# CHAPER III

# RESULTS AND DISCUSSION

## 3.1 Synthesis of diacetylene monomers containing boronic acid head group

In this study, diacetylene monomers containing boronic acid head groups were synthesized (Figure 3.1). Monomers **1a-3**a possess an amide group while monomers **4e-6e** have an ester linkage. Since all six monomers had not been reported; the chromic properties of the corresponding PDAs against various external stimuli would have been very interesting. The effects of amide and ester group on the chromic properties of PDAs supramolecular were studied, including thermochromism, affinochromism, solvatochromism and alkalinochromism.

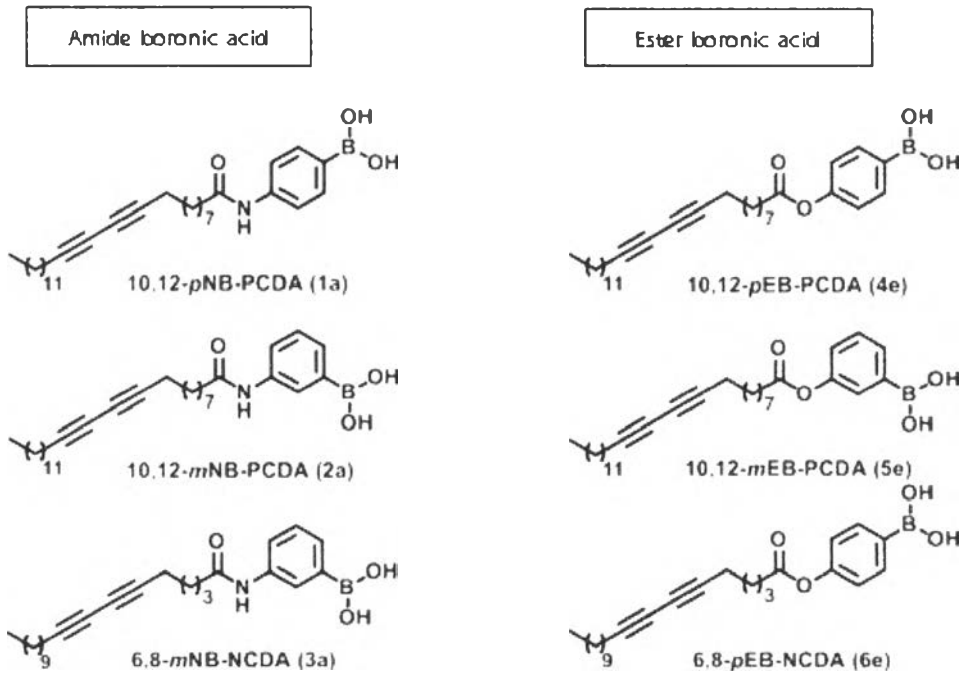
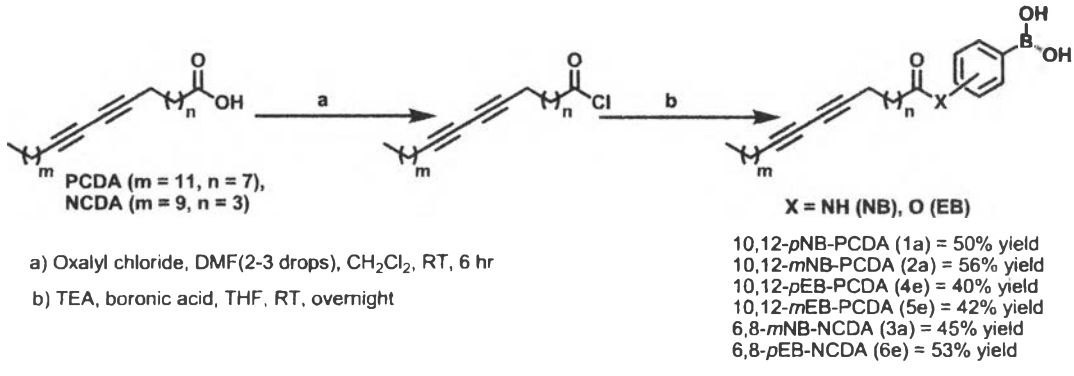



**Figure 3.1** Structure of diacetylene monomers in this study.

### 3.1.1 Synthetic method for diacetylene monomers containing boronic acid head group (1a-6e)

To synthesize diacetylene monomers containing boronic acid (**1a-6e**): pentacosadiynoic acid (PCDA) and nonacosadiynoic acid (NCDA) were first transformed into the corresponding acid chloride in $CH_2Cl_2$ (Scheme 3.1). Subsequently, the crude acid chloride was reacted with a boronic acid for example 4-aminophenylboronic acid, 3-aminophenylboronic acid, 4-hydroxyphenylboronic acid and 3-hydroxyphenylboronic acid. In this reaction, these boronic acids act as nucleophile in the presence of triethylamine (TEA) as a base to give the desired diacetylene monomers (**1a-6e**) shown in Scheme 3.1. Target monomers were purified by recrystallization in methanol to give the white solids of **1a-6e**.




**Scheme 3.1** Synthetic route of boronic acid diacetylene monomers (**1a-6e**).

The $^1$H-NMR spectra of the target monomers containing amide boronic acid in DMSO-$d_6$ are shown in Figure 3.2. All signals can be assigned according to their structures. For example, the signals at approximately 6.71 (u) and 7.39 (v) ppm belong to the para-substituted aromatic proton of 10,12-*p*NB-PCDA (**1a**). 10,12-*m*NB-PCDA (**2a**) and 6,8-*m*NB-NCDA (**3a**) have similar signals. The signal at approximately 9.80 ppm corresponds to NH proton and the signals at approximately 7.25-9.80 ppm belong to the aromatic proton and OH proton of boronic acid. The $^1$H-NMR of monomer (**2a-3a**) indicates that they contain amino and boronic acid group. Thus, the results confirmed that the structures of the desired products.

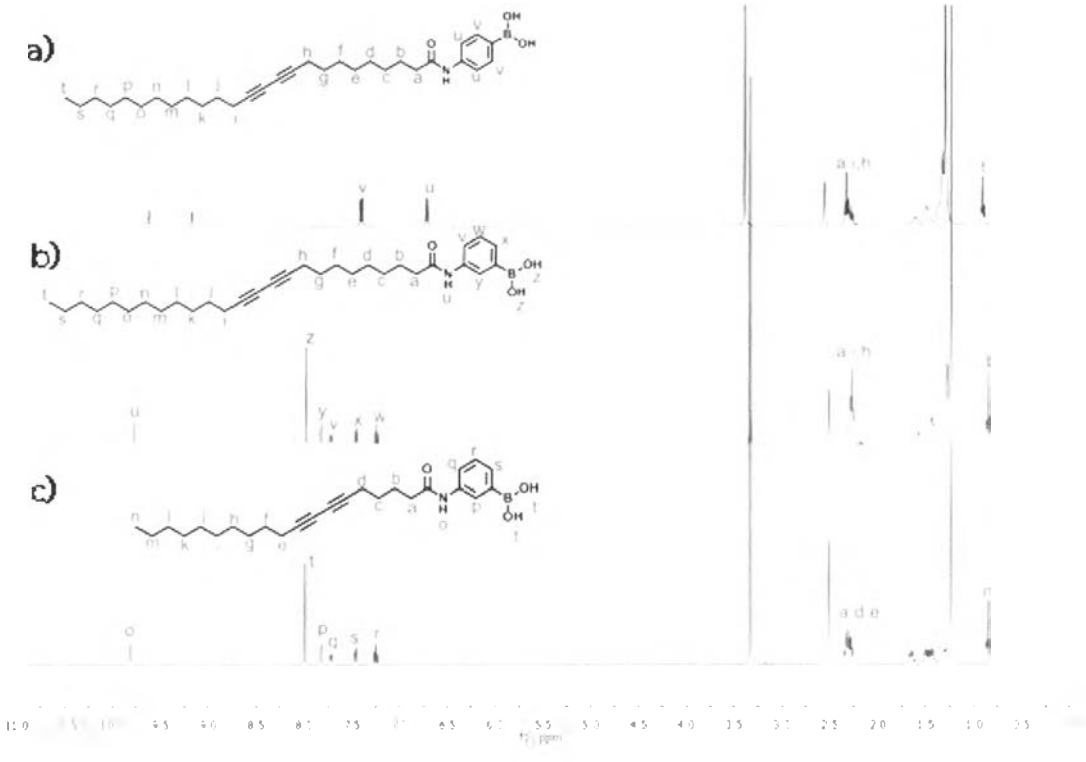





**Figure 3.2** $^{1}$H-NMR spectra of amide boronic acid diacetylene monomers: a) 10,12-*p*NB-PCDA (**1a**), b) 10,12-*m*NB-PCDA (**2a**) and c) 6,8-*m*NB-NCDA (**3a**).

Similarly, the $^{1}$H-NMR spectra of the target monomers containing ester boronic acid (**4e**-**6e**) in $CDCl_3$ are shown in Figure 3.3. All signals can be assigned according to their structures. For example, the signals at approximately 6.71 (u) and 7.39 (v) ppm belongs to the *para*-substituted aromatic proton of 10,12-*p*EB-PCDA (**4e**) and 7.01 (o) and 7.73 (p) of 6,8-*p*EB-PCDA (**6e**). The signals at approximately 7.25-9.80 ppm belong to the aromatic proton and OH proton of 10,12-*m*EB-PCDA (**5e**). The resulting $^{1}$H-NMR confirm the structure of all prepared monomers.

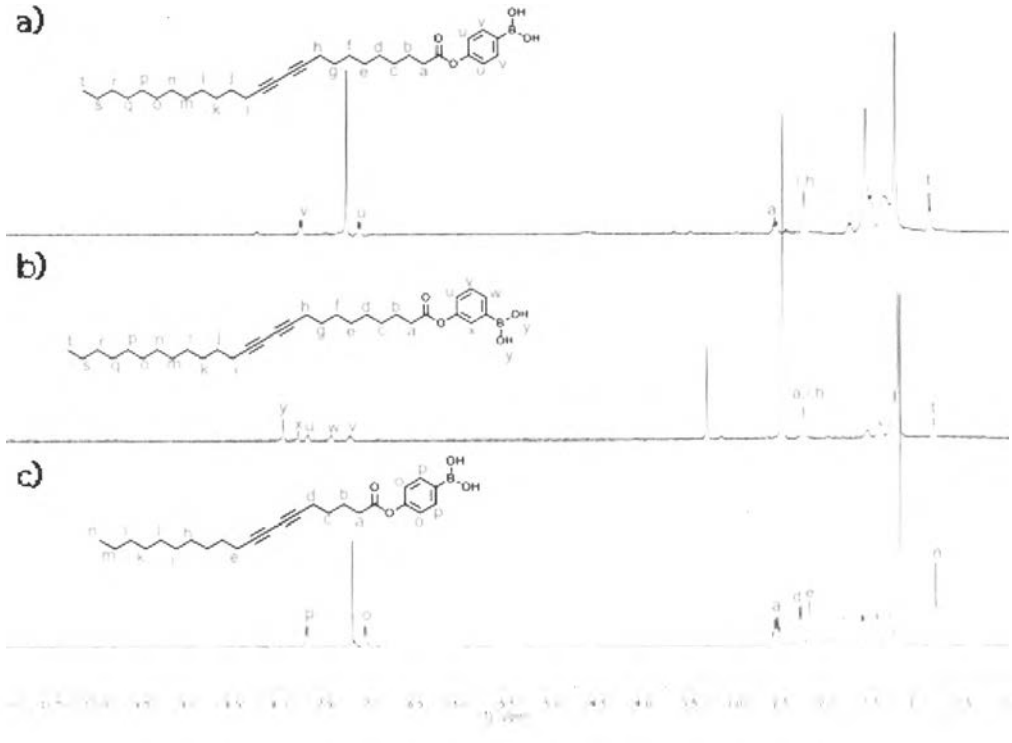



**Figure 3.3** $^{1}$H-NMR spectra of ester boronic acid diacetylene monomers a) 10,12-*p*EB-PCDA (**4e**), b) 10,12-*m*EB-PCDA (**5e**) and c) 6,8-*p*EB-NCDA (**6e**).



