

CHAPTER I

INTRODUCTION AND THEORY

1.1 Overview

Recently, development of conjugated polymers as sensing materials have gained much attention because changes in their absorption, emission, and redox properties. A major advantage of using conjugated polymer-based sensors over small molecules found in their potential for signal amplification [1]. Along this development, polydiacetylenes (PDA) have been shown for their unique color changing properties under various external perturbations such as temperature, pH, solvent, mechanical stress and ligand-receptor interactions [2-11].

PDA can be prepared in various forms such as bulk crystal, monolayer or multilayer films, polymerized vesicles or incorporated into inorganic host matrices to form nanocomposites [12]. PDA is typically obtained from topopolymerization of appropriate diacetylene monomers [13]. Diacetylene lipids have recently emerged as one of the most studied class of monomers because they can form nano-structured vesicles uniformly dispersed in an aqueous medium. The vesicle solution can in turn be polymerized efficiently by UV-irradiation. One of the most commonly used lipid monomer for preparation of vesicles is 10,12-pentacosadiynoic acid (PCDA) [14] that give intense blue-colored solution of poly(PCDA) solution upon photopolymerization. Poly(PCDA) vesicle solution shows irreversible color transition from blue to red by increasing the temperature and changing of solvent or pH. The color change has also been utilized in the construction of biosensors for naked eye detection of influenza virus, cholera toxin, Escherichia coli, glucose and cyclodextrin [15].

Temperature is one of the most important physical parameters affecting biological and chemical systems. There are various circumstances in which the temperature history must be monitored and recorded, for examples, the need to know whether a frozen food product has been exposed to an unacceptable level of temperature during storage and distribution or whether a person traveling through a broader or strictly controlled hygienic zone having a high fever. A disposable, economical and simple to use device can be very useful for such applications.

Irreversible thermochromic films, of which the color transition temperatures (CTT) are tunable, meet those criteria.

In this work, the key component of thermochromic films with tunable color transition temperature (CTT) is the thermochromic agent, polydiacetylene (PDA) vesicles. Since the color change of PDA vesicles is closely related to the interaction between the side chains of the ene-yne conjugated backbone, the modification of this interaction through two different approaches is the main subject of this thesis. The first approach involves a simple mixing of a widely used diacetylene lipid monomer, 10,12-pentacosadiynoic acid (PCDA), with a fatty acid of different aliphatic chain length at various mole ratios. The insertion of the fatty acid molecules into the vesicle lipid bilayers should moderate the perfect packing between the aliphatic chains of the diacetylene monomer and thus limit the polymerization as well as the interaction between the polymer side chains resulting in the lowering of the CTT and the experimental results should provide useful quantitative data for further insight into packing pattern in mixed lipid vesicles. The second approach deals with modification of the carboxylic head group of PCDA. The modification of the carboxylic head group should cause significant change in the orientation and strength of the hydrogen bonds between the head groups. Two amide derivatives *N*-(2-aminoethyl)pentacosadiynamide (AEPCDA) and *N,N'*-(ethan-1,2-diyl)bispentacosadiynamide (EBPCDA) derived from the condensation of ethylenediamine with one and two equivalents of PCDA, respectively. Moreover, *N*-(2-stearamidoethyl)pentacosadiynamide (SEPCDA) was synthesized by condensation reaction between *N*-(2-aminoethyl)stearamide and 10,12-pentacosadiynoyl chloride. These amide diacetylenes may be polymerized to form PDA vesicles possessing CTT higher than PCDA.

1.2 Theory

1.2.1 Polydiacetylene vesicles

Polydiacetylene (PDA) form a unique class of polymeric material that couple highly aligned conjugated backbone with tailorable pendent side groups and terminal functionalities. PDA is conjugated polymers resulted from topopolymerization of diacetylene monomers via 1,4-addition reaction to form alternating ene-yne polymer chains (Figure 1.1) upon heat, irradiation with light or γ -irradiation [1].

