การสังเคราะห์และพอลิเมอไรเซชันของนาโนแอสเซมเบิลไดแอเซทิลีนลิพิดที่มีหมู่แอมิโน

นางสาวสุริชา พุ่มแตง

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2553

SYNTHESIS AND POLYMERIZATION OF NANO ASSEMBLED DIACETYLENE LIPIDS CONTAINING AMINO GROUPS

Miss Suricha Pumtang

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2010

Thesis Title	SYNTHESIS AND POLYMERIZATION OF NANO ASSEMBLED DIACETYLENE LIPIDS CONTAINING AMINO GROUPS
By	Miss Suricha Pumtang
Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Anawat Ajavakom, Ph.D.
Thesis Co-advisor	Associate Professor Mongkol Sukwattanasinitt, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

.....Dean of the Faculty of Science
(Professor Supot Hannongbua, Dr.rer.nat.)

THESIS COMMITTEE

.....Chairman
(Associate Professor Supawan Tantayanon, Ph.D.)

.....Thesis Advisor
(Anawat Ajavakom, Ph.D.)

.....Thesis Co-advisor
(Associate Professor Mongkol Sukwattanasinitt, Ph.D.)

.....Examiner
(Associate Professor Voravee Hoven, Ph.D.)

.....External Examiner
(Gamolwan Tumcharern, Ph.D.)

สุริชา พุ่มแตง : การสังเคราะห์และพอลิเมอไรเซชันของนาโนแอสเซมเบิลไดแอเซทิลีนลิพิดที่มีหมู่แอมิโน. (SYNTHESIS AND POLYMERIZATION OF NANO ASSEMBLED DIACETYLENE LIPIDS CONTAINING AMINO GROUPS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : อ.ดร.อนวัช อาชวาคม, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม : รศ.ดร.มงคล สุขวัฒนาสินิทธิ์, 86 หน้า.

การสังเคราะห์ไดแอเซทิลีนลิพิดมอนอเมอร์กลุ่มใหม่ประกอบด้วยหมู่แอมิโด หรือคาร์บอกซิลเป็นส่วนหัว ที่มีความแปรผันความยาวของสายโซ่แอลคิล (n = 2, 3, 4) ระหว่างหมู่คาร์บอนิลกระทำผ่านการควบแน่นของ 10,12-เพนตะโคซะไดไอนามีนกับ ไดแอซิดต่างๆ หรืออนุพันธ์แอนไฮดรายด์แบบวงของมัน เราได้ตรวจสอบปฏิกิริยาการพอลิเมอไรเซชันและสมบัติการเปลี่ยนสีของพอลิไดแอเซทิลีน (PDA) ที่สังเคราะห์ได้ ซึ่งมอนอเมอร์เปลี่ยนเป็นสีน้ำเงินหรือม่วงในสถานะของแข็ง ในขณะที่เปลี่ยนอย่างทันทีทันใดเป็นสีที่แตกต่างกันในสถานะฟิล์ม ขึ้นอยู่กับความยาวของสายโซ่แอลคิลระหว่างหมู่คาร์บอนิล บ่งชี้ถึงการฟอร์มตัวของ PDA หลังนำเอาไดแอเซทิลีนลิพิดมอนอเมอร์มาโซนิเคตในน้ำที่มีสภาพความเป็นกรด-ด่างต่างๆ มันจะสามารถกระจายตัวและพอลิเมอไรซ์ด้วยรังสียูวี 254 นาโนเมตร ได้เป็น PDA โซล สมบัติการเปลี่ยนสีของ PDA โซลด้วยความร้อนสามารถติดตามด้วยยูวีวิสิเบิล-สเปกโตรสโกปี สำหรับ PDA ที่ประกอบด้วยหมู่เอไมด์หนึ่งหมู่ ค่า n ต่ำจะแสดงอุณหภูมิการเปลี่ยนสีต่ำกว่า ในขณะที่ PDA ที่ประกอบด้วยหมู่เอไมด์สองหมู่แสดงแนวโน้มในทางตรงข้าม ในอีกทางหนึ่งของ PDA ที่ประกอบด้วยหมู่เอไมด์หนึ่งหมู่การเพิ่มขึ้นของค่า n เป็นการทำให้ระดับความสามารถในการผันกลับได้ของสีน้ำเงินเพิ่มขึ้น PDA ที่ประกอบด้วยหมู่เอไมด์สองหมู่แสดงแนวโน้มในทางตรงข้ามอีกเช่นเดิม การทำ PDA เป็นเซ็นเซอร์เปลี่ยนสีบนกระดาษนำไปตรวจสอบตัวทำละลายอินทรีย์ 14 ชนิดและสารลดแรงตึงผิว 9 ชนิด จากผลที่ได้เราสามารถพัฒนาตัวตรวจวัดสำหรับตรวจสอบตัวทำละลายอินทรีย์ 11 ชนิดและสารลดแรงตึงผิวประเภทประจุบวกได้โดยใช้วิธีการแยกทางสถิติ (ปรินซิปัลคอมโพแนนท์แอนาไลซิส, PCA)

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต.....สุริชา พุ่มแตง.....

ปีการศึกษา 2553 ..... ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก.....

ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม.....

5072535723: MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEYWORDS: POLYDIACETYLENE/ THERMOCHROMISM/ NANOVESICLES

SURICHA PUMTANG: SYNTHESIS AND POLYMERIZATION OF NANO ASSEMBLED DIACETYLENE LIPIDS CONTAINING AMINO GROUPS. ADVISOR: ANAWAT AJAVAKOM, Ph.D., CO-ADVISOR: ASSOC. PROF. MONGKOL SUKWATTANASINITT, Ph.D., 86 pp.

The synthesis of a novel class of diacetylene lipid monomers containing amido or carboxyl head groups with various length methylene spacer ($n = 2,3,4$) between carbonyl group was accomplished by condensation of 10,12-pentacosadiynamine with various diacids or their cyclic anhydride derivatives. The polymerization and chromic properties of the synthesized polydiacetylenes (PDAs) were investigated. The monomers turned into blue or purple colors in solid state while instantaneously turned colored with different blue shade in film state depending on the alkyl chain length between carbonyl groups indicating the formation of PDAs. After diacetylene lipid monomers were sonicated in various pH of water, they can be dispersed and polymerized by 254 nm UV-irradiation to PDA sols. Thermochromic property of these PDA sols was monitored by UV-vis spectroscopy. For PDA possessing single amide head group, the low *n* value exhibits the lower transition temperature while PDA having two amide head groups presents the inverse tendency. On the other hand, the increasing of *n* value enhances the degree of reversibility of one amide PDA. Again, two amide series illustrated the opposite tendency. Fabrication of the PDAs for paper-based colorimetric sensors for 14 organic solvents and 9 types of surfactants were also achieved. As the results, sensors for 11 organic solvents and cationic surfactants by using the statistical discriminating method (Principal component analysis, PCA) were successfully developed for such detection.

Field of Study: Petrochemistry and Polymer Science Student's Signature: Suricha Pumtang
Academic Year: 2010.....Advisor's Signature: Anawat Ajavakom
Co-advisor's Signature: Mongkol Sukwattanasinitt

ACKNOWLEDGEMENTS

I would like to express my appreciation to my advisor, Dr. Anawat Ajavakom, and my co-advisor, Associated Professor Dr. Mongkol Sukwattanasinitt for their invaluable suggestion, generousness and extremely encouragement during the course of this research. This research is completely impossible to succeed without their helpfulness.

I would like to express my sincere gratitude to my supervisor in JAIST Associated Professor Dr. Ken-ichi Shinohara for his suggestion, generousness, and supports me throughout I studied the AFM in JAIST. Especially for giving me a chance to have a wonderful experience in Japan.

I would like to express my sincere gratitude to Dr. Gamolwan Tumcharern from National Nanotechnology Center (NANOTEC) for AFM, and DLS data. I also would like to show my appreciation to Dr. Sumrit Wacharasindhu for his guidance, and helpful suggestion.

I would like to show gratitude to Associated Professor Dr. Supawan Tantayanon, chairperson of thesis defense committee, for their kind attention and recommendations. I also would like to thank Assistant Professor Dr. Paitoon Rashatasakhon for his attention and suggestion during our group meeting.

My appreciation is also given to many people in our research group; Dr. Anupat Potisatityuenyong and Miss Sansanee Bunchit for training; Miss Jasuma and Mr. Thoedtoon for their experiences; Mr. Chaiwat, my greatest colleague; Miss Warathip, Mr. Nakorn, and Mr. Thirawat for their helpful suggestion. Miss Pagasukon, Miss Yamonporn, Miss Surareewan, Mr. Thanakrit, and everyone in MSGroup for a great friendships and encouragement;

I would like to thanks Center for Petroleum, Petrochemicals and Advanced Materials and my financial support from ADB under the Petroleum & Petrochemical Technology Consortium, 90th anniversary of Chulalongkorn University Fund, and JENESYS scholarship under JAIST and Japan government.

Finally, I would like to express my thankfulness to my beloved parents who always stand by my side during both of my pleasant and hard time.

CONTENTS

Page

LIST OF TABLES

Table **Page**

LIST OF FIGURES

Figure **Page**

Figure **Page**

Figure **Page**

Figure **Page**

Figure **Page**

LIST OF SCHEMES

Scheme **Page**

LIST OF ABBREVIATIONS

PDA	Polydiacetylene
PCDA	10,12-pentacosadiynoic acid
PCDAmide	10,12-pentacosadiynamide
PCDAmine	10,12-pentacosadiynamine
PCDAS	4-Oxo-4-(pentacosa-10,12-diynylamino)butanoic acid
PCDAG	5-Oxo-5-(pentacosa-10,12-diynylamino)pentanoic acid
PCDAA	6-Oxo-6-(pentacosa-10,12-diynylamino)hexanoic acid
diPCDAS	N^1,N^4-Di(pentacosa-10,12-diynyl)succinamide
diPCDAG	N^1,N^5-Di(pentacosa-10,12-diynyl)glutaramide
diPCDAA	N^1,N^6-Di(pentacosa-10,12-diynyl)adipamide
CTT	Color transition temperature
CR	Colorimetric response
NMR	Nuclear magnetic resonance spectroscopy
AFM	Atomic force microscopy
DLS	Dynamic light scattering
DSC	Differential scanning calorimetry
°C	Degree celsius
g	Gram
mL	Millilitre
µL	Microlitre
mM	Millimolar
µM	Micromolar
nm	Nanometre
µm	micrometre
min	Minute
%	Percent
DR	Degree of reversibility

CHAPTER I

INTRODUCTION AND THEORY

1.1 Overview

To develop a novel colorimetric indicating materials that is clearly observable by the naked eye and also can be used safely and economically, the conjugated polymer have been receiving attention. Particularly polydiacetylene (PDA), one of the most well known practical conjugated polymers, has unique chemical structures which are amphiphilic molecule. Accordingly allow diacetylene lipid monomer to form a various nanostructure such as bilayer, vesicle, micelle, ribbon, or rod that associate diacetylene can disperse in aqueous media and can be polymerized effectively by UV-irradiation [1]. Interestingly, under an external stimulation, for example, raising temperature (thermochromism) [2-7], changing pH (alkalinochromism/acidochromism) [8-10], adding an organic solvent (solvatochromism) [11-16], and adding a chemical (chemochromism) [17], PDAs undergoes a drastic color transition from blue to red. This is suitable and easy for use as various sensing applications.

The sensing properties of the conjugated polymers associate with the electronic states of the extensively delocalized π-conjugated system of the polymer backbone. Because of the optical absorption of blue and red forms of PDAs is a consequence of a $\pi - \pi^*$ transition of electron within linear π-conjugated backbone. Whenever, the external stimuli disturb the electronic states of the delocalized π-conjugated system, their absorption, and emission properties will be induced to change and tune a color of PDA from blue to red.

Understanding in detail of the color transition will advance to design the suitable sensing materials for difference applications. Thermochromism is probably one of the most widely investigated for structure and property relationships as well as their mechanism. The color transition of PDAs can be either reversible or irreversible and is usually measured experimentally as a shift of the absorption band from low to high energy in the visible spectrum. Although the variation of the total chain length, the

position of the diyne unit within the chain can provide diverse colorimetric responses to temperature and have been reported, the reports were limited to study the effect of chain length, and the position of the diyne unit but the effect from amino head group and the position of carbonyl within the chain on the thermochromic behaviors have reported a minimal information available. The positions of amide head groups can affect thermochromic property of PDAs by induce the weak or strong hydrogen bonds between the head groups. In this thesis have synthesized a novel series of diacetylene monomeric lipids containing either one or two amino group with various alkyl chain length spacer between carbonyl head groups. The monomeric lipids were then dispersed in water and photopolymerized to form PDA sols. The thermochromic studies of the synthesized PDA sols were carried out based mainly on variable temperature UV-Vis spectroscopy. The spectroscopic data were then analyzed in order to gain more information about how the position of amide groups and the alkyl chain length linkers influence the thermochromic properties of the PDAs. The results from this investigation increased the assortment of temperature sensing materials as well as guidelines for designing new PDAs for universal temperature indicators. Because of the temperature is one of the most important physical parameters that affect the quality of various products, especially food and medicine which can affect directly to the customers. Mercury is the earliest and most widely used for temperature sensing but it is too toxic into fabricated on consumer products [8].

In addition, solvents are essential for chemical and related industry but their misuses and careless disposals can cause catastrophic danger and global environmental pollution. Many solvents are also considered to be toxic volatile organic compounds (VOCs) that can put human into serious health risks by prolonged exposure through high dose inhalation, particularly some carcinogenic aromatic and chlorinated solvents [18]. For proper safety management, detection and identification of solvents are important among the initial assessments. Many VOC sensors using electrochemical [19,20], cholesteric liquid crystals (CLCs) [21], electrical and optical [22-24] techniques have been developed. Among these, the optical mode is the most promising to be developed into a simple naked-eye and instrumentless detection practical for an on-site analysis by a non-technician.

In another way, surfactant is also a commonly chemicals were used for many purposes, especially in industrial field and household. High quantitative disposal without a proper treatment can cause the catastrophic environmental pollutant. The simple method needs to be developed in order to an on-site detection without using the instruments.

1.2 Theory

1.2.1 Polydiacetylene vesicles

Polydiacetylene (PDA) forms 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 [25,26].

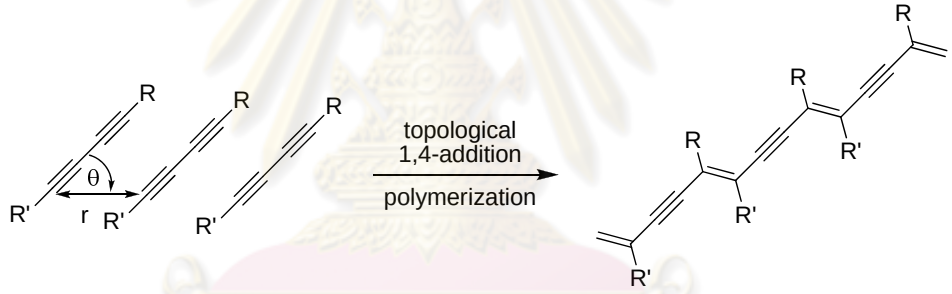


Figure 1.1 Polymerization of diacetylene monomers by irradiation with UV light.

The topopolymerized diacetylene crystals are nearly perfectly ordered crystals which cannot be occurred by solution polymerization or recrystallization of a preformed polymer from solution or melt. The resulting PDA, if generated under optimized conditions appears 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 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. 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, PDA-embedded polymer matrix films, 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).

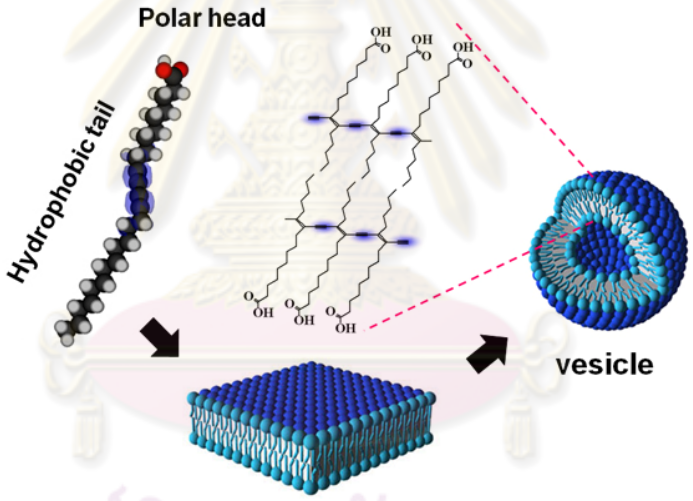


Figure 1.2 Structure and formation of a PDA lipid vesicle [3].

1.2.2 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 appears blue in color. The exposure of PDA to environmental perturbations 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.

1.2.3 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 [27,28].

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.

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) [29].

1.2.4 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

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

Where $PB = A_{blue}/(A_{blue}+A_{red})$, 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 10 to 90 °C.

1.2.5 RGB color model

According to development of paper based colorimetric respond of polydiacetylene is a simple method and suitable to use as a sensors application, since evaluate the results into a quantitative analysis can be collected by using the RGB color model. The RGB color model is an additive color model in which red, green, and blue color are added together in various component ratio to reproduce a broad array of colors as show in Figure 1.3. The name of the model comes from the initials of the three additive primary colors, red, green, and blue. The main purpose of the RGB color model is for the sensing, representation, and display of images. The RGB color model was used to descript how much of each red, green, and blue color is included in the photographic images [30].

Figure 1.3 The RGB color model

1.3 Literature survey

1.3.1 Thermochromism

In 1998, Okada *et al.* [3] studied the self-assembly in vesicles form of diacetylene containing carboxylic in hydrophilic head group and its derivatives which various alkyl chain length within the chain and between diacetylene and carboxyl group(Figure 1.4) in water media. Then polymerized by UV-irradiation 254 nm and studied the thermochromic properties monitoring by UV-vis spectrometer. It was found that

polydiacetylene which have the short alkyl chain length between diacetylene and carboxyl group (compound 3 and 4) were more sensitive to the thermal changes than long alkyl chain length(compound 1 and 2).

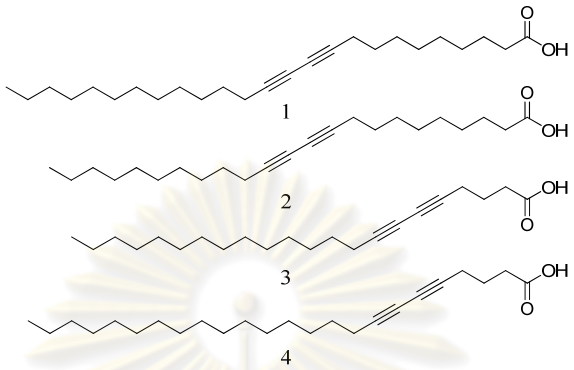


Figure 1.4 Structure of diacetylene monomers used in investigations of thermochromism in vesicles.

In 2000, Cheng *et al.* [31] reported the synthesis of a series of novel PDA microstructures and the characterization of their morphology and chromatic transition using TEM and UV-*vis* and FTIR spectroscopies. The microstructures are formed by single-chained 10,12-pentacosadiynoic acid lipid derivatized with different amino acids (Figure 1.5). The linkage of the head groups to the diacetylenic chains is via an amide bond. Amino acids were chosen as head groups to create a compatible surface on the microstructures for protein-related applications. In addition, amino acids are chiral and possess various charges, allowing surface charge and hydrophilicity to be manipulated in a controllable manner. This work is the continuation of their previous study on PDA chromism where the focus was on optical properties of bilayer vesicles formed with these amino acid terminated PDA lipids. The authors recommended that the head group structure and hydrophilicity effects on the morphology and chromatic transitions of the PDAs microstructures. They purposed that only hydrophilic amino acid terminated lipids can readily form bilayer vesicles and allow polymerization, whereas hydrophobic amino acid terminated lipids do not form vesicles. The colorimetric properties of these PDAs, the microstructures with hydrophobic head groups are more sensitive to thermal and pH changes.

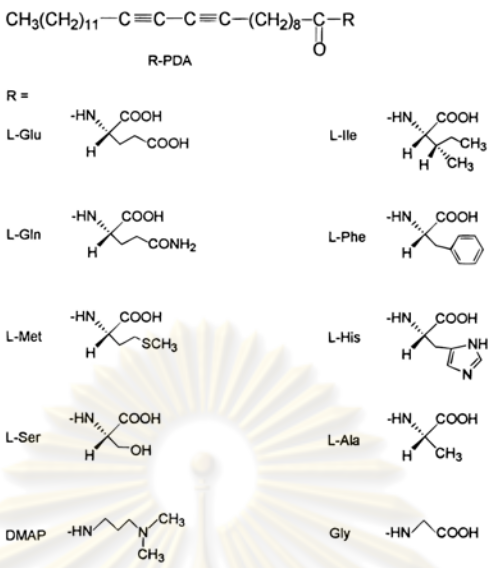


Figure 1.5 Molecular structure of the amino acid terminated lipids from 10,12-pentacosadiynoic acid (PDA). The amine terminated DMAP lipid was synthesized for comparison experiments.

In 2003, Ahn *et al.* [4] synthesized derivatives of 10,12-pentacosadiynoic acid having an anilide and carboxylanilides (ortho-, meta-, and para-) (Figure 1.6). The thermochromism of the prepared diacetylene monomers were studied as Langmuir-Schaefer film form. The film obtained from meta-carboxylanilide derivative (PCDA-*m*BzA) displayed a completely reversible color transition upon removal of both thermal and pH stimuli. The authors recommended 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.

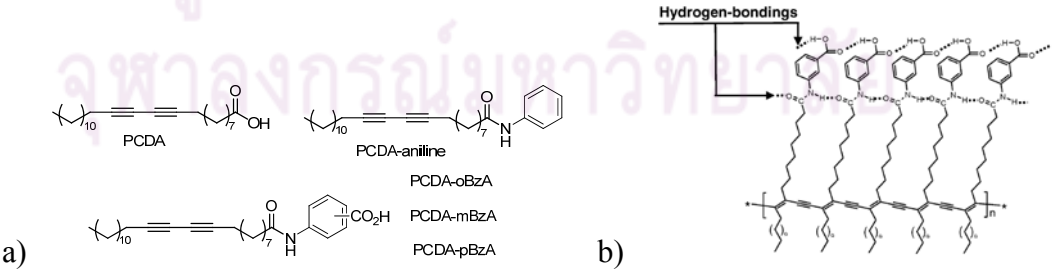


Figure 1.6 a) Structure of diacetylene monomers used in investigations of reversible thermochromism in Langmuir-Schaefer films, b) Schematic of enhanced hydrogen-bonding at terminal carboxyl and amide-carbonyl groups.

In 2004, Song *et al*. [32] reported the design, preparation, and characterization of bolaamphiphilic diacetylene lipids (BPDAs) terminated with different polar functionalities. The chemical nature of the functional groups displayed on the surface of BPDAs directly affects the optical properties of the self-assembling polymers under ambient conditions, the authors suggested that this is presumably due to the different hydrogen-bonding and electrostatic interactions at the polar surfaces of the assembly that either strengthen or weaken the van der Waals association between lipid monomers. The thermochromism properties monitored UV-vis spectrometer and TEM suggested that BPDA-1, modified with L-aspartate, showed very different optical properties with another BPDAs system. Because of containing two carboxylate groups more closely spaced at the polar end, the aspartate-modified (BPDA-1) presumably displayed less favorable hydrogen bonding and/or stronger electrostatic repulsion between polar surface residues than its glutamate-modified (BPDA-3) counterpart, significantly reducing the crystallinity of its lipid packing and also reduced effective conjugation length of the poly (ene-yne) backbone.

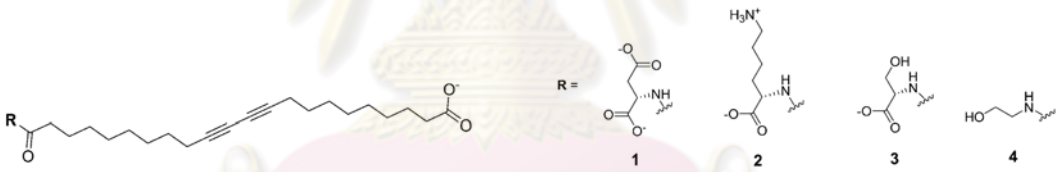


Figure 1.7 Bolaamphiphilic diacetylene lipids, with various head group modifications (1-4).