### 3.2 Preparation of PDA sols and characterization

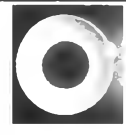
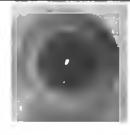
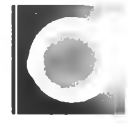
#### 3.2.1 Polymerization of diacetylene monomers

To study the chromic properties such as affinochromism, thermochromism, solvatochromism, alkalinochromism and photochromism of PDA derived from monomers **1a-6e**, all prepared diacetylene monomers were first transformed into PDA sols. Firstly, all synthesized monomers were dissolved in chloroform (1 mL). Subsequently the solvent were evaporated using $N_2$ gas followed by suspension in Milli-Q water as described in Chapter II. The appearance of disperse monomers were presented in Table 3.1 (second row) showing colorless to pale blue color. Next, resulting aqueous sols were irradiated with UV light (254nm) for 5 minutes at 0°C to give a blue-color solution as illustrated in Table 3.1 (third row). These results indicated the formation of ene-yne conjugated polydiacetylenes. The blue color corresponds to an increase in conjugation length of conjugated polymer. The ability to be hydrated and the color of polymerized diacetylenes were also presented in Table 3.1. Upon exposure to UV light (254 nm) for 5 minutes at 0°C, 10,12-*p*NB-PCDA

(**1a**), 10,12*m*NB-PCDA (**2a**) and 6,8-*m*NB-PCDA (**3a**) were transformed into blue sols while 10,12-*p*EB-PCDA (**4e**) and 10,12-*m*EB-PCDA (**5e**) appeared as pale blue sols. However, 6,8-*p*EB-NCDA (**6e**) cannot be polymerized giving a clear solution. Intensity of PDA color positively correlates with polymerizability of their monomers, which is dependent on its packing efficiency. Thus, strong blue appearance from 10,12-*p*NB-PDA (**1a**), 10,12-*m*NB-PDA (**2a**) and 6,8-*m*NB-PDA (**3a**) are indicative of strong hydrogen bonding between amide group and $\pi$-$\pi$ aromatic stacking in the side chain of polymers. When amide group is replaced with ester group in case of PDA from 10,12-*p*EB-PCDA (**4e**) and 10,12-*m*EB-PCDA (**5e**), hydrogen bonding is weakened leading to poor packing efficiency. In case of unpolymerizable PDA of 6,8-*p*EB-NCDA (**6e**), the shorter methylene chain length creates increased stress in polymer backbone that inhibits polymerization [39, 40].

These hypotheses are also supported by the melting point trend of these monomers. The monomers containing amide groups (**1a**-**3a**) have higher melting point than the monomers containing ester group (**4e**-**6e**); suggesting a strong interaction among the former. This will be further discussed in later section.

**Table 3.1** Color appearance of PDA vesicles derived from monomers (**1a-6e**).

| Monomers | Before polymerization | After polymerization | Melting point (°C) |
|---|---|---|---|
| 10,12-*p*NB-PCDA(**1a**) |  |  | 109-111 |
| 10,12-*m*NB-PCDA(**2a**) |  |  | 173-176 |
| 6,8-*m*NB-NCDA(**3a**) |  |  | 190-191 |
| 10,12-*p*EB-PCDA(**4e**) |  |  | 74-75 |
| 10,12-*m*EB-PCDA(**5e**) |  |  | 50-52 |
| 6,8-*p*EB-NCDA(**6e**) |  |  | 89-90 |



### 3.2.2 Morphology of polydiacetylene sols

The size of the PDA sols derived from boronic acid PDA (10,12-*p*NB-PDA (**1a**), 10,12-*m*NB-PDA (**2a**), 6,8-*m*NB-PDA (**3a**), 10,12-*p*EB-PDA (**4e**) and 10,12-*m*EB-PDA (**5e**)) were determined by dynamic light scattering (DLS) technique. The DLS size distribution revealed that average hydrodynamic diameter of the particles was in the range of 76-352 nm (Figure 3.4). These results suggested that the prepared PDA sols have a high homogeneity and the same average size.

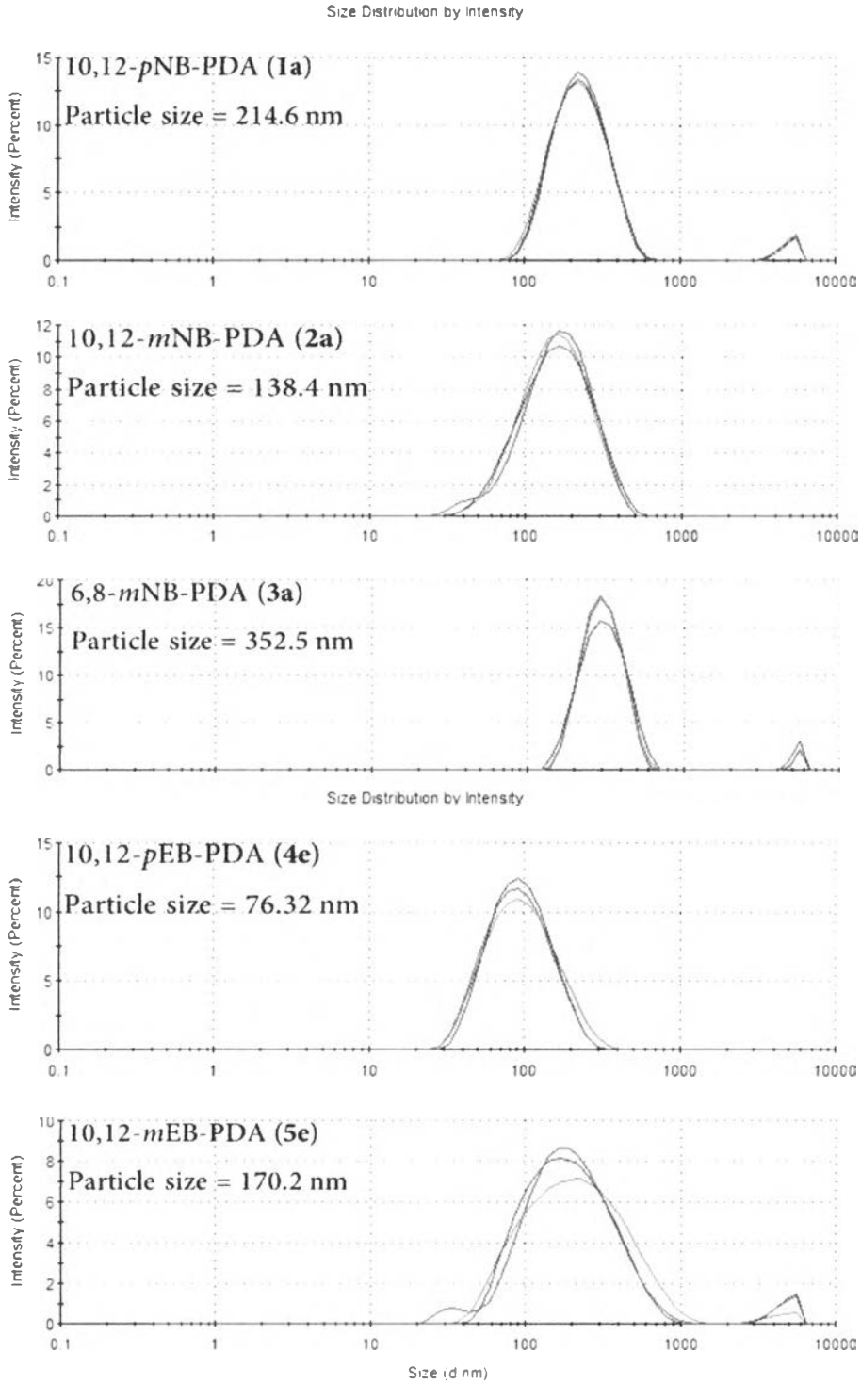



**Figure 3.4** Particle size distribution of 10,12-*p*NB-PDA (**1a**), 10,12-*m*NB-PDA (**2a**), 6,8-*m*NB-PDA (**3a**), 10,12-*p*EB-PDA (**4e**) and 10,12-*m*EB-PDA (**5e**) from dynamic light scattering.

### 3.2.3 UV-vis spectra of PDA sols

In this part, all PDA sols were characterized by UV-visible spectrophotometer. The characteristic absorption peaks ($\lambda_{max}$) of all PDA were illustrated in Figure 3.5. The results corresponded to the naked eye observation made in previous section (Table 3.1). The deep blue colored PDA of amide boronic acid diacetylene monomers **1a**, **2a** and **3a** showed stronger absorption in comparison with pale blue colored PDA of ester diacetylenes **4e** and **5e**. Absorption maxima of PDA derived from the amido boronic acid diacetylene monomer (**1a-3a**) appear in the range of 625-658 nm. Similarly, the PDA generated from ester boronic acid diacetylene monomer (**4e, 5e**) show the absorption maxima at 632 nm and 635 nm respectively.

