.1.4 Transonic 460/H from Elma®

Transonic was used for sonicate in order to mix the composition in the solution. Finally, homogeneous solution was received.

### 3.2.1.5 Thermometer

Thermometer was used for measure the temperature, when the soaping solution was heated by hot plate for dye release test.

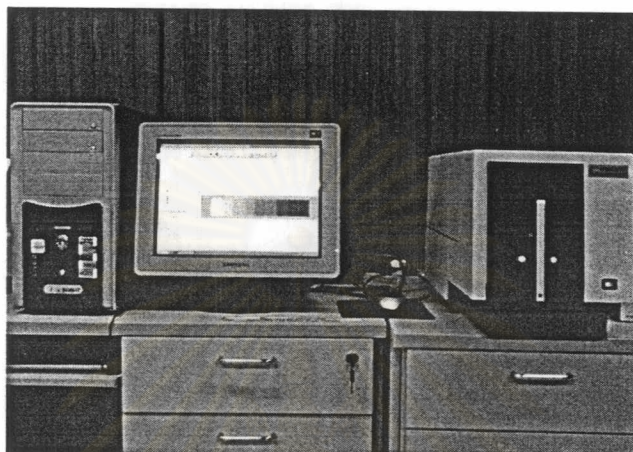
## 3.2.2 Characterized equipments

### 3.2.2.1 Macbeth COLOR EYE® 7000 spectrophotometer

Because the sample was a multifilament, it was too small for the small channel of the instrument. The test sample was prepared by wrapping the coated-multifilament two times on plastic  $1 \times 4 \text{ cm}^2$  to ensure that the multifilament covered the plastic uniformly. The instrument analyzes the light being reflected from the sample and produces an absorption spectrum. The ratio between the sorption coefficient (K) and the scattering (S) can be extracted from the reflectance data where R is the reflectance of the fabric at 510 nm. The K/S value is commonly used to represent the amount of dye fixation or dye content of a given textile fiber. The



measurement parameters of the spectrophotometer were selected as followed: 10 from the observer, D65 illuminant, specular and UV-Vis included. Color strength of coated-multifilament was received from K/S value at wavelength from 360 to 750 nm. Macbeth COLOR EYE® 7000 spectrophotometer is shown in Figure 3.11

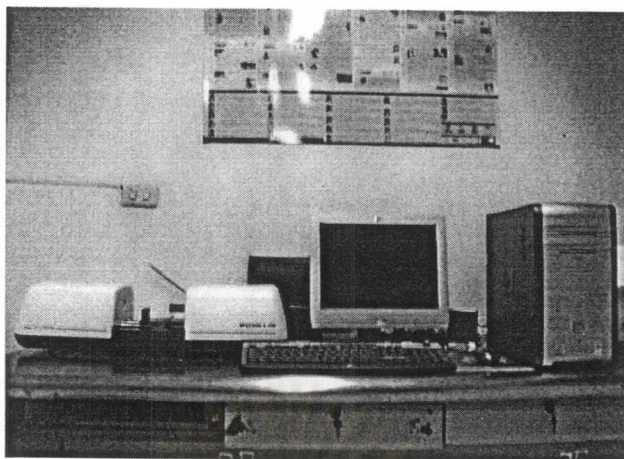


**Figure 3.11** Macbeth COLOR EYE® 7000 spectrophotometer.

#### **3.2.2.2 UV-Vis Spectrophotometer (SPECORD S 100, Analytikjena)**

Prior to any spectrophotometric measurements, a bare clean glass slide was first introduced and recorded as a background. For the measurements, the PEM coated glass slide was measured. The absorbance of the thin film was measured in the 400 to 700 nm visible range, which includes the absorbance peak of the Scarlet G dye. UV-Vis spectrophotometer (SPECORD S 100, Analytikjena) is shown in Figure 3.12