In 2005, Kim *et al*. [33] expanded their previous works. To evaluate the structural effect on thermochromism of polydiacetylene, panels of diacetylene monomer were synthesized in order to investigate the effect of 1) amide hydrogen bonding, 2) aromatic interactions, 3) alkyl chain lengths, and 4) carboxylic groups of diacetylene lipid as showed in Figure 1.8. The observations from temperature dependent UV-Vis spectrometry and FTIR suggested that cooperative and integrated interactions between amide, aromatic, and carboxylic acid head groups is the requirement for reversibility of polydiacetylene. Furthermore, the alkyl chain length between functional head group is also affect the reversible color transition of polydiacetylene.

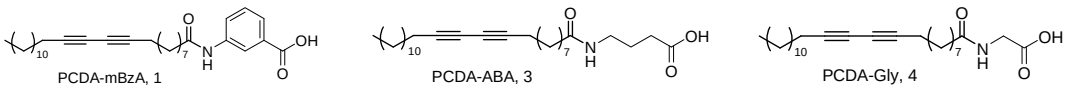


Figure 1.8 Structures of diacetylene lipids investigated for thermochromism.

In 2006, Dautel *et al*. [34] synthesized a novel ureido substituted diacetylenic derivatives (Figure 1.9). Then the relationships between chemical structures and color transition behavior of these synthesized derivatives were investigated in organogel form. It has been suggested that the urea function and its perfectly defined hydrogen-bond pattern allowed reversible chromic transitions (jointly monitored by UV-vis and Infrared spectroscopies).

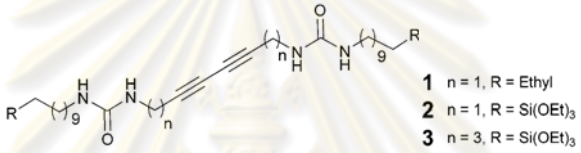


Figure 1.9 Structures of ureido substituted diacetylenic derivatives investigated for thermochromism.

In 2007, Fujita *et al*. [35] proposed that molecular modeling to seek a stable conformation of PDA prepared from **G*n***s in the gel state which is useful in predicting the effective conjugation length (ECL) in PDA where the odd-even number of alkyl chains (*n*) is a key factor for determining the blue and red phases of the PDAs.

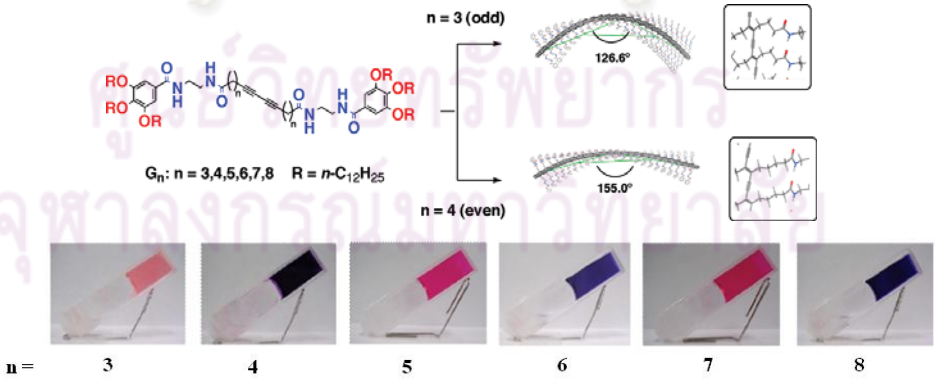


Figure 1.10 Chemical structure of G_n and the optimized conformation of 24 mers of (upper) polyG_3 and (lower) polyG_4.

In 2009, S. Wacharasindhu and co-worker [6] have synthesized the novel series of amido-PCDA derivatives from condensation of PCDA with various aliphatic and aromatic diamines. After studied their thermochromic properties by temperature variable UV-vis spectrometry, the authors have suggested that the color transition temperatures and thermochromic reversibility of these polymers are varied depended on the number of amide groups and the structure of the aliphatic and aromatic linkers.

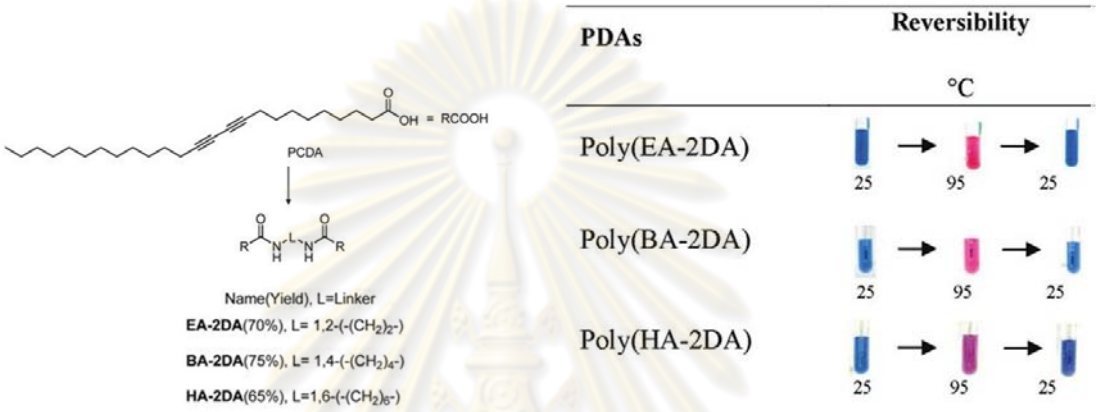


Figure 1.11 Thermochromic reversibility of the PDA sols illustrated by color photographs

In 2010, C. Pollookin and co-worker [7] have reported the novel class of diacetylene lipid monomer. A series of bisdiynamide lipids containing various lengths of methylene spacer between the diynes and the diamide head group and number of methylene units in their hydrophobic tails were synthesized. The authors have suggested that tuning of color transition temperature of thermochromically reversible bisdiynamide series of polydiacetylenes (PDAs) can be achieved 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.

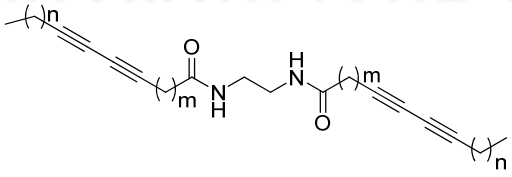


Figure 1.12 Chemical structure of bisdiynamide series of diacetylene lipids.

1.3.2 Alkalinochromism and Acidochromism

Alkalinochromism and acidochromism were chromic properties that material can change color by deprotonation in case of alkalinochromism and protonation in case of acidochromism. Either alkalinochromism or acidochromism, the role of head group of diacetylene monomer had directly impact on the colorimetric transition as reported by several researchers.

In 1998, Cheng and coworkers [8] had been synthesized and studied the colorimetric response in various pH solutions of a series of amino acid-derivatized 10, 12-pentacosadiynoic acid. The result showed a different colorimetric response based on type of head groups. For example, Glu-PDA which has dicarboxylic head group changed the color from blue to red at pH 6 by deprotonation of the carboxylic group. The protonation of the tertiary amine head group of DMAP-PDA changed its color at pH 5. His-PDA which has both of carboxylic and imidazole changed the color at pH below 0 and pH 8-9 (Figure 1.13).

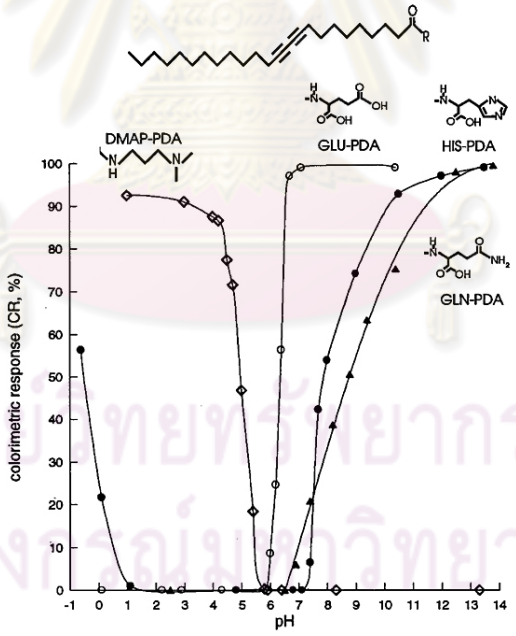


Figure 1.13 Colorimetric response (%CR) of amino acid terminate polydiacetylene vesicle as a function of solution pH.

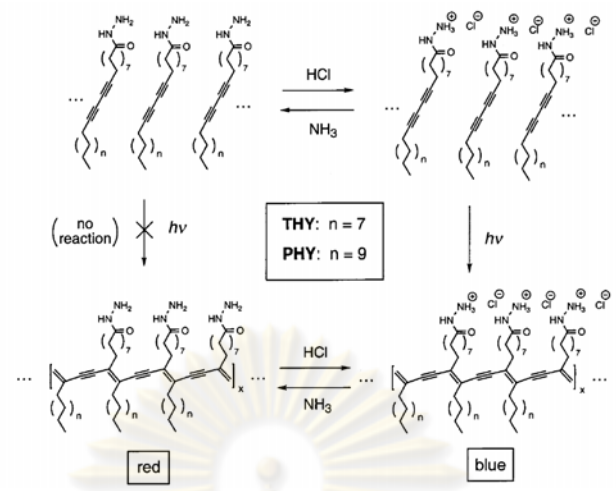


Figure 1.14 Schematic representations of the polymerization behavior and colorimetric changes of the diacetylene hydrazides PHY and THY in the presence of HCl or NH_3.

In 1999, Jonas *et al.* [9] studied a novel system based on hydrazide derivatives of single chain diacetylene lipids which are 10,12-Tricosadiynohydrazide (THY) and 10,12-Pentacosadiynohydrazide (PHY). These materials showed an unusual aggregation and polymerization behavior in organic solution, in contrast to the parent carboxylic acids. In addition, these hydrazide lipids undergo an unprecedented reversible color change (blue/red) in polymerized vesicles when the pH of the surrounding aqueous medium is cycled between acidic and basic conditions. This unusual behavior is attributed to the unique hydrogen-bonding pattern of the hydrazide head group (Figure 1.14).

In 2006, Kew *et al.* [10] have reported that the poly10,12 tricosadiynoic acid (poly(TCDA)) exhibited the alkalinochromic by changing its color from blue to red during the addition of basic solution. The titration of poly(TCDA) vesicle by NaOH solution produced a red vesicle. The pKa of polydiacetylene was in the range of 9.5-9.9 depending on a kind of metal hydroxide (Figure 1.15). The author proposed the color transition mechanism which started by 1) deprotonation of carboxylic proton, 2) metal ion binding with the carboxylate anion and 3) the alkyl chain changed conformation which caused a color change of poly(TCDA).

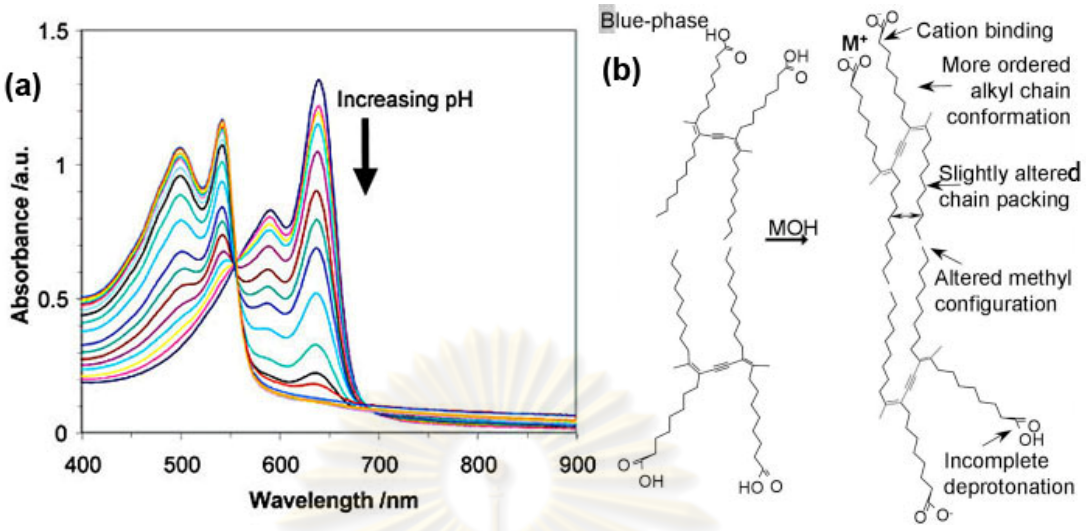


Figure 1.15 a) Optical absorption of the titration of 0.5 mM poly(TCDA)vesicle with 0.1 N NaOH solution, b) propose of color transition mechanism by alkalinochromism.

1.3.3 Solvatochromism

The efficient monitoring of volatile organic compounds (VOCs) has gained prominence in environmental and public safety control due to the potential health hazards posed by exposure to these substances. Indeed, the development of efficient sensors for the detection of VOCs has become the subject of intensive study.

In 2007, Kim *et al.* [36] have developed the efficient sensors for the detection of volatile organic compounds (VOCs) based on conjugated polymer-embedded electrospun fibers. The observation of an organic solvent induced, blue-to-red color transition of PDA embedded electrospun fibers suggests that the colorimetric response might vary in an organic solvent-dependent manner on the structure of diacetylene monomer. They show different colorimetric responses upon exposure to the 4 organic solvents such as chloroform, tetrahydrofuran (THF), ethyl acetate (EA), or *n*-hexane as illustrated in Figure 1.16.

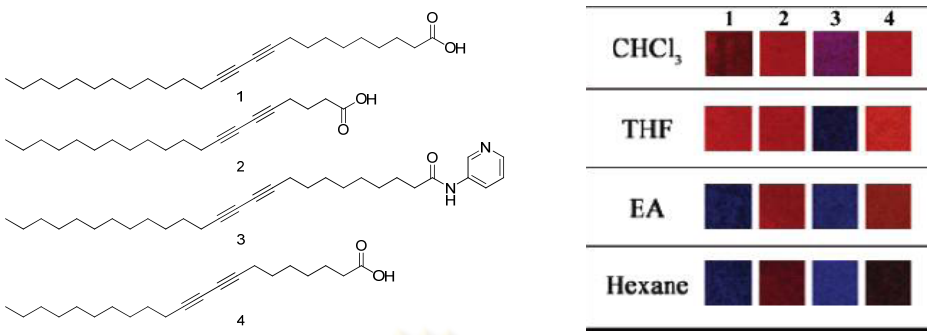


Figure 1.16 Photographs of the PDA-embedded electrospun fiber mats prepared with diacetylene monomers **1**-**4** after exposure to organic solvent

In 2009, Kim *et al*. [37] have generated the electrospun fiber mats from PDA-embedded polymer matrix that can be used to detect volatile organic compounds (VOCs). The results display the different color patterns of the fiber mats derived from different combinations of PDA-ABA 1 and PCDA-AN 2 as illustrated in Figure 1.17.

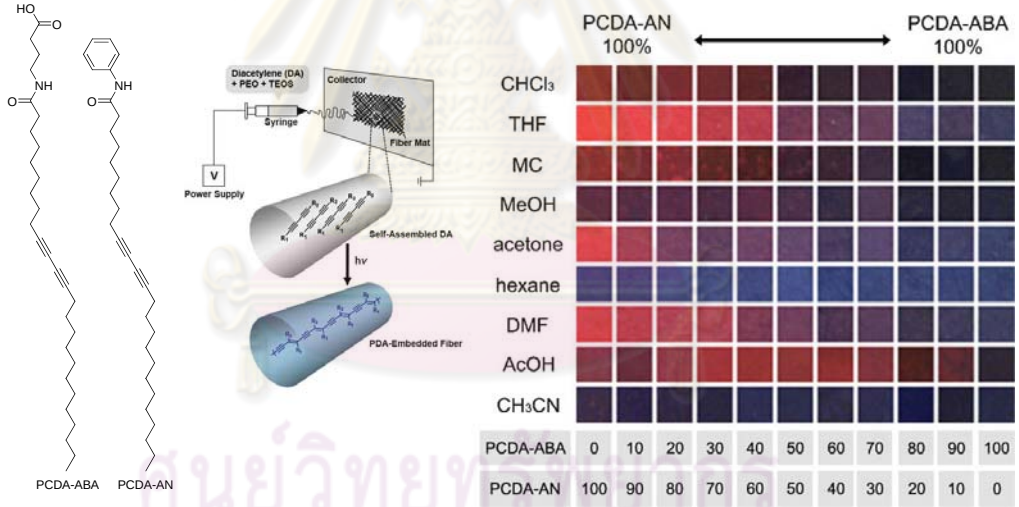


Figure 1.17 Schematic representation of the preparation of PDA-embedded electrospun microfibers and photographs of the polymerized PDA-embedded electrospun fiber mats after exposure to organic solvents at 25 ºC for 30 s.

In 2010, H. Jiang and colleagues [38] have also reported the development of a novel polydiacetylene (PDA)-based sensitive colorimetric microarray sensor for the detection and identification of volatile organic compounds. PDA-embedded polymer matrix films as the multi-layer PDA-based micro patterns (Figure 1.18) could be prepared by the spin-

coating method combined with the sol–gel process. Polydimethylsiloxane Sylgard 184 (PDMS) was employed to enhance the stability of the PDA films when dipped in VOCs, especially chlorinated solvent.

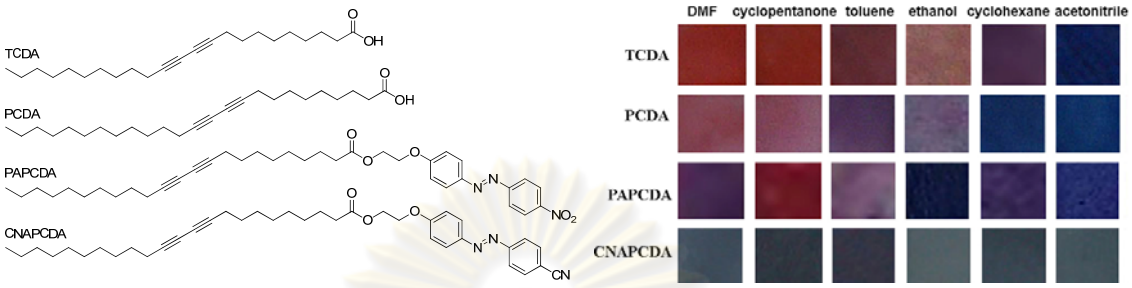


Figure 1.18 photographs of the PDA-embedded polymer matrix films derived from TCDA, PCDA, PAPCDA and CNAPCDA after dipped in organic solvents at room temperature.

In 2010, S. Wu and colleagues [39] investigated the effects of solvents on structure of micelle-like assemblies of an azo chromophore-functionalized polydiacetylene (polyAzoDA) and polymerized tricosa-10,12-diynoic acid (polyTDA). They used the mixtures of water with glycol, DMSO, ethanol and THF to observe blue-to-red color changes of polydiacetylenes. They found that the colors of polyTDA and polyAzoDA change at certain contents of organic solvents. The results in Figure 1.19 exhibit the strength of the polyTDA-solvent interaction in the following order: THF>ethanol> DMSO>glycol. According to the results, THF is a solvent which can effected on blue-to-red color transitions of polyAzoDA in THF/water mixtures. However, they do not observe color transitions in the other solvents/water mixtures. The authors have proposed that the stability to several solvents of polyAzoDA caused by the H- and J-like aggregates of azo chromophores in polyAzoDA.

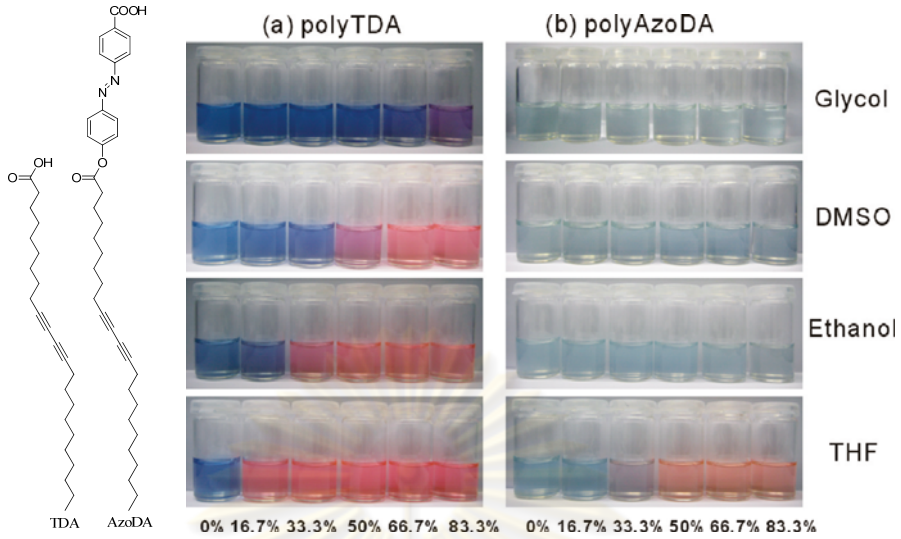


Figure 1.19 Photographs of micelle dispersions in different water-solvent mixtures. At increasing solvent content, the color of (a) polyTDA and (b) polyAzoDA changes from blue to purple/red depending on type of solvent and its relative content, respectively.

In 2008, A. Potisatityuenyong and co worker [3] conduced extensively investigation poly-10,12-pentacosadiynoic acid (poly(PCDA)) vesicle solution in the aspect of thermochromism, solvatochromism and alkalinochromism. In the case of solvatochromic and alkalinochromic experiment, UV-vis absorption and observation by eye show the similar pattern, blue to red color transformation. The decreasing and increasing in absorbance of red and blue phase without peak shifting indicate directly to quantitative conversion between blue and red vesicle. Solvatochromism and alkalinochromism involve hydrogen bond breaking turning the blue vesicle into red color. The author proposed the mechanism of color transition of PCDA as shown in Figure 1.20.

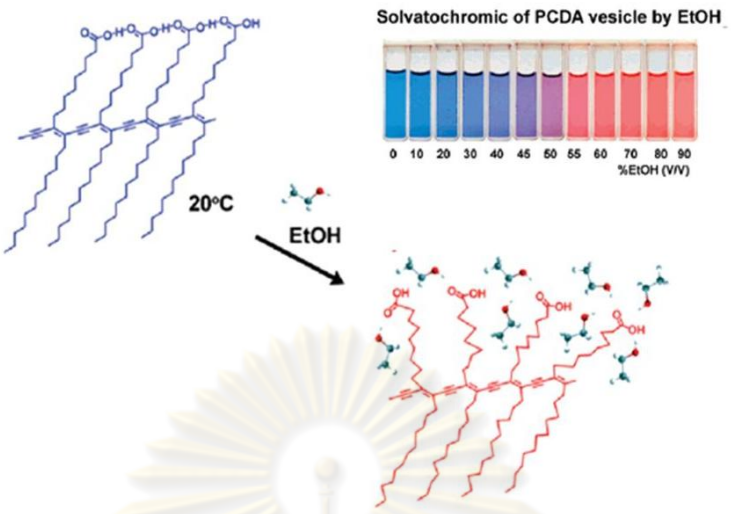


Figure 1.20 Proposed side-chain movements in the chromic transitions of poly(PCDA) vesicles upon organic solvent.

1.3.4 Affinochromism

The development of selective optical signaling systems for ions has received considerable attention for a few decades due to their important roles in biological and environmental processes. Cationic surfactants have been reported as environmental pollutants since they are heavily used as surface cleaning agents, such as soaps, shampoo, etc. Accordingly, it is necessary to develop convenient methods for the detection of such quaternary ammonium surfactants. It is especially difficult to determine non-aromatic cationic surfactants due to their lack of chromophores. These cationic surfactants can be monitored by two-phase titration, mass spectrometry, high performance liquid chromatography (HPLC), or GC-MS methods by converting quaternary ammonium salts to their corresponding tertiary amines. Due to the need for simple methods to detect these surfactants, there have been some reports adopting either fluorescent or UV changes.