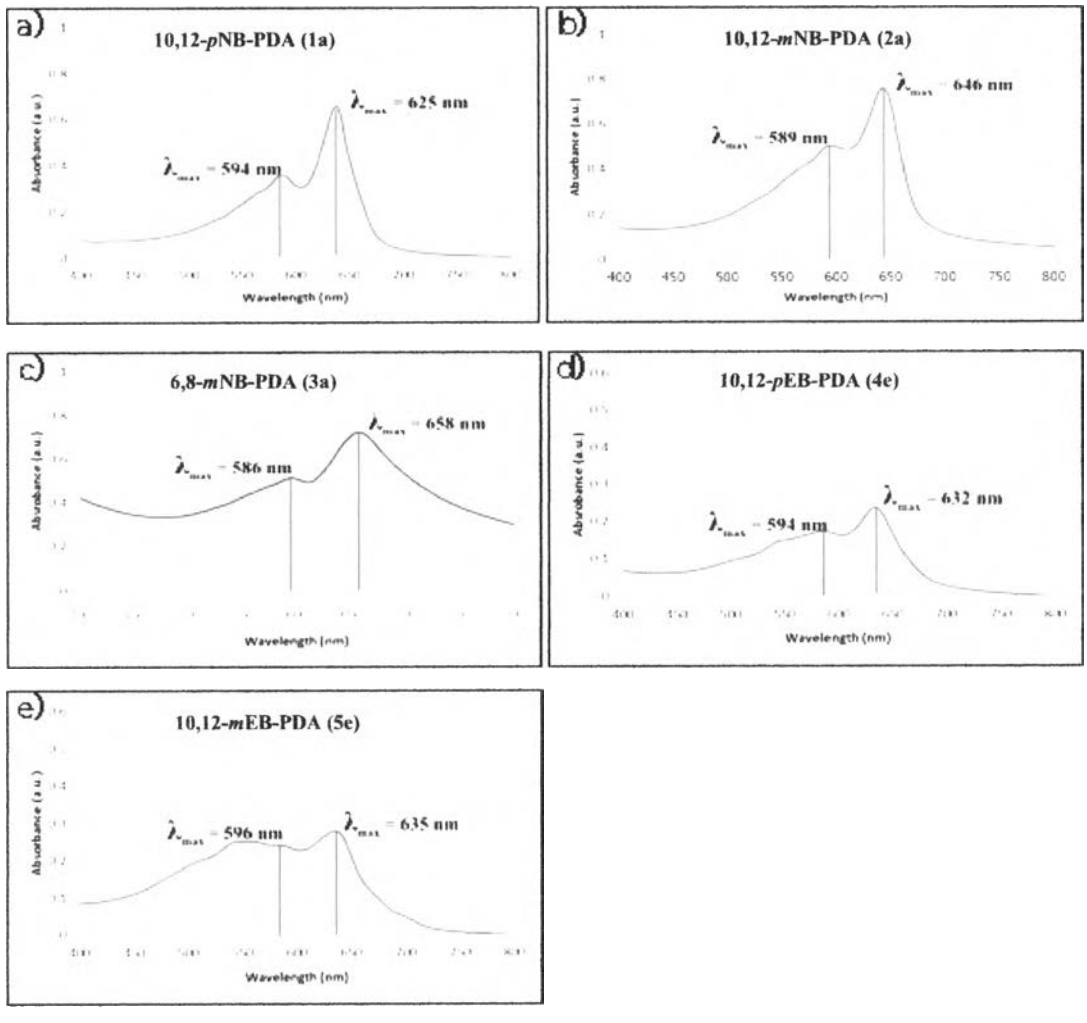



**Figure 3.5** UV-vis spectra of 0.1 mM PDA containing boronic acid from a) 10,12-*p*NB-PDA (**1a**), b) 10,12-*m*NB-PDA (**2a**), c) 6,8-*m*NB-PDA (**3a**), d) 10,12-*p*EB-PDA (**4e**) and e) 10,12-*m*EB-PDA (**5e**).

### 3.3 Thermochromic study of PDA sols

In this section, the thermochromic properties of all PDA sols derived from five boronic acid diacetylene monomers were recorded by photography upon heating the vesicles from 25°C to 90°C. The UV-vis spectra were recorded from temperature variable spectrometer. During the heating from 25°C to 90°C of all PDA vesicles, the absorption peak around 540 nm gradually increased while the absorption peak around 635 nm dramatically decreased corresponding to the blue to red color transition shown in Figure 3.6. However, the color transition temperature (CTT) of each PDA which is the temperature that PDA was transformed from blue to red color is diverse among them. Based on observation by naked eyes, it is demonstrated that PDA from amide boronic acid diacetylene monomer have higher CTT than PDAs from ester boronic acid diacetylene monomer. The CTT of PDA from amide **1a**, **2a** and **3a** were found at 70-80°C, 75-85°C and 45-55°C respectively (Figure 3.6 a-c). While the CTT of PDA prepared from ester **4**e and **5e** display CCT at 35-40°C and 55-60°C respectively (Figure 3.6 c and d).



These results show that PDA structures have a direct effect on CTT. CTT is raised when the interaction amongst monomers is stronger as indicated by higher CCT of amide boronic acid PDA such as 10,12-*p*NB-PDA (**1a**), 10,12-*m*NB-PDA (**2a**) and 6,8-*m*NB-PDA (**3a**). In addition, the strength of interaction is influenced by positioning of boronic acid substituent on PDA backbone. Boronic subsistent at *meta* position exhibits stronger binding in comparison to boronic substituent at *para* position in both amide and ester derivatives. For example, PDA of **2a** has higher CTT than **1a** whilst PDA of **5**e has higher CTT than **4e**.

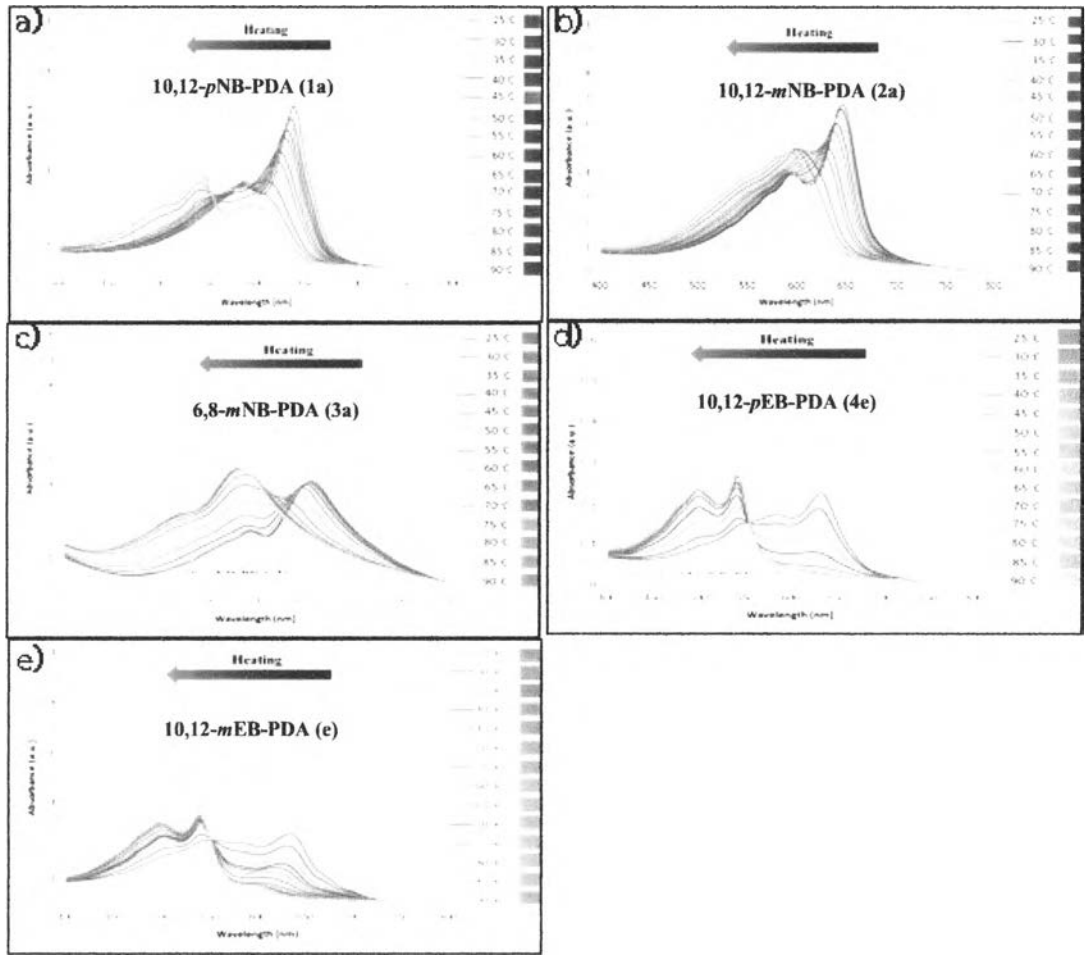



**Figure 3.6** Absorption spectra of 0.1 mM PDA containing boronic acid from a) 10,12-*p*NB-PDA (**1a**), b) 10,12-*m*NB-PDA (**2a**), c) 6,8-*m*NB-PDA (**3a**), d) 10,12-*p*EB-PDA (**4e**) and e) 10,12-*m*EB-PDA (**5e**) upon heating from 25-90°C and color appearance of PDA sols.

### 3.3.1 Colorimetric response (%CR)

To quantify the color transition temperature, the absorbance data of all PDA sols from heating process (Figure 3.6) were converted to colorimetric response (%CR) that is defined as percent change in the maximum absorption of the blue phase with the respect to the total absorption at both red and blue phases. The colorimetric response calculated from the following equation

$$\%CR = 100 \times (FB_0 - FB)/FB_0$$

FB is the fraction of blue calculated from $A_{blue}/(A_{blue}+A_{red})$ where $A_{blue}$ and $A_{red}$ are the absorbance at the $\lambda_{max}$ of the blue and the red forms respectively of the PDA sols.

$FB_0$ is the fraction of blue of the original PDA prior to heating. The plot of colorimetric response against the temperature of all PDA studied yielded sigmoidal curve as a result of color transition upon raising temperature (Figure 3.7).

The slope of these sigmoidal curves corresponds to sensitivity of PDA thermochromism. Ester boronic acids PDA have sharp slope responses rapidly within a narrow temperature range. Amide boronic acids PDA have flatter slope has a broader response range but the color transition may not be obvious. The color transition temperature estimated from %CR for the PDA derived from 10,12-*p*NB-PDA (**1a**), 10,12-*m*NB-PDA (**2a**), 6,8-*m*NB-PDA (**3a**), 10,12-*p*EB-PDA (**4e**) and 10,12-*m*EB-PDA (**5e**) and are found in the following order: 10,12-*p*EB-PDA (**4e**) < 10,12-*m*EB-PDA (**5e**) < 6,8-*m*NB-PDA (**3a**) < 10,12-*p*NB-PDA (**1a**) = 10,12-*m*NB-PDA (**2a**). The %CR plot showed that the ester boronic acid PDA (10,12-*p*EB-PDA (**4e**) and 10,12-*m*EB-PDA (**5e**)) reached 20 %CR in the narrow temperature range of 5°C and 10°C respectively. While the amide boronic acid PDA (6,8-*m*NB-PDA (**3a**), 10,12-*p*NB-PDA (**1a**) and 10,12-*m*NB-PDA (**2a**)) reached 20 %CR in the wide temperature range (~20°C).