จุฬาลงกรณ์มหาวิทยาลัย



**Figure 3.12** UV-Vis Spectrophotometer (SPECORD S 100, Analytikjena)

### 3.3 Methodology

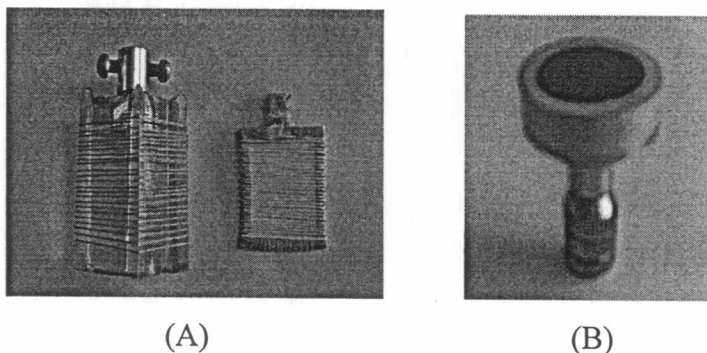
#### 3.3.1 Substrate Preparation

##### 3.3.1.1 Cleaned substrate

Silicon wafer and glass slide were cleaned in 70% $\text{H}_2\text{SO}_4$  (concentrated) / 30%  $\text{H}_2\text{O}_2$  (aq) (“piranha”; caution, piranha is a strong oxidizer and should not be stored in closed containers) and then in hot  $\text{H}_2\text{O}_2$ /ammonia/water, 1:1:7 v/v, rinsed in water, and blow dry with stream of air. Multifilaments were used as received without any further treatment.

##### 3.3.1.2 Substrate onto holder

Nylon or silk multifilament were wrapped onto the holder before dipping in the solutions while the planar substrates as silicon wafer or glass slide were affixed to a stainless steel shaft with parafin film. The substrate onto holder are shown in Figure 3.13



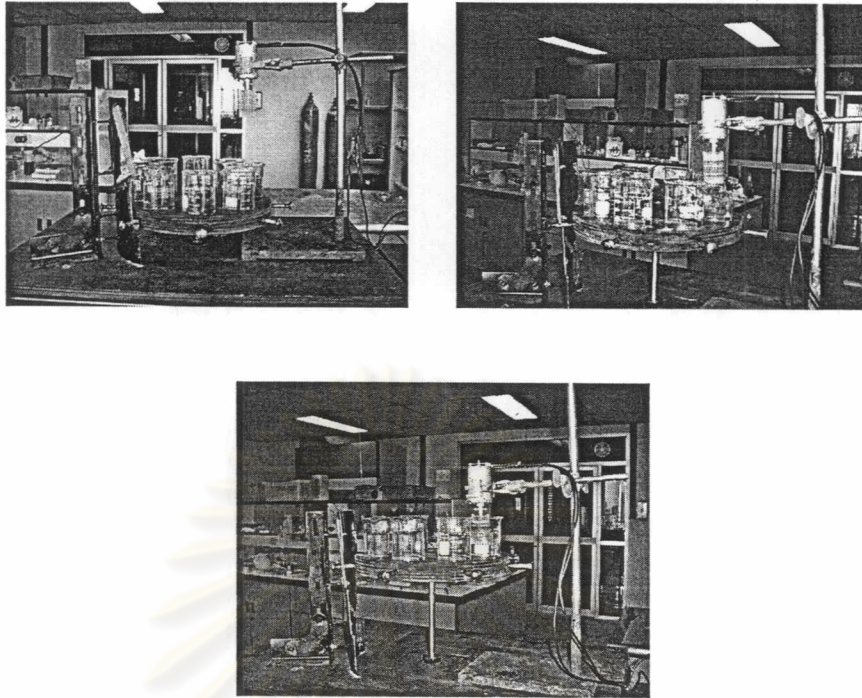
**Figure 3.13** Different substrates onto holder ; multifilament (A) , silicon wafer substrate (B).

### 3.3.2 Solution Preparation

The solution in this system composed eight 100 ml beakers, two beakers consist of dilute cationic and anionic polyelectrolyte solutions, other beakers were rinse water. Solutions of various pH were prepared by mixing the appropriate amount of acetic acid with sodium acetate trihydrate and 1 M sodium hydroxide solution was used to adjust the pH to 11. In both cationic and anionic polyelectrolyte solutions sodium chloride salt was added, then sonicated in order to dissolve. After added salt, pH of solutions were measured pH again for certain pH condition.