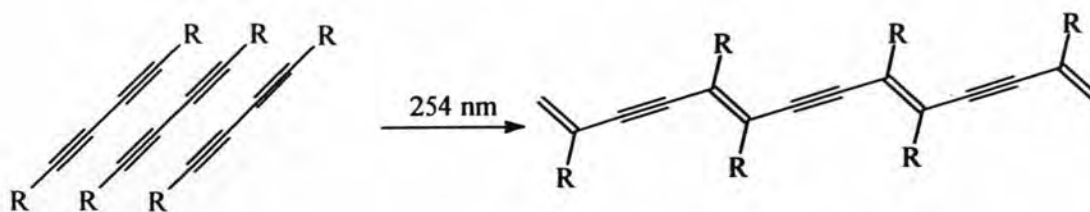


Figure 1.1 Polymerization of diacetylene monomers by irradiation with UV light.

The topopolymerized diacetylene crystals are nearly perfectly ordered crystals which can not be occurred by solution polymerization or recrystallization of a preformed polymer from solution or melt [16,17]. The resulting PDA, if generated under optimized conditions appear as an intense blue-colored PDA. PDA can change color from blue to red, having the maximum absorption peak at 630 nm and 540 nm in the blue and red form, respectively, under external perturbation such as temperature, pH, solvent, mechanical stress and ligand-receptor interactions [2-11] due to reduction of the effective conjugation length resulted from strain and torsion imposed onto the backbone induced by order-disorder transitions in the side chains [18-19]. Owing to these color changing properties, PDA-based sensors have been prepared in a wide range of organized structures such as single crystals, thin films on solid supports using Langmuir-Blodgett or Langmuir-Schaefer techniques, self-assembled monolayers, liposomes or vesicles in water.

Diacetylene lipid acids are known to spontaneously organize into vesicle structure in aqueous media which can be further photopolymerized by UV light to provide spherical nanostructure of polydiacetylene vesicles. One of the most commonly used lipid monomer for preparation of vesicles is 10,12-pentacosadiynoic acid (PCDA). PCDA monomers have carboxylic group that can dissociate in water and make these monomers hydrophilic but long hydrocarbon chain make these monomers hydrophobic. PCDA monomer can thus assemble in the form of lipid bilayer vesicles in water and can be polymerized by irradiation with UV light (Figure 1.2).

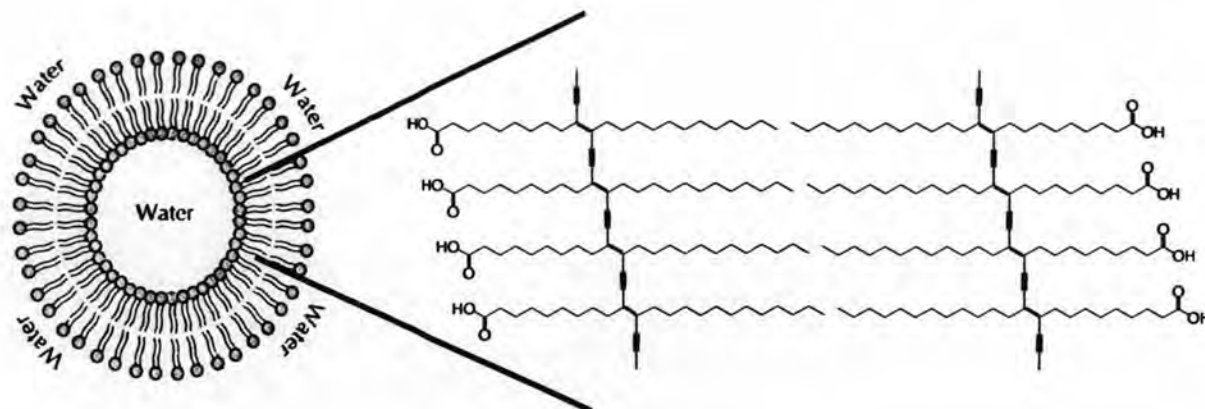


Figure 1.2 Illustration of poly(PCDA) vesicle.

Electronic transition of polydiacetylene

Optical absorption in polydiacetylene occurs via $\pi \rightarrow \pi^*$ absorption within the linear π -conjugated polymer backbone. Upon polymerization, frequently the first chromogenically interesting state of PDA appear blue in color. The exposure of PDA to environmental perturbations such as heat (thermochromism), mechanical stress (mechanochromism), or solvent (solvatochromism) involve a significant shift in absorption from low to high energy bands of the visible spectrum, so the polydiacetylene transforms from blue to red color 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 [20].

The color transition of the polymerized vesicles was monitored by measuring the absorbance differences between the vesicles before and after stimulation by an interesting parameter. This information is often converted to a percentage, termed the Colorimetric Response (CR) [21].