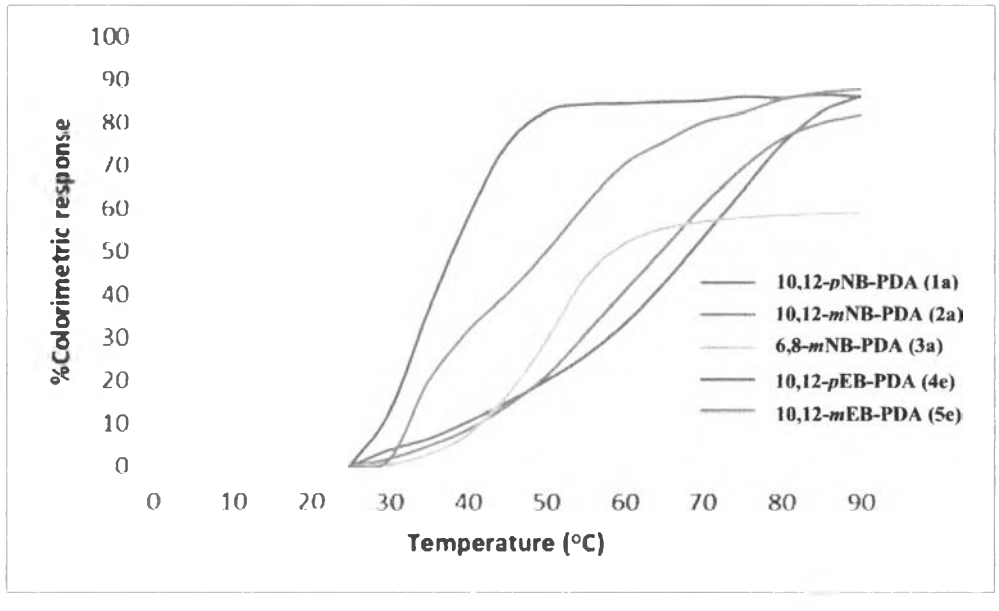



**Figure 3.7** The colorimetric responses (%CR) of boronic acid PDA.

### 3.4 Thermochromically reversibility of PDA sols

The thermochromic reversibility of PDA sols are investigated in this section. The objective of this part is to compare the thermochromic reversibility of PDAs containing amide and ester group of boronic acid. To study thermochromic

reversibility, PDA sols were heated up to 90°C and cooled down to 25°C while the color change was observed by photographic recorder and UV-vis spectroscopy (Figure 3.8). When started at 25°C the amide boronic acid PDA (**1a**, **2a** and **3a**) showed a typical blue color corresponding to absorption maximum wavelength around at 640 nm. When the temperature was increased to 90°C, the absorption maximum was shifted to 550 nm along with blue to purple color change in case of longer methylene PDA **1**a and **2a** (Figure3.8 a and b) and blue to red color change in case of shorter methylene PDA **3a** (Figure 3.8 c). When cooled down to the original temperature, the UV spectrum returned to the original blue phase and shown the blue color in case of meta amide boronic acid PDA (Figure 3.8 b and c) and purple in case of *para* amide boronic acid PDA (Figure 3.8 a). The result suggested that thermochromic reversibility and partial thermochromic reversibility relies on the strength of hydrogen bonding between amide group and π-π stacking of aromatic side chain.

On the other hand, the thermochromic reversibility properties of ester boronic acid PDA are different from the amide derivative. At 25°C, the ester boronic acid PDA showed a typical blue color corresponding to absorption maximum wavelength around at 630 nm (Figure 3.8 d and e). When the temperature was raised to 90°C, the absorption maximum shifted to 550 nm along with blue to red color transition. When cooled down to the original temperature, the UV spectrum remains unchanged and color did not return to original blue phase but showed the red color (Figure 3.8 c and d). The results reveal that both *para* and *meta* ester boronic acid PDA: 10,12-*p*EB-PDA (**4e**) and 10,12-*m*EB-PDA (**5e**) are thermochromically irreversible due to weak hydrogen bonding and π-π stacking in the side chain of polymers.

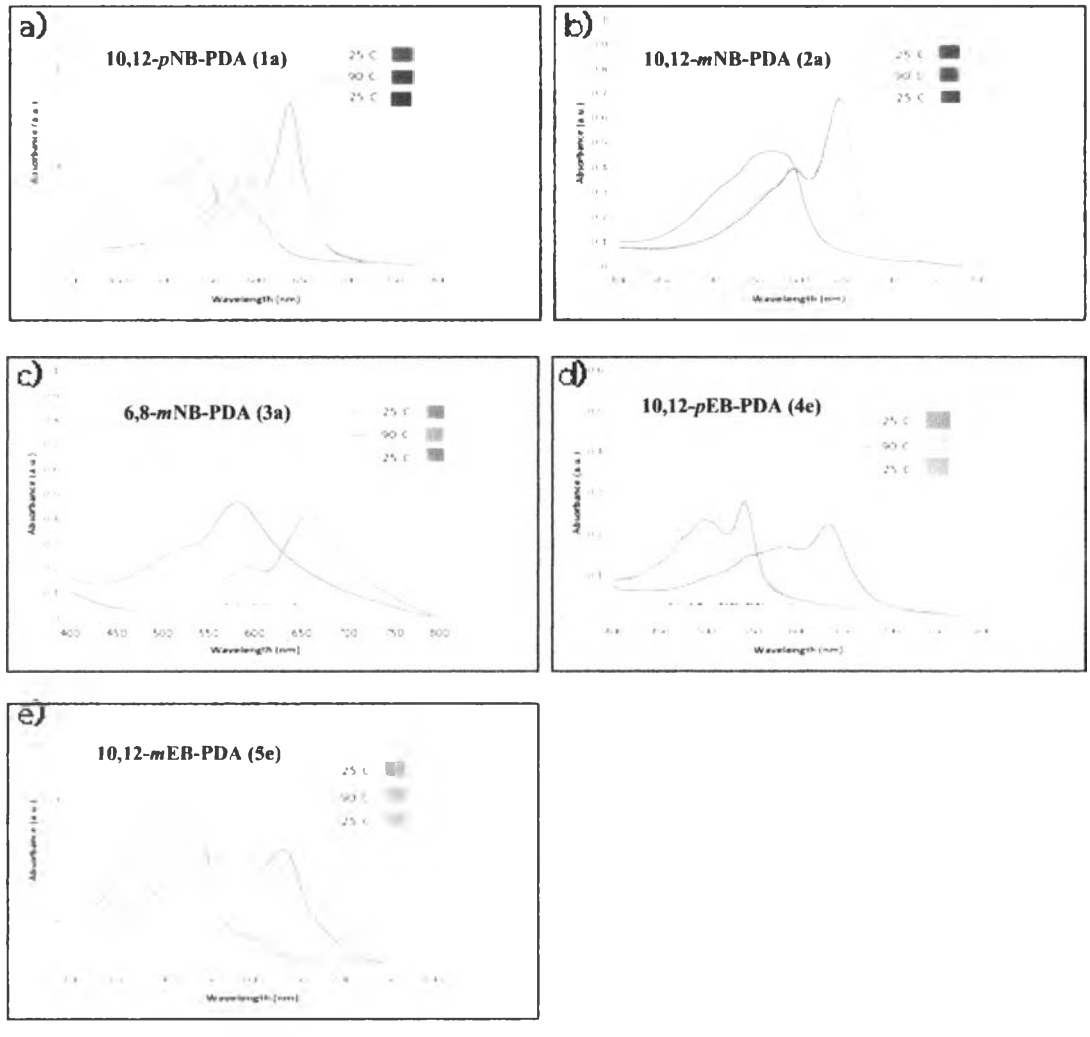





**Figure 3.8** UV-vis spectra and photograph of PDA containing boronic acid from a) 10,12-*p*NB-PDA (**1a**), b) 10,12-*m*NB-PDA (**2a**), c) 6,8-*m*NB-PDA (**3a**), d) 10,12-*p*EB-PDA (**4e**) and e) 10,12-*m*EB-PDA (**5e**) during thermal cycles.

### 3.4.1 Degree of reversibility (%DR)

To investigate the stability of thermochromically reversibility, we tested PDA sols to 10 heating-cooling cycles between 25°C to 90°C. To calculate the %DR, we monitored absorbance of PDA sols at their initial $\lambda_{max}$ at blue phase for 10 heating-cooling cycles between 25-90°C. We plotted absorbance against cycle number on a graph as shown in Figure 3.9. After the first heat treatment, the blue absorbance of all PDAs decreased and upon the second heat treatment, the intensity of initial $\lambda_{max}$ at blue phase recovered differently among the PDAs.

In case of the ester boronic acid PDAs: 10,12-*p*EB-PDA (**4e**) and 10,12-*m*EB-PDA (**5e**), little recovery was observed. On the other hand, amide boronic acid PDAs: 10,12-*m*NB-PDA (**2a**) and 6,8-*m*NB-PDA (**3a**) demonstrated virtually full recovery of the initial absorbance in all cycles while 10,12-*p*NB-PDA (**1a**) showed half color recovery.

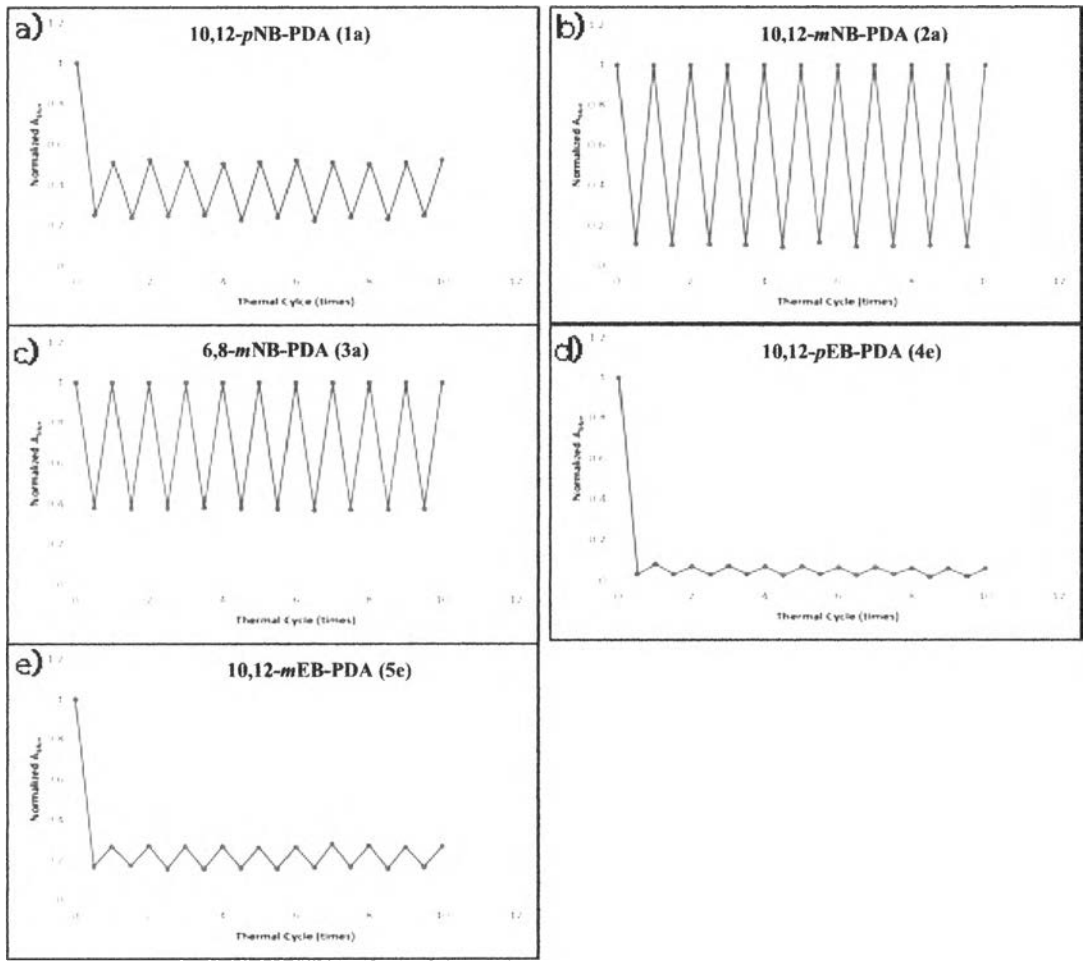



**Figure 3.9** Thermal cycle of 0.1 mM PDA containing boronic acid from a) 10,12-*p*NB-PDA (**1a**), b) 10,12-*m*NB-PDA (**2a**), c) 6,8-*m*NB-PDA (**3a**), d) 10,12-*p*EB-PDA (**4e**) and e) 10,12-*m*EB-PDA (**5e**) in the temperature of 25-90°C.