In 2009, X. Chen *et al*. [40] have reported the colorimetric detection of cationic surfactants based on conjugated polydiacetylene supramolecules (Figure 1.21a). They found that the colorimetric responses of the conjugated polymers can be attributed to the disruption of the hydrogen bonding in head group, for which both ammonium groups and long alkyl chains are required. Because of the addition of CTAC can disturb the regularly arrayed hydrogen bonding between head groups by ionic interactions between the

phenolate of the head group and the ammonium group as show in the Figure 1.21b. The disruption of the hydrogen bonding could allow the release of the strain energy imposed on the alkyl side chains generated during polymerization. The release of the side chain strain can cause partial distortion of the arrayed *p*-orbitals, leading to a decrease in the effective conjugation length of the polymer.

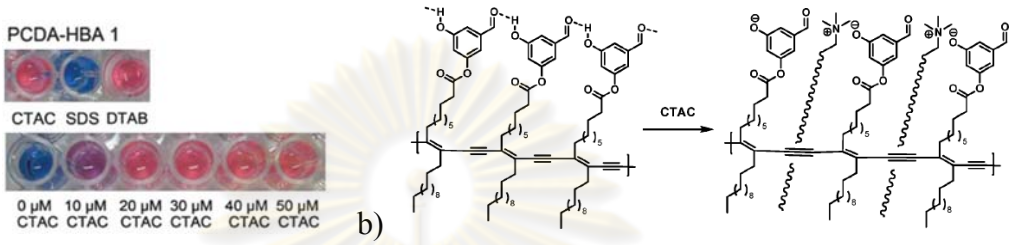


Figure 1.21 Colorimetric titrations of PCDA-HBA 1 with various surfactants and various amounts of CTAC (a), proposed head group structures of the PDAs derived from PCDA-HBA 1 in the presence of CTAC (b).

From the above review, functional head group and alkyl chain length between diyne unit and carbonyl head group in diacetylene are a crucial factor in controlling chromic properties of polydiacetylene. We believe that the appropriate modification of functional group and alkyl chain length manipulated on polar head part of diacetylene may give us the opportunity to control colorimetric reversibility and color transition temperature of polydiacetylene. This will assist us developing polydiacetylene-based materials into sensors, actuators, devices and other purposes. Furthermore, almost previous literatures studied the applications of all polydiacetylenes only in solution or even in an electrospun film case; addition of polymer matrix was needed to enhance the film stability. They are still not suitable for the on-site uses or commercial purposes. Interestingly, if it can be developed into a simple method in order to use as sensor application.

1.4 Objectives and scope of the research

The objective of this thesis is to synthesize, polymerize, study the thermochromic properties of amino group(s) containing self-assemble polydiacetylene and develop into sensor applications. To achieve the objectives, the work scope includes 1) synthesis of amide derivatives from 10,12-pentacosadiynamine, 2) preparation and polymerization of

polydiacetylene nanoparticles from 10,12-pentacosadiynamine and its derivatives, at various optimum conditions, 3) characterization of the morphology and particle sizes of the prepared self-assemble PDAs by using atomic force microscopy (AFM), transmission electron microscopy (TEM) and dynamic light scattering (DLS), 4) study of thermochromic properties of the prepared PDAs sols monitoring by UV-vis spectrometer, 5) develop the polydiacetylenes into sensor applications using a paper based method and principal component analysis (PCA).

CHAPTER II

EXPERIMENTAL

2.1 General Information

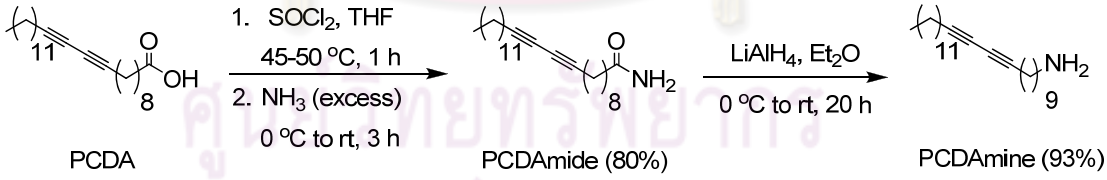
2.1.1 Chemicals

1. 10,12-Pentacosadiynoic acid (PCDA), GFS, USA
2. *N*,*N*'-Dicyclohexylcarbodiimide (DCC), Fluka, Switzerland
3. 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC), Fluka, Switzerland
4. 4-Dimethylaminopyridine (DMAP), Fluka, Switzerland
5. *N*-Ethyl-*N*'-isopropylpropan-2-amine (DIPEA), Fluka, Switzerland
6. Malonic acid, Fluka, Switzerland
7. Malonyl chloride, Fluka, Switzerland
8. Succinic acid, Fluka, Switzerland
9. Glutaric acid, Fluka, Switzerland
10. Adipic acid, Fluka, Switzerland
11. Succinic anhydride, Fluka, Switzerland
12. Glutaric anhydride, Fluka, Switzerland
13. Thionyl chloride, Fluka, Switzerland
14. Lithium aluminuimhydride ($LiAlH_4$), Aldrich, USA
15. Ammonia solution, Merck, Germany
16. Diethylether (Et_2O), reagent grade, Lab-Scan, Ireland
17. Chloroform (CH_3Cl), AR grade, Lab-Scan, Ireland
18. Dichloromethane (CH_2Cl_2), commercial grade, Lab-Scan, Ireland
19. Hexane, commercial grade, Lab-Scan, Ireland
20. Ethyl acetate (EtOAc), commercial grade, Lab-Scan, Ireland
21. Tetrahydrofuran (THF), AR grade, Lab-Scan, Ireland
22. propan-1-ol (methanol, CH_3OH), commercial grade, Lab-Scan, Ireland
23. Sodium hydroxide (NaOH), Merck, Germany
24. Hydrochloric acid (HCl), Merck, Germany
25. Magnesium sulfate ($MgSO_4$) anhydrous, Riedel-deHaën®, Germany
26. Silica gel 60, Merck, Germany

2.1.2 Apparatus and equipments

1. Rotary evaporator, R200, Buchi, Switzerland.
2. Ultrasonicator, Elma, Germany
3. Magnetic stirrer, Fisher Scientific, USA
4. Hot plated magnetic stirrer, Corning, USA
5. pH meter, Twin pH B 212, Japan
6. Pipette man (P20, P200 and P5000), Gilson, France
7. Pipette man (Le100 and Le1000), Nichiryo, Japan
8. Freeze-dryer, Freezone 77520, Benchtop, Labconco, USA
9. Nuclear Magnetic resonance spectrometer (NMR) 400 MHz, Mercury 400, Varian, USA
10. Mass spectrometer, Quattro micromass, Waters, France
11. Fourier transform infrared spectrometer (FTIR), Impact 410, Nicolet, USA
12. UV-vis spectrophotometer, Cary 100 Bio, Varian, Australia
13. Dynamic light scattering spectrometer (DLS), Nanosizer, Malvern Instrument, England
14. Atomic force microscopy (AFM), Pico Scan^{TM} 2500, Japan
15. Transmission electron microscope (TEM), JEOL TEM-2100, Japan
16. Differential scanning calorimetry (DSC)

2.2 Synthetic procedures



PCDA PCDAmide (80%) PCDAmine (93%)

Scheme 2.1 Synthesis of pentacosa-10,12-diynamine (PCDAmine)

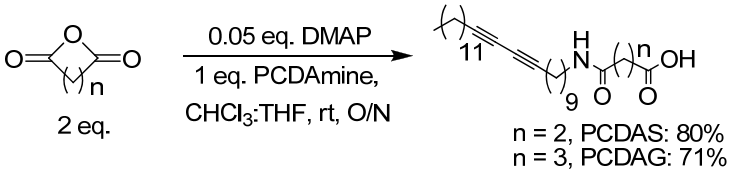
Pentacosa-10,12-diynamide: Thionyl chloride (0.36 mL, 5.0 mmol) was added dropwise into a solution of PCDA (330 mg, 0.9 mmol) in dry THF (3 mL). The mixture was stirred and heated at 45-50 ºC for 1 hour. The solvent was evaporated under reduced pressure to give pentacosa-10,12-diynoyl chloride and, without further purification, it was then quickly transferred into an excess cold ammonia solution (25%, 15 mL). The reaction mixture was stirred for 3 hours and the product was extracted into CH_2Cl_2 (3 × 200 mL). The product solution was washed with water (2

× 50 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure to give a yellow solid residue. The crude solid was then washed by hexane (250 mL) to yield pure pentacosa-10,12-diynamide as a colorless solid (269 mg, 80% yield), mp 100-102 ºC.

^{1}H NMR ($CDCl_3$): δ_H 0.87 (t, J = 6.6 Hz, 3H, CH_3), 1.27-1.35 (m, 26H, CH_2), 1.50 (dt, J = 7.1, 14.4 Hz, 4H, ≡CCH_2CH_2), 1.62 (dd, J = 8.6, 16.0 Hz, 2H, $CH_2CH_2CONH_2$), 2.23-2.25 (m, 6H, CH_2CONH_2 and ≡CCH_2), 5.20-5.40 (br, 2H, NH_2CO). LMRS (ESI): MH^+ found 374.39 ($C_{25}H_{43}NO$ requires 373.33).

Pentacosa-10,12-diynamine (PCDAmine): A suspension of amide (251 mg, 0.6 mmol) in Et_2O (25 mL) was added $LiAlH_4$ (250 mg, 6.5 mmol) at 0 ºC. After the reaction mixture was allowed to room temperature, it was stirred for 20 hours. Then the reaction was cooled down to 0 ºC and followed by dropwise of water 0.25 mL, 15% NaOH solution 0.25 mL, and water 0.75 mL, respectively. The mixture was filtered, and the filtrate was dried ($MgSO_4$). The solvent was evaporated under reduced pressure to yield PCDAmine as a colorless solid (201 mg, 93% yield), mp 60–62 ºC. ^{1}H NMR ($CDCl_3$): δ_H 0.81 (t, J = 6.8 Hz, 3H, CH_3), 1.20-1.35 (m, 30H, CH_2), 1.43-1.50 (m, 6H, $CH_2CH_2NH_2$ and ≡CCH_2CH_2), 2.17 (t, J = 6.9 Hz, 4H, ≡CCH_2), 2.60 (t, J = 7.0 Hz, 2H, CH_2NH_2). LMRS (ESI): MH^+ found 360.46 ($C_{25}H_{45}N$ requires 359.36).

Preparation of monoamide diacetylene monomers (PCDAS, PCDAG) from cyclic anhydride: DMAP (0.05 equiv) in CH_3Cl (0.05 M) was added into an acid anhydride (2 equiv) in CH_3Cl and THF (4:1 v/v, 0.4 M) at room temperature. The mixture was stirred for 5-10 minutes before adding into the solution of PCDAmine (1 equiv) in CH_3Cl (1 M) at room temperature. The reaction mixture was stirred overnight, and the solvent was evaporated under reduced pressure. The crude oil was purified by the precipitation in EtOAc to yield 4-(pentacosa-10,12-diynyl-amino)-4-oxobutanoic acid (PCDAS) and 5-(pentacosa-10,12-diynylamino)-5-oxo-pentanoic acid (PCDAG).



Scheme 2.2 The ring opening reactions of PCDAmine toward the cyclic anhydrides

PCDAS was synthesized according to above procedure from succinic anhydride (203 mg, 2.0 mmol) as a colorless solid (396 mg, 80%), mp 120-121 ºC.

^{1}H NMR ($CDCl_3$): δ_H 0.87 (t, J = 6.8 Hz, 3H, CH_3), 1.26-1.35 (m, 28H, CH_2), 1.49-1.50 (m, 6H, CH_2CH$_2$NHCO and ≡CCH$_2$CH_2), 2.23 (t, J = 6.9 Hz, 4H, ≡CCH_2), 2.52 (d, J = 6.7 Hz, 2H, CH_2COOH), 2.69 (d, J = 6.7 Hz, 2H, CH_2CONH), 3.26 (dt, J = 6.8, 13.3 Hz, 2H, CH_2NHCO), 5.60-5.75 (br, 1H, CH$_2$NHCO).

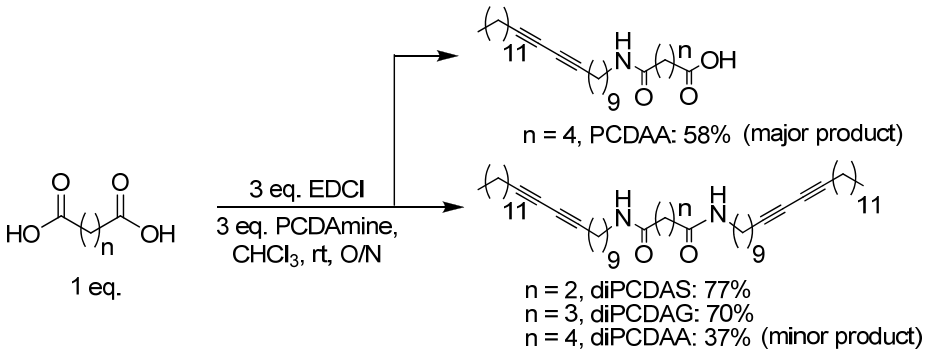
^{13}C NMR ($CDCl_3$): δ_C 174.7, 172.5, 77.6, 77.5, 65.3, 65.2, 40.0, 31.9, 30.8, 30.0, 29.63, 29.61, 29.60, 29.5, 29.4, 29.33, 29.30, 29.14, 29.10, 29.0, 28.9, 28.8, 28.4, 28.3, 26.8, 22.7, 19.2, 19.18, 14.1. LMRS (ESI): MH$^-$ found 458.79 ($C_{29}H_{49}NO_3$ requires 459.37).

PCDAG was synthesized according to above procedure from glutaric anhydride (229 mg, 2.0 mmol) as a colorless solid (339 mg, 71%), mp 114-115 ºC.

^{1}H NMR ($CDCl_3$): δ_H 0.81 (t, J = 6.8 Hz, 3H, CH_3), 1.20-1.35 (m, 28H, CH_2), 1.43-1.50 (m, 6H, CH_2CH$_2$NHCO and ≡CCH$_2$CH_2), 1.91 (quintet, J = 7.2 Hz, 2H, CH_2CH$_2$COOH), 2.19-2.25 (m, 6H, CH_2COOH and ≡CCH_2), 2.37 (t, J = 7.0 Hz, 2H, CH_2CONH), 3.18 (dt, J = 6.9, 13.2 Hz, 2H, CH_2NHCO), 5.45-5.60 (br, 1H, CH$_2$NHCO).

^{13}C NMR ($CDCl_3$): δ_C 177.0, 172.4, 77.6, 77.5, 65.3, 65.2, 39.7, 35.3, 33.0, 31.9, 29.63, 29.61, 29.60, 29.53, 29.50, 29.33, 29.31, 29.2, 29.1, 29.0, 28.9, 28.8, 28.4, 28.3, 26.8, 22.7, 20.8, 19.20, 19.18, 14.1. LMRS (ESI): MH$^-$ found 472.77 ($C_{30}H_{51}NO_3$ requires 473.39).

Preparation of mono- and diamide diacetylene monomers (PCDAA, diPCDAS, diPCDAG, diPCDAA) from dicarboxylic acid: EDC (3 equiv) in CH_3Cl (0.6 M) was added into a dicarboxylic acid (1 equiv) in CH_3Cl and THF (4:1 v/v, 0.08 M). The mixture was stirred for 1 hour at room temperature and then added dropwise into the mixture of PCDAmine (3 equiv) and DIPEA (3 equiv) in CH_3Cl (1.2 M) at room temperature. The reaction mixture was stirred for 24 hours when the white precipitate was clearly observed. The reaction mixture was concentrated under reduced pressure to yield the crude product as a white solid. The white solid was dissolved in CH_3OH under sonication and allowed to precipitate in a refrigerator to yield 6-(pentacosa-10,12-diynylamino)-6-oxohexanoic acid (PCDAA), N^1,N^4-Di(pentacosa-10,12-diynyl)succinmide (diPCDAS), N^1,N^5-Di(pentacosa-10,12-diynyl)glutaramide (diPCDAG), N^1,N^6-Di(pentacosa-10,12-diynyl)adipamide (diPC DAA).



Scheme 2.3 The condensations of PCDAmine with dicarboxylic acids

PCDAA was synthesized according to above procedure from adipic acid (68 mg, 0.46 mmol) as a colorless solid (132 mg, 58%), mp 125-127 ºC.

^{1}H NMR ($CDCl_3$): δ_H 0.81 (t, J = 6.5 Hz, 3H, CH_3), 1.20-1.60 (m, 28H, CH_2), 1.45-1.55 (m, 6H, C*H*$_2$CH$_2$NHCO and ≡CCH$_2$C*H*$_2$), 1.59 (q, J = 6.8, 13.4 Hz, 4H, C*H*$_2$C*H*$_2$CH$_2$CONH), 2.16-2.30 (m, 6H, C*H*$_2$COOH and ≡CC*H*$_2$), 3.08 (t, J = 6.9 Hz, 2H, C*H*$_2$CONH), 3.17 (dt, J = 6.0, 12.8 Hz, 2H, C*H*$_2$NHCO), 5.64 (s, 1H, CH$_2$N*H*CO).

^{13}C NMR ($CDCl_3$): δ_C 172.7, 77.6, 77.5, 65.3, 65.2, 51.5, 44.9, 44.3, 41.9, 39.5, 36.3, 33.7, 33.2, 31.9, 29.64, 29.62, 29.60, 29.5, 29.42, 29.40, 29.3, 29.1, 29.0, 28.9, 28.8, 28.4, 26.8, 22.7, 19.2, 14.1. LMRS (ESI): MH^- found 486.60 ($C_{31}H_{53}NO_3$ requires 487.40).

diPCDAA was isolated as a minor product of PCDAA (141 mg, 37%), mp 96-97 ºC.

^{1}H NMR ($CDCl_3$): δ_H 0.87 (t, J = 6.8 Hz, 6H, CH_3), 1.26-1.40 (m, 56H, CH_2), 1.49-1.60 (m, 12H, C*H*$_2$CH$_2$NHCO and ≡CCH$_2$C*H*$_2$), 1.75 (dd, J = 7.6, 14.8 Hz, 4H, C*H*$_2$CH$_2$CONH), 2.23 (t, J = 7.0 Hz, 8H, ≡CC*H*$_2$), 2.97 (t, J = 7.6 Hz, 4H, C*H*$_2$CONH), 3.14 (dt, J = 6.6, 12.9 Hz, 4H, C*H*$_2$NHCO).

^{13}C NMR ($CDCl_3$): δ_C 172.8, 77.5, 65.30, 65.2, 40.9, 39.6, 36.1, 31.9, 30.0, 29.64, 29.62, 29.60, 29.5, 29.3, 29.2, 29.1, 28.99, 28.97, 28.9, 28.8, 28.4, 28.3, 26.9, 26.8, 24.9, 22.7, 19.2, 14.1. LMRS (ESI): MH^+ found 829.88 ($C_{56}H_{96}N_2O_2$ requires 828.75).

diPCDAS was synthesized according to above procedure from succinic acid (19 mg, 0.17 mmol) as a colorless solid (105 mg, 77%), mp 129-130 ºC.

^{1}H NMR ($CDCl_3$): δ_H 0.81 (t, J = 6.8 Hz, 6H, CH_3), 1.20-1.30 (m, 56H, CH_2), 1.30-1.50 (m, 12H, C*H*$_2$CH$_2$NHCO and ≡CCH$_2$C*H*$_2$), 2.17 (t, J = 6.9 Hz, 8H,

≡CC*H*$_2$), 2.43 (s, 4H, C*H*$_2$CONH), 3.14 (dt, *J* = 6.8, 13.3 Hz, 4H, C*H*$_2$NHCO), 5.80-5.85 (br, 2H, CH$_2$N*H*CO).

^{13}C NMR ($CDCl_3$): δ_C 172.1, 77.6, 77.5, 65.3, 65.2, 40.7, 39.6, 32.1, 31.9, 30.2, 29.63, 29.61, 29.60, 29.53, 29.50, 29.3, 29.2, 29.1, 29.0, 28.9, 28.8, 28.4, 28.3, 26.8, 22.7, 19.2, 14.1. LMRS (ESI): MH^+ found 802.28 ($C_{54}H_{92}N_2O_2$ requires 800.72).

diPCDAG was synthesized according to above procedure from glutaric acid (19 mg, 0.4 mmol) as a colorless solid (216 mg, 70%), mp 119-120 ºC.

^{1}H NMR ($CDCl_3$): δ_H 0.81 (t, *J* = 6.8 Hz, 6H, CH_3), 1.20-1.35 (m, 56H, CH_2), 1.45-1.60 (m, 12H, C*H*$_2$CH$_2$NHCO and ≡CCH$_2$C*H*$_2$), 1.88 (quintet, *J* = 7.0 Hz, 2H, C*H*$_2$CH$_2$CONH), 2.20-2.30 (m, 12H, C*H*$_2$CONH and ≡CC*H*$_2$), 3.16 (dt, *J* = 6.9, 13.2 Hz, 4H, C*H*$_2$NHCO), 5.65-5.75 (br, 2H, CH$_2$N*H*CO).

^{13}C NMR ($CDCl_3$): δ_C 172.5, 77.6, 77.4, 65.3, 65.2, 39.5, 35.7, 35.4, 31.9, 29.61, 29.60, 29.58, 29.57, 29.56, 29.4, 29.3, 29.2, 29.1, 29.0, 28.8, 28.76, 28.34, 28.30, 26.9, 22.6, 22.1, 19.2, 14.1. LMRS (ESI): MH^+ found 815.74 ($C_{55}H_{94}N_2O_2$ requires 814.73).

2.3 Preparation of polydiacetylene sols

The diacetylene (DA) monomers were dissolved in CH_3Cl (5 mM) to provide the stock solution. The DA monomer (1.5 mL) was pipetted from the stock solution and then removed under N_2 gas blow. A volume of milli Q water was added to provide the DA lipid concentration of 0.5 mM. The suspensions were heated to 75-85 ºC, followed by sonication in an ultrasonicating bath for 0.5-2.0 hours forming semitransparent or transparent DA sol. Then the DA sol was kept at 4 ºC for overnight. The DA sol was irradiated with UV light (254 nm) at room temperature 1 min for PCDAmine, 2 min for mono amide, and 3 min for diamide DA monomers, except in the case of PCDAmine and diPCDAA need to control the temperature at 0 ºC in an ice bath during polymerization process. Finally, the PDA sol was filtered through a filter paper (No.1) to give a clear intense blue-colored PDA sol.

2.4 Characterization of polydiacetylene sols

2.4.1 Atomic force microscopy (AFM)

The PDA sol was deposited on a freshly cleaved mica plate and dried at room temperature in dessicator for 12 hours. Pico Scan™ 2500: Pico SPM II controller operating in tapping mode using an OMLC-AC 200TS-C3 cantilever was used to

observe the morphology and particle size of the deposited PDA sol. The image of the particles was measured on an air-dried sample of PDA sol at room temperature.

2.4.2 Transmission Electron Microscopy (TEM)

TEM images were completed using a JEOL, Japan, model; JEM-2100 electron microscope equipped with a CCD camera. The accelerating voltage was 200 KV.

2.4.3 Dynamic light scattering (DLS)

The mean size of particles and the size distribution were determined by nanosizer (zeta sizer Nano ZS Malvern Instruments). The samples (2.0 mL) were taken into a quartz cuvette. Each experiment was repeated 3 times in order to acquire an average data, which will be analyzed and reported by using intensity statistics mode to plot range of particle size graph.

2.4.4 Differential scanning calorimetry (DSC)

The melting points of PDA monomers were determined by using DSC (NETZSCH DSC 204 F1). Monomer was added 2 mg sealed in aluminum pan and heated at a rate of 25K/10min.

2.5 Study of thermochromism properties of PDA sols

2.5.1 UV-visible spectroscopy

The visible absorption of the PDA sol was taken in a quartz cuvette with 1 cm. optical path length on a temperature controlled UV-vis spectrometer. The spectra were collected from 800 to 400 nm with the zero absorbance set at 800 nm. The λ_{max} of the blue and red phase of each sample was determined at 10 and 70°C (for PPCDAmine sol), 25 and 90°C (for mono- and diamide PDA sol). The initial absorbance was controlled in the range of 0.2-0.9 by adjusting the concentration of the PDA sols.

2.5.2 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 $\%CR = (PB_0\text{-}PB)/PB_0 \times 100$.