### 3.3.3 Preparation of polyelectrolyte multilayer thin films

The holder was rotated by a small DC motor. A home-built robotic platform, accommodating eight 100 ml beakers, was programmed to expose the substrate alternately to two polyelectrolyte solutions with three rinses of water or buffer depend on type of polyelectrolyte in between. The substrate was dipped at the first step in cationic polyelectrolyte solution. The sample was then washed by dipping three times in water or buffer (total washing time 2 minutes). The sample was then dipped in the anionic polyelectrolyte solution. The dipping and washing procedure described above was repeated to construct multilayer. The demonstration of the construction PEM on multifilament is shown in Figure 3.14.



**Figure 3.14** Demonstration of the construction PEM on multifilament.

### 3.3.4 Dyeing process

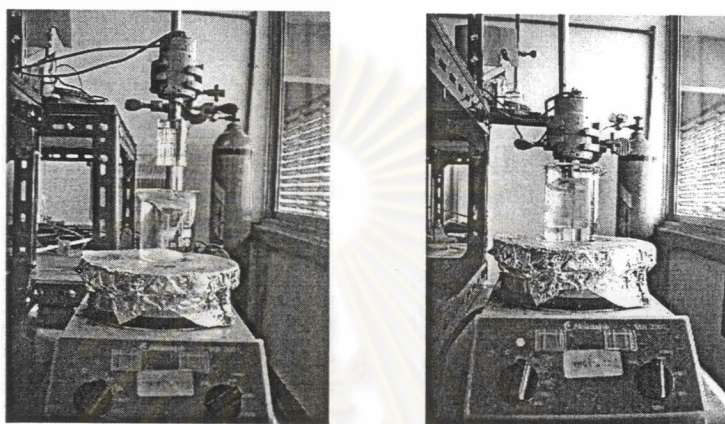
Silk multifilament which were wrapped onto a plastic holder, were dyed with Scarlet G concentration 0.5 mM, pH 3 at room temperature for 30 minutes. The ionic strength of the Scarlet G solution was adjusted to 0.1 M NaCl. Dyed silk multifilament were rinsed in distilled water pH 3 and fresh water 2 times, then dried in order to construct PEM in the next step.

### 3.3.5 Color fastness to washing test

The samples which were prepared from this research were multifilament, without twist. Although the samples were not enough to weave and be prepare into fabrics, color fastness to washing test in this research could be applied from standard testing : ISO 105-C01: 1989.

Coated silk were wrapped on the resin holder, then the holder was spun from small DC motor. The standard soap concentration 0.5 %wt, volume 80 ml was heated up previously at temperature  $40 \pm 2$  °C. The substrate was immersed in

standard soap for 30 minutes, rinsed two times in cold distilled water and dried. The multifilament K/S value after washing was monitored using Macbeth COLOR EYE<sup>®</sup> 7000 spectrophotometer and the standard soap solution after wash was monitored using UV-Vis Spectrophotometer. The demonstration of color fastness to washing test is shown in Figure 3.15.



**Figure 3.15** Color fastness to washing test

### 3.3.6 Specific experimental conditions

#### 3.3.6.1 Preliminary study of the construction of polyelectrolyte multilayers on glass slide by Layer-by-Layer technique

The construction of polyelectrolyte multilayers (PEM) by Layer-by-Layer deposition technique is a relatively new technology in Thailand. So the preparation method of construction of PEM and the step of using the automatic dipping machine were studied before the research was done. The dye was selected to construct PEM with positive charged polyelectrolyte because film growth could be observed and monitored the increasing color strength of PEM on glass slide by using UV-Vis spectrophotometer

In this study, PEM were constructed from cationic Chitosan and anionic acid dye (Nylosan). The Nylosan dye molecule contains two sulfonate groups, which can electrostatically interact with the positively charged Chitosan on the glass slide and therefore can be used to prepare PEM. The Layer-by-Layer deposition of the

Chitosan-Nylosan thin films was monitored using UV-Vis spectroscopy as a function of the number of layers.

In addition, the characteristic solvatochromism of the resulting thin films was investigated as a function of the ethanol concentration in water for its potential use as ethanol sensor.

**Table 3.1** Experimental condition of the possibility construction of PEM from Chitosan and Nylosan dye on glass slide.