Colorimetric Response (CR)

A quantitative value for the extent of blue-to-red color transition is given by the colorimetric response (%CR) which is defined as

$$\%CR = (PB_0 - PB) / PB_0 \times 100$$

Where $PB = A_{\text{blue}} / (A_{\text{blue}} + A_{\text{red}})$, A_{blue} and A_{red} are the absorbance of the blue and the red phase at 630 and 540 nm, respectively. The visible absorbance was measured by a temperature controlled UV-Vis spectrometer. PB_0 is the initial percent blue of the

vesicle solution and film before heated. All blue-colored PDA vesicle solution and film samples were heated from 25 to 90 °C.

1.2.2 Thermochromism of polydiacetylene vesicles

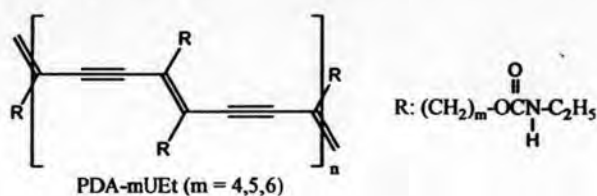
Thermochromism, the color transition upon the rise of temperature, is one of the interesting chromic properties of polydiacetylenes both for its applications and fundamental understanding. Thermochromism in polydiacetylenes arises from the conformational changes of the conjugated backbone from planar to non-planar due to movement of the side chains. The color transition is thus resulted from the increase of energy gap between the HOMO and LUMO level. The color transition of polydiacetylenes is driven by the relief of mechanical strain in their structures [21].

For polydiacetylene vesicles, hydrogen bonding between the head groups of the lipid monomers is usually responsible for the planarity of the conjugated backbone. Thermal energy can break or weaken the hydrogen bonding between the head groups resulting in random movement of the side chains and lower the planarity of the backbone and hence the average conjugation length of π electrons along the polymer backbone inducing the color change from blue to red [12].

1.3 Literature Survey

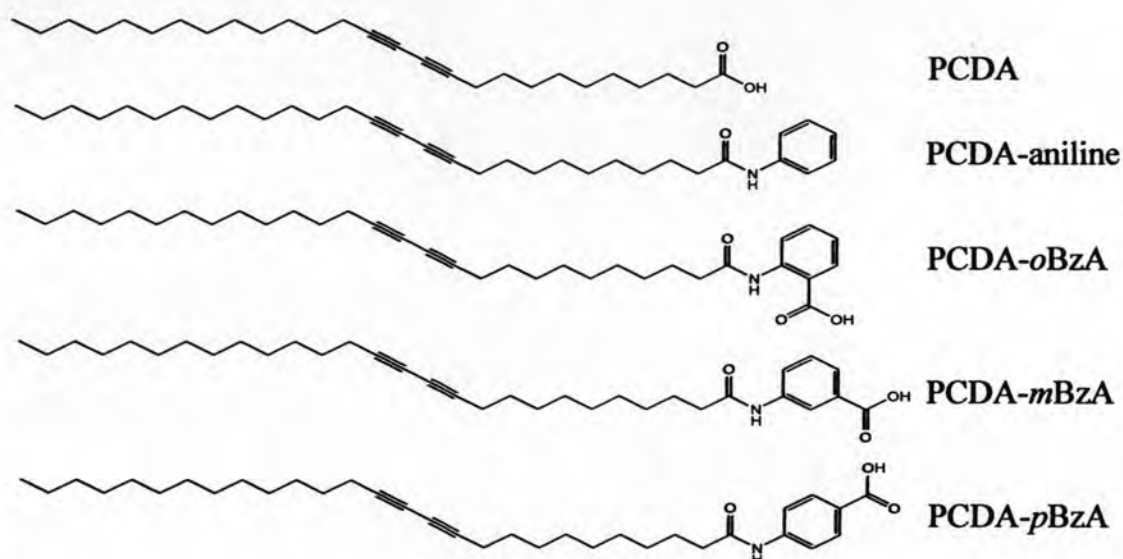
In 1997, Lio *et al.* [22] studied thermochromism of polydiacetylene Langmuir-Schaefer film of 10,12-pentacosadiynoic acid (PCDA) and sialic acid derivatives of PCDA. It was found that the blue-colored film at 25 °C gradually changed to blue-purple at 50 °C and eventually complete converted to red at temperatures between 70 and 90 °C that color change from blue to red arises from reduction of the effective conjugated length of the polymer en-yne backbone influenced by the pendant side groups.