Where $PB = A_{blue}/(A_{blue}+A_{red})$, 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 PDA sols before heated. All blue-colored PDA sols samples were heated from 10 to 70°C (for PPCDAmine sol), 25 to 90°C (for mono- and diamide PDA sol).

2.5.3 Degree of reversibility (%DR)

To obtain a quantitative value of the degree of reversibility (%DR), the average value of the absorbance change (ΔA_{avg}) from the second to tenth heating is compared against the absorbance change in the first heating (ΔA_1) according to the following equation:

$$\%DR = 100 \times \Delta A_{avg}/\Delta A_1 \text{ where } \Delta A = A_{25\,^{\circ}C} - A_{95\,^{\circ}C}$$

2.6 Preparation of polydiacetylene paper based sensors application

2.6.1 Preparation of paper-based PDA indicators

A piece of filter paper (5 × 5 cm^2) was pretreated by dipping in THF and allowed for air-dry. A diacetylene monomer solution in THF (0.5% w/v, 10 µL) was dropped on the pretreated filter paper. The dropping process was repeated at 3 different areas on the filter paper and the wet spots were quickly dried with air blow. The treated filter paper was irradiated with UV light (254 nm, 900 µW/cm^2) at room temperature for 2 min. The resulting blue PDA spots were cut into circular discs (∅ 0.5 cm) and used as solvent and surfactant indicators.

2.6.2 Study the colorimetric response of diacetylene lipid monomers upon organic solvent and surfactant based on filter paper

Three pieces of each paper-based indicator were dipped into an organic solvent and surfactant tested at room temperature (~ 30 ºC) for 5 min. The indicator pieces were withdrawn from the solvent/surfactant and allowed to dry in the air on tissue paper. Fourteen organic solvents, and nine surfactants were tested and milli Q water was used for the blank test. The colors of the indicators were recorded by a commercial scanner (Epson Perfection 640U) in 3 repeating scans to generate 9 images (3 pieces × 3 scans) for each pair of solvent/surfactant and indicator.

Quantitative analysis was determined using RGB values according to the following equation:

$\Delta R = R_s - R_b$ where R_s is Red value of sample, and R_b is Red value of blank

$\Delta G = G_s - G_b$ where G_s is Green value of sample, and G_b is Green value of blank

$\Delta B = B_s - B_b$ where B_s is Blue value of sample, and B_b is Blue value of blank

The red, green and blue (RGB) values of the color images were evaluated by a photography processing software. The set of RGB numerical data were then tabulated and analyzed by the statistic method, principal component analysis (PCA), to generate clusters of data in the PCA score plots.

CHAPTER III

RESULTS AND DISCUSSION

The applications of polydiacetylene (PDA) have been extensively studied, especially, the application for thermal sensors. However, the mechanisms of color transition in molecular level have not been clearly understood. In order to investigate color transition of this kind, the synthesis of target diacetylene lipid monomers was achieved by using PCDA as starting material (Figure 3.1). Amide coupling reaction with ammonia followed by the lithium aluminium hydride ($LiAlH_4$) reduction gave 10, 12-pentacosadiynamine (PCDAmine). The mono and diamide derivatives were synthesized by treating PCDAmine with the corresponding anhydride and diacid compounds.

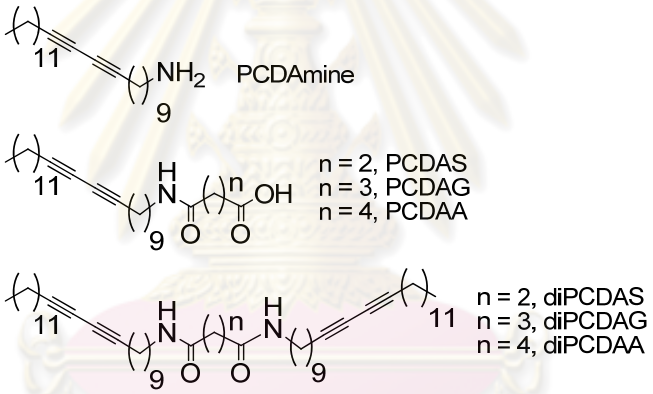
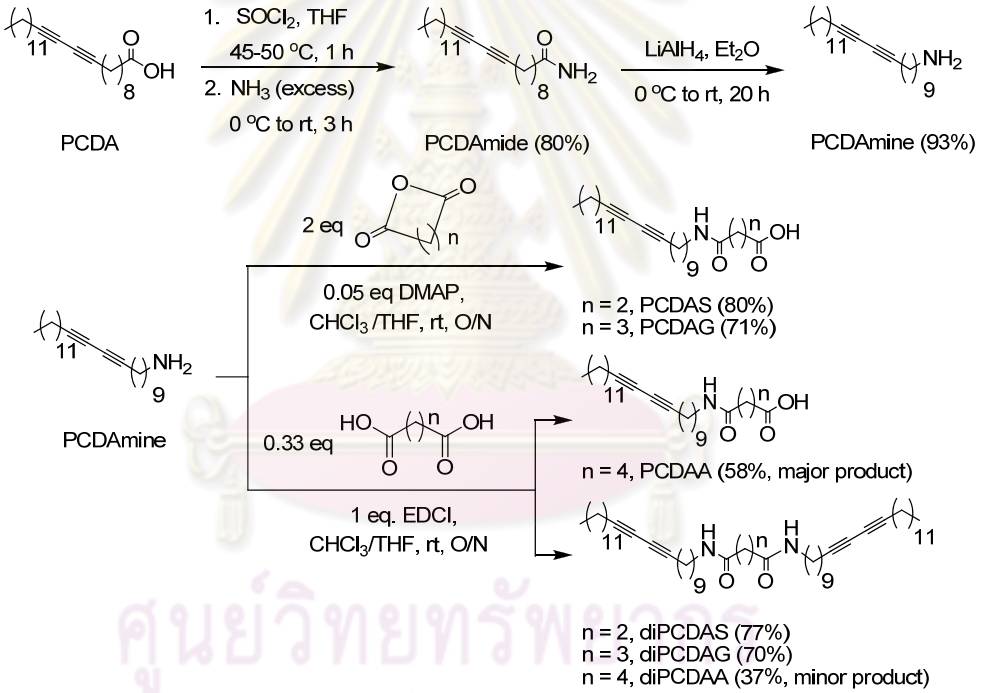


Figure 3.1 Chemical structures of 10, 12-pentacosadiynamine, its monoamide, and diamide derivatives.

3.1 Synthesis of diacetylene lipid monomers

The synthesis of the diacetylene lipid monomers containing hydrophilic carboxylic and amide head groups began with the preparation of 10,12-pentacosadiynamine (PCDAmine) by reacting PCDA with excess ammonia in THF followed by a reduction with $LiAlH_4$ [36] to afford PCDAmine in 93% total yield (Scheme 1). The condensation of PCDAmine with two equivalents of acid anhydride i.e. succinic or glutaric anhydride at room temperature in the presence of catalytic amount of 4-dimethylaminopyridine (DMAP) coupling reagent gave PCDAS and PCDAG in 70-80% yields. On the other hand, the diamide monomers (diPCDAS and diPCDAG) were obtained in good yields (70-77%) from the reaction of PCDAmine

with 0.33 equivalents of the corresponding dicarboxylic acid i.e. succinic or glutaric acid in the presence of EDCI coupling reagent. However, the condensation of PCDAmine with adipic acid (0.33 equiv) gave the monoamide (PCDAA) in 58% yield along with the expected diamide (diPCDAA) as a minor product in 37% yield. The relatively poorer formation of the diamide product suggests that the second carboxyl group within the longer chain of adipic acid reacts to the amino group much slower than the shorter diacids, succinic or glutaric acid (Scheme 3.1). The monoamide diacetylenes were purified by precipitation in ethyl acetate while the diamide products were precipitated in methanol for compound. ^{1}H NMR, ^{13}C NMR and low-resolution ESI quadrupole mass analyzer were used to confirm their structures and purities prior to the study of their photopolymerization and sensing application.



Scheme 3.1 Synthesis of diacetylene lipid monomers containing amide and diamide groups.

The ^{1}H NMR signals of PCDAmide, and PCDAmine lipid were quite similar to PCDA spectra (Figure 3.2). The most indicative signal for the formation of the carboxylic, amide or amine products appeared at 2.28, 2.23, 2.60 ppm corresponding to the methylene protons next to carboxyl group (t), amide group (t), and amino group (u), respectively. The less distinctive signal was a broad signal at 5.35 ppm belonging to the amide N-H protons. For PCDAmide, the signal of methylene protons connected to diacetylene (l,m) also observed at 2.23 ppm belonging to the methylene protons (t)

next to the amide group while another two lipids; methylene protons connected to diacetylene moiety (l,m) were observed at 2.17 ppm. Most of the protons in the aliphatic chain in all three products give the signals in the range of 1.62-0.81 ppm.

^{1}H NMR spectra of PCDAmide and PCDAmine are shown along with the spectrum of PCDA in Figure 3.2.

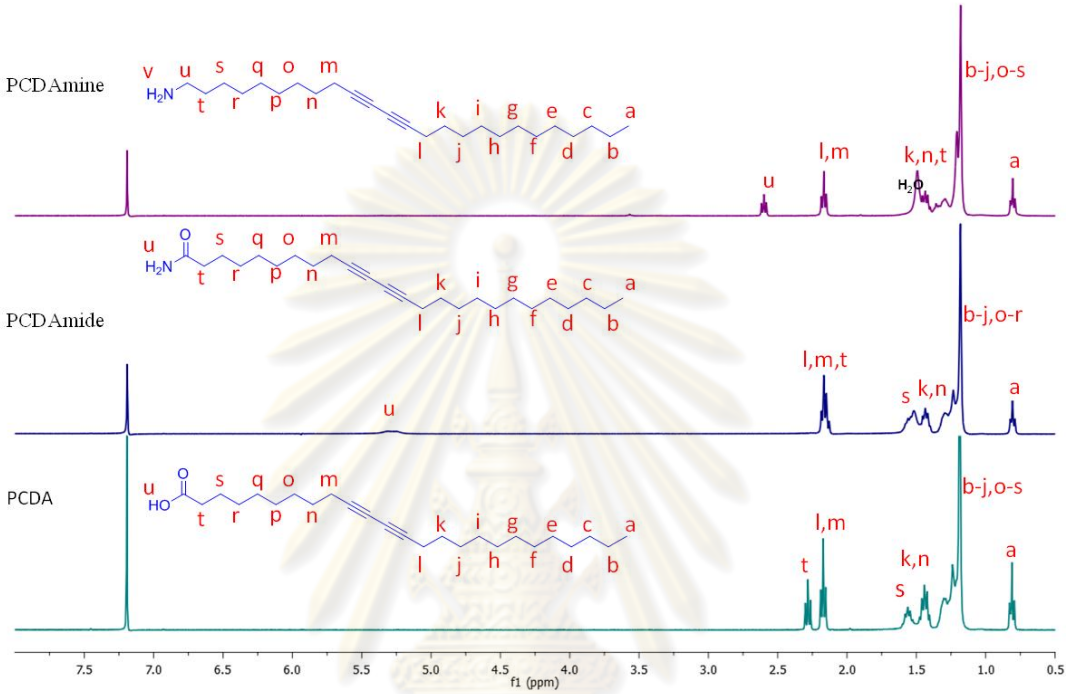


Figure 3.2 ^{1}H NMR spectra of PCDA, PCDAmide, and PCDAmine in $CDCl_3$.

^{1}H NMR spectra of PCDAS and diPCDAS are shown along with the spectrum of PCDAmine in Figure 3.3. The spectra of the products show the signals of amide protons in the chemical shift range of 5.7-5.8 ppm. The signals of the methylene protons next to the amino group in PCDAmine shifted slightly low field from 2.6 to 3.1-3.3 ppm upon the conversion to the amide groups. The extra singlet signal in diPCDAS at 2.4 ppm belongs to the symmetric methylene protons (w, x) in monoamide PCDAS between carbonyl groups of diamide derivatives. On the other hand, the signals of the asymmetric methylene protons are observed in the range of 2.5 to 2.7 ppm represent to monoamide compounds. In advertently, the other methylene protons connected to the amide group remained at relatively the same chemical shift of the methylene protons connected to the amine group of the parent PCDAmine.

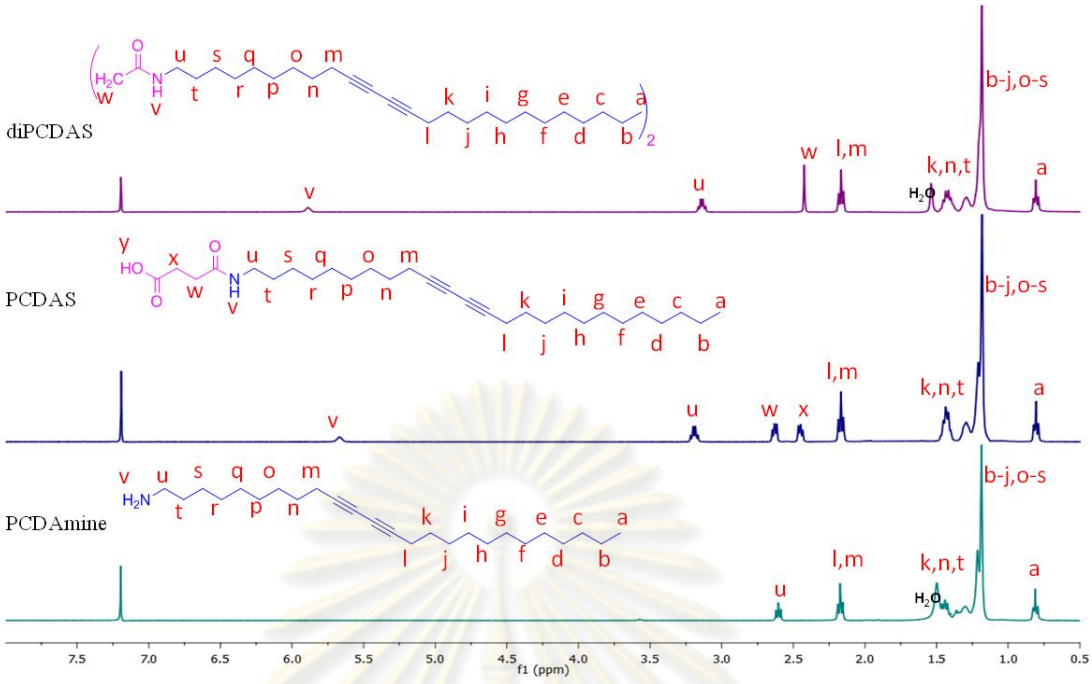


Figure 3.3 ^{1}H NMR spectra of PCDAmine, PCDAS, and diPCDAS in $CDCl_3$.

For the PCDAG, and diPCDAG derivatives, the spectra show the signals of N-H protons in the chemical shift range of 5.5-5.7 ppm. The signals of the methylene protons next to the amine group in PCDAmine also shifted slightly low field from 2.6 to 3.1-3.2 ppm upon the conversion to the amide groups. The extra signals in the range of 1.8 to 2.4 ppm belong to the methylene protons between carbonyl groups indicated the different pattern spectra of mono and diamide derivatives. However, the methylene protons connected to the amide group remained at relatively the same chemical shift of the methylene protons connected to the amine group of the parent PCDAmine and also the methylene protons adjacent to diyne units as well.

^{1}H NMR spectra of PCDAG and diPCDAG are shown along with the spectrum of PCDAmine in Figure 3.4.

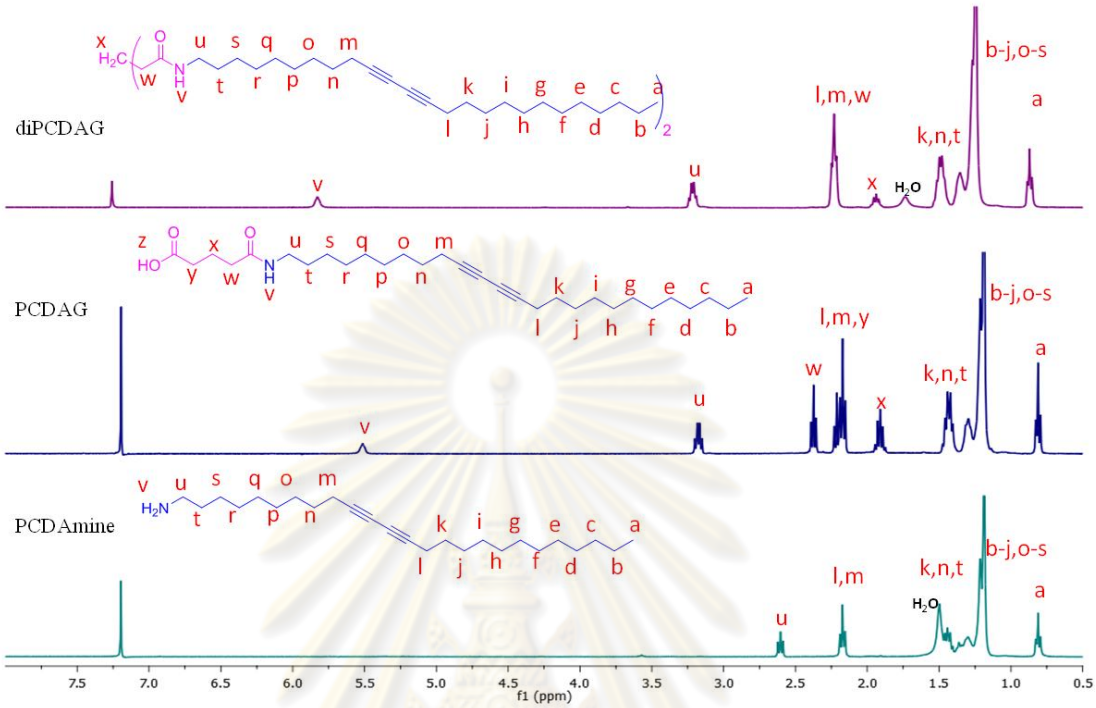


Figure 3.4 ^{1}H NMR spectra of PCDAmine, PCDAG, and diPCDAG in $CDCl_3$.

^{1}H NMR spectra of PCDAA and diPCDAA are shown along with the spectrum of PCDAmine in Figure 3.5. In the case of PCDAA, and diPCDAA derivatives, the general pattern of ^{1}H NMR signals was similar to PCDAmine. The indicative signals for the formation of mono and diamide products appeared in the chemical shift range of 1.5-3.1 ppm corresponding to the methylene protons between carbonyl groups. For asymmetric diacetylene compound, the methylene protons between carbonyl groups were observed at 1.59 (x, y), 2.16 (z), and 3.08 (w) ppm. On the other hand, the methylene protons between carbonyl groups of symmetric diacetylene derivatives appeared at 1.75 (x), and 2.97 (w) ppm. The doublet of doublet signal at 3.14, and 3.17 ppm corresponding to the methylene protons connected to amide N-H group (u). The signal was a broad signal in the chemical shift range of 4.2-5.7 ppm belonging to the amide N-H protons (v).

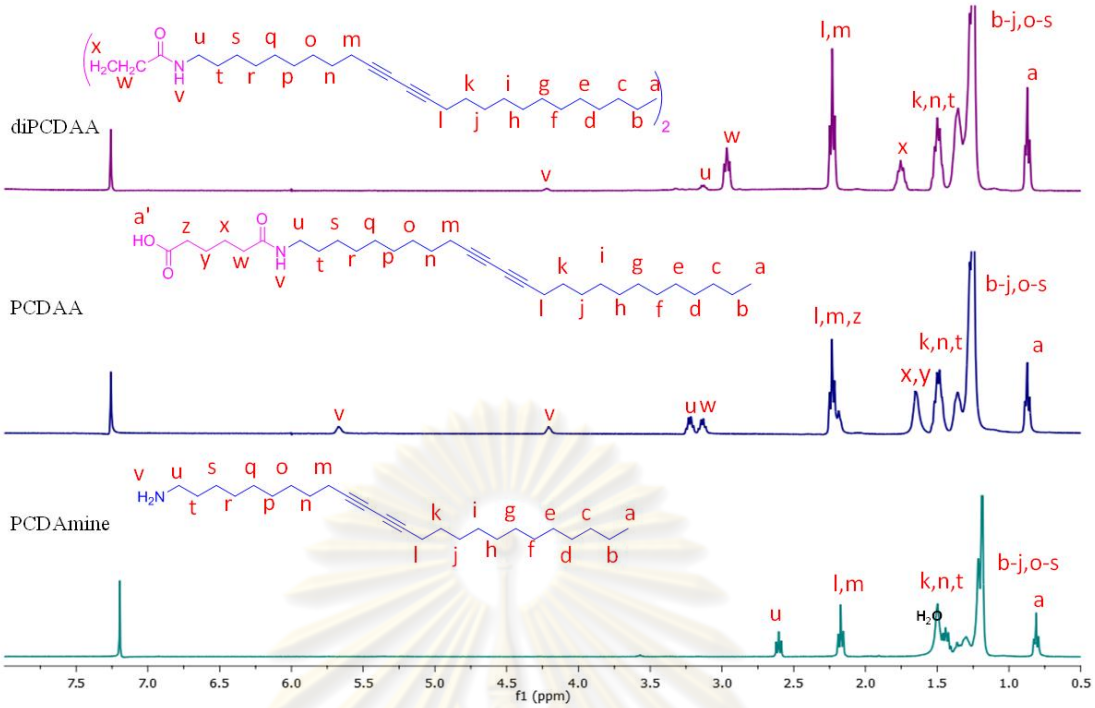
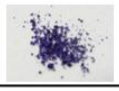
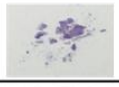
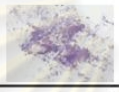
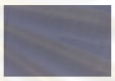
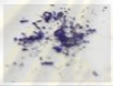
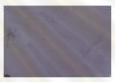
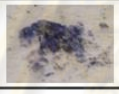


Figure 3.5 ^{1}H NMR spectra of PCDAmine, PCDAA, and diPCDAA in $CDCl_3$.

3.2 Polymerization of diacetylene monomers

In order to compare the UV irradiation onto the synthesized diacetylene monomers in solution state, solid state, and film state on the filter paper were attempted, and the results were shown in Table 3.1. Upon UV irradiation (UV lamp 900 μw/ cm^2), the white powders of PCDAS, PCDAG and diPCDAS rapidly turned into purple color (within 1 min) while the white color of PCDAmine, PCDAA, diPCDAG and diPCDAA turned into intense blue color. To develop these PDAs into practical sensors, we studied the polymerization of diacetylene monomers coated on filter papers. The results showed that all diacetylene monomers were polymerized on filter paper to give intense blue and purple color with slightly different shade, except PCDAmine and diPCDAA which gave red PDA. The red color of poly(PCDAmine) and poly(diPCDAA) on the filter paper suggested a weaker PDA side chain packing upon the adsorption on the cellulose substrate.

Table 3.1 Polymerization of diacetylene monomers at room temperature.

PDA monomers	Solid state (1 min)	Film state (2 min)	Solution state (2-3 min)
PCDAmine			
PCDAS			
PCDAG			
PCDAA			
diPCDAS			
diPCDAG			
diPCDAA			

In addition, the polymerization of PDAs sol was also investigated at room temperature. The PCDAS and PCDAG gave intense blue color. On the other hand, PCDAmine and diPCDAA exhibited in red shade. It suggested that their functional head group a weak formed intermolecular hydrogen bond. Furthermore, a weaker side chain packed of PCDAA, diPCDAS, and diPCDAG also caused the light blue color in the sols at room temperature.

3.3 Preparation of polydiacetylene (PDA) sols and characterization

The synthesized monomers were made into aqueous polydiacetylene (PDA) sols. The vesicles were prepared by sonication of lipid monomer in both milli Q water and in the mixture of DMSO with milli Q water (1mL/14mL) followed by irradiation with 254 nm UV-light. The self assembling ability and the color of polymerized diacetylenes are presented in Table 3.2. All monomers were able to be hydrated to give colorless solution in milli Q water prior to UV light irradiation. However, the dispersion had to be improved by repeating the heating and the sonication process until the translucent sols were obtained. On the other hand, they gave poor dispersion after sonication in DMSO with milli Q water condition. Due to their poor solubility in DMSO, the diacetylene lipid precipitated upon exposure to UV irradiation. The

dispersed monomers were subsequently irradiated with 254 nm light at 900 μW/cm^2 for 2 min in the case of PCDAmine, and monoamide diacetylene and 3 min for diamide one. After UV exposure, the colorless sols of PCDAS, PCDAG, and diPCDAS diacetylene lipids readily turned to distinct blue sols signifying the polymerization of diacetylene monomers to form ene-yne conjugated PDAs. On the contrary, PCDAA, diPCDAG and diPCDAA sols appeared in purple shade. These results also supported by UV-vis spectra of the corresponding PDAs.