No. of bi-layers	Chitosan concentration (%w/w)	Nylosan concentration (mM)	Salt concentration (M)	Dipping time (min)	pH
5,10,15,20, 25,30,35,40	0.1	0.14	0.1	2	4

**Table 3.2** Experimental condition of the solvatochromic behavior of the Nylosan dye solution.

Nylosan concentration (mM)	pH	3, 4, 5, 7
0.14	Ionic strength (M)	0, 0.1, 0.5, 1
	Ethanol content (%)	0, 10, 20, 30, 40

**Table 3.3** Experimental condition of the potential use of Chitosan-Nylosan thin films as an alcohol sensor

Construction of PEM condition		Demonstration of Chitosan-Nylosan thin films as an alcohol sensor
Dipping time (min)	2	PEM was immersed in different ethanol content 10,20,25,30,35,40, and 45%wt
Salt concentration (M)	0.1	
Chitosan concentration (%w/w)	0.1	
Nylosan concentration (mM)	0.14	
pH	4	
Number of layers	40	

The next experiment, PEM from dye and oppositely charged polyelectrolyte were constructed on nylon multifilament. Nylosan was not selected because solvatochromism property of Nylosan depend on ionic strength and pH of solution. This reason might affect to the experiment, so Scarlet G dye was selected because it is more stable in various solution.

### 3.3.6.2 Investigation of the constructed condition of PEM on nylon multifilament

Dye ability on nylon multifilament was pre-study in order to find non-dyeable condition of dyeing nylon with Scarlet G solution. A certain pH of non-dyeable condition from this study was used to construct PEM. PEM from PDADMAC and anionic acid dye (Scarlet G) were coated on nylon multifilament compare with dipped nylon in the Scarlet G solution at same condition in order to prove that the dye appearance indicated that PEM could grow on nylon multifilament.

**Table 3.4** Experimental condition of dye ability on nylon multifilament.

Substrate	Dye concentration (mM)	Salt concentration (M)	pH	Exhaustion time (hr)
Nylon multifilament length 3 m	0.5	0	3, 5, 7, 9, 11, 12	1

**Table 3.5** Experimental condition of the preparation of PEM on nylon multifilament at pH11

Experiments	No. of layers	PDADMAC concentration (mM)	Scarlet G concentration (mM)	Salt concentration (M)	Dipping time (sec)
Construction of PEM	4, 8, 12, 16, 20, 24, 30, 40, 60, 80	1	0.5	0.1	30
Dyeing	4, 10, 16, 20, 30, 40, 60	Rinse water			

### 3.3.6.3 Parameters controlling the growth of PEM on nylon multifilament

The different growth of PEM from the experiment 3.3.6.2 was assured that PEM could construct on nylon multifilament. The next interesting topic was the parameters controlling the growth of PEM on nylon multifilament. PEM were constructed on nylon multifilament and varied some parameters such as deposition time, salt concentration, polyelectrolyte and dye concentration which were expected to affect to control the growth of PEM.

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย



**Table 3.6** Experimental condition of the study of parameters controlling the growth of PEM on nylon multifilament.

Parameters	No. of layers	Deposition time (min)	Salt concentration (M)	PDADMAC concentration (mM)	Scarlet G dye concentration (mM)
1 Deposition time	20	15s, 30s, 1, 2, 5	0.1	1	0.5
1.1 Same deposition time in both solutions					
1.2 Fixed deposition time 5 min in PDADMAC					
1.3 Fixed deposition time 5 min in ScarletG		0, 0.1, 0.3, 0.5, 0.7, 1	30 sec	0.1	0.01, 0.1, 1, 10, 20
2 Salt concentration					
2.1 Nylon substrate					
2.2 Glass slide		0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.75, 1	30 sec	0.1	0.01, 0.1, 1, 10, 20
3 Polyelectrolyte and dye concentration					
3.1 Same concentration in both solutions					
3.2 Fixed PDADMAC concentration 1 mM		0.001, 0.01, 0.1, 1, 10, 50	30 sec	0.1	0.005, 0.05, 0.5, 5, 50
3.3 Fixed ScarletG concentration 0.5 mM					

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

Dye loading and release behaviors were studied in order to better understand the parameters which were exhaustion time, speed of spinner, salt concentration, and pH condition of dye solution for dyeing process. Dye release was studied because the relationship between length, time and pH which was adjusted in soaping solution with sodium hydroxide for high pH and acetic acid for low pH, can affect the dye release behavior.