To execute a quantitative analysis of thermochromically reversibility, we calculated degree of reversibility (%DR) of PDA which is the average value of the absorbance change ($\Delta A_{avg}$) from the 2$^{nd}$ to 9$^{th}$ heating is compared against the absorbance change in the first heating ($\Delta A_1$) according to the following equation

$$\%DR = 100 \times \Delta A_{avg}/\Delta A_1$$

Where $\Delta A = A_{25}(°C) - A_{90}(°C)$. The %DR value, allowed us to classify the reversibility class of PDA such as fully reversible (%DR > 90%), partially reversible (10% < %DR < 90%) and irreversible (%DR < 10%). The absorbance of PDA during the heating and cooling cycles were evaluated using the above equation and summarized in Table 3.2

**Table 3.2** Classification of PDA sols.

| PDA | Degree of reversibility (%DR) | Classification of PDA |
|---|---|---|
| 10,12-*p*NB-PDA(**1a**) | 37 | Partially reversible |
| 10,12-*m*NB-PDA(**2a**) | 100 | Fully reversible |
| 6,8-*m*NB-PDA(**3a**) | 100 | Fully reversible |
| 10,12-*p*EB-PDA(**4e**) | 4 | Irreversible |
| 10,12-*m*EB-PDA(**5e**) | 13 | Partially reversible |



Based on our results, we would like to propose a mechanism for thermochromic reversibility. We believe that degree of thermochromic reversibility is governed by the strength of interaction between polar head groups on PDA side chains such as amide, ester, aromatic and *meta* or *para* boronic acid groups.

When PDA possess strong side chain interaction as in the case of amide boronic acid PDAs such as 10,12-*m*NB-PDA (**2a**) or 6,8-*m*NB-PDA (**3a**) (Figure 3.10 a), head group conformation is maintained during the heating cycle. When heat is removed, original PDA conformation is restored and it can reverse back to its original blue form.

However, for PDA with weak side chain interaction as in the case of ester boronic acid PDA 10,12-*p*EB-PDA (**4e**) and 10,12-*m*EB-PDA (**5e**) or *para* amide boronic acid PDA 10,12-*p*NB-PDA (**1a**); the polar head group cannot maintain its original form during the heating cycle. Thus, when heat is removed, PDA cannot return to its original conformation and the blue form is lost. The PDA is maintained in its purple or red form. These PDA have weak head group interaction because of a lack of either amide group or miss position of boronic acid substituent (Figure 3.10 b and c).

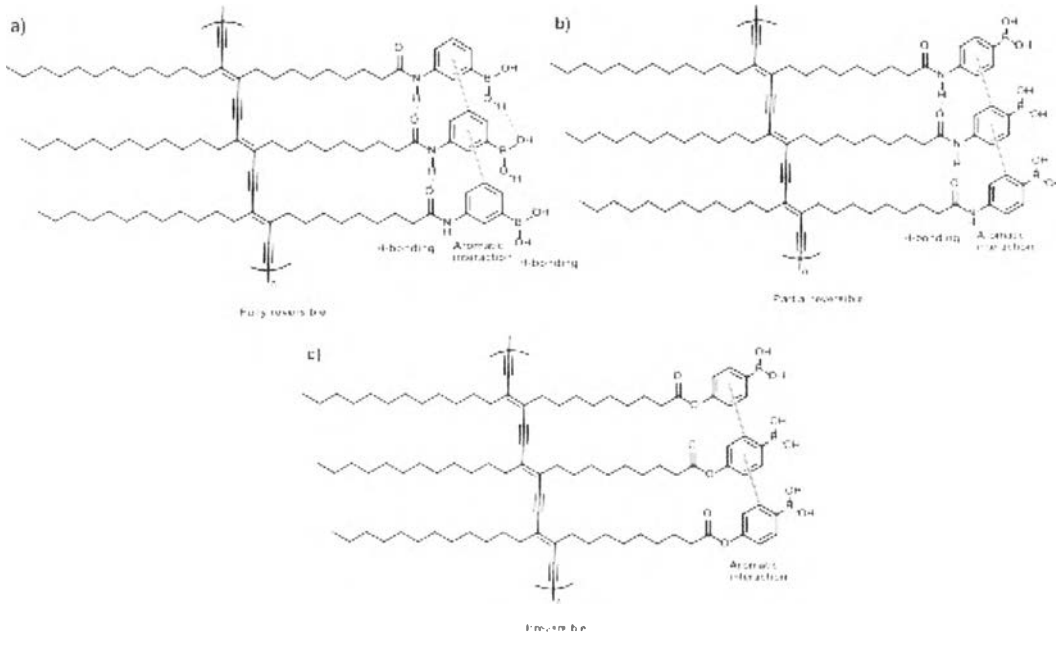


**Figure 3.10** Proposed the head group interaction of PDAs of a) 10,12-*m*NB-PDA (**2a**), b) 10,12-*p*NB-PDA (**1a**) and c) 10,12-*p*EB-PDA (**4e**).

### 3.5 Solvatochromic study of PDA containing boronic acid

To study solvatochromism, prepared PDAs are fabricated into solid state before testing with VOC vapor. Boronic acid diacetylene monomers (**1a, 2e, 4e and 5e**) were fabricated onto filter paper sheets. To begin with all diacetylene solution were dropped onto filter paper and dried in the dark at room temperature. Filter paper coated with multiple dots of diacetylene monomer was irradiated with UV light (254nm, 500 μW/cm$^2$) for 1 minute as depicted in Figure 3.11.

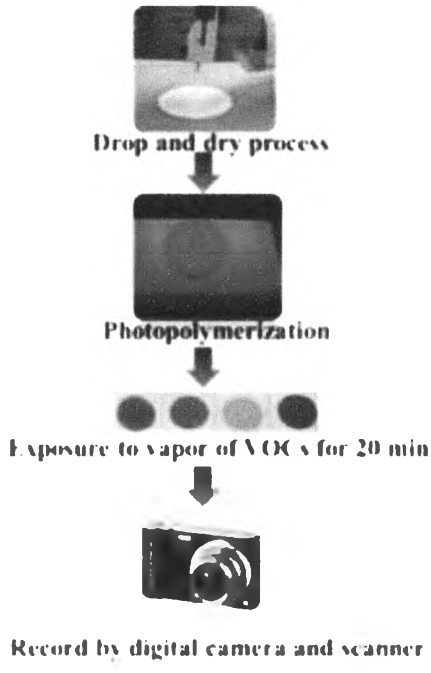





**Figure 3.11** Preparation of blue PDA dots for VOC sensing.

Four diacetylene monomers **1a**, **2a**, **4e** and **5e** can be converted to give blue dots of the corresponding PDA as shown in Figure 3.11 (first row), confirming that the topopolymerization occurred. The PDA of **3a** and **6e** were not able to produce the desired blue dots of the corresponding PDA. This is perhaps due to the improper hydrophobic packing of monomer from the short methylene chain length in diacetylene monomer **3a** and **6e**.

Subsequently, PDA coated papers were tested by attaching them on the inner surface of petri dishes which were saturated with various VOC vapor. A variety of PDA coated papers were exposed to 15 solvents for 20 minutes. We observed that 10,12-*p*NB-PDA (**1a**) and 10,12-*m*NB-PDA (**2a**) having the amide group maintained their blue color when exposed to all VOC. However, PDA derived from ester diacetylene derivatives such as 10,12-*p*EB-PDA (**4e**) and 10,12-*m*EB-PDA (**5e**) were sensitive to vapor of VOC and displayed color changes form blue to red in response to chloroform, acetone, dichloromethane and tetrahydrofuran.

Based on this result, it appears that VOC cannot solvate a strong polar head group interaction found in PDAs having amido head group 10,12-*p*NB-PDA (**1a**) and 10,12-*m*NB-PDA (**2a**), thus no color changes were observed. On the other hand,

weaker bonding found in ester PDAs 10,12-*p*EB-PDA (**4e**) and 10,12-*m*EB-PDA (**5e**) were affected by VOC vapor and color changes occurred. Ability of amide PDA to response specifically to temperature changes without being affected by VOC level is highly beneficial. This property makes it suitable as a temperature indicator in a high VOC environment as the color changes would occur only in response to changes in temperature without it being affected by surrounding VOC.

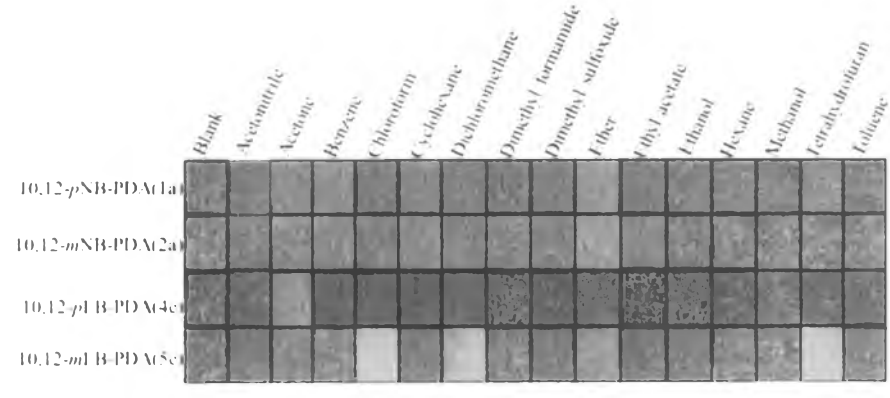



**Figure 3.12** Solvatochromic properties of four diacelyene monomers against 15 VOC.



### 3.6 Photochromic study of PDA containing boronic acid

To study the effect of duration of UV exposure, 1%w/v of each diacetylene monomer in THF was dropped (2 μL) onto filtrate paper and then dried in the dark for 30 min. Diacetylene dots were photopolymerized for 30s, 1min, 2 min, 3 min, 4 min, 5 min or 10 min and the results were depicted in Figure 3.13. The results shown that at 30s, all PDA exhibited pale blue color. Increasing exposure time led to an increase in PDA color intensity. UV irradiation cannot induce blue to red color changes, indicating a close packing of polymer side chain due to strong hydrogen bonding and $\pi$-$\pi$ stacking.