In 2001, Tachibana *et al.* [23] prepared polydiacetylene series containing urethane groups with different alkyl chain length in the side chain (PDA-mUEt, $m = 4, 5, 6$) by irradiation of diacetylene monomer crystals.



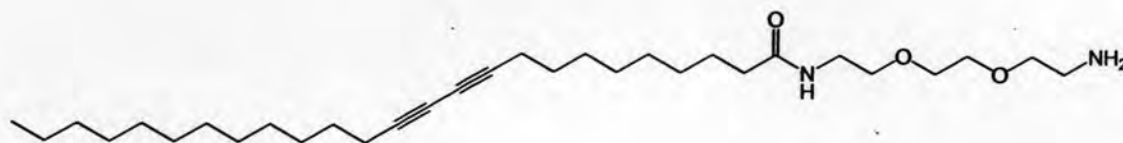
The thermochromic reversibility was found to depend on the alkyl chain length. PDA-5UEt showed full reversibility while PDA-4UEt was not fully reversible and PDA-6UEt was irreversible. No clear explanation for these observation was provided.

In 2003, Ahn *et al.* [24] synthesized derivatives of 10,12-pentacosadiynoic acid containing an anilide and carboxylanilides (ortho-, meta-, and para-).



The thermochromism of the polymerized Langmuir-Schaefer films of these derivatives was studied. The film obtained from meta-carboxylanilide derivative was found to have a remarkable reversibility upon removal of both thermal and pH stimuli. The authors suggested that the orientation of the terminal carboxyl and amide groups in meta-carboxylanilide was suitable for a formation of double hydrogen-bonding required for the recovery of the original conformation. In 2005, Kim *et al.* [1] found similar results that the thermochromism of polydiacetylene of PCDA-*m*BzA prepared in the form of vesicles was also fully reversible.

In 2003, Kim *et al.* [20] prepared blue polydiacetylene vesicles from an amine-terminated diacetylene monomer, PCDA-NH₂.



Direct immobilization of these polydiacetylene vesicles onto the aldehyde modified glass substrate resulted in the blue-to-red color transition probably due to mechanical

stress induced by reaction between the amine groups of the polydiacetylene vesicles and the aldehyde groups on the glass substrates. However, immobilization of diacetylene monomer vesicles followed by photopolymerization gave blue-colored immobilized polydiacetylene. Incubation of this blue film in a solution containing poly(acrylic acid) gave a colorimetric change from blue-to-red. It is expected that the amine moieties of the immobilized PDA vesicles should form ionic bonding with the carboxylic groups of poly(acrylic acid). These multivalent ionic interactions may force the movement of the polydiacetylene side chain and consequently the reduction of the π -conjugation in the backbone.

In 2004, Su *et al.* [25] synthesized antibodies which were covalently coupled with mixed vesicles of 10,12-tricosadiynoic acid and dimyristoylphosphatidylcholine (DMPC). After mixing with an appropriate antigen, specific immunoreactions took place at the vesicle surface altering polydiacetylene conformation that led to a color change from blue to red. Incorporation of DMPC in the mixed vesicles increased the sensitivity of the chromatic immunoassay that the color change was readily discernible by naked eyes when the concentration of the antigen was greater than 1 ng/mL.

In 2005, Su *et al.* studied interaction between surfactants and lipid vesicles composed of DMPC and polymerized 10,12-pentacosadiynoic acid in aqueous solution by using colorimetric method. The electrostatic interaction and hydrophobic interaction play a key role in the interaction between the mixed lipid vesicles and surfactant that the cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS) and Triton X-100 were selected as a cationic, anionic and nonionic surfactant, respectively. The addition of surfactants into mixed vesicles induced color change from blue to red that resulted from electrostatic interaction between the head groups of the surfactants and the vesicles promoting the insertion of alkyl chain of surfactants into the hydrophobic domain of the vesicles. The insertion of alkyl chain of the surfactants perturbed the conformation of polymer backbone in mixed vesicles and led to color change of the mixed vesicles. Again, incorporation of DMPC in mixed lipid vesicles interrupted molecular packing of PCDA that facilitated the insertion of surfactants [26]. Moreover, DMPC-polymerized PCDA vesicles functionalized with glycolipid was applied as biosensor for detection of *E. coli* [27]. In the same year, Su also prepared multi-layer film of polydiacetylene vesicles on PEI-modified quartz

slide by electrostatic layer-by-layer deposition using negatively charged 10,12-pentacosadiynoic acid vesicles and polyelectrolyte polyethylenimine (PEI) or positively charged PCDA-2'-aminiethylamide (PCDANH₂) vesicles. The color change of this film from blue to red was observed at 60 °C [28].