Note: Dye release experiment, soaping solution was received from pH adjusted of standard detergent solution by sodium hydroxide and acetic acid.

#### 3.3.6.4.1 *Dye loading behavior*

**Table 3.7** Experimental condition of the study of parameters controlling of dye loading.

Factors	Length (m)	Scarlet G concentration (mM)	pH	Salt concentration (M)	Dipping time (min)	Speed of spinner (V)
1 Deposition time	2	0.5	3	0.1	30s, 1,	0
2 Speed of spinner					2, 5, 10,	
3 Salt concentration and pH condition			20, 30,	60		
			3, 6, 9	0, 0.1, 0.3, 1	30	0, 3, 6
						0

### 3.3.6.4.2 Dye release behavior

**Table 3.8** Dye loading condition of each experiment.

Experiments	Length (m)	Scarlet G concentration (mM)	pH	Exhaustion time (hr)
1 Dye release of different length	0.5, 1, 1.5, 2, 3, 4	0.5	3	1
2 Kinetic of dye release	3			
3 Effect of pH of soaping solution which adjusted by sodium hydroxide and acetic acid on dye release	2			

**Table 3.9** Experimental condition of the study of dye release behavior.

Experiments	Soaping solution concentration (%wt)	pH of soaping solution which were adjusted pH by sodium hydroxide and acetic acid	Temperature (°C)	Exhaustion time (min)
1 Dye release of different length	0.4	9.78	50 ± 3	30
2 Kinetic of dye release		9.78		Monitored using UV-Vis at 1, 2, 3, 4, 5, 7, 12, 15, 30
		6		1, 3, 6, 9, 12, 15, 20, 30
3 Effect of pH of soaping solution on dye release		4, 5, 6, 7, 8, 9		30

Note :

- Kinetic of dye release: at pH 6, the soaping solution after washing were added NaOH in order to make the solutions clear.
- Effect of pH of soaping solution on dye release: at pH 4-9 were added NaOH 1 M 35 drops and KOH 2-3 pellets in order to make the solutions clear.

### 3.3.6.5 Study the stability of PEM on silicon wafer

The stability of PEM on silicon wafer was the important experiment which had to be done before constructing PEM on silk. Because of the suitable constructed condition, approximately thickness, and the stability of PEM in soaping solution must be studied on a substrate which would be easier to see the changed phenomenon. When the suitable conditions were found, PEM were constructed on dyed silk.

Positive and negative charge densities of PEM were selected by suitable type of polyelectrolyte. If the PEM contributed to high negative charge barrier, it indicated that PEM reversed excess negative charge was washed in standard detergent in order to repel anionic dye which might be released at high pH. If PEM was positive charged barrier, it indicated that PEM had the excess positive charge in order to attract the anionic dye to protect dye release.

Polyelectrolyte pairs were selected to construct PEM in order to compare their potential growth of PEM on silicon wafer. The important parameters as salt concentration and pH condition which were affected to the growth of the PEMs, were studied. PEM from this experiment was tested about the stability in soaping solution in order to check the color change on silicon wafer when the PEM was decomposed. Finally, the suitable condition was selected in order to coat dyed silk for protecting dye release.

Note: Soaping solution in this experiment means that standard detergent solution.

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

**Table 3.10** Experimental condition of selected the suitable polyelectrolyte pairs to construct PEM on silicon wafer.

Type	No. of layers	Dipping time (min)	Salt conc. (M)	PDADMAC conc. (mM)	Anionic polyelectrolyte conc. (mM)		pH
					Alginic acid	PSS-co-MA	
PDADMAC / Alginate	20, 30,	1	1	1	1	-	4.5
PDADMAC / PSS-co-MA	40, 50				-	1	3

**Table 3.11** Effect of salt concentration and pH condition on the growth of PEM from PDADMAC/PSS-co-MA on silicon wafer.

No. of layers	Dipping time (min)	Salt conc. (M)	pH	PDADMAC conc.(mM)	PSS-co-MA conc. (mM)
40	1	0.5,1	3, 4.5, 6, 9	1	1
20		0.2, 0.5, 1	4.5, 6, 9		

### Stability testing of PEM on silicon wafer

PEM on silicon wafer was immersed half part in soaping solution 0.4 %wt overnight. The resulting film was opaque and looked thicker because the soaping solution could penetrate in thin film and complex. We could therefore not see the changed of film thickness clearly. This problem was resolved by preparing a solution with similar pH than the soaping solution and immersed thin film in order to avoid the interference from anionic surfactant. The induced decomposition of PEM was checked by changed of color on silicon wafer.