Table 3.2 Properties of prepared PDA sols.

PDA monomers	Vesicle formation in MQ water	Polymerization (vesicle form)	Vesicle formation in DMSO/MQ water 1mL/14mL	Polymerization (vesicle form)
PCDAmide	ND	ND	ND	ND
PCDAmine	(pH 2-6) 			
PCDAS	(pII 8) 			
PCDAG	(pH 10) 			
PCDAA	(pH 6.8) 			
diPCDAS	(pH 8) 			
diPCDAG	(pII 10) 			
diPCDAA	(pH 6.8) 			

*ND= not determine

3.4 Particle size and morphology of polydiacetylene sols

3.4.1 Dynamic light scattering (DLS)

The average size of polydiacetylene suprastructure was investigated by using DLS technique. The DLS results suggested that an average size of assembled polydiacetylene is in nanoparticle range (200 nm). Furthermore, DLS spectra in Figure 3.6 also indicated the odd-even number of alkyl chains (*n*) between carbonyl groups in mono and diamide diacetylene monomer having effect on the average size. That is, an even number of alkyl chains in diamide diacetylene induces a particle size

smaller than that of odd number one. However, an even number of alkyl chains in monoamide diacetylene formed a larger particle size.

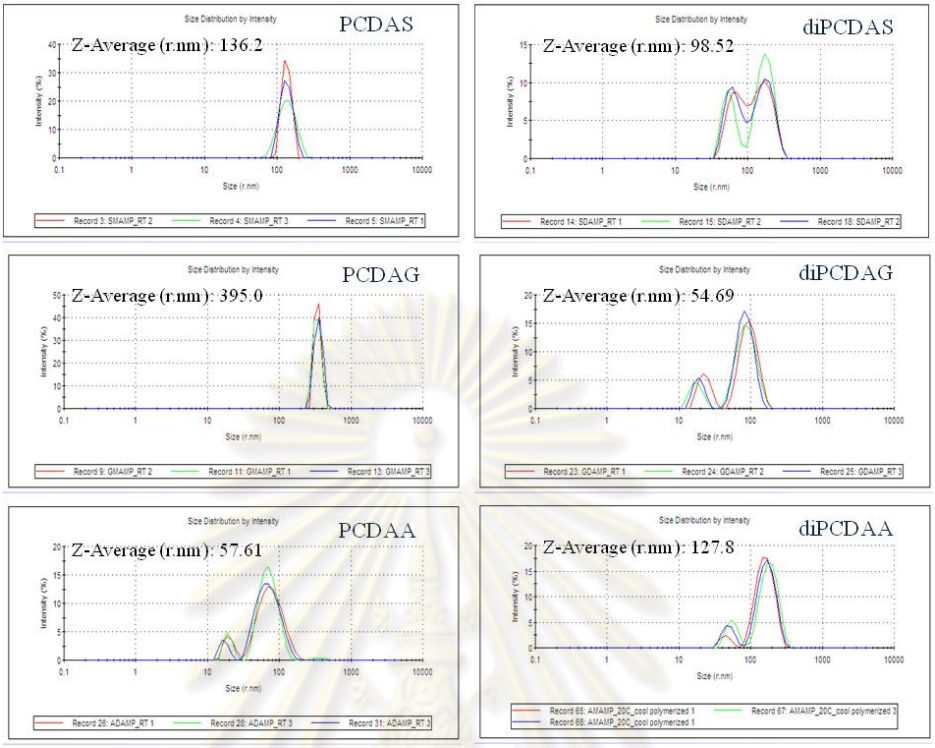


Figure 3.6 Average sizes of PDAs vesicles

3.4.2 Atomic force microscopy (AFM) and Transmission electron microscopy (TEM)

AFM was utilized to observe the shape and size of the air-dried PDA sols. The AFM images showed spherical structures of all PDA sols. In addition, the morphology of PDAs in different filtration method was also investigated. Figure 3.8a exhibit the small spherical of PDAs sols which were filtrated by a 0.45 µm syringe solely obtaining 50 nm, size of particles. In another way, PDAs sols which were filtrated by a filter paper showed some aggregation and the larger size of the particles as shown in the Figure 3.8b. However, the AFM results were in good agreement with the TEM and DLS results.

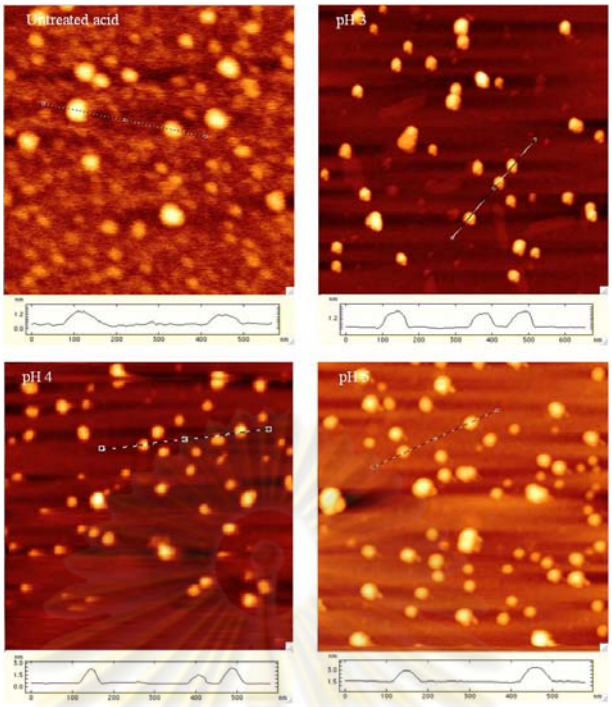
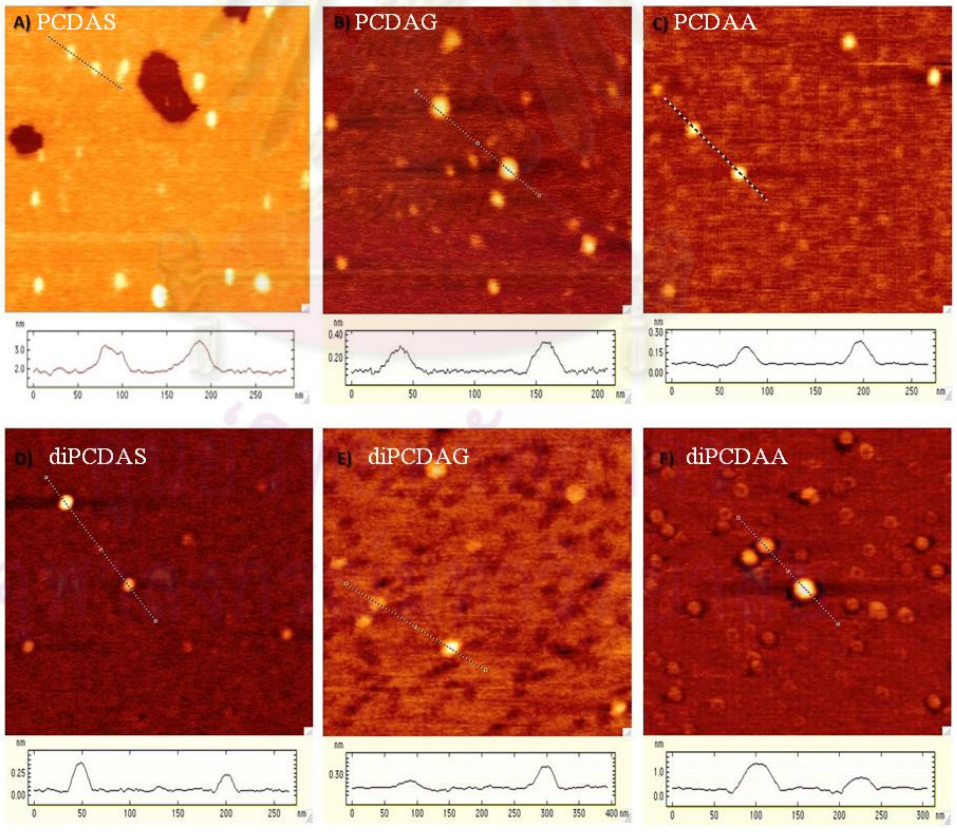
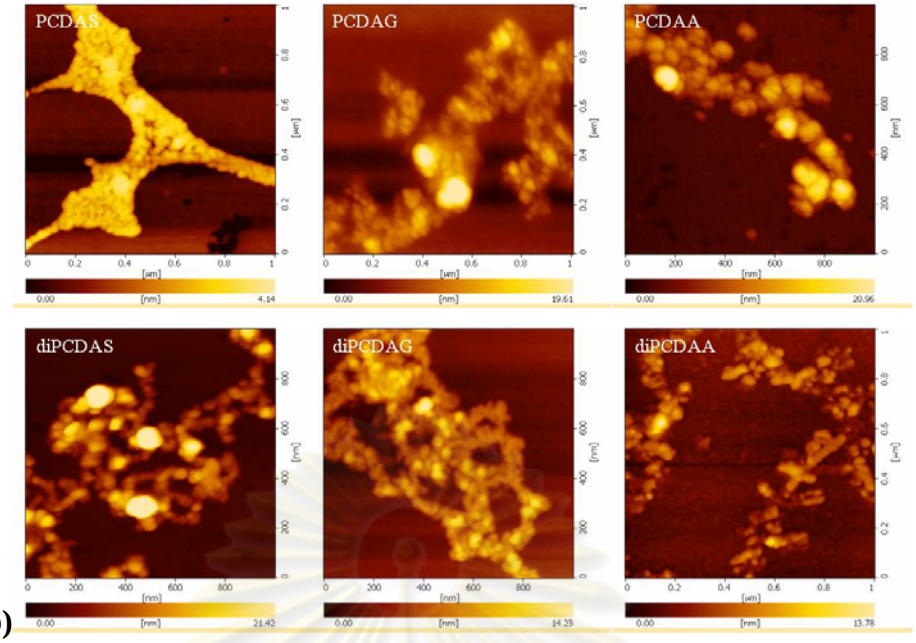


Figure 3.7 AFM images of PCDAmine in acidic conditions



a)



b)

Figure 3.8 AFM images of mono- and diamide diacetylene derivatives. a) using syringe filter, b) using paper filter No.1

3.4.3 Transmission electron microscopy (TEM)

TEM images of PDA sols also confirmed the results obtained from DLS and AFM. PDA sols were prepared from monoamide diacetylene monomers such as PCDAS, PCDAG, and PCDAA uniformly exhibiting the nanoparticles. On the contrary, diamide diacetylene vesicles show a little distribution of the particle size related to the DLS result.

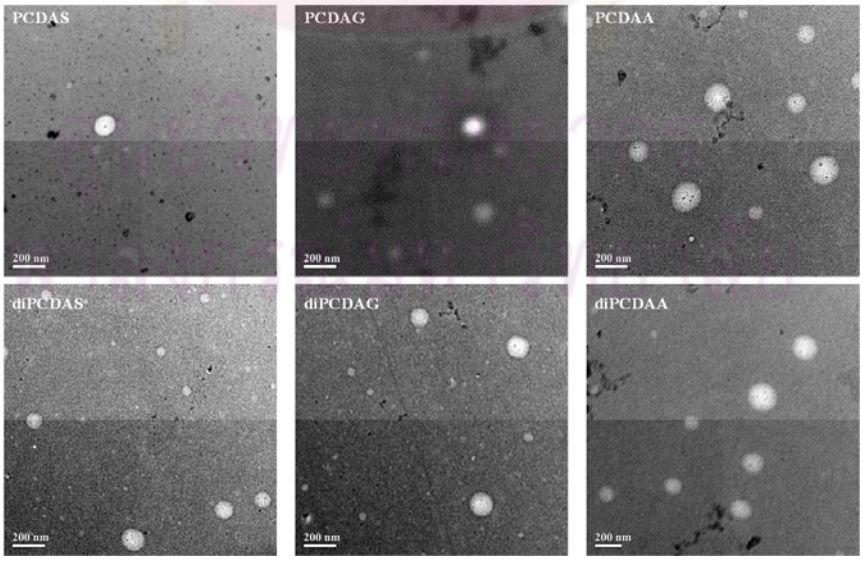


Figure 3.9 TEM images of mono- and diamide diacetylene derivatives

3.5 Thermochromic properties of PDA sols

3.5.1 Thermal transition temperature

Having prepared PDA sols, the next stage of investigation focused on thermochromic properties. Initially, they were filtered and subjected to the stepwise heating from 10 to 70 ºC for PCDAmine and from 20 or 25 to 90 ºC for mono and diamide PDAs sols within the heating cell of variable temperature UV-vis spectrometer. Figure 3.10 illustrates the annealing temperature dependence of UV-vis absorption spectrum. The blue sols prepared from PCDAmine in various acidic conditions (pH2-6) possess a maximum wavelength around 640 nm with the phonon side band approximately at 592 nm. Upon increasing temperature, the absorbance band is decreased and shifted to shorter wavelength. At 70 ºC, the red solution of all PCDAmine sols showed the maximum absorption at 540 nm, indicating the larger band gap between the ground and excited states. As shown by the color images in Figure 3.10, the color changes from blue to red took place in the range of 30-55 ºC.

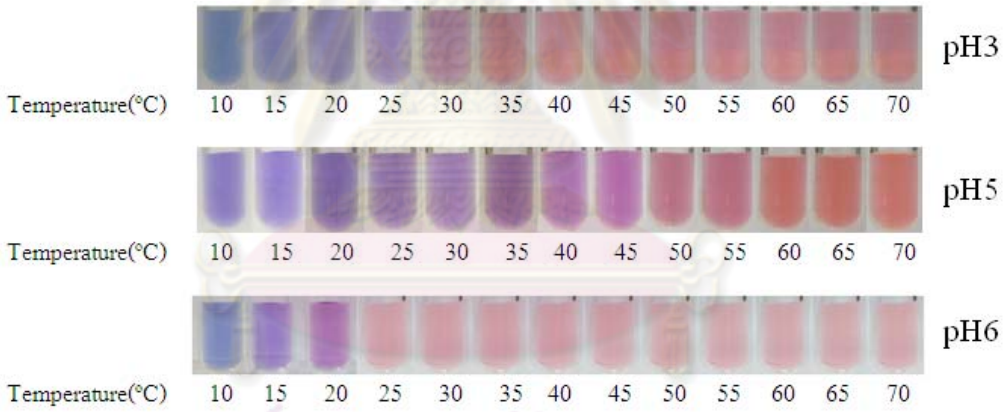


Figure 3.10 Colorimetric responses to temperature of the poly(PCDAmine) sols in acidic conditions (pH 3, 5, and 6).

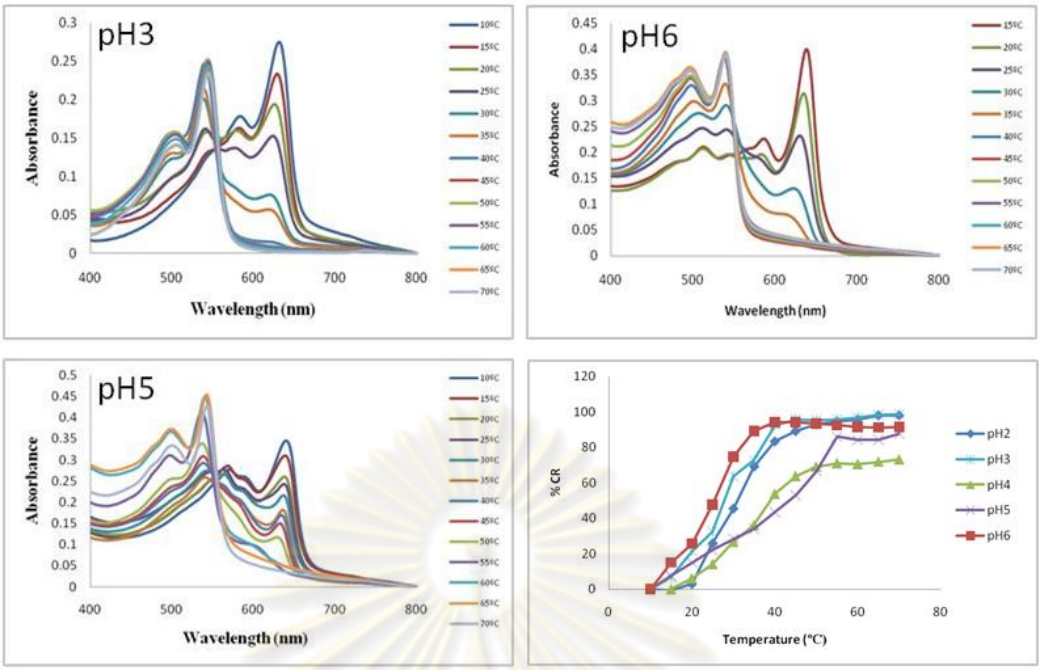


Figure 3.11 UV-spectra of the poly(PCDAmine) sols in acidic conditions (pH 3, 5, and 6) upon stepwise heating to various temperatures and colorimetric responses to temperature of poly(PCDAmine) sols in pH 2-6.

To evaluate the color transition of PDA sols from the UV-vis absorption spectra of all PDA sols were translated into colorimetric response percentage (%CR). The %CR is defined as percent change compared to the one at room temperature (20-25 ºC) in the maximum absorption of the blue phase with the respect to the total absorption at both red and blue phases. The plot of %CR against the temperature of all PDA gave sigmoidal curves as a result of blue to red transition upon raising temperature (Figure 3.11). %CR curves suggested that pH of poly(PCDAmine) sol has an extreme impact to the thermal transition of poly(PCDAmine). The order of the color transition temperature (CTT) of poly(PCDAmine) in various pH following by pH6 < pH3, pH2 < pH4, pH5. According to the results, we hypothesized that in pH6 the amine head group can form relatively weak electrostatic interaction between protonated nitrogen atom and lone pair of the unprotonated one resulting in the lowest color transition temperature, and with pH4 and pH5 conditions, some of the amino groups can be protonated and able to form more electrostatic interactions than that of pH6 case. However, the extreme protonation in pH2 and pH3 cases probably caused the charge repulsion in a head group as shown in Figure 3.12. It is a reason of why in

the lower pH (2 and 3) gave the lower color transition temperature comparing to the pH 4 and 5 cases.

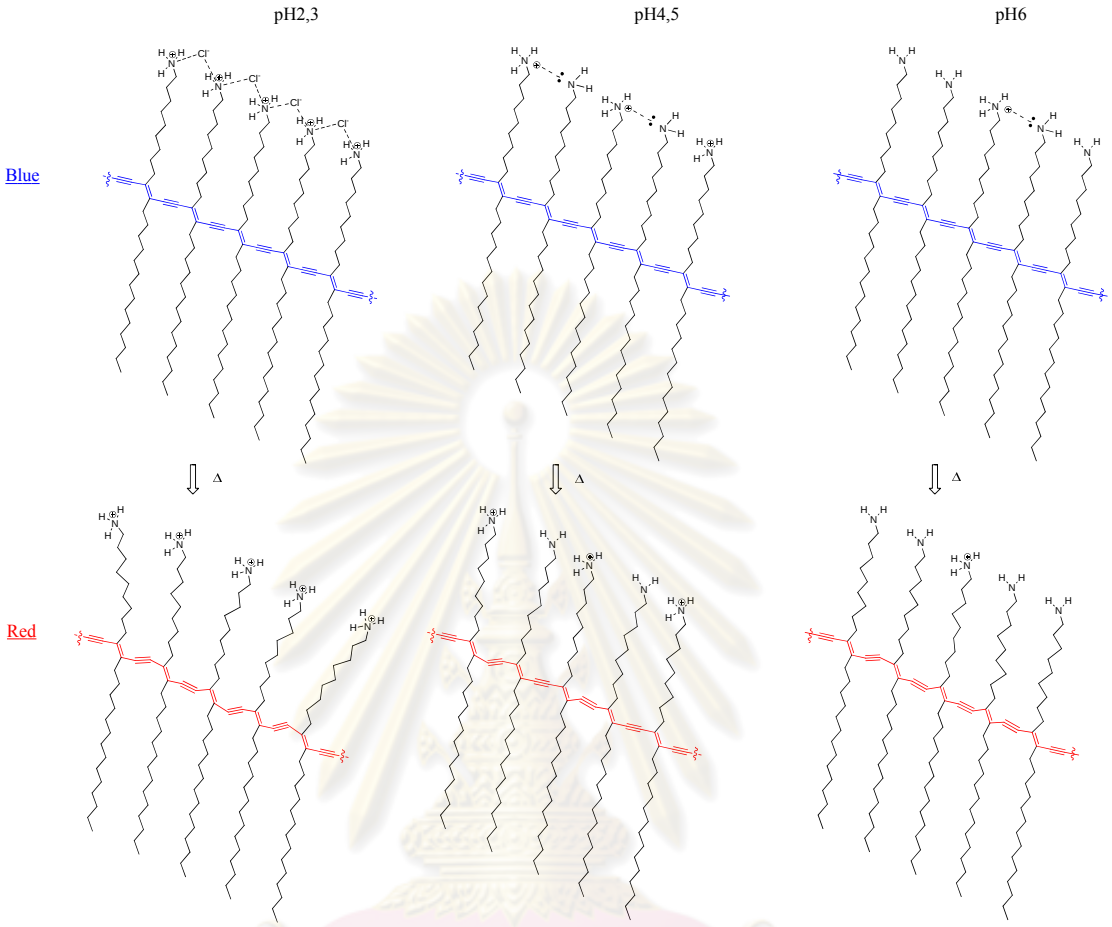


Figure 3.12 Mechanism of the color transition of poly(PCDAmine) in various acidic pH

The thermochromic transition of the monoamide and diamide PDA sols was studied by UV-vis absorption spectroscopy and photographic observation. The %CR is determined from the change of the blue absorbance fraction (B) which is the ratio between the blue absorbance (A_{blue}) and the summation of the blue and red absorbance ($A_{blue} + A_{red}$). The A_{blue} and A_{red} are measured at the maximum absorption wavelength (λ_{max}) of the corresponding blue and red phases of PDAs, typically around 640 and 540 nm, respectively. The order of color transition temperatures assessed from %CR of 50% level was found in the following order: poly(PCDAA) > poly(PCDAG) > poly(PCDAS) for the monoamide PDAs (Figure 3.13). The monoamide monomers, such as PCDAS, PCDAG, and PCDAA contain the same C25 aliphatic structure with different alkyl chain length between carbonyl groups in polar

head. Therefore the number of methylene group between carbonyl groups may affect the strength of the hydrogen bonding and the hydrophobic packing. Since the longer methylene chains give higher color transition temperatures, hydrophobic interaction is probably more important than the odd even effect [6].