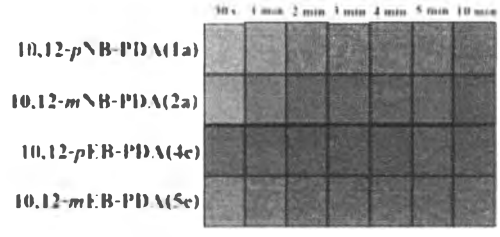



**Figure 3.13** The PDA coated paper for photochromic study in various time (30s-10min).

### 3.7 Alkalinochromic study of PDA sols

To test the stability of PDA under various pH, all PDA vesicles were added hydrochloric acid and potassium hydroxide for pH adjustment between 2-14 (Figure 3.14). The results showed that PDAs containing amide boronic acid (10,12-*p*NB-PDA (**1a**) and 10,12-*m*NB-PDA (**2a**)) were stable in the wide pH range between 2-14. The original blue color and absorption peak around 635 nm remained unchanged (Figure 3.14 a and b). On the other hand, PDAs containing ester boronic acid (10,12-*p*EB-PDA (**4e**) and 10,12-*m*EB-PDA (**5e**)) appeared as purple-red color under basic condition at pH 10-14 corresponding to the decrease of absorption peak around 653 nm and the increase of absorption peak around 540 nm (Figure 3.14). Again, strong head group interaction resulting from amide groups are respond for the pH stable behavior of PDA from amide diacetylene **1a** and **2a**.

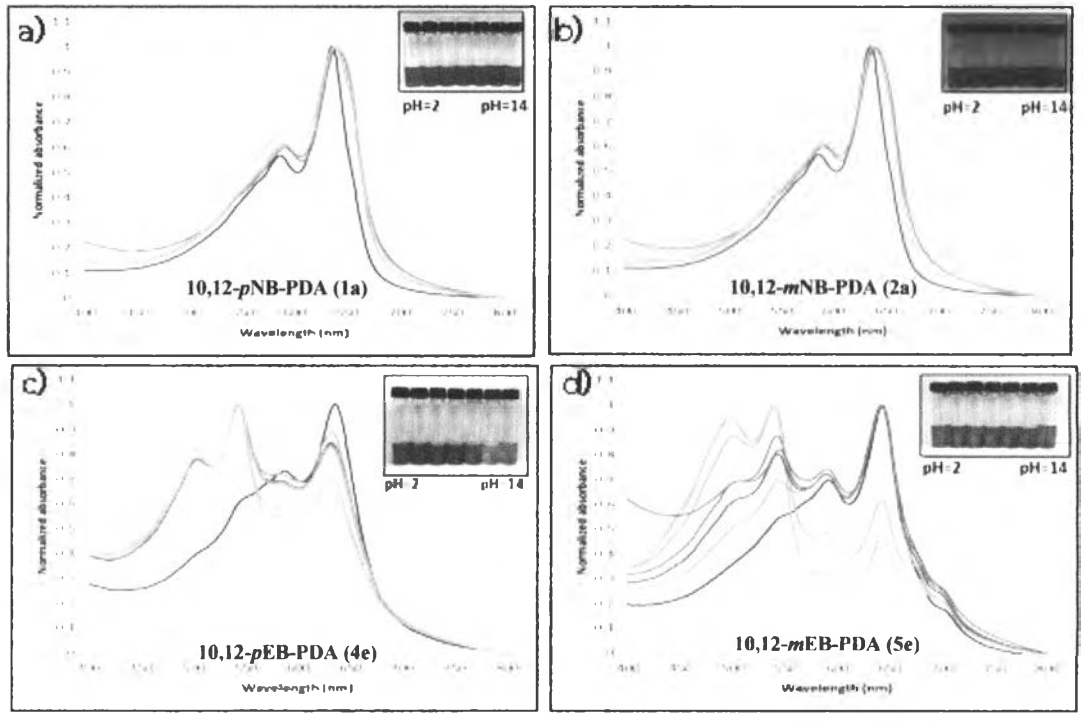





**Figure 3.14** UV-vis spectra of 0.1 mM PDA from a) 10,12-*p*NB-PDA (**1a**), b) 10,12-*m*NB-PDA (**2a**), c) 10,12-*p*EB-PDA (**4e**) and d) 10,12-*m*EB-PDA (**5e**) against various pH (2-14).

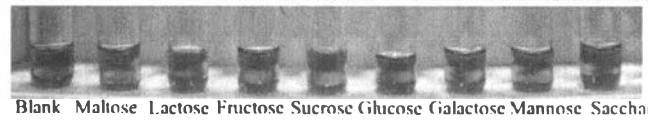
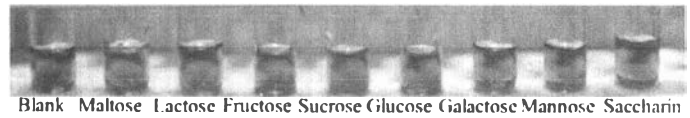
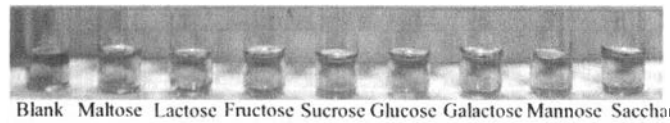
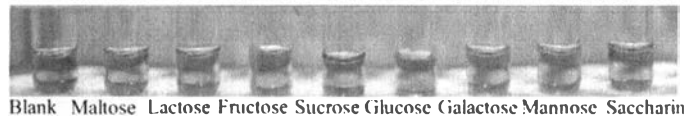
### 3.8 Affinochromic study of PDA sols

#### 3.8.1 Sugar sensing properties

As mentioned in the introduction, we installed the boronic acid group to enhance polar head group interaction in order to fine tune thermochromic reversibility of PDAs and to create a sugar chemo sensor using boronic acid-sugar interaction.

To investigate the sugar sensing ability, we prepared our PDA sols in HEPES buffer pH = 7.4 to the final concentration 0.1 mM leading to blue PDA solution as seen in Table 3.3 (first row). Eight different types of 1mM sugar solution were added to all prepared PDA sols and the results are shown in Table 3.3. Unfortunately, no color changes were observed. Sugar-boronic acid binding may have occurred in solution but the strength of interaction might not be enough to cause distortion to the PDA conjugated backbone.

**Table 3.3** Photograph of 0.1 mM PDAs (HEPES buffer pH = 7.4) in the present of sugars (1 mM).

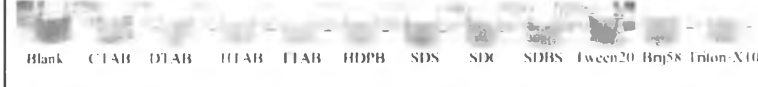
| PDA | Screening of sugars |
|---|---|
| 10,12-*p*NB-PDA (**1a**) |  Blank Maltose Lactose Fructose Sucrose Glucose Galactose Mannose Saccharin |
| 10,12-*m*NB-PDA (**2a**) |  Blank Maltose Lactose Fructose Sucrose Glucose Galactose Mannose Saccharin |
| 10,12-*p*EB-PDA (**4e**) |  Blank Maltose Lactose Fructose Sucrose Glucose Galactose Mannose Saccharin |
| 10,12-*m*EB-PDA (**5e**) |  Blank Maltose Lactose Fructose Sucrose Glucose Galactose Mannose Saccharin |



### 3.8.2 Surfactant sensing properties

Next, affinochromic properties of all PDAs vesicles were tested with 11 surfactants comprising of non-ionic, anionic and cationic surfactants at 50 μM concentration. The result indicated that the colorimetric response from naked eye (Table 3.4) of amide boronic acid PDA such as 10,12-*p*NB-PDA (**1a**) and 10,12-*m*NB-PDA (**2a**) remained unchanged. Similarly, the UV spectrum of amide boronic acid PDA as shown in Figure 3.15 a and b are stable with all tested surfactants and remained unchanged. The UV absorption peak around 635 nm did not decreased except TTAB which is perhaps due to aggregation of PDA sols. On the other hand, the colorimetric response from naked eye of ester boronic acid PDA namely 10,12-*p*EB-PDA (**4e**) and 10,12-*m*EB-PDA (**5e**) (Table 3.4) displayed strong color changes with cationic surfactant at the concentration of 50 μM. This is perhaps caused by the formation of boronate. In basic condition (pH = 7.4), boronic acid moieties were converted into boronate anion upon the addition of cationic surfactants. This columbic interaction will cause the insertion of cationic surfactant into the PDA vesicle leading to the color transition as seen in the increase of the absorption peak at 540 nm and the decrease of absorption peak around 635 nm (Figure 3.15 c and d)

**Table 3.4** Photograph of 0.1 mM boronic acid PDA (HEPES buffer pH = 7.4) in the present of surfactants (50 μM).

| PDA | Screening of surfactants |
|---|---|
| 10,12-*p*NB-PDA (**1a**) |   |
| 10,12-*m*NB-PDA (**2a**) |   |
| 10,12-*p*EB-PDA (**4e**) |   |
| 10,12-*m*EB-PDA (**5e**) |   |

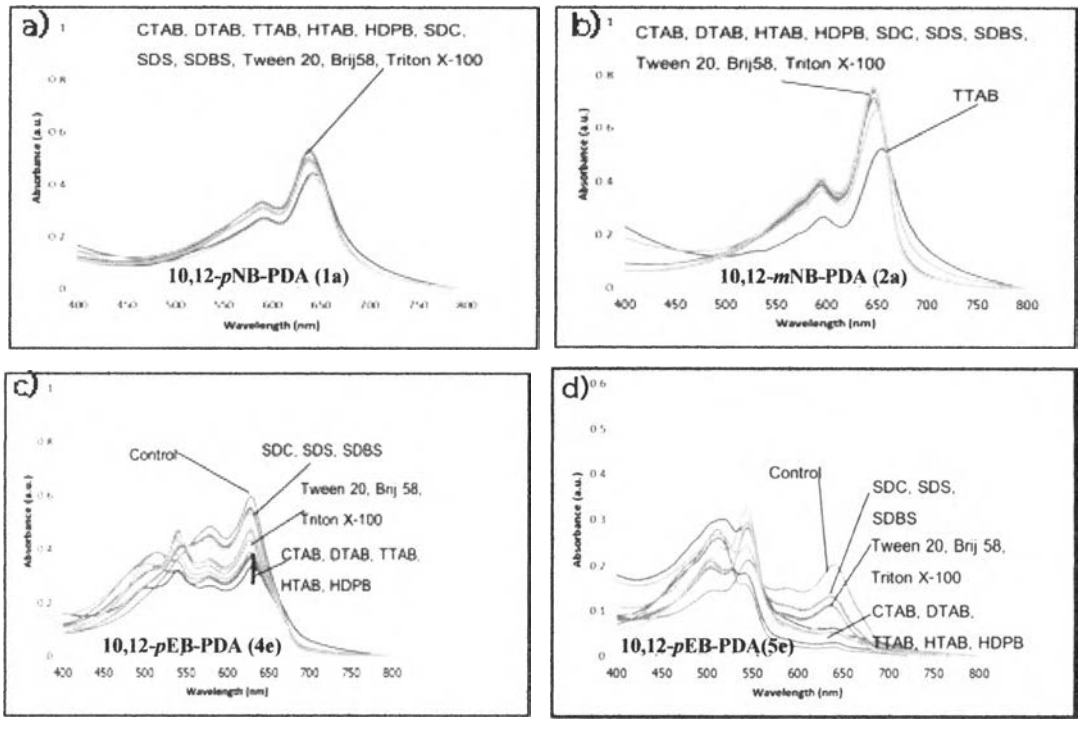



**Figure 3.15** UV-vis spectra of all PDA sols (0.1mM) from a) 10,12-*p*NB-PDA (**1a**), 10,12-*m*NB-PDA (**2a**), c) 10,12-*p*EB-PDA (**4e**) and d) 10,12-*m*EB-PDA (**5e**) in the present of surfactants (50 μM).