In 2006, Potisatityuenyong *et al.* [29] prepared polyelectrolyte multilayer (PEM) thin films on glass substrates using 10,12-pentacosadiynoic acid (PCDA) vesicles as a polyanion and chitosan as a polycation. The intact vesicles were shown by AFM image and the color intensity of the films can be controlled through the number of vesicle layers deposited. The PEM films retained all chromic properties *i.e.* solvatochromism, pH sensing, and thermochromism of the vesicles dispersed in water.

In 2006, Kim *et al.* [30] prepared polydiacetylene vesicles embedded in PVA film using a mixing-dyeing process and thermochromic properties were investigated by heating process. The blue-colored PVA film at 25 °C gradually changed to purple at 80 °C and eventually changes to red above 100 °C. In addition, incubation of polymerized PCDA-embedded PVA film prepared with silica gel particles in α -cyclodextrin solution promoted the blue-to-red color change due to the formation of inclusion complex between the polydiacetylene side chains and α -cyclodextrin .

In 1980, Yee *et al.* [31] patented on the use of polydiacetylene containing urethane groups, prepared from solid state polymerization of the corresponding monomer, for temperature sensing. The patent described that polydiacetylene exhibited reversible color change at transition temperature in the range -180 to 220 °C, wherein the thermochromic cycles can be repeated many times with no apparent degradation and little change in spectroscopic properties.

In 1992, Thierry and Le Moigne [32] patented the symmetrical and unsymmetrical alkyl diacetylene compounds which exhibited a particular thermochromic behavior. These polydiacetylene compounds showed an irreversible color change from blue to red which took place at the threshold temperature depended on the length of the alkyl chain on the starting monomer. A polydiacetylene compound could be deposited on a substrate or mixed with thermoplastic such as polyethylene to be used as temperature indicators.

In 2003, Ribi *et al.* [33] patented on ingestible thermochromic materials prepared from polydiacetylene microcrystalline that can be used in association with compositions in food to show the change of food temperature [34].

In 2004, Disalvo *et al.* [35] patented on the temperature sensing composition comprised of a thermochromic dye (thermochromic powder LD-P, red no. 058TC or Dyancolor Red Poster Screen Ink or thermochromic powder no. 058C8T) which is dispersed or dissolved in a hardened matrix forming resin (The resin can be a thermoset such as epoxy, polyurethane, phenolic or other thermoset or it can be a thermoplastic such as polyethylene, polypropylene, polyvinyl chloride, polyester or other thermoplastic). The temperature sensing dye underwent a color change when the prevailing temperature entered the range of 4 to 7 °C that this invention can be used as an indicator that indicates when the temperature of a refrigerator or other food storage container rise above 4 to 7 °C which is the optimum temperature range for storage of food.

In 2005, Heys and 3M [36] patented on diacetylene derivatives and their polymers over 100 types that containing different side chain lengths mostly derivitized from the diacetylene alcohols. as the polymers were also claimed for temperature indicator which can change color at the threshold temperature.

1.4 Objective and scope of this thesis

The objective of this thesis is to prepare films containing polydiacetylene vesicles that can change color at various temperatures. To achieve the objective, the scope of this research work includes 1) synthesis of amide derivatives of 10,12-pentacosadiynoic acid (PCDA), 2) preparation of polydiacetylene vesicles from PCDA and its derivatives, 3) preparation of polydiacetylene vesicles from PCDA mixed with various fatty acids, 4) characterization of the prepared vesicles by AFM, TEM and dynamic light scattering, 5) study of thermochromic properties of the prepared vesicle solutions, 6) preparation of thermochromic films containing the prepared vesicles and 7) study of thermochromic properties of the prepared films.