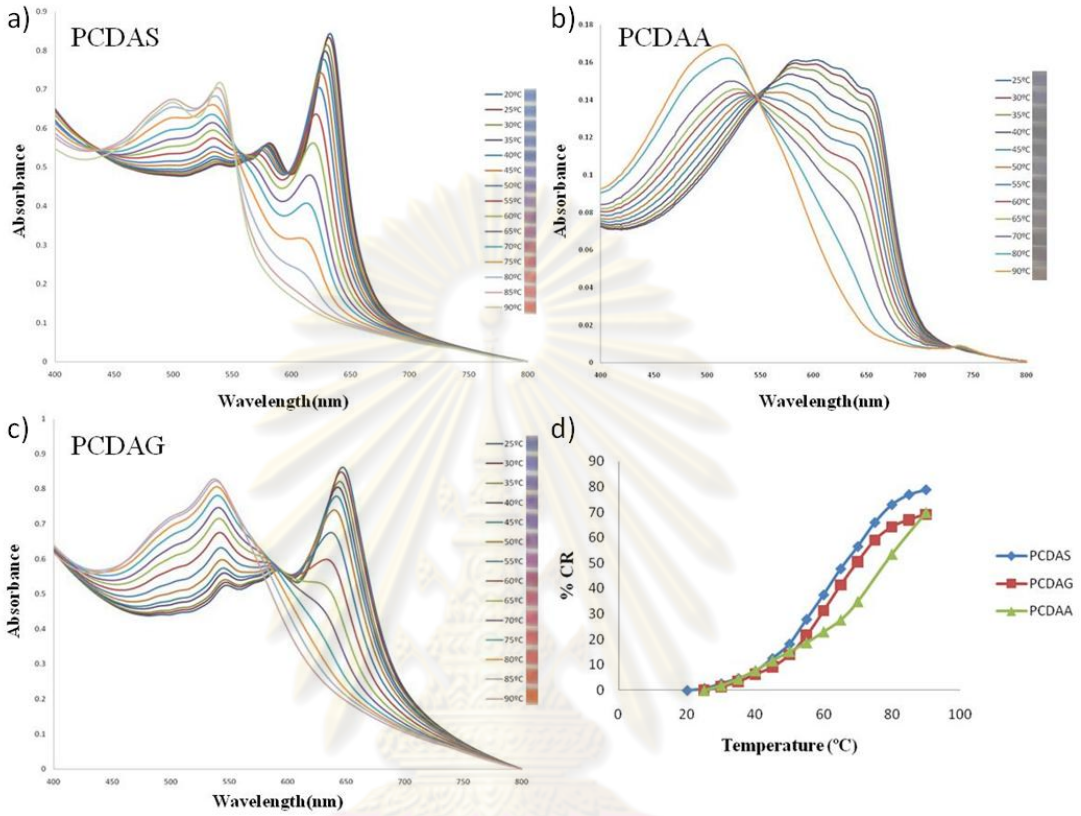


Figure 3.13 UV-vis spectra along with color photographs (at the side bar) of monoamide PDA sols prepared from the diacetylene lipids containing one amide group upon stepwise heating and their colorimetric responses (%CR).

To find relationships between the color transition temperatures of the PDAs possessing one amide group and the thermal behavior of the diacetylene monomers, melting points of the monomers were investigated by DSC. The DSC thermograms of PCDAS and PCDAA exhibited 2 endothermic peaks while that of PCDAG showed only one sharp endothermic peak (Figure 3.14 right). These results suggest that the melting process of PCDAS and PCDAA involves breaking two hydrogen bonds but the melting of PCDAS may involve only one. The proposed two dimensional packing of the monomers (Figure 3.14 left) indicates that both amide and carboxylic acid groups in PCDAS and PCDAA are well positioned for hydrogen bond formation but only one of the two functional groups of PCDAG can be in a position to form a linear

hydrogen bond corresponding to the numbers of DSC peaks observed. Interestingly, the weight averaged melting points of these monomers (111.2, 114.9 and 117.8) are in a similar trend with the color transition temperatures which is PCDAS < PCDAG < PCDAA. However, a clearer picture of this relationship requires more thorough investigation.

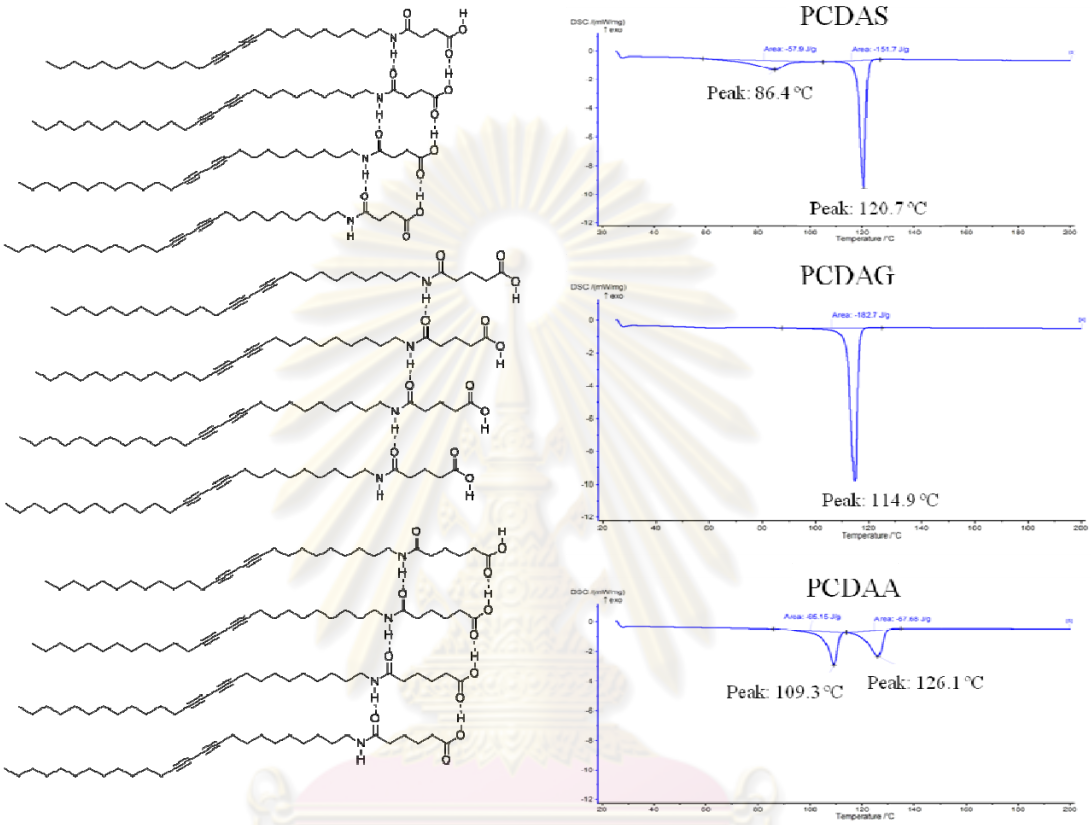


Figure 3.14 Monomers forms and DSC thermograms of monoamide diacetylene monomers

In contrast, the color transition temperatures of the diamide PDAs were found in the following order: poly(diPCDAS) > poly(diPCDAG) > poly(diPCDAA) (Figure 13.5). The order of the color transition temperatures of PDAs obtained from %CR is in good agreement with those observed from eyes and photographic records. The %CR plots also provided valuable information. Evidently, PDAs derived from diPCDAA exhibited a sharp color transition with %CR increased from 20% to 50% within the temperature range of no more than 10 ºC. On the other hand, PDAs obtained from other two diacetylene lipids showed more gradual change in %CR upon heating.

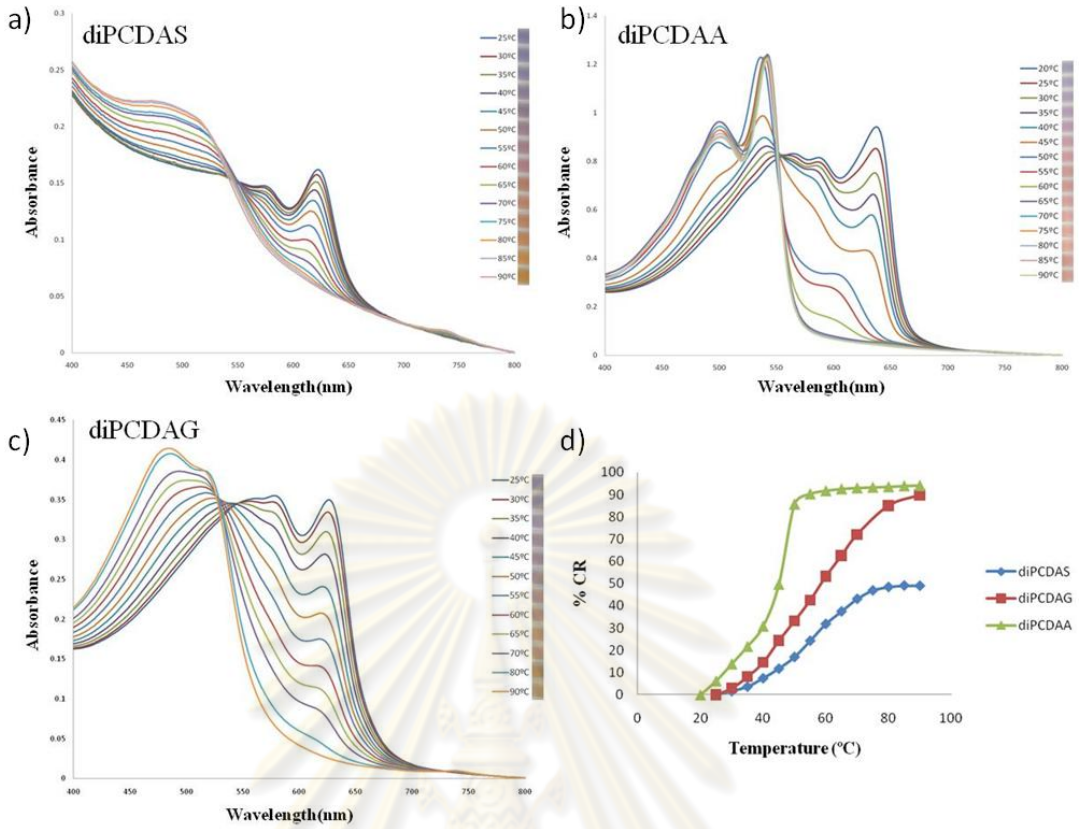


Figure 3.15 UV-vis spectra along with color photographs (at the side bar) of PDA sols prepared from the diacetylene lipids containing two amide group upon stepwise heating and their colorimetric responses (%CR).

In addition, to find the relationships between the color transition temperatures of the PDAs possessing two amide group and the thermal behavior of the diacetylene monomers, melting points of the monomers were again investigated by DSC. The DSC thermograms of diPCDAA displayed 2 endothermic peaks while that of diPCDAS and diPCDAG showed only one endothermic peak (Figure 3.16 right). These results suggest that the melting process of diPCDAA involves breaking two hydrogen bonds but the melting of diPCDAS and diPCDAG may involve only one. The proposed two dimensional packing of the monomers (Figure 3.16 left) indicates that only one of the two amide functional groups of diPCDAG can be in a position to form a linear hydrogen bond. Even though, both amide groups in diPCDAS and diPCDAA are well positioned for hydrogen bond formation, a shorter methylene chain linker of diPCDAS may caused the behavior of diPCDAS involves breaking hydrogen bond only one while diPCDAA posses a longer methylene chain linker, it probably occupied breaking two hydrogen bond corresponding to the numbers of

DSC peaks observed. Interestingly, the weight averaged melting points of these monomers (129.6, 119.4 and 89.0) are in a similar trend with the color transition temperatures which is diPCDAS > diPCDAG > diPCDAA. However, a clearer picture of this relationship requires more thorough investigation.

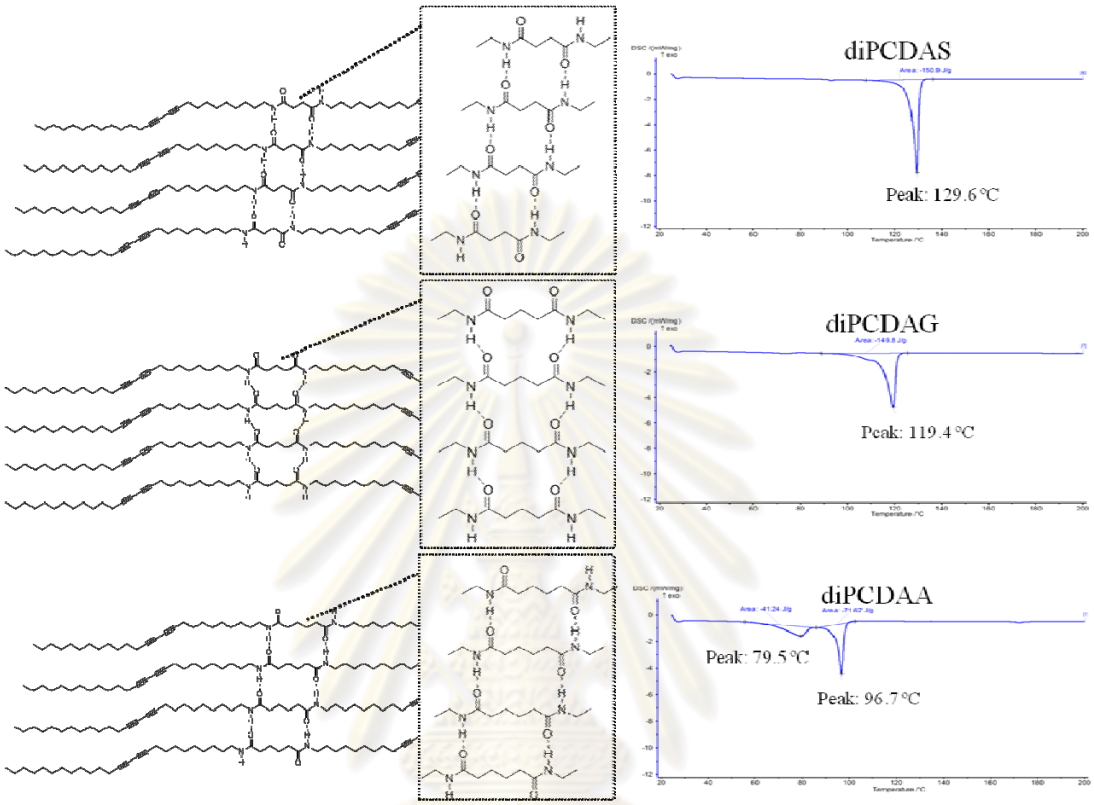
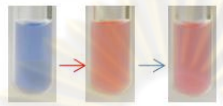
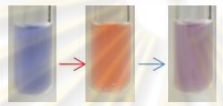
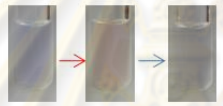
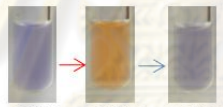
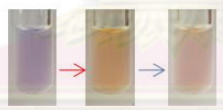


Figure 3.16 Monomers forms and DSC thermograms of diamide diacetylene monomers

The worth pointing out trend described above is that the lower the color transition temperature, the sharper the temperature induced colorimetric response. Both hydrogen bonding and hydrophobic packing probably simultaneously contribute to this trend. The blue-to-red color transition is associated with the movement of the side chains resulting in the release of backbone strain and disturbing the ene-yne planarity upon thermal stimulation. The side chain movement will be more sluggish and requires more energy if the hydrophobic interaction between the side chains and the hydrogen bonding between the head groups are strong.

3.5.2 Reversibility of the color transition

Table 3.3 Color photographs showing approximate degrees of reversibility (% DR) of the color transition of the PDA sols observed by eyes.

DA monomers	Reversibility	%DR	Classification of PDA
PCDAmine	 10°C 70°C 10°C	ND	Irreversible
PCDAS	 25°C 90°C 25°C	11.5%	Irreversible
PCDAG	 25°C 90°C 25°C	34.0%	Partially reversible
PCDAA	 25°C 90°C 25°C	84.8%	Fully reversible
diPCDAS	 25°C 90°C 25°C	92.8%	Fully reversible
diPCDAG	 25°C 90°C 25°C	67.8%	Partially reversible
diPCDAA	 25°C 90°C 25°C	0.0%	Irreversible

During the course of the thermochromism studies, the reversibility of the color transition has come to our attention. When the PDA sols were heated up to 90 ºC and cooled back to 25 ºC, the recorded color photographs before heating, after heating and after cooling provided an approximate idea about the reversibility of these PDAs (Table 3.3).

The photograph of PDAs possessing one amide head group such as poly(PCDAS), and poly(PCDAG) exhibited irreversibility and partially reversibility, respectively. Exceptionally poly(PCDAA) presented full reversibility of the color transition. On the other hand, the corresponding PDAs having two amide head groups, poly(diPCDAS),

poly(diPCDAG), and poly (diPCDAA) displayed complete reversibility, partially reversibility, and irreversibility, respectively.

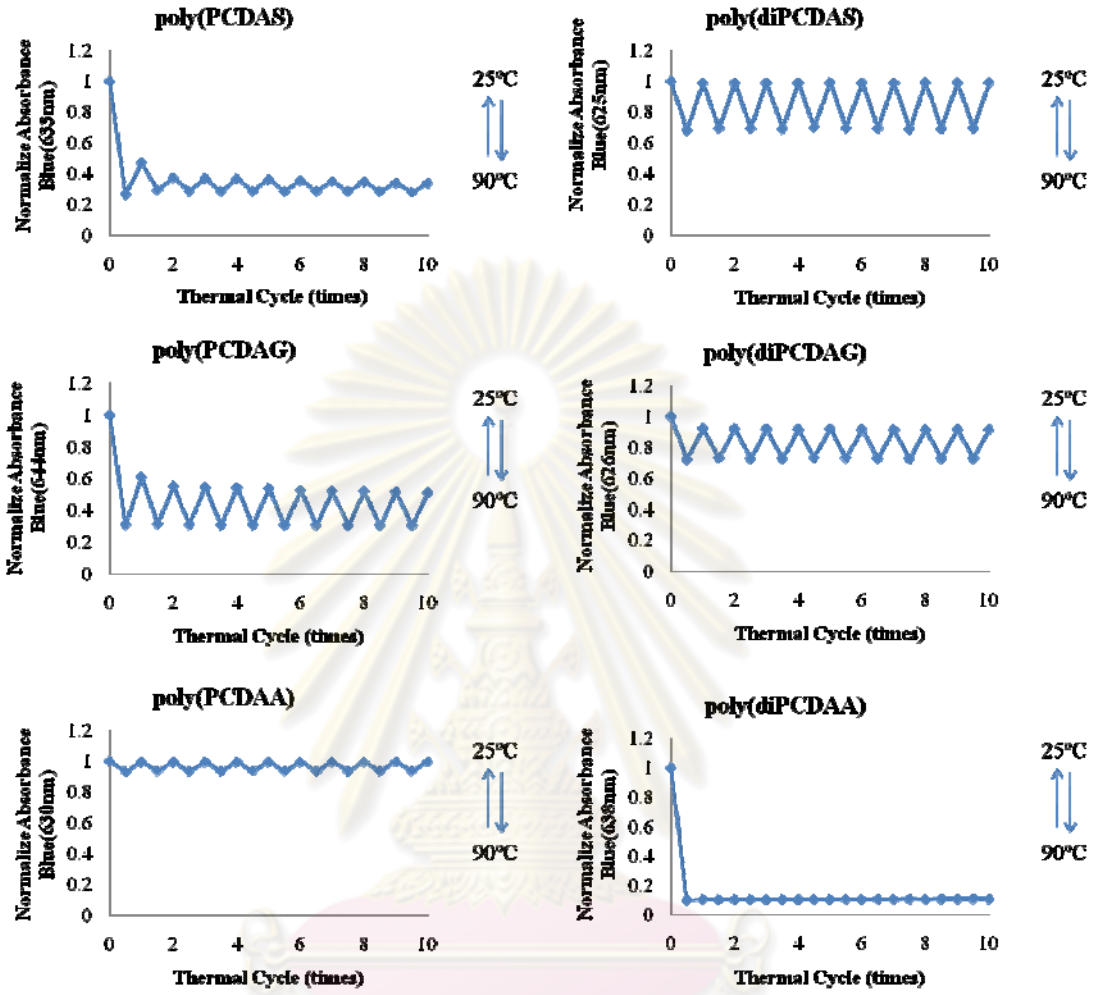


Figure 3.17 Absorbance at the λmax of the blue phase of the PDA sols at 25 and 90 ºC in the heating-cooling 10 cycles.

To assess the degree of thermochromic reversibility of the PDAs, the blue absorbance, defined as the absorbance at the λmax of "blue from", was monitored for 10 cycles of heating and cooling between 90 and 25 ºC. The plots between the absorbance and the cycle numbers of poly(PCDAA), and poly(diPCDAS) displayed a zigzag pattern with virtually full recovery of the initial absorbance in every cycles (Figure 3.17), indicating the complete thermochromic reversibility of these PDAs. The result suggested that % DR for monoamide PDAs increasing the number of methylene carbon between carbonyl groups gained higher. Proportionately, the complete reversibility of PDAs containing two amide head groups depends on the

decreasing of methylene between carbonyl group. This result is probably caused by the long alkyl chains on the both side of the monomeric molecule implying that the amide head groups cannot reform strong hydrogen bonds after the heat disturbance.

Some PDAs such as, poly(PCDAS), poly(PCDAG), and poly(diPCDAG) were studied in the same manner, and the plots between the blue absorbance and repeating the number of cycles showed a low degree of reversibility but consistent recovery of the absorbance after the second heating-cooling cycle. The following equation was used to determine the quantitative value of % DR. $\%DR = 100 \times \Delta A_{avg}/\Delta A_1$ where ΔA_{avg}, the average $A_{25\text{-}90^oC}$ of blue from the 2nd to 10th cycle of heat and ΔA_1 is $A_{25\text{-}90^oC}$ of blue of 1st cycle of heat. According to % DR presented in Table 3.3, the PDAs investigated in this work were classified into three categories *i.e.* 1) fully reversible PDA (%DR > 80%), partially reversible PDA (15 < %DR < 80%) and irreversible PDA (%DR < 15%) related to the photographs of the color transition of the PDA sols observed by eyes. Based on the criteria mentioned above, poly(diPCDAA) possess irreversible thermochromic property as it shows the % DR of 0.0%. After the 2nd heating-cooling cycle, poly(diPCDAA) sol appeared as red color at both 90 and 25 ºC (Table 3.3). Although, poly(diPCDAA) having two amide group, the behavior of the color irreversibility probably caused by the reformation of the intermolecular hydrogen bonding unachievable due to the flexible movement of methylene chain between carbonyl head group and very small recovery of hydrophobic interaction of alkyl side chain.

3.6 Sensing Application of PDAs

3.6.1 Solvatochromism

As the PDA films coated on filter papers are particularly interesting for the economical and practical sensing applications, the naked eye solvent sensing capabilities of the PDA films prepared from the synthesized diacetylene monomers were investigated. Fourteen common organic solvents (hexane, CH_3CN, CH_3OH, acetone, EtOH, Et_2O, toluene, 2-propanol, EtOAc, CH_2Cl_2, DMSO, $CHCl_3$, THF, and DMF) were tested. From visual observation, poly(PCDAS) and poly(PCDAG) showed blue-to-red color change upon the exposure to only THF and DMF while the others did not give any colorimetric response to any solvents (Figure. E2). We arbitrarily selected PCDAS for further investigation partly due to its more availability from the higher synthetic yield.

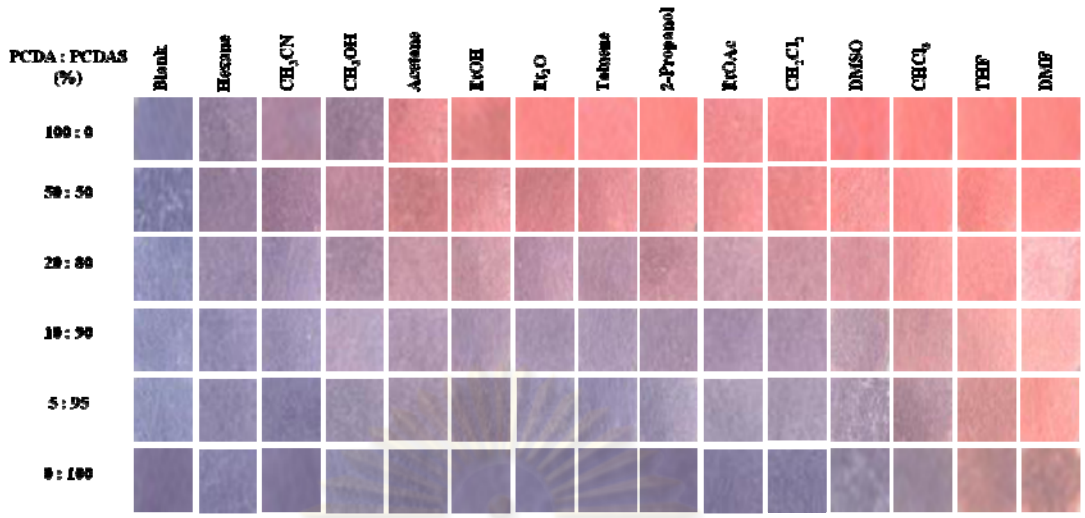


Figure 3.18 Array of cropped photographic images of PDAs on filter paper fabricated from PCDA and PCDAS responding to various organic solvents.

Previously, poly(PCDA) has been reported to show blue-to-red colorimetric responses to a variety of solvents [36, 38]. This high solvent sensitivity of poly(PCDA) is potentially useful for tuning the colorimetric responses of our lower solvent sensitive poly(PCDAS) to produce a sensing array with a wide range of responses for solvent identification. The PDA films on filter paper were fabricated from mixed solutions of PCDA and PCDAS (0.5% w/v) at various weight ratios. The photographic images of the films after solvent exposure vividly showed the array of color pattern for each solvent (Figure 3.18). With an aid of color evaluating program (turning the color image into RGB values) and pattern recognition by a multivariate statistical analysis method such as PCA, this array is potentially useful for solvent identification.

The color images of PDAs on filter paper were quantitatively analyzed by photography processing software to obtain the RGB values (Figure 3.19). The histogram of RGB values showed promising distinguishable pattern for each solvent.

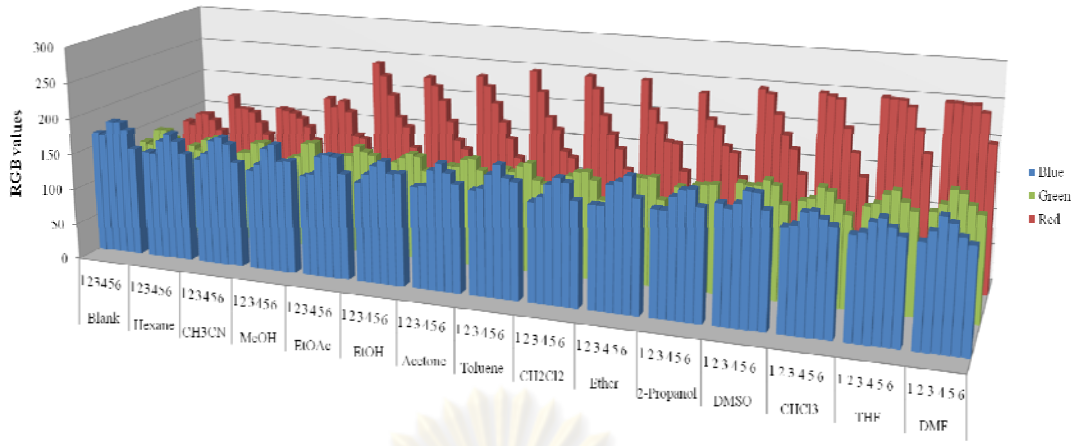


Figure 3.19 RGB plot of colorimetric responses in the presence of solvent of PCDA and PCDAS in various mixture ratios; PCDA(1); 50:50(2); 20:80(3); 10:90(4), 5:95(5), and PCDAS(6).

The statistical PCA method was utilized to verify the solvent identifying ability of the sensor by transforming the data set of RGB values into PCA scores projected on the orthogonal axes of principal components (PCs) resulting in the PCA score plot. The plot in the first three PCs obtained from a single sensor prepared only from PCDA showed highly overlapping data points without separable clusters (Figure 3.20) indicating a totally indiscriminating ability. However, the data from the sensing array prepared from PCDA/PCDAS mixtures gave 9 clusters of data (Figure 3.21). Eight clusters can be assigned to water (blank) and seven organic solvents while the other cluster contained the data points of seven solvents. With close inspection of the plot, three solvents (EtOH, EtOAc, and Et_2O) possessing the data points highly overlapping to the others were excluded to produce a new PCA score plot with twelve well separated clusters (Figure 3.22) corresponding to water (blank) and 11 organic solvents (CH_3CN, hexane, CH_3OH, THF, CH_2Cl_2, $CHCl_3$, acetone, toluene, DMF, DMSO, and 2-propanol). It is important to note that the distances from the solvent cluster to the blank cluster are well correlated to the degree of the colorimetric responses of the sensors; the further the distance is, the higher the colorimetric responds (the redder the sensor appears).

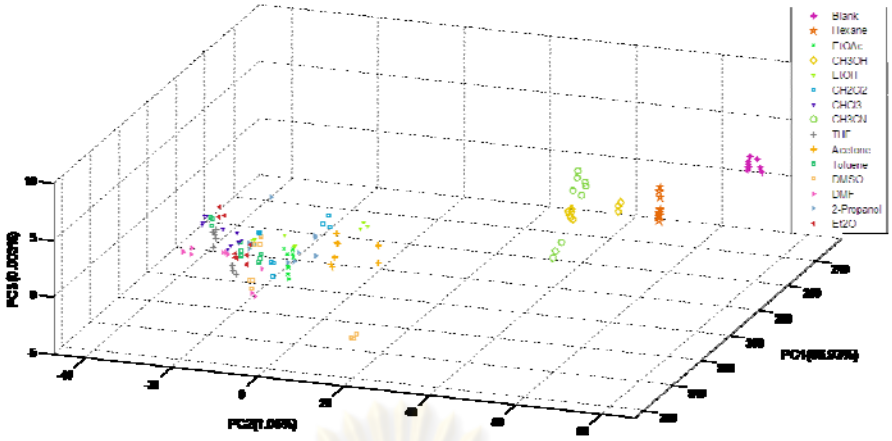


Figure 3.20 PCA score plots of the RGB values obtained from water (blank) and 14 organic solvents tested by a single sensor of PCDA.

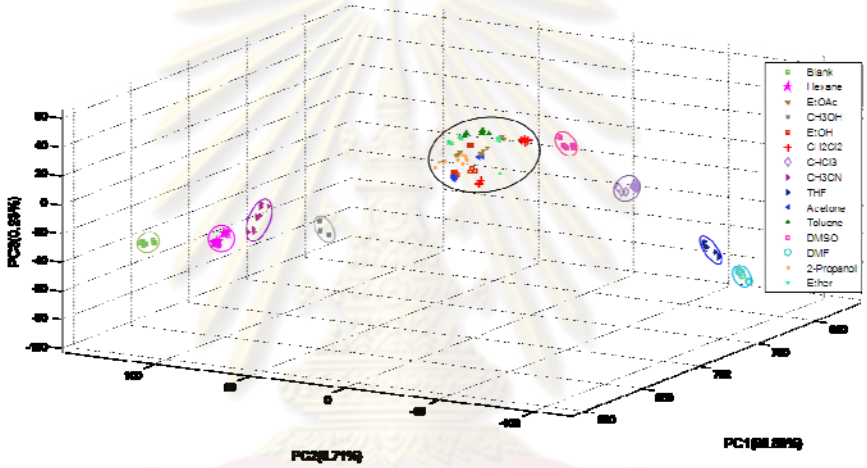


Figure 3.21 PCA score plots of the RGB values obtained from water (blank) and 14 organic solvents tested by a sensing array of PCDA/PCDAS mixtures.

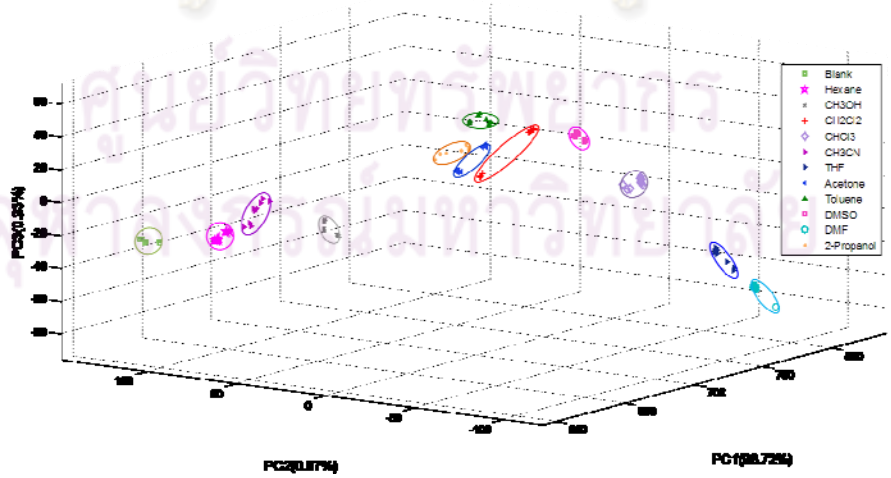


Figure 3.22 PCA score plots of the RGB values obtained from water (blank) and 11 organic solvents tested by a sensing array of PCDA/PCDAS mixtures without the data of EtOH, EtOAc, and Et_2O.

The qualitative identification of 9 organic solvents by PDA sensors using mixed diacetylene monomers in polysiloxane matrix has been presented [37]. In this work, the statistical analysis such as PCA could be applied to quantitatively assess the scope of solvents which can be identified. As the analysis suggested, the paper based sensing array is capable of identifying 11 common organic solvents via its colorimetric responses.

3.6.2 Affinochromism

The PCDA, PCDAG and their mixed lipid solutions (0.5%w/v) can be served as a surfactant sensor array. The photographic colorimetric response of the array to 9 types of surfactants i.e. cationic (DTAB, HTAB, TTAB), anionic (SDC, SDBS, SDS) and nonionic (Triton X-100, Tween 20, Brij® 58) is illustrated in Figure 3.23. The photographs clearly show that the array fabricated from PCDA, PCDAG and their mixtures at different ratios selectively responded to generate the distinctive color pattern for cationic surfactant. The RGB histogram of each surfactant and PDAs shows different color transitions of PDAs. With an aid of RGB pattern recognition, this array is capable of identifying the type of cationic surfactants (Figure 3.23).

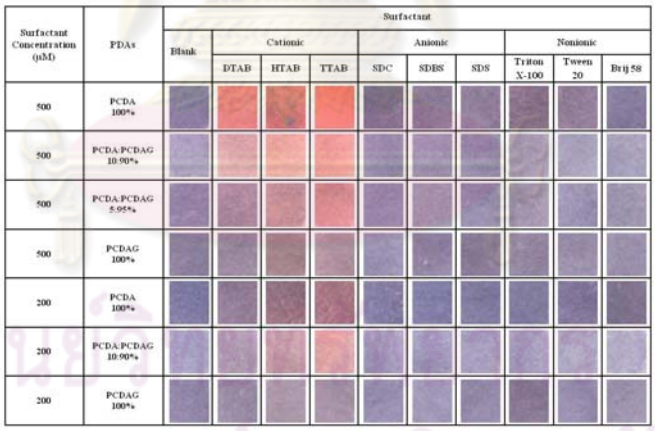


Figure 3.23 Array of cropped photographic images of PDAs on filter paper fabricated from PCDA and PCDAG responding to various surfactants.

In addition, RGB histogram in Figure 3.24 also supported the results from the paper based array, the poly(PCDAG) and their mixture can identify three types of cationic surfactants at concentration 200 and 500 μM while using only poly(PCDA) cannot indicate the different of those ones.

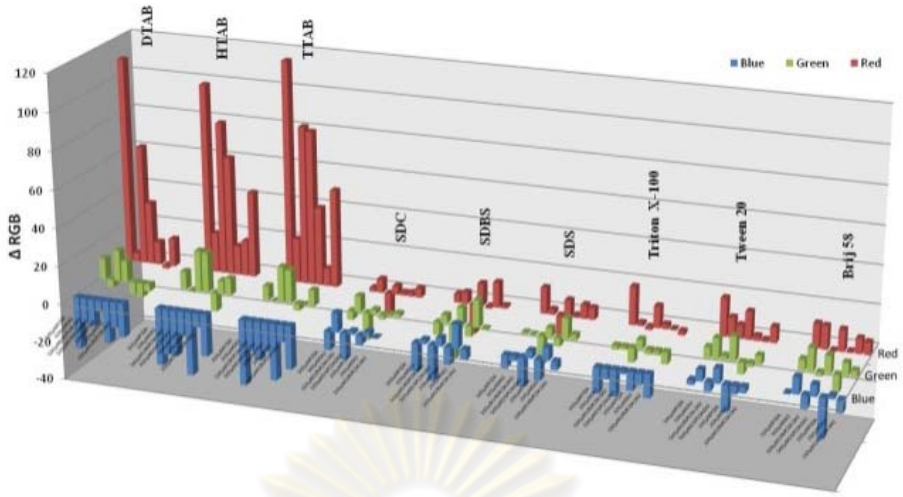


Figure 3.24 RGB histogram of colorimetric responses of polydiacetylene in the presence of surfactant.

From the results, we hypothesize that the surfactant molecule could disturb the intermolecular hydrogen bond between hydrophilic head groups of polydiacetylene and also inserted itself into position between diacetylene alkyl chains resulting in the reduction in length of the conjugated system. Therefore the color change from blue to red was observed.

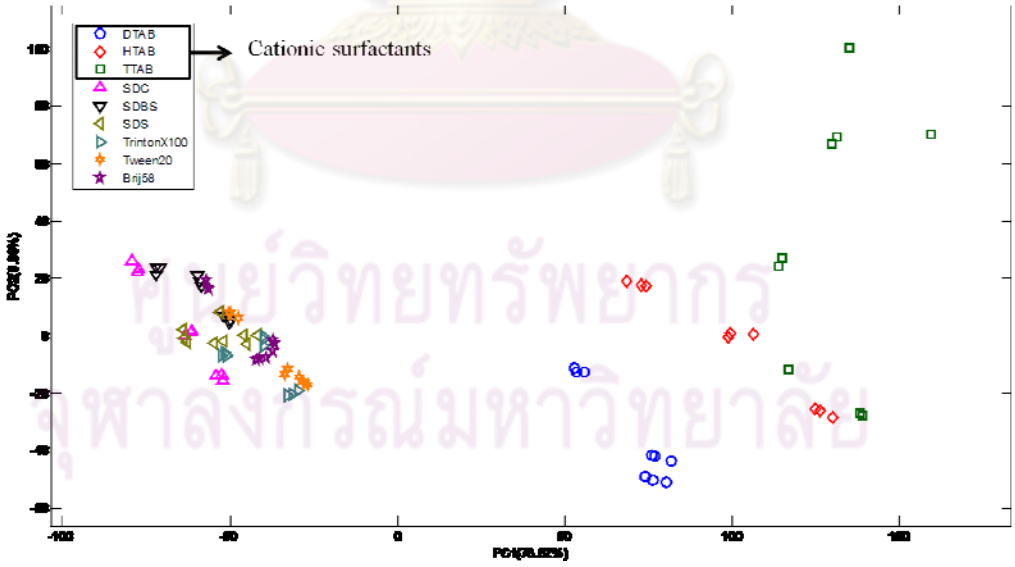
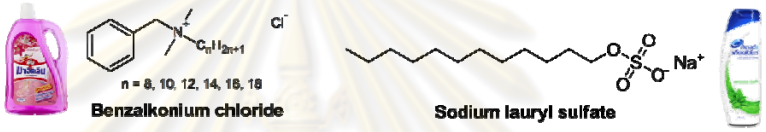


Figure 3.25 PCA score plots of the RGB values obtained from water (blank) and 9 surfactants tested by a sensing array of PCDA/PCDAG mixtures.

The plot of PCA score obtained from a paper based sensor prepared from the mixture of PCDA and PCDAG showed highly overlapping data points without

separable clusters of anionic and non-ionic surfactants, indicating a discriminating ability of cationic surfactant from those anionic and non-ionic ones (Figure 3.25).

In order to practically examine with the commercial products, PCDA and PCDAG were used to detect cationic surfactant in a cleaning agent (Magic clean) which have cationic (benzalkonium chloride) mixed with nonionic (ethoxylated and propoxylated alcohols) or anionic surfactant (sodium lauryl sulfate) in shampoo (Head & Shoulder) as an ingredient. Either control (in HEPES buffer pH 7.4) or no control (milli Q water pH 5) pH conditions, these paper based PDAs appear in red shade only when tested with the cationic surfactant containing sample (Figure 3.26). Even though, there are metal ions such as Ca^{2+} and Mg^{2+} dissolved in media, no interference can be observed in any cases (Figure 3.27).



DAs	Media: MQ water (pH 5) HEPES buffer (pH 7.4)	Blank	Sufactant: Magic clean (cationic+ non-ionic)[1] No dilution	Magic clean D10X	Magic clean D100X	Magic clean D1000X	Head & Shoulder (anionic)[2] No dilution
PCDA	MQ water						
	HEPES buffer						
PCDAG	MQ water						
	HEPES buffer						

*** [1] Product band: Magic clean: Benzalkonium Chloride 1.0 % w/w , Ethoxylated and Propoxylated Alcohols 2.0 % w/w
[2] Product band: Head & Shoulder: Sodium lauryl sulfate (SLS)

Figure 3.26 Cropped photographic images of PDAs on filter paper fabricated from PCDA and PCDAG responding to surfactants which were used in commercial products.

DAs	Blank (MQ water)	Metal ions (1 mM) Na^{1}	Ca^{2+}	Fe^{2+}	Mg^{2+}	Hg^{2+}	Cd^{2+}
PCDA							
PCDAG							

Figure 3.27 Cropped photographic images of PDAs on filter paper fabricated from PCDA and PCDAG responding to metal ions (1 mM M^{n+}).

CHAPTER IV

CONCLUSION

4.1 Conclusion

In conclusion, we have successfully synthesized a novel series of diacetylene lipid monomers containing one and two amide head groups with various length methylene spacers between carbonyl groups. The polymerization and chromic properties of the resulted PDAs have shed some light on the roles of the amide head group and its spacer length on the polymerizability of the diacetylene lipids and the color transition properties of the PDAs. The UV-vis results of this PDA series suggested that the number of methylene carbons between carbonyl groups impacted on the thermochromic properties both transition temperature and degree of reversibility. The diacetylene lipids can be fabricated onto filter paper and photopolymerized by UV-irradiation of 254 nm. The monoamide diacetylene (PCDAS and PCDAG) can be used in combination with PCDA to generate a new paper-based sensing array for detection and identification of 11 organic solvents by using PCA and classification of cationic surfactants from anionic and nonionic surfactants.

REFERENCES

[1] Shimizu, T.; Masuda, M.; and Minamikawa, H. Supramolecular Nanotube Architectures Based on Amphiphilic Molecules. Chem. Rev. 105 (2005): 1401-1443.

[2] Gill, I.; and Ballesteros, A. Immunoglobulin-polydiacetylene sol-gel nanocomposites as solid-state chromatic biosensors. Angew. Chem. Int. Ed. 42 (2003): 3264-3267.

[3] Okada, S.; Peng, S.; and Spevak, W. Color and Chromism of Polydiacetylene Vesicles. Acc. Chem. Res. 31 (1998): 229-239.

[4] Ahn, D. J.; Chae, E.-H.; and Lee, G. S. Colorimetric Reversibility of Polydiacetylene Supramolecules Having Enhanced Hydrogen-Bonding under Thermal and pH Stimuli. J. Am. Chem. Soc. 125 (2003): 8976-8977.

[5] Song, J.; Cisar, J. S.; and Bertozzi, C. R. Functional Self-Assembling Bolaamphiphilic Polydiacetylenes as Colorimetric Sensor Scaffolds. J. Am. Chem. Soc. 126 (2004): 8459-8465.

[6] Wacharasindhu, S.; Montha, S.; and Boonyiseng, J.; and Sukwattanasinitt, M. Tuning of Thermochromic Properties of Polydiacetylene toward Universal Temperature Sensing Materials through Amido Hydrogen Bonding. Macromolecules 43 (2010): 716–724.

[7] Phollookin, C.; Wacharasindhu, S.; Ajavakom, A.; and Sukwattanasinitt, M. Tuning Down of Color Transition Temperature of Thermochromically Reversible Bisdiynamide Polydia-cetylenes. Macromolecules 43 (2010): 7540–7548.

[8] Cheng, Q.; and Stevens, C. Charge-induced chromatic transition of amino acid-derivatized polydiacetylene liposomes. Langmuir 14 (1998): 1974-1976.

[9] Jonas, U.; Shah, K.; Norvez, S.; and Charych, D.H. Reversible color switching and unusual solution polymerization of hydrazide-modified diacetylene lipids. J. Am. Chem. Soc. 121 (1999): 4580-4588.

[10] Kew, S.J.; and Hall, E. H. pH response of carboxy-terminated colorimetric polydiacetylene vesicles. Anal. Chem. 78 (2006): 2331-2338.

[11] Potisatityuenyong, A.; Rojanathanes, R.; Tumcharern, G.; and Sukwattanasinitt, M. Electronic Absorption Spectroscopy Probed Side-Chain Movement in Chromic Transitions of Polydiacetylene Vesicles. Langmuir 24 (2008): 4461-4463.

[12] Wu, S.; and Zhang, Q. Solvent Effects on Structure, Morphology, and Photophysical Properties of an Azo Chromophore-Functionalized Polydiacetylene. Macromolecules 43 (2010): 6142–6151.

[13] Pires, A.C. S.; Soares, N. D. F. F.; da Silva, L. H. M. Thermodynamic Study of Colorimetric Transitions in Polydiacetylene Vesicles Induced by the Solvent Effect. J.Phys. Chem. B. 114 (2010): 13365-13371.

[14] Yoon, J.; Chae, S. K.; and Kim, J.-M. Colorimetric Sensors for Volatile Organic Compounds (VOCs) Based on Conjugated Polymer-Embedded Electrospun Fibers. J. Am. Chem. Soc. 129 (2007): 3038-3039.

[15] Jiang, H.; Wang, Y.; and Ye, Q. Polydiacetylene-based colorimetric sensor microarray for volatile organic compounds. Sensors and Actuators B 143 (2010): 789-794.

[16] Yoon, J.; Jung, Y.-S.; and Kim, J.-M. A Combinatorial Approach for Colorimetric Differentiation of Organic Solvents Based on Conjugated Polymer-Embedded Electrospun Fibers. Adv. Funct. Mater. 19 (2009): 209-214.

[17] Su, Y. Preparation of polydiacetylene/silica nanocomposite for use as a chemo-sensor. Reactive & Functional Polymers 66 (2006): 967–973.

[18] Labre`che, F. P.; and Goldberg, M. S. Exposure to Organic Solvents and Breast Cancer in Women: A Hypothesis. American Journal of Industrial Medicine 32 (1997): 1-14.

[19] Gardner, J.W.; and Bartlett, P.N. Electronic Noses: Principles and Applications. Oxford University Press: Oxford, UK (1999).

[20] Sotzing, G.A.; Briglin, S.M.; and Grubbs, R.H. Preparation and properties of vapour detector arrays formed from poly(3,4-ethylenedioxy)thiophene-poly(styrene sulfonate) / insulating polymer composites. Anal. Chem. 72 (2000): 3181-3190.

[21] Mujahid, A.; Stathopulos, H.; and Lieberzeit, P. A. Solvent Vapour Detection with Cholesteric Liquid Crystals-Optical and Mass-Sensitive Evaluation of the Sensor Mechanism. Sensors 10 (2010): 4887-4897.

[22] Beenen A.; and Niessner, R. Development of a photo acoustic trace gas sensor based on fiber-optically coupled NIR laser diodes. Appl. Spectrosc. 53 (1999): 1040-1044.

[23] Walt, D.R.; Dickinson, T.; and White, J. Optical sensor arrays for odor recognition. Biosens. Bioelectron. 13 (1998): 697–699.

[24] Nakagawa, M.; Okabayashi, T.; and Fujimoto, T. A new method for recognizing organic vapour by spectroscopy image on cataluminescence-based gas sensor. Sensors and Actuator B 51 (1998): 159–162.

[25] Aoki, K.; Kudo, M.; and Tamaoki, N. Novel Odd/Even Effect of Alkylene Chain Length on the Photopolymerizability of Organogelators. Org. Lett. 6 (2004): 4009-4012.

[26] Lim, C.; Sandman, D. J.; and Sukwattanasinitt, M. Topological Polymerization of tert-Butylcalix [4] arenes Containing Diynes. Macromolecules 41 (2008): 675-681.

[27] Carpick, R.W.; Sasaki, D.Y.; and Marcus, M.S. Polydiacetylene films: a review of recent Investigations into chromogenic transitions and nanomechanical properties. J. Phys.: Condens. Matter 16 (2004): R679.

[28] Kuriyama, K.; Kikuchi, H.; and Kajiyama, T. Chromatic Phase of Polydiacetylene Langmuir-Blodgett Film. Langmuir 14(1998): 1130-1138.

[29] Su, Y.L.; Li, J.R.; and Jiang, L. Chromatic immunoassay based on polydiacetylene vesicles. Colloids Surf. B. 38(2004): 29-33.

[30] http://en.wikipedia.org/wiki/RGB_color_model.