### 3.3.6.6 Improving color fastness to wash of dyed silk multifilament by coating with PEM

The suitable condition which were found from 3.6.6.5 were used to construct PEM on dyed silk multifilament in order to investigate the efficiency of protect dye release from PEM coated silk. The experiments in this study had 3 parts as follows, construction of PEM from PDADMAC/PSS-co-MA and PDADMAC/PSS. Both of them were observed the different potential protecting dye release which effected from charged density.

**Table 3.12** Dyed silk condition before coating PEM.

Experiments	Length (m)	Scarlet G concentration (mM)	pH	Exhaustion time (hr)
1 PEM from PDADMAC/PSS-co-MA	3	0.5	3	1
2 PEM from PDADMAC/PSS				

#### 3.3.6.6.1 *Construction of PEM from PDADMAC/PSS-co-MA on dyed silk multifilament*

This experiment describes the effect of PEM which were constructed at different salt concentration and the number of layers on the potential protecting dye release.

**Table 3.13** Experimental condition of constructed PEM from PDADMAC /PSS-co-MA.

Experiments	No. of layers	Dipping time (min)	Salt concentration (M)	PDADMAC concentration (mM)	PSS-co-MA concentration (mM)	pH
Effect of the number of layers	6, 10, 20, 30, 46, 60	1	1	1	1	4.5

**Table 3.14** Washing condition of coated dyed silk with PEM from PDADMAC/PSS-co-MA.

Experiments	Soaping solution concentration (%wt)	Temperature (°C)	Exhaustion time (min)
Effect of the number of layers of PEM on color fastness to wash.	0.5	40 ±2	30

*3.3.6.6.2 Construction of PEM from PDADMAC/PSS on dyed silk multifilament*

This experiment describe the effect of PEM which were constructed at different salt concentration and opposite top layer on the potential protecting dye release

**Table 3.15** Experimental condition of constructed PEM from PDADMAC /PSS.

Experiments	No. of layers	Dipping time (min)	Salt concentration (M)	PDADMAC concentration (mM)	PSS concentration (mM)	pH
1 Effect of salt conc.	10, 20, 30	1	0.5, 1, 2	1	1	3
2 Effect of type of top layers	10, 11, 20, 21, 30, 31		1			

**Table 3.16** Washing condition of coated dyed silk with PEM from PDADMAC/PSS.

Experiments	Soaping solution concentration (%wt)	Temperature (°C)	Exhaustion time (min)
1 Effect of salt conc.	0.5	40 ±2	30
2 Effect of type of top layer			

Note :

1. Effect of PEM which were constructed at different salt concentrations on color fastness to wash.
2. Effect of type and charge density on top layer

### 3.3.6.7 Comparison the efficiency of protected dye release

First time, PEM from PDADMAC/PSS-co-MA and PDADMAC/PSS were constructed on silicon wafer in order to find the condition which could construct PEM with equal thickness. Then this condition was used to construct PEM with different type of top layer on dyed silk and observed dye release behavior compare with uncoated dyed silk.

**Table 3.17** Experimental condition of construction PEM from PDADMAC /PSS-co-MA and PDADMAC/PSS at same thickness on dyed silk.

Types of top layer	No. of layers	Dipping time (min)	Salt conc. (M)	PDADMAC conc. (mM)	PSS-co-MA conc. (mM)	PSS conc. (mM)	pH
Uncoated dyed silk	0	1	1	-	-	-	-
PSS-co-MA	30			1	1	-	4.5
PSS	20			1	-	1	3
PDADMAC	21			1	-	1	3



**Table 3.18** Washing condition of coated PEM from PDADMAC/PSS-co-MA and PDADMAC/PSS at same thickness on dyed silk.

Types of top layer	Soaping solution concentration (%wt)	Temperature (°C)	Exhaustion time (min)
Uncoated dyed silk	0.5	40 ±2	30
PSS-co-MA			
PSS			
PDADMAC			

Note: Coated dyed silk was then washed in soaping solution which was 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.

ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย