

# CHAPTER I

## INTRODUCTION

### 1.1 Overviews

Polydiacetylene (PDA) is a class of conjugated polymer which can change color from blue to red in response to external stimuli including temperature (thermochromism), solvent (solvatochromism), pH value (alkalinochromism), ligand-receptor interaction (affinochromism) and physical stress (mechanochromism). This color change of the high molecular weight supramolecule is observable by naked eye. The polymer is relatively non-toxic, does not easily leach into solution and does not require toxic metal catalysts for polymerization; thus it is an ideal sensing element for many types of biological and environmental sensors. The sensing capability of PDA can be modified by adjusting the structure of diacetylene monomers that polymerize to form PDA supramolecule. Many research groups have designed and synthesized various monomers to provide PDA with specific sensing properties.

Among many chromic properties of PDA, thermochromism is the most commercially promising application. To produce a high quality temperature sensing element, one must be certain that color changes only occur in response to changes in temperature and but not to other types of external stimuli. Thus, it is the goal of the current research project to synthesize a diacetylene monomer to achieve a PDA sensing element that is only responsive to temperature changes but stable to other stimuli such as solvent, pH changes, surfactant and UV light. In addition, it is also of interest to fine tune the color transition temperature and thermochromic reversibility of the resulting PDA. By changing the structure of diacetylene monomers that form PDA supramolecule, thermochromic properties can be modified. There are two types of thermochromic materials: irreversible and reversible, depending on the behavior of the color change. Irreversible thermochromism is a phenomenon of thermochromic material that can change color permanently when temperature is changed. The original color cannot be recovered even the temperature is back to the starting point. Reversible thermochromism is a phenomenon whereby original color of thermochromic material can be regained after the temperature is reversed to the starting point.

In this work, boronic head group is selected to be attached to the diacetylene lipids to provide hydrogen bonding that potentially could affect the supramolecular

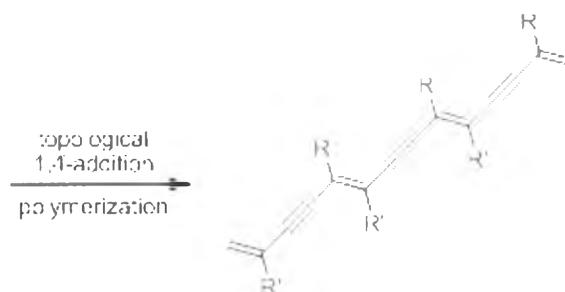


interaction and thereby should influence PDA thermochromism. Furthermore, since boronic is also known to interact with sugar in solution, the resulting PDA will be tested against various sugar molecules in solutions.

## 1.2 Theory

### 1.2.1 Polydiacetylene

Polydiacetylene (PDA) is a class of conjugated polymer which has ene-yne conjugated backbone. The unique property of PDA is color change from blue to red color transition that can be observed by naked eye. PDA can be prepared from topopolymerization of diacetylene monomer using heat, UV irradiation and  $\gamma$ -irradiation [1,2] to form ene-yne alternating polymer. The unique color changing from blue to red under external stimuli turns PDA into an important chromic material for naked eye chemo-bio sensors [3-6].



**Figure 1.1** Topopolymerization of diacetylene monomer [2].

### 1.2.2 Polydiacetylene vesicles

Lipid bilayer vesicle is one of the most widely used forms of polydiacetylene for sensing applications such as chemosensor [7,8], thermal sensor [9,10] and biosensor [11,12]. It is a water filled spherical assembly of lipid bilayer. The formation of vesicle is thermodynamically driven so that the hydrophobic surface of the lipid molecules is not exposed to water. Only the hydrophilic head group of the lipid is exposed to water inside and outside of the bilayer membrane. A number of lipids containing diyne unit can self-assemble into vesicle that have the right packing parameters for topological polymerization to form PDA vesicles (Figure 1.2). In the form of vesicle, PDA can be homogeneously dispersed in an aqueous media to form a sol type colloid, which is convenient for further characterization, fabrication and

applications. The most studied diacetylene lipids are 10,12-pentacosadiynoic acid (PCDA). The interest in these lipid vesicles is mainly related to sensor application [13-15].

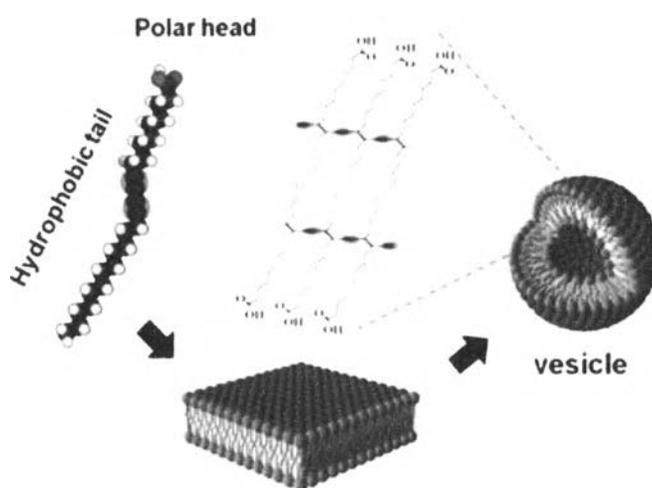
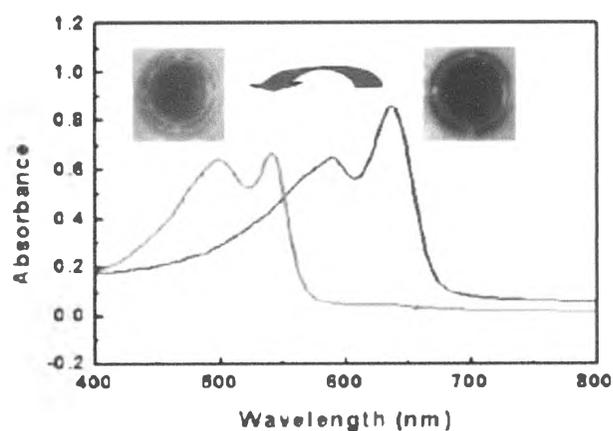


Figure 1.2 Structure and formation of PDA vesicle [13].

### 1.2.3 Optical properties of PDA sols

Optical absorption of polydiacetylene occurs via  $\pi \rightarrow \pi^*$  absorption within the linear  $\pi$ -conjugated polymer backbone. Upon polymerization, the first chromogenically interesting state of PDA appears blue color ( $\lambda_{\text{max}} = 640 \text{ nm}$ ). The exposure of PDA to external stimuli involve a significant shift in absorption from low to high energy bands of the visible spectrum then the polydiacetylene changes from blue to red color ( $\lambda_{\text{max}} = 550 \text{ nm}$ ) that resulted from molecular conformational changes such as side chain packing, ordering, and orientation, impart stresses to the polymer backbone that alter its conformation, thus changing the electronic states and the corresponding optical absorption.



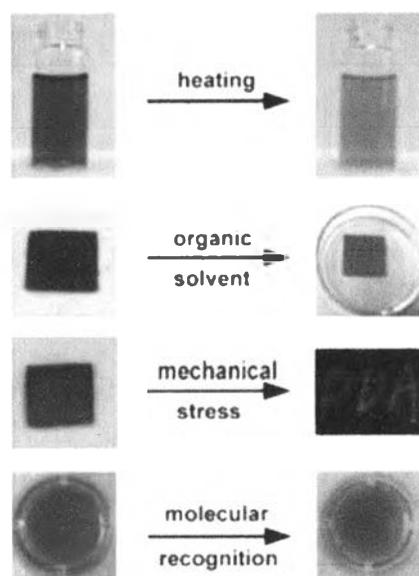


**Figure 1.3** UV-vis spectrum of PDA show characteristic peak of blue phase ( $\lambda_{\text{max}} = 640 \text{ nm}$ ) and red phase ( $\lambda_{\text{max}} = 550 \text{ nm}$ ) [16].

#### 1.2.4 Chromism of PDA sols

The most attractive properties of PDA is color change upon its exposure to various external stimuli such as thermochromism (heat), solvatochromism (solvent), mechanochromism (stress), affinochromism (ligand-receptor interaction) and alkalionchromism (pH). This factors can induce the color change from blue to red corresponding to the absorption maximum ( $\lambda_{\text{max}}$ ) in the blue phase at 640 nm was shifted to red phase is the absorption maximum ( $\lambda_{\text{max}}$ ) at 550 nm [17]. Even though, the mechanism of colorimetric change is unclear, possible explanation from Kim [18] is the distortion of PDA conjugate back bone generating from the polymer side chain movement in response to external stimulation.



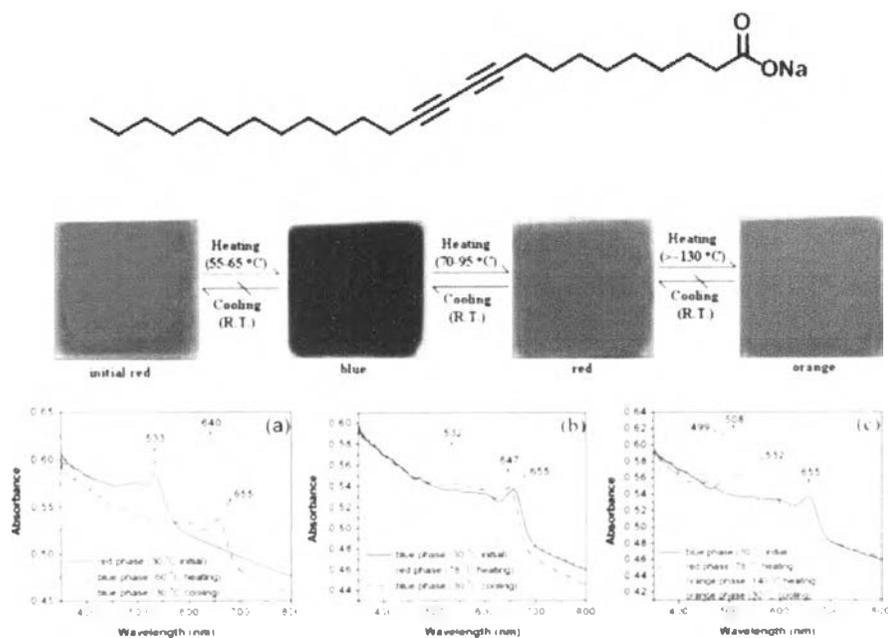


**Figure 1.4** Chromism of polydiacetylene by external stimuli [18].

### 1.3 Thermochromic reversible polydiacetylene

Thermochromism is the change in color of material when treated with heat. It is probably the earliest chromism property found for PDA. The most notable thermochromism involves the color change from blue to red that have been developed for various colorimetric sensing applications. The thermochromic PDA can be either reversible or irreversible depending on the interaction between the side chain substituents and side chain head groups. There are many dedicated effort research to elucidate the mechanisms of color change in PDA materials which is still not fully understood. It is likely that more than one mechanism causing thermochromic change depending on the nature of polymer. The report has shown that both side chain order and head group hydrogen bonding affect the chromic state [19].

In 2006, Pang *et al.* [20] reported the photopolymerization of Na-PCDA microcrystals. The results showed the lattice dimensional change of the metastable PDA crystals prepared by photopolymerization of Na-PCDA microcrystals. Releasing the internal strain by thermal agitation increased the effective conjugation length, producing an irreversible red to blue color change. The electrostatic interaction also resulted in stable PDA crystals that showed a reversible blue to red thermochromism in the temperature range 70-95°C (Figure 1.5)



**Figure 1.5** Structure of diacetylene monomer, photograph of color transition and UV-Vis spectrum for the color transitions: a) irreversible red to blue, b) reversible blue to red and c) irreversible red to orange [20].

In 2007, Lee *et al.* [21] studied the colorimetric reversibility of polydiacetylene supramolecules systemically. Diacetylene monomers used in the study are shown in Figure 1.6. Irreversible color change of PCDA **1** derived PDA solution was demonstrated by monitoring of the chromic transition during the heating and cooling process. PDAs derived from PCDA-*m*BzA **2** showed complete thermally promoted colorimetric reversibility. In contrast, a solution of PDA sols prepared from PCDA-*m*CPE **3**, an ester analog of PCDA-*m*BzA **2**, did not display thermally stimulated colorimetric reversibility, indicating the significant role played by internal H-bonding of amide group in governing the reversibility of the color change. Another key factor in controlling the reversibility of thermochromism is aromatic interactions between the head groups. The colorimetric irreversibility observed with PDAs made from PCDA-ABA **4** demonstrated this feature. The *para*-substituted diacetylene monomer PCDA-*p*BzA **5** generated stable, blue-colored PDA sols in aqueous media that displays complete colorimetric reversibility. This observation indicated that the position of the carboxylic acid group did not affect the reversible thermochromism. Alkyl chain length was found to have a negligible effect on the colorimetric reversibility of the resulting polymerized vesicles, as demonstrated by the complete reversibility

observed for solutions containing PDA sols made from HCDA-mBzA 6. The amine and hydroxyl-terminated diacetylene monomers PCDA-EDEA 7 and PCDA-EA 8 produced colorimetrically irreversible PDAs. Finally, the naphthyl group diacetylene monomer derived from PCDA-NPA 9 showed reversible thermochromism.

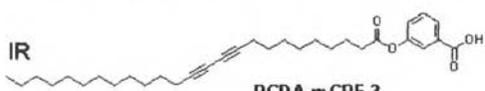
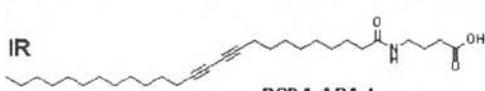
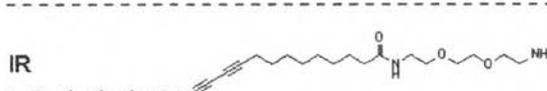
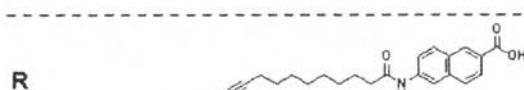
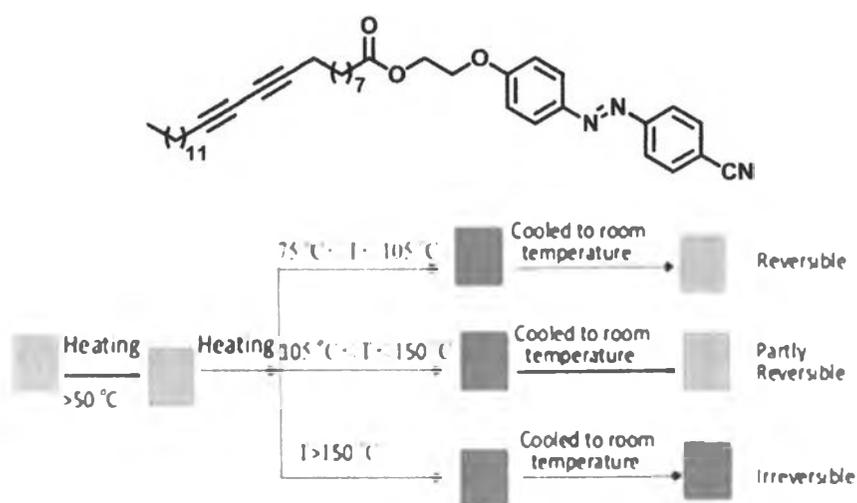
DA monomers	Thermochromism
IR  PCDA 1	 heating →  cooling → 
R  PCDA-mBzA 2	 heating →  cooling → 
IR  PCDA-mCPE 3	 heating →  cooling → 
IR  PCDA-ABA 4	 heating →  cooling → 
R  PCDA-pBzA 5	 heating →  cooling → 
R  HCDA-mBzA 6	 heating →  cooling → 
IR  PCDA-EDEA 7	 heating →  cooling → 
IR  PCDA-EA 8	 heating →  cooling → 
R  PCDA-NPA 9	 heating →  cooling → 

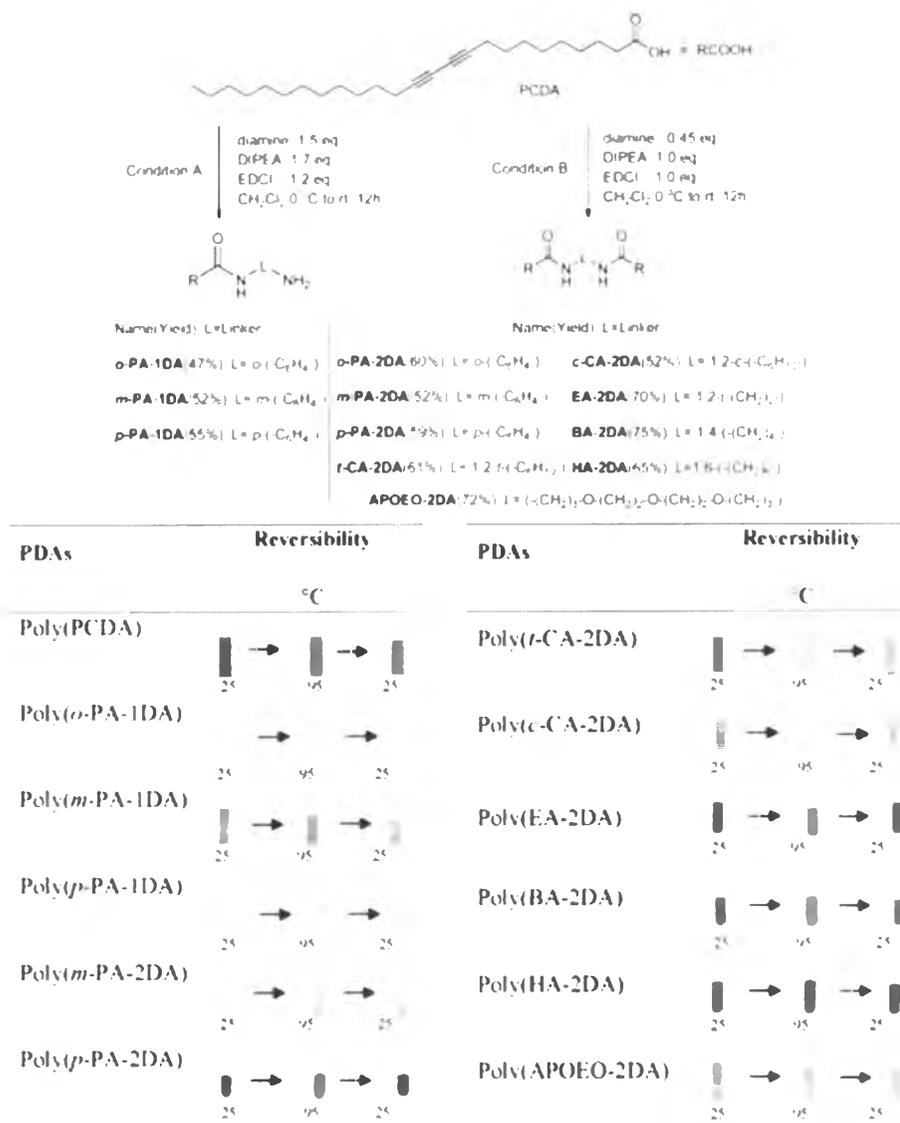
Figure 1.6 Structure of diacetylene monomers and photograph of PDA sols that demonstrate irreversible and reversible thermochromism [21].

In 2008, Ye *et al.* [22] reported the morphology, structure and chromic properties of azobenzene polydiacetylene (Figure 1.7). It showed a reversible chromic transition with a wide thermochromic transition temperature range. The critical transition temperature was 105°C for completely reversible thermochromic transition and 150°C for partially reversible thermochromic transition, respectively. The results showed the strong intermolecular aromatic interaction between side chain and the maintenance of lamellar crystal structures at high temperature were essential requirement for the complete reversibility of thermochromic of PDA film.



**Figure 1.7** Structure of diacetylene monomer and diagram of the thermochromic phase transition of PDA film [22].

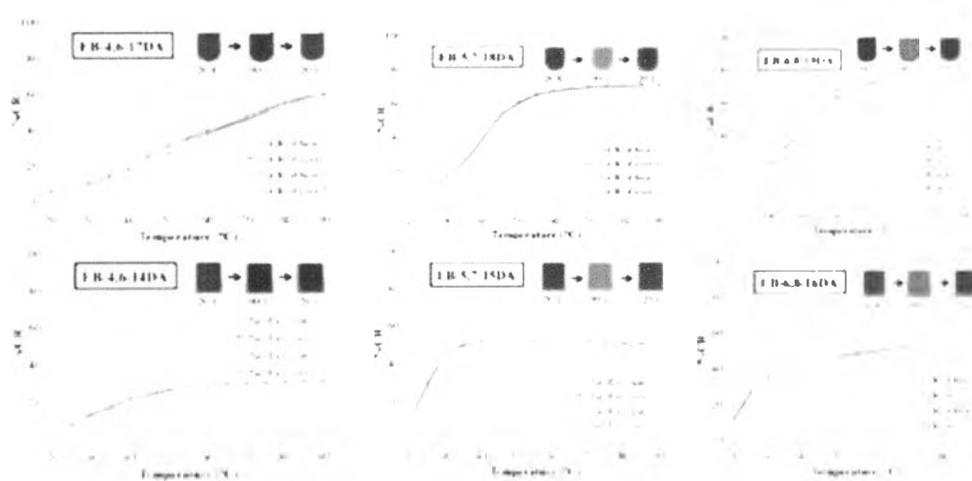
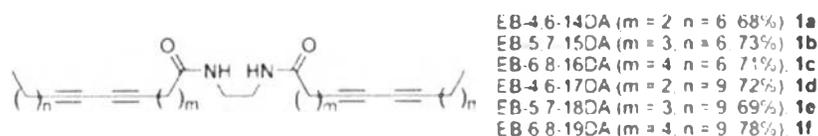
In 2010, Wacharasindhu *et al.* [23] reported a new strategy for tuning thermochromic properties of polydiacetylene through amido hydrogen bonding to create a universal temperature sensing material (Figure 1.8). The results indicated that color transition temperature and thermochromic reversibility of polydiacetylenes can be tuned by the structures of the linkers between the amide groups. Both color transition temperature (CTT) and reversibility of polydiacetylenes were found to be mainly associated with the number and orientation of the hydrogen bond forming group.