[31] Cheng, Q.; Yamamoto, M.; and Stevens, R. C. Amino Acid Terminated Polydiacetylene Lipid Microstructures: Morphology and Chromatic Transition. Langmuir 16 (2000): 5333-5342.

[32] Song, J.; Cisar, J. S.; and Bertozzi, C. R. Functional Self-Assembling Bolaamphiphilic Polydiacetylenes as Colorimetric Sensor Scaffolds. J. Am. Chem. Soc. 126 (2004): 8459-8465.

[33] Kim, J. M.; Lee, J. S.; and Choi, H. Rational Design and in-Situ FTIR Analyses of Colorimetrically Reversible Polydiacetylene Supramolecules. Macromolecules 38 (2005): 9366-9376.

[34] Dautel, O. J.; Robitzer, M.; and Re-Porte, J.-P. L. Self-Organized Ureido Substituted Diacetylenic Organogel. Photopolymerization of One-Dimensional Supra-molecular Assemblies to Give Conjugated Nanofibers. J. Am. Chem. Soc. 128 (2006): 16213-16223.

[35] Fujita, N.; Sakamoto, Y.; Shirakawa, M. Polydiacetylene Nanofibers Created in Low-Molecular-Weight Gels by Post Modification: Control of Blue and Red Phases by the Odd-Even Effect in Alkyl Chains. J. Am. Chem. Soc. 129 (2007): 4134-4135.

[36] Yoon, J.; Chae, S. K.; and Kim, J.-M. Colorimetric Sensors for Volatile Organic Compounds (VOCs) Based on Conjugated Polymer-Embedded Electrospun Fibers. J. Am. Chem. Soc. 129 (2007): 3038- 3039.

[37] Yoon, J.; Jung, Y.-S.; and Kim, J.-M. A Combinatorial Approach for Colorimetric Differentiation of Organic Solvents Based on Conjugated Polymer-Embedded Electrospun Fibers. Adv. Funct. Mater. 19 (2009): 209-214.

[38] Jiang, H.; Wang, Y.; and Ye, Q. Polydiacetylene-based colorimetric sensor microarray for volatile organic compounds. Sensors and Actuators B 143 (2010): 789-794.

[39] Wu S.; and Zhang, Q. Solvent Effects on Structure, Morphology, and Photophysical Properties of an Azo Chromophore-Functionalized Polydiacetylene. Macromolecules 43 (2010): 6142–6151.

[40] Chen, X.; Lee, J.; Jung Jou, M. Colorimetric and fluorometric detection of cationic surfactants based on conjugated polydiacetylene supramolecules. Chem. Commun. (2009): 3434–3436.

APPENDICES

Appendix A

Appendix A: ^{1}H NMR and ^{13}C NMR spectra of synthesized diacetylene monomers

Figure A1: ^{1}H NMR; PCDAmide

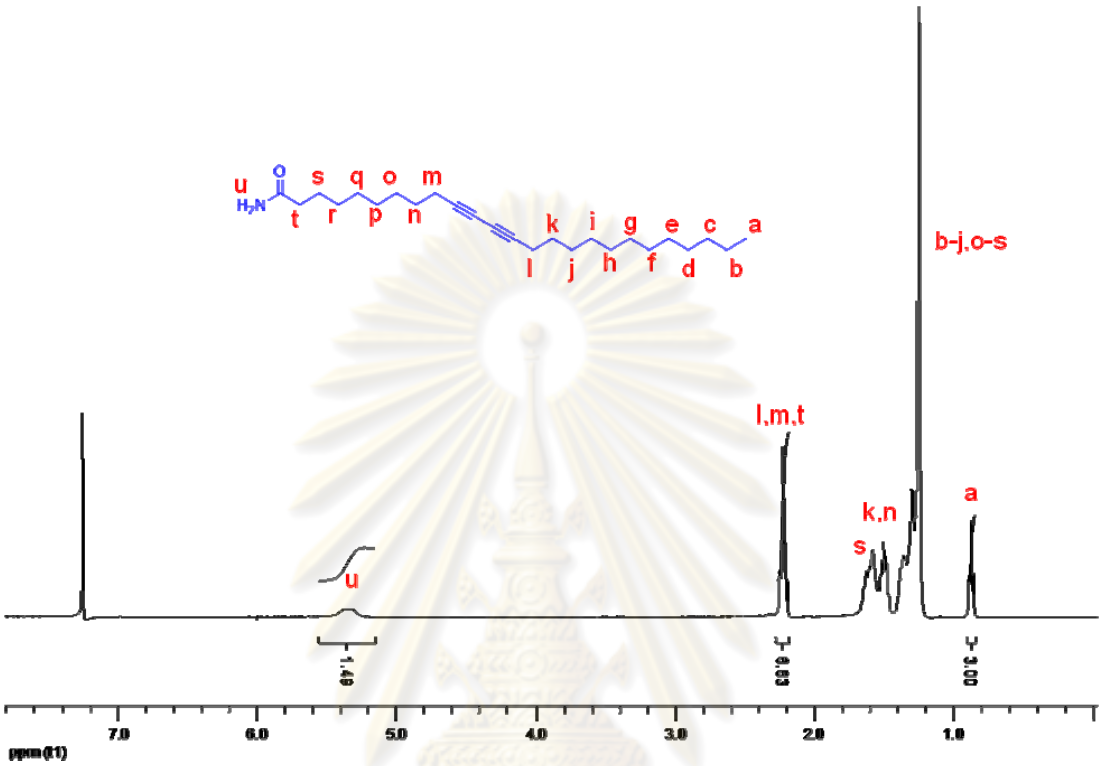


Figure A2: ^{1}H NMR; PCDAmine

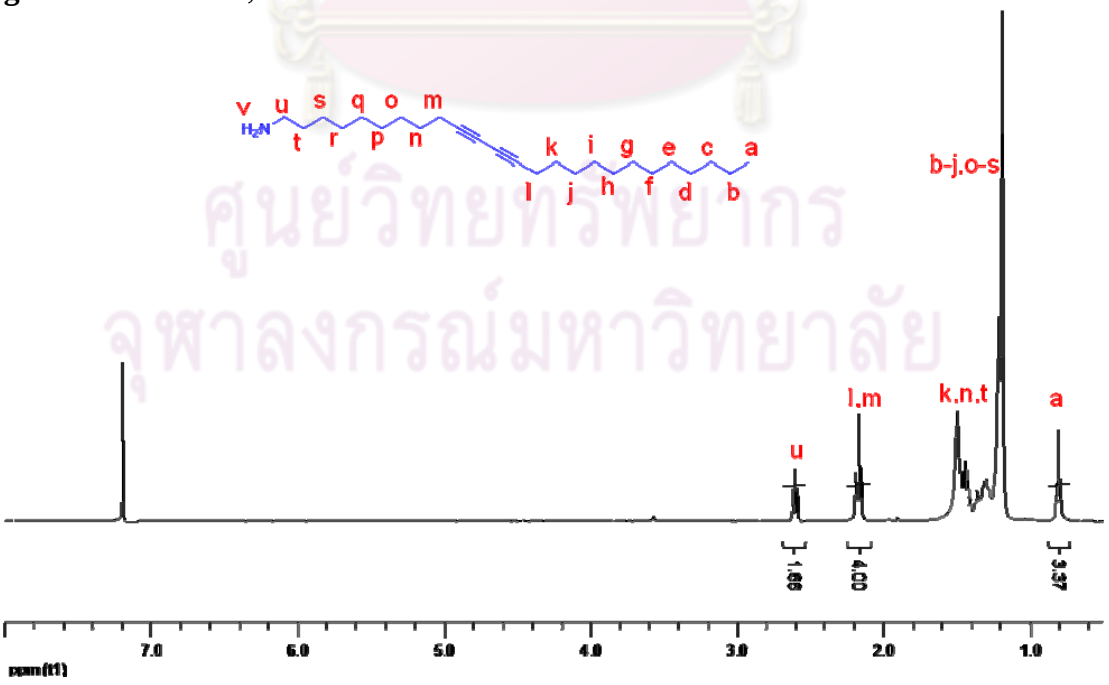


Figure A3: ^{1}H NMR; PCDAS

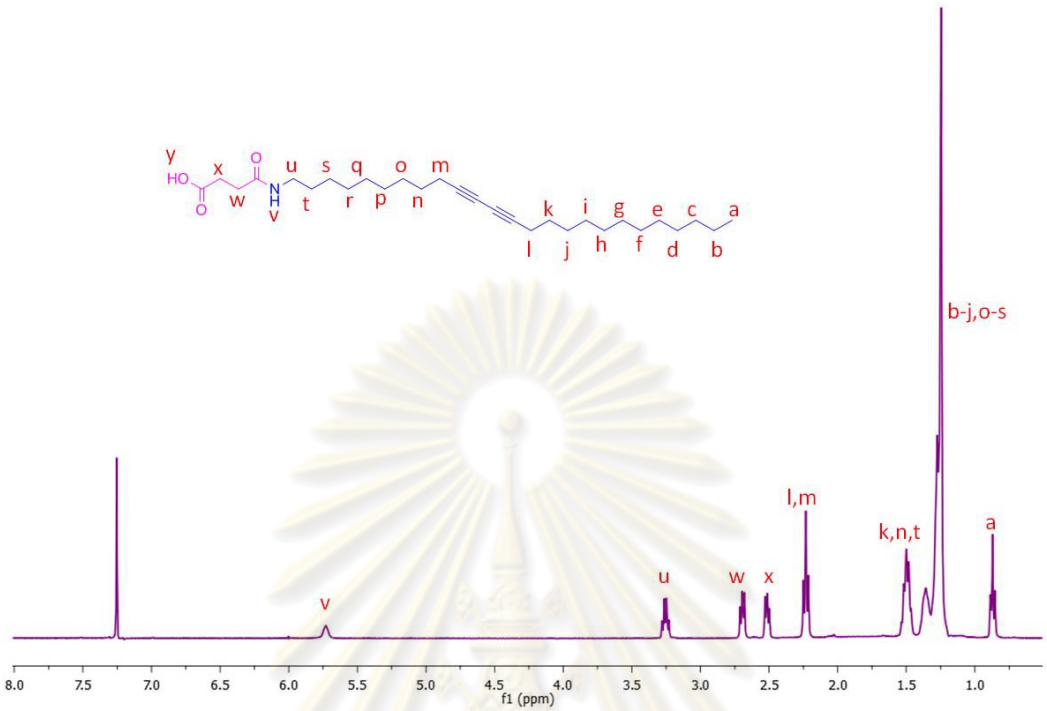


Figure A4: ^{1}H NMR; PCDAG

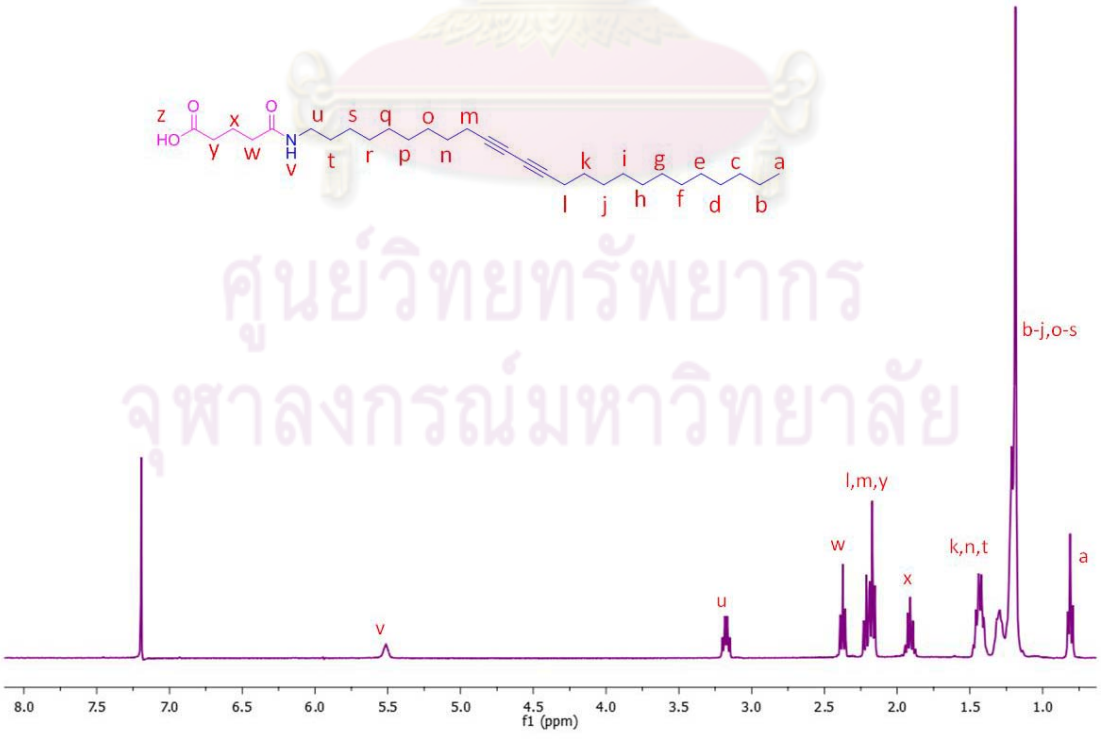


Figure A5: ^{1}H NMR; PCDAA

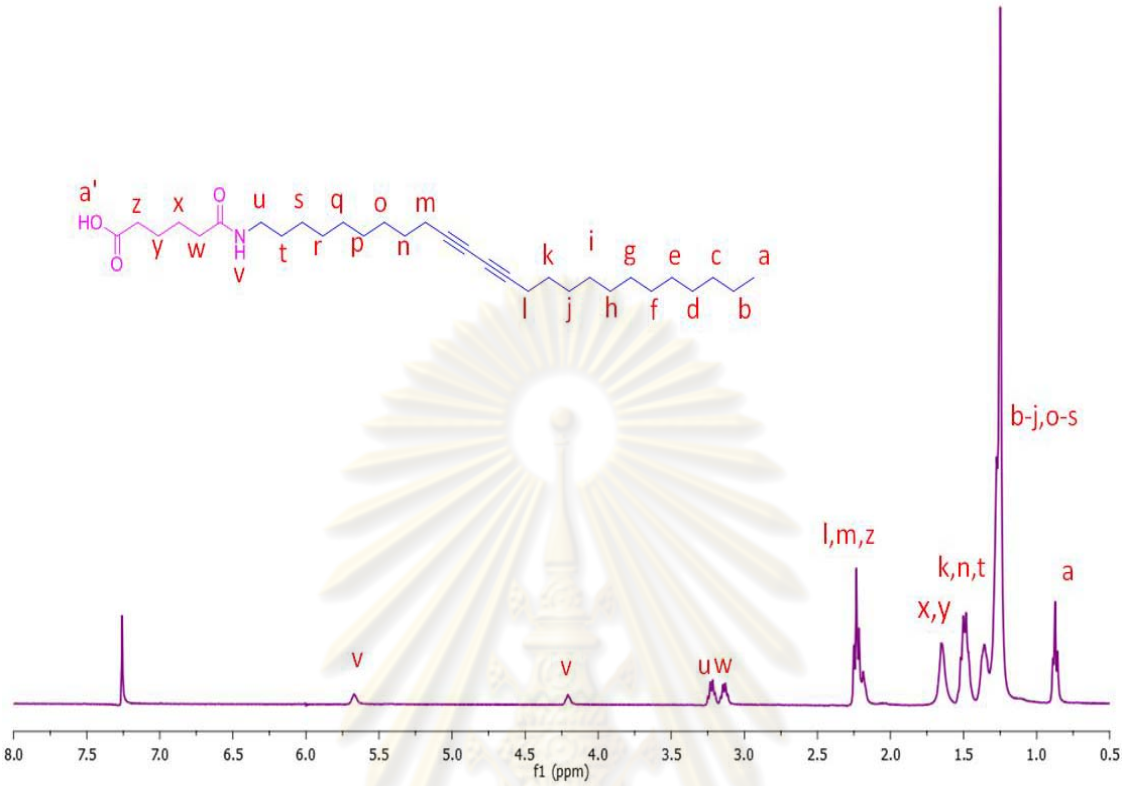


Figure A6: ^{1}H NMR; diPCDAS

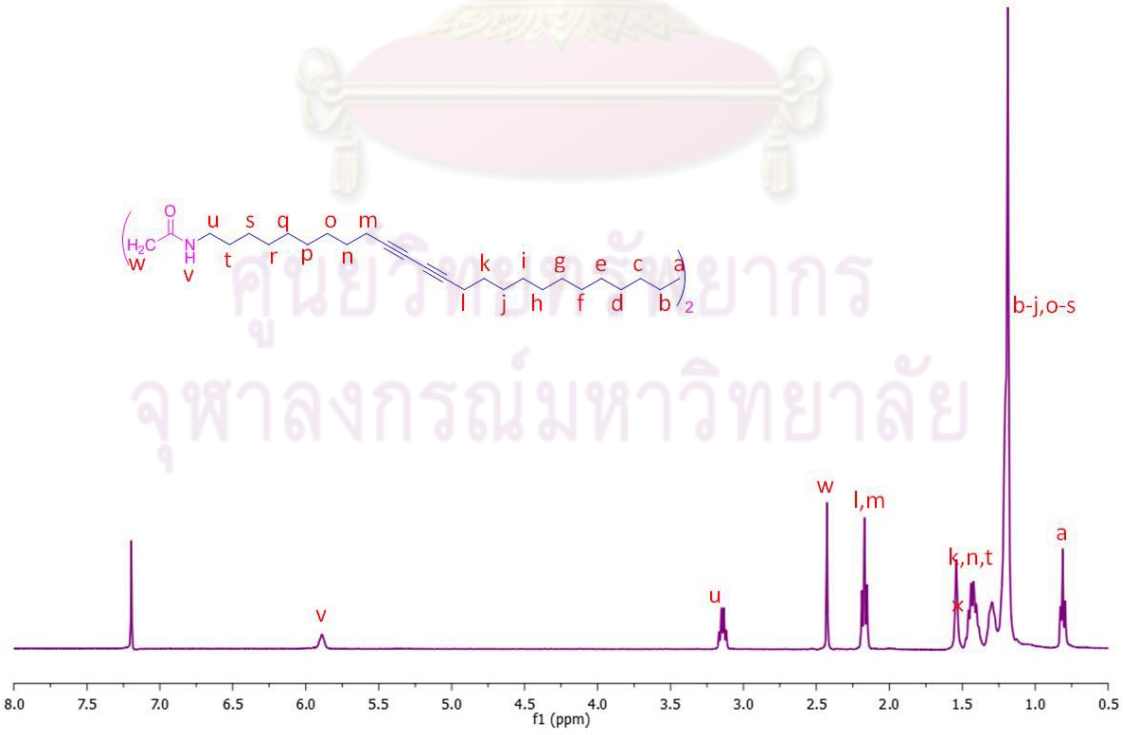


Figure A7: ^{1}H NMR; diPCDAG

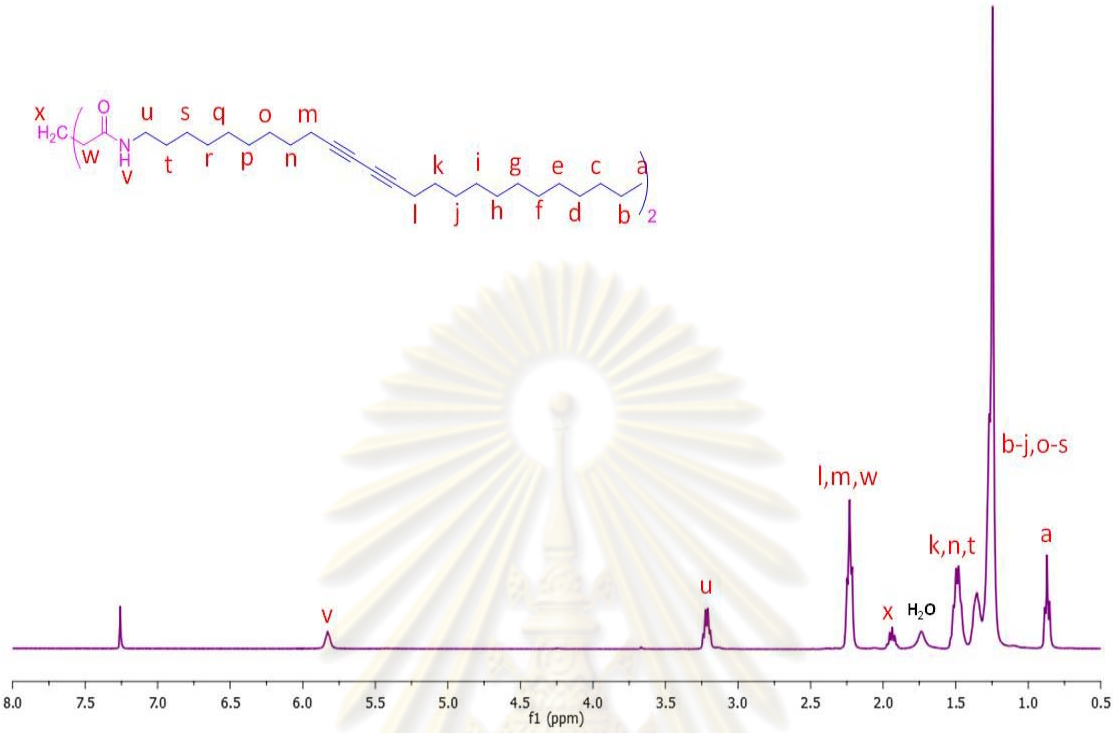


Figure A8: ^{1}H NMR; diPCDAA

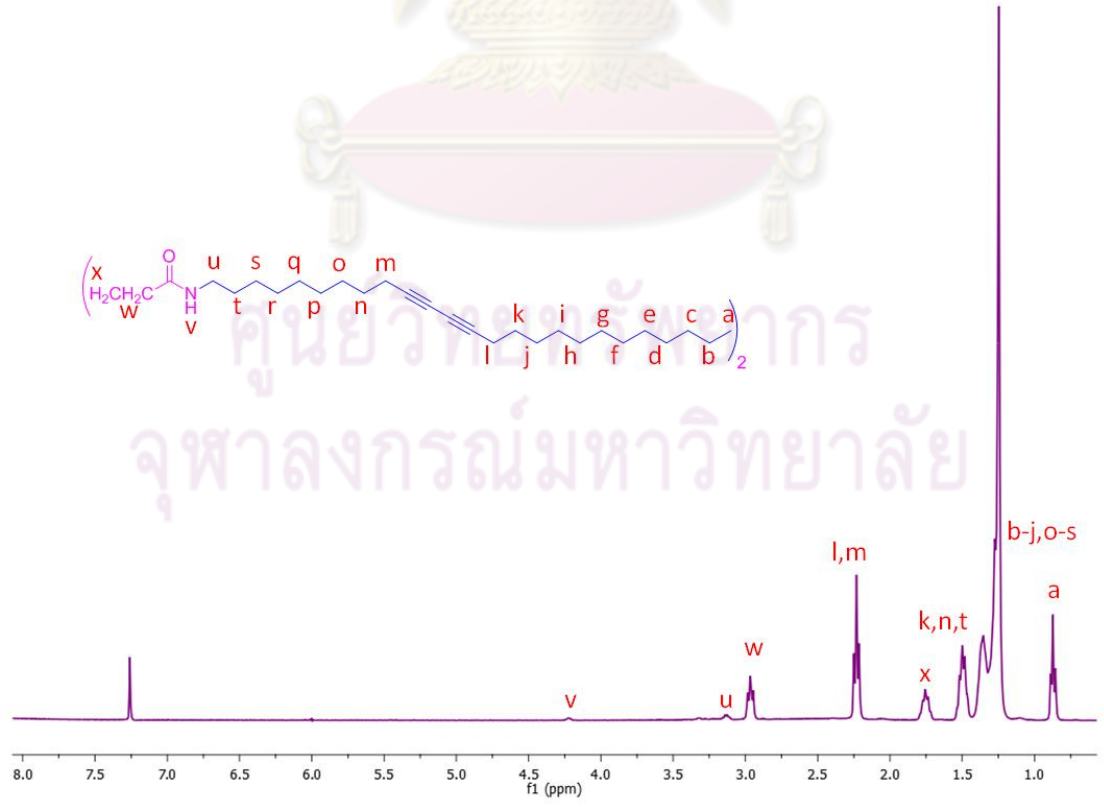


Figure A9: ^{13}C NMR; PCDAS