### 3.9 Salicylic diacetylene monomers synthesis

Recently, Sirilaksanapong and co-worker [41] reported the synthesized of 1,3,5-Triphenylbenzene fluorophore containing salicylic acid group as receptor for $Cu^{2+}$ sensing (Figure 3.16). This sensor show superior selectivity toward $Cu^{2+}$ with the high sensitivity.

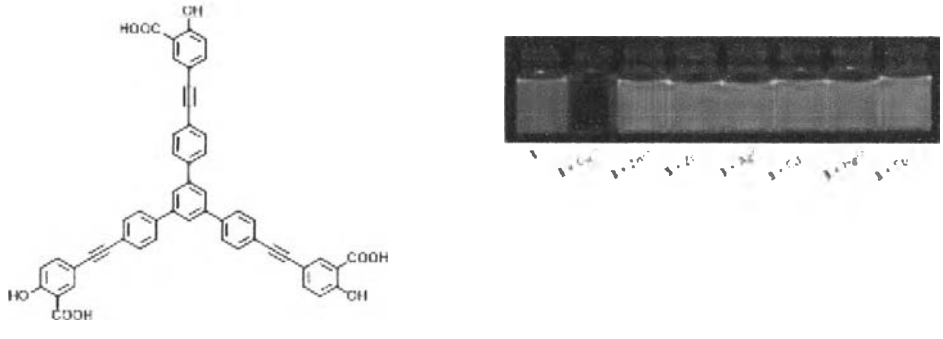



**Figure 3.16** The structure of fluorophore and the photograph of fluorophore under black light in the present of various metal ions.

Inspired by this work, we therefore designed and synthesized three diacetylene monomers containing salicylic acid (**7s-9s**) as the pendant group as seen in Scheme 3.2. We hypothesized that these PDAs would undergo colorimetric change upon addition of copper ion and allowed us to create the naked eye metal sensor based on polydiacetylene.

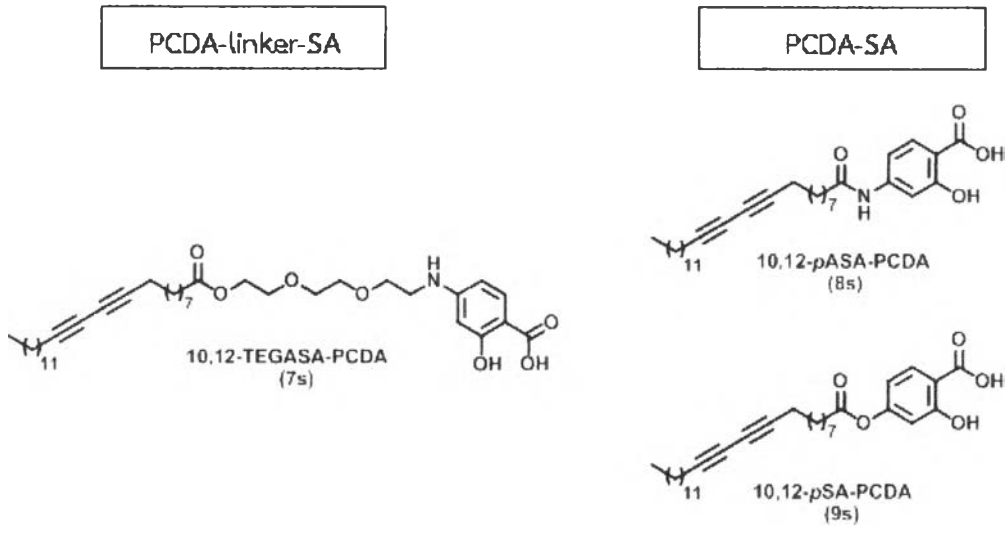
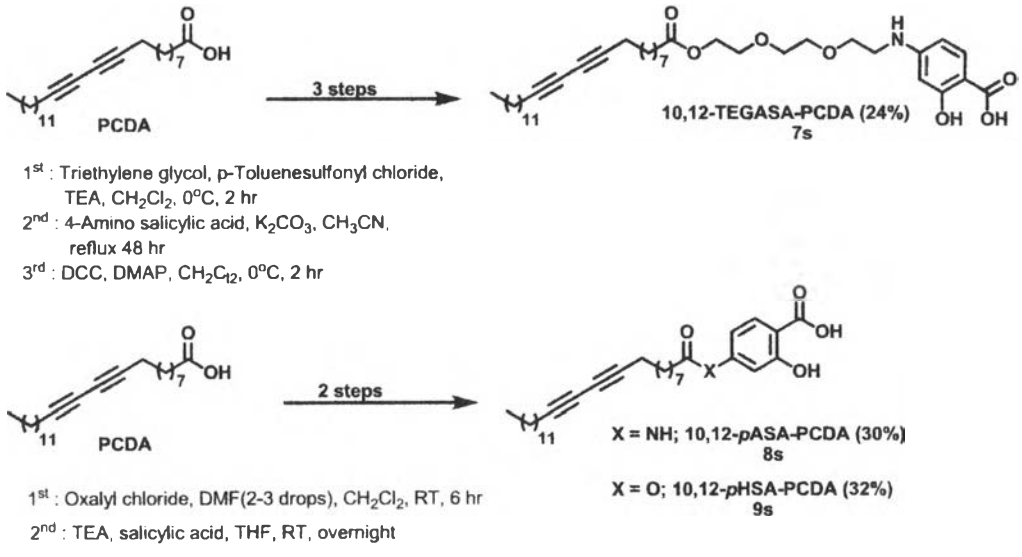



**Figure 3.17** Structure of salicylic acid diacetylene monomers (**7s-9s**).

### 3.9.1 Synthetic method of diacetylene monomers containing salicylic acid head group (7s-9s).

To synthesize the desired diacetylene monomers containing salicylic acid, PCDA was reacted with linker-salicylic acid as a nucleophile in the presence of DCC and DMAP as a coupling agent to give the diacetylene monomer (**7s**) as shown in Scheme 3.2. Also, pentacosadiynoic acid (PCDA) was first transformed into corresponding acid chloride in DCM solvent. Subsequently, the crude acid chloride was reacted with reacted with 4-amino salicylic acid and 2,4-dihydroxy benzoic acid as a nucleophile in the presence of triethylamine (TEA) as a base to give the diacetylene monomers **8s** and **9s** as shown in Scheme 3.2. Target monomer (**7s**) was purified by column chromatography and target monomers (**8s**, **9s**) were purified by recrystallization in methanol to give the white solids of **7s-9s**.




**Scheme 3.2** Synthetic route of salicylic acid diacetylene monomers (**7s-9s**).



The $^1$H-NMR spectra of target monomers containing salicylic acid in $CDCl_3$ are shown in Figure 3.18. All the signals can be assigned according to their structures. In case of salicylic acid diacetylene monomer with glycol as a linker 10,12-TEGASA-PCDA (**7s**), the signals about 3.61-4.37 ppm belong to the $-OCH_2$ proton of **7s** (Figure 3.16a). While the signals about 6.13 ppm (a, b) and 7.60 ppm (c) belong to the aromatic proton and 10.81 ppm (D) belong to –OH proton adjacent to carbonyl group. The proton NMR of 10,12-TEGASA-PCDA (**7s**) confirmed the structure of **7s**. Moreover, the proton NMR of 10,12-*p*ASA-PCDA (**8s**) and 10,12-*p*HSA-PCDA (**9s**) have a similar pattern (Figure 3.18 b and c). The signals at ca 6.66 ppm (u), 7.18 ppm (v) and 7.74 ppm (w) belong to the aromatic proton indicating that PCDA were attached to salicylic acid.

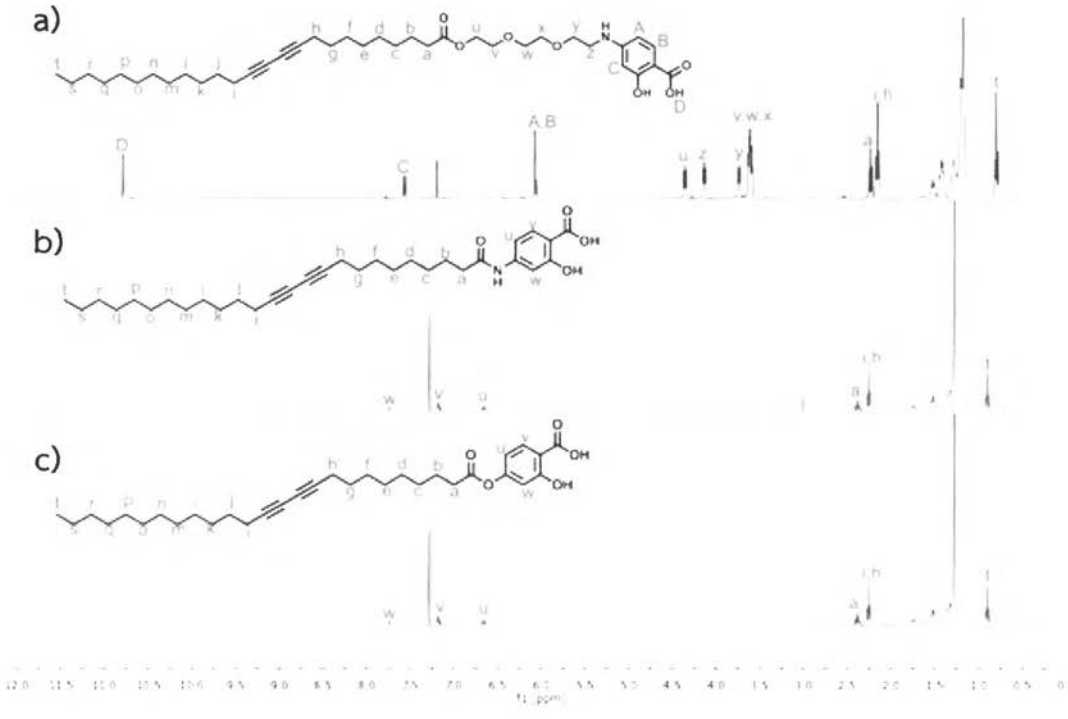





**Figure 3.18** $^{1}$H-NMR spectra of salicylic acid diacetylene monomers a) 10,12-TEGASA-PCDA (**7s**), b) 10,12-*p*ASA-PCDA (**8s**) and c) 10,12-*p*HSA-PCDA (**9s**).