**Figure 1.8** Investigated structures of diacetylene monomers and photograph of thermochromic reversibility [23].

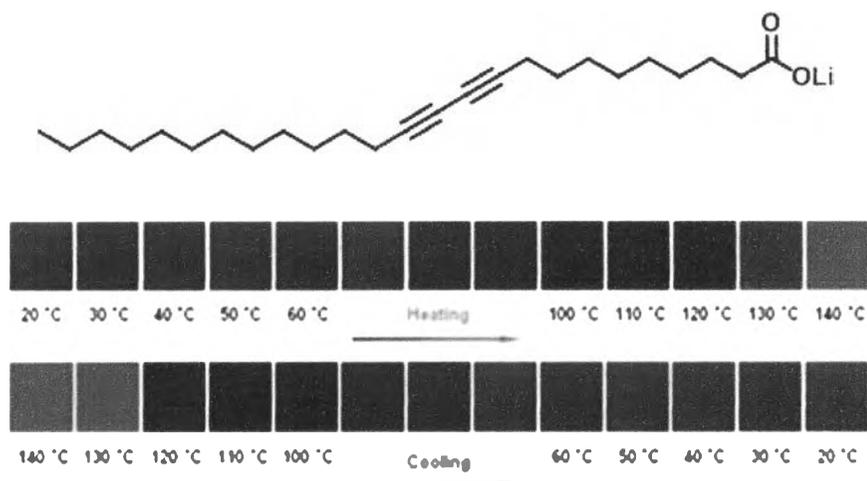
In 2010, Phollookin *et al.* [24] reported the thermochromic reversibility of polydiacetylene (Figure 1.9). They found that tuning of color transition temperature (CTT) of thermochromically reversible diindiamide series of PDA can be success by systematic variation of the length of methylene spacer (*m*) between the diyne and the diamide head group as well as the number of methylene units (*n*) in the hydrophobic tail. On the other hand, the decrease of *n* value enhances the thermal sensitivity resulting in lower color transition temperature, the effect of *m* value is not as straight forward. Therefore even number (*m* = 2,4), the diamide side-chain of the PDA form extraordinary strong hydrogen bonding accommodate by the well

positioned ene-yne conjugated backbone in opposite to the odd number ( $m = 3$ ). Thus  $m$  played the odd-even effect on thermal stability.



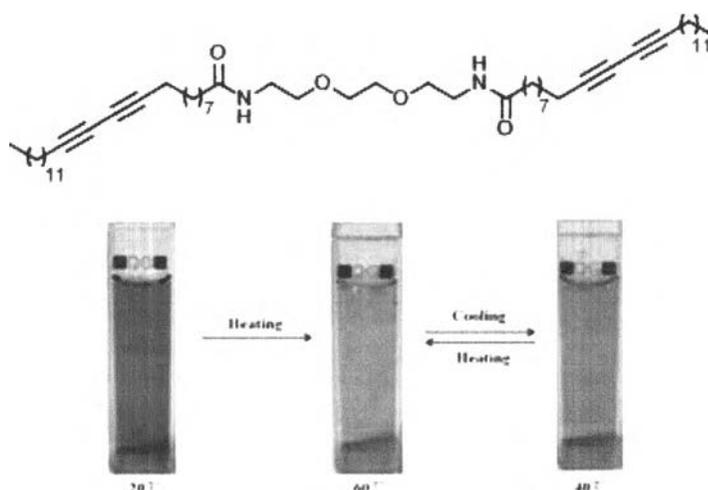
**Figure 1.9** Diacetylene structure and colorimetric response of PDA sol along with photograph of color change [24].

In 2010, Balakrishnan *et al.* [25] reported that the Li-PCDA was successfully synthesized. Photopolymerization of diacetylene monomer in solid state is prepared. Interestingly, the colorless Li-PCDA sols generated a brilliant blue color upon UV irradiation for 30 second while colorless PCDA sols displayed a very slight color change in the same time. The thermal treatment of PVA films showed reversible thermochromism which heated to 140°C the color change from blue to stable red. Upon removal of the heat, the red film gradually retraced its color to original blue, as shown in Figure 1.10



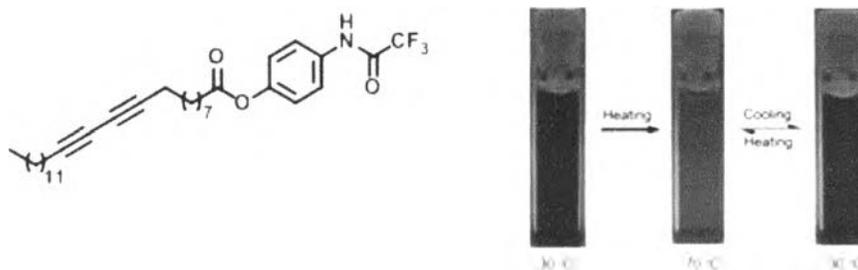
**Figure 1.10** Structure of diacetylene monomer and photograph of Li-PCDA embedded PVA film upon heating 20-140°C [25].

In 2010 Lee *et al.* [26] investigated the thermally reversible PDA containing ethylene oxide bisdiacetylene (Figure 1.11). The PDA sols were prepared in aqueous media. The thermochromism was studied that the temperature initially increased to 60 °C when decreased temperature to 40 °C the color change from red to purple. The author suggested that the steric hindrance introduced between side chains could relax with a thermodynamic process during the first heating step ranging from room temperature to 60 °C. In case of thermochromic phase (from blue to red), the slight reorganization of the aliphatic side chains may produce a slight distortion of the linker with a less effective conjugated backbone.



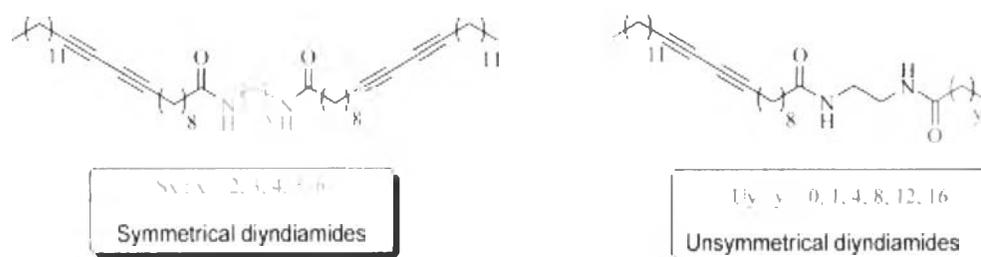
**Figure 1.11** Investigated structure of diacetylene monomer and photograph of PDA sol upon heating process [26].

In 2011, Chen *et al.* [27] reported that the new thermochromic reversible PDA is synthesized. PDA sols displayed a reversible color change from purple to red as the temperature is varied between of 30-70°C and repeated heating-cooling cycles can lead to the switches between red and purple colors (Figure 1.12). Moreover, the thermochromic reversible of PDA embedded PVA film was demonstrated.



**Figure 1.12** Structure of monomer and photograph of color change upon heating cycle 30-70°C [27].

In 2012, Ampornpun *et al.* [28] reported that two series of symmetrical (*Sx*) and unsymmetrical (*Uy*) diacetylene monomers containing diamide groups with different methylene units are successfully prepared (Figure 1.28). Photopolymerization of their vesicles dispersed in water is carried out by irradiation at 254 nm affording blue sols of the corresponding PDAs. The degree of thermochromic reversibility (%DR) of the PDA sols are determined using UV-Vis spectroscopy in order to probe effects of the number of the methylene units *x* and *y* within the linker and hydrophobic tail, respectively. The complete color reversibility (%DR > 89%) is observed only when *x* is an even number while partially reversible or irreversible thermochromism (%DR < 65%) is displayed in the case of odd *x* number. For the *Uy* series, the color recovering ability within the heating and cooling process increases along with the *y* number; %DR = 3, 62, and 90% for *y* = 0, 4, and 16, respectively. This work is the first direct demonstration of the roles of number of methylene units within the diacetylene monomers on the thermochromic reversibility of their PDAs that provide additional dimensions for rational molecular design in the development of PDA thermal sensors.



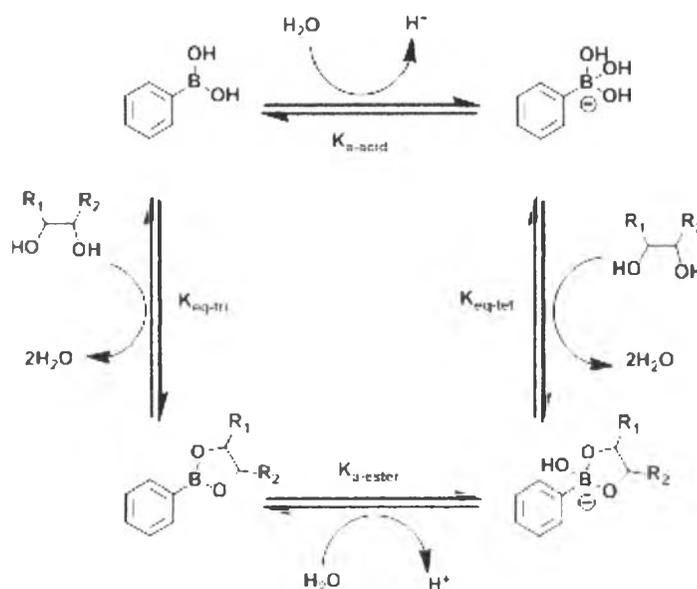
**Figure 1.13** Structure of diacetylene monomers: symmetrical diyndiamides (Sx) and unsymmetrical diyndiamide monomers (Uy) [28].

In summary, the key important factors that affect thermochromic reversibility are the enrichment of polar head group hydrogen bonding [21, 23, 24, 26], incorporation of  $\pi$ - $\pi$  aromatic interaction [22, 27] and hydrophobicity of alkyl side chain [28].

#### 1.4 Sensor from Boronic acid

Boronic acids are Lewis acid that can interact with Lewis bases to generate boronate anions, and they can also bind with diol compound to form cyclic boronate esters. Boronic acid as receptor designs originated when Lorand and Edwards published the first quantitative evaluation of the interaction between various diol compounds and phenylboronic acid in 1959 [29]. The inherent acidity of the boronic acid is enhanced when 1,2-, 1,3-, or 1,4-diols react with boronic acids to form cyclic boronic esters (5, 6, or 7 membered rings) in aqueous media, and these interactions form the cornerstone of diol-based receptors used in the construction of sensors [30].





**Scheme 1.1** Demonstrated binding process of boronic acid and diol compound [31].

There are many researches in fluorescence sensor base on boronic acid as receptor. For example, fluorophore 10 containing boronic acid show the fluorescence response with fluoride ion detection [32] while the naphthoimidazolidione derivative fluorophore 11 display fluorescence quenching toward  $\text{CN}^-$  in aqueous solution [33]. Moreover, the rhodamine derivative fluorophore 12 containing boronic acid as a receptor demonstrated high selectivity and sensitivity against  $\text{Hg}^{2+}$  in aqueous solution [34]. Recently, the use of boronic as the sugar receptor were reported for instant tetraphenylethene derivative 13 show the fluorescence quenching toward D-glucose in aqua media [35] and the BODIPY derivative 14 showed the fluoresce enhancement toward receptor D-Fructose [36].

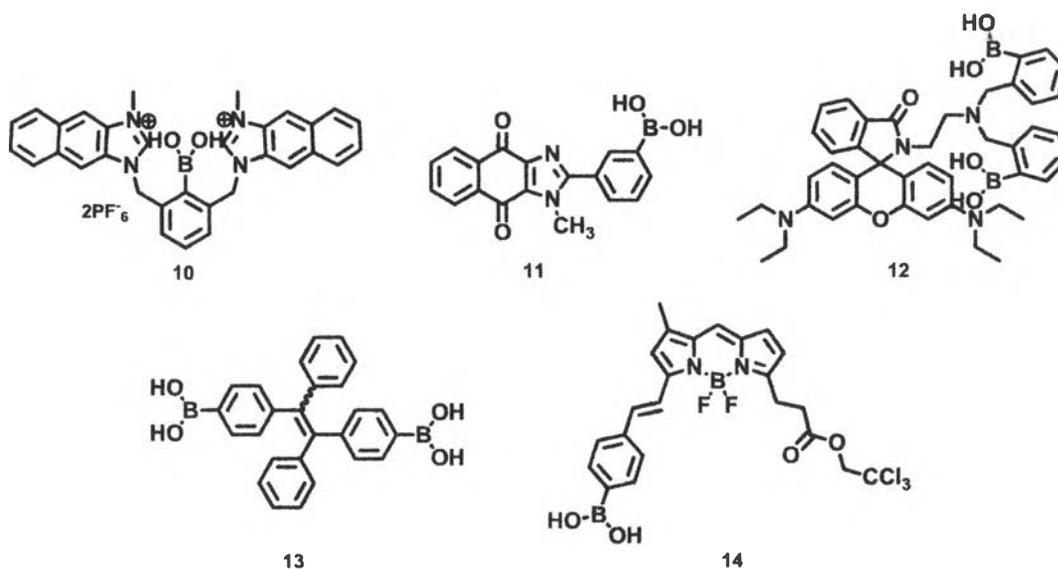
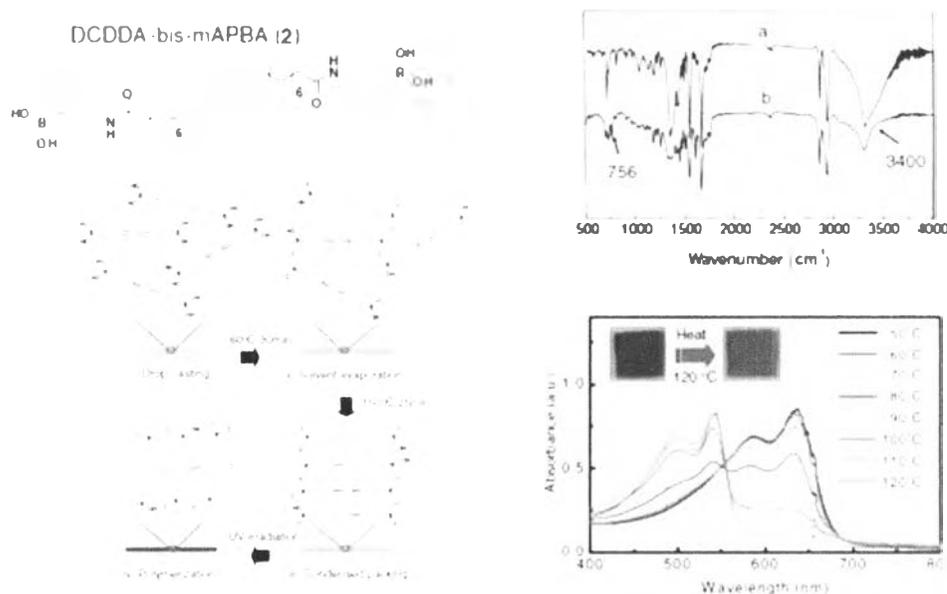


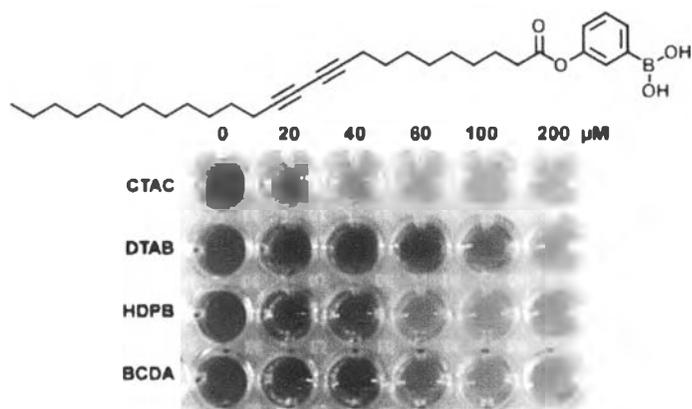
Figure 1.14 The structure of fluorophore containing boronic acid as a receptor.

Recently others have studied attachment of boronic acid to diacetylenes. In 2011, Kim *et al.* [37] reported the synthesized of diboronic acid diacetylene monomers (Figure 1.15). The monomers were fabricated on to glass substrate by drop casting, thermal annealing and photopolymerization. The author claimed that boronic acid were converted to boronic anhydride during thermal annealing which confirmed by FTIR analysis. The thermochromism of PDA film was investigated when PDA film was heated up to 120°C the color change from blue to red while cool down to 50°C the color is not recovered to original blue PDA film.



**Figure 1.15** Structure of diacetylene monomer, preparation of PDA film on glass substrate, FTIR spectrum of DCDDA-bis-mABA (2): a) before annealing and b) after annealing and UV spectrum of PDA film upon heating 50-120°C [37].

Unfortunately, while carrying out our research, in 2013, Lee *et al.* [38] reported the utilization of oxy-boronic acid diacetylene monomer which is the first report on PDA carrying boronic acid (Figure 1.16). Affinochromic property of surfactant toward PDA was studied and results showed that the oxy-boronic acid PDA sols have a colorimetric color change in different color with cationic surfactants. Unfortunately, these PDA are not able to undergo colorimetric change with any kind of sugar. With the interception of our interest with this group however, there are no report on the thermochromism on the PDA carrying boronic acid.



**Figure 1.16** Structure of diacetylene monomer and photograph of PDA sols (250  $\mu\text{M}$ ) in the present of various amounts of CTAC, DTAB, HDPB, and BCDA in HEPES buffer (10 mM, pH = 7.4): 0, 20, 40, 60, 100, 200  $\mu\text{M}$  [38].

### 1.5 Objectives and scope of the thesis

The objectives of this thesis are study colorimetric chemosensor for sugar sensing and thermochromism of PDA containing boronic acid. In this study, six diacetylene monomers containing amide boronic acid (**1a-3a**) and ester boronic acid (**4e-6e**) were designed in order to study the relationship between the chromic properties of PDA with their structures ester group versus amide group, the position of boronic acid on benzene moiety and methylene chain length. The chromic properties of these PDAs will be tested against temperature, VOC, UV light, acid-base and chemical such as sugars and surfactants. The outcome of this study would lead to the understanding of the basic knowledge to create new PDA toward chemo and thermo sensor.

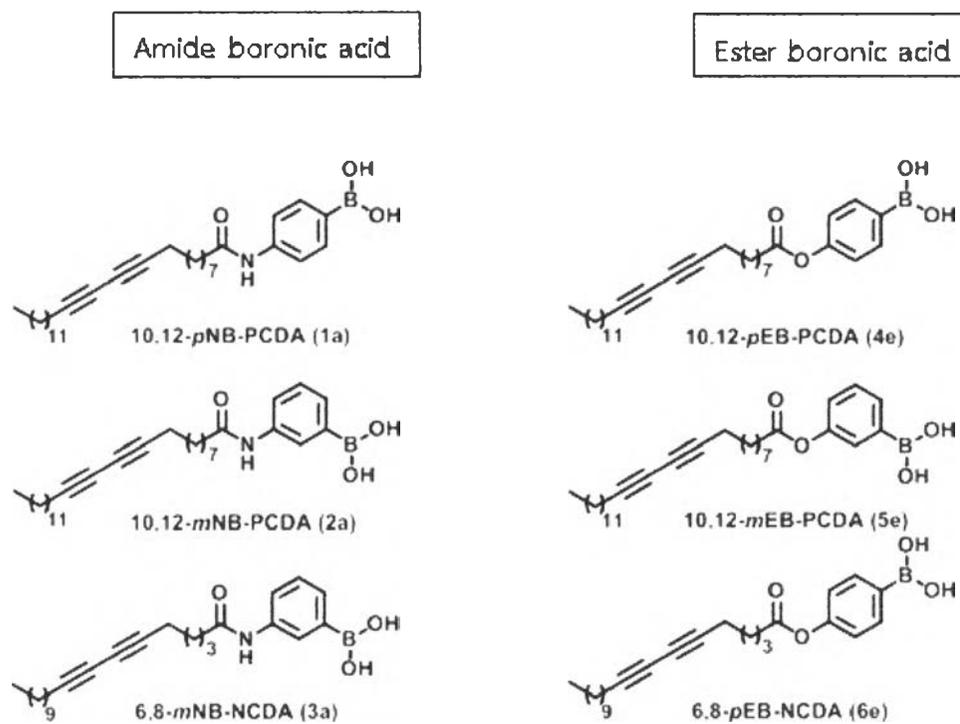


Figure 1.17 Structure of boronic acid diacetylene monomers in this study.