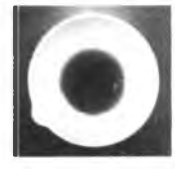
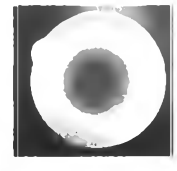
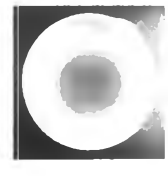
### 3.10 Preparation of PDA sols and characterization

#### 3.10.1 Polymerization of diacetylene monomers

To study the affnochromic properties against metal ions of target monomers, all prepared diacetylene monomers were transformed to PDA sols. Firstly, all synthesized monomers were dissolved in chloroform (1 mL) after that the solvent were evaporated by using $N_2$ gas followed by suspension in Milli-Q water as described in Chapter II. Then aqueous sols were then irradiated with UV light (254nm) for 5 minutes at 0°C to performed photo polymerization into PDA. The colors of polymerized diacetylenes were presented in Table 3.5. Upon UV light (254nm) exposure for 5 minutes at 0°C, the 10,12-*p*ASA-PCDA (**8s**) and 10,12-*p*HSA-PCDA (**9s**) were transformed into blue sols while 10,12-TGASA-PCDA (**7s**) was still transparent. This might be caused by the effect of ethylene glycol moieties prohibiting the close packing of monomer leading to the poor polymerization. To solve this problem, we mixed PCDA into 10,12-TEGASA-PCDA (**7s**) in the ratio of 1: 9 V/V to reduce the charge repulsion of ethylene glycol. Such condition provided the blue sols of 10,12-

TEGASA-PCDA/PCDA (**7s**). The color appearance of all sols 10,12-TEGASA-PCDA/PCDA (**7s**)(1:9), 10,12-*p*ASA-PCDA (**8s**) and 10,12-*p*HSA-PCDA (**9s**) are depicted in Table 3.5.

**Table 3.5** Color appearance of PDA vesicles derived from 10,12-TEGASA-PCDA (**7s**)/PCDA, 10,12-*p*ASA-PCDA (**8s**), 10,12-*p*HSA-PCDA (**9s**).

| Monomers | Before polymerization | After polymerization | Melting point (°C) |
|---|---|---|---|
| 10,12-TEGASA-PDA (**7s**)/PCDA |  |  | - |
| 10,12-*p*ASA-PDA (**8s**) |  |  | 95-97 |
| 10,12-*p*HSA-PDA (**9s**) |  |  | 74-76 |



### 3.10.2 UV-Vis spectra of PDA sols

After the successful transformation of all diacetylene into the desired PDA sols in aqueous solution. All PDA sols were further characterized by UV-Visible spectrophotometer. The characteristic absorption peaks ($\lambda_{max}$) of all PDA were showed in the Figure 3.19. The results corresponded to the naked eye observation made in previous section (Table 3.5). The color of 10,12-TEGASA-PDA (**7s**) is deep blue and 10,12-*p*ASA-PDA (**8s**) are pale blue On the other hand, the color of 10,12-*p*HSA-PDA (**9s**) is unstable pale violet due to weaker hydrogen bonding and $\pi$-$\pi$ aromatic stacking in the side chain of polymers. Absorption maxima of PDA of 10,12-TEGASA-PDA (**7s**)/PCDA, 10,12-*p*ASA-PDA (**8s**) and 10,12-*p*HSA-PDA (**9s**) show the absorption maxima at 638, 643 and 641 nm respectively.

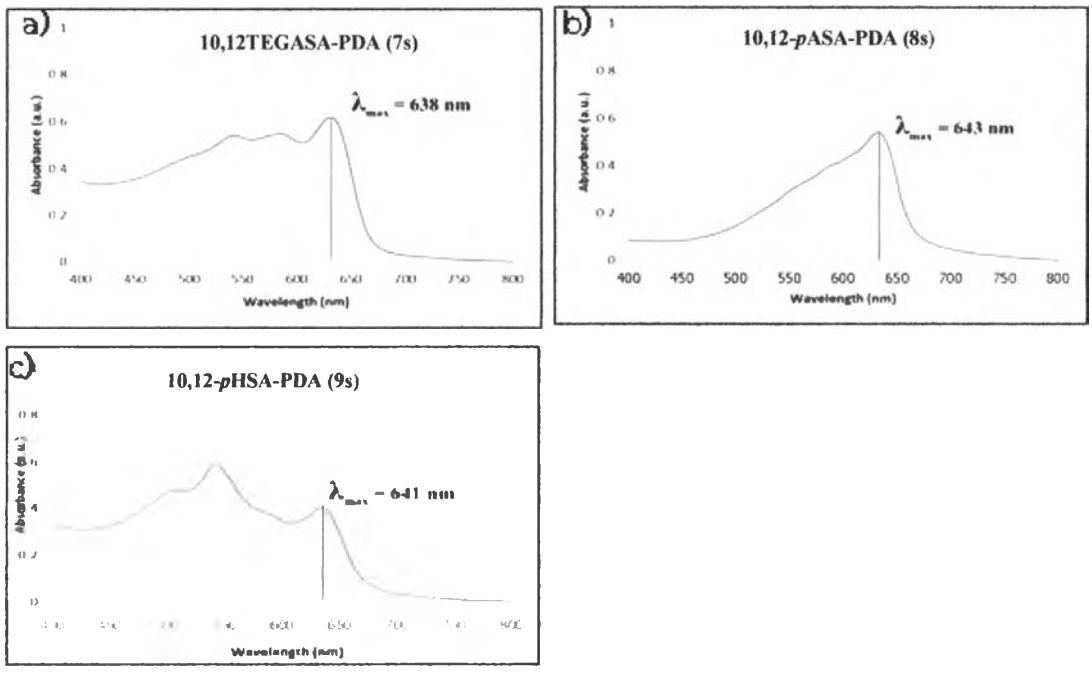


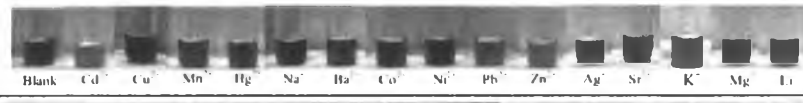
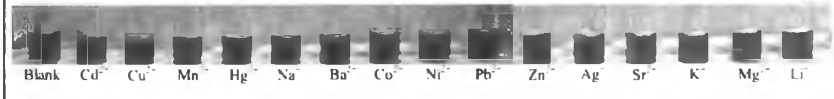
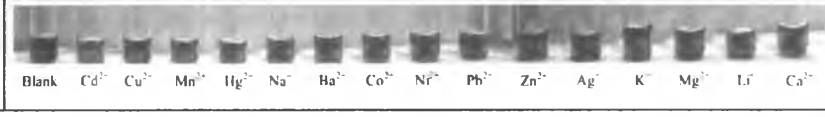

**Figure 3.19** UV-vis spectra of salicylic acid PDA sols of a) 10,12-TEGASA PCDA/PCDA (**7s**)(1:9), b) 10,12-*p*ASA-PCDA (**8s**) c) 10,12-*p*HSA-PCDA (**9s**).



### 3.11 Metal ions sensing

To investigate the sensing ability of salicylic group as a receptor for metal ions, we prepared PDA sols in HEPES buffer pH = 7.4 to the final concentration of 0.1 mM. Metal ions (50 μM) were added to prepared PDA sols including poly (PCDA) and the results are shown in Table 3.6. The blue PDA sols of poly(PCDA) exhibited color change with $Pb^{2+}$, $Cd^{2+}$ and $Zn^{2+}$ similarly with the blue PDA sols of 10,12-TEGASA-PDA (**7s**)/PCDA and 10,12-*p*HSA-PDA (**9s**).

**Table 3.6** Photograph of 0.1 mM salicylic acid PDA (HEPES buffer pH = 7.4) in the present of metal ions (50 μM).

| PDA | Screening of metal ions |
|---|---|
| 10,12-TEGASA-PDA(**7s**)/PCDA |  |
| 10,12-*p*ASA-PDA(**8s**) |  |
| 10,12-*p*HSA-PDA(**9s**) |  |



In our previous work, Narkwiboonwong and co-workers [42] reported the synthesized of EG-PCDA, 3EG-PCDA and 5EG-PCDA and then monomers was blend with PCDA for $Pb^{2+}$ detection. The results showed that color changes occurred due to the interaction between $Pb^{2+}$ and carboxylate group of blended PCDA but not ethylene glycol chelated with $Pb^{2+}$.

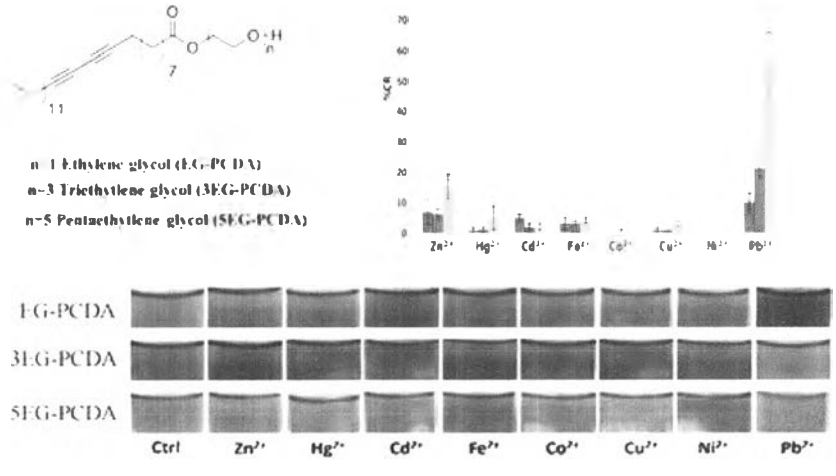



**Figure 3.20** The structure of DA monomer and photograph of PDA sol in the present of various metal ions.

The result implied that color changes observed in Table 3.6 occurred because of carboxylate group not the chelation of metal ions by salicylate. Lack of color changes of the blue PDA sols 10,12-*p*ASA-PDA (**8s**) could be caused by a strong H-bonding of amide head group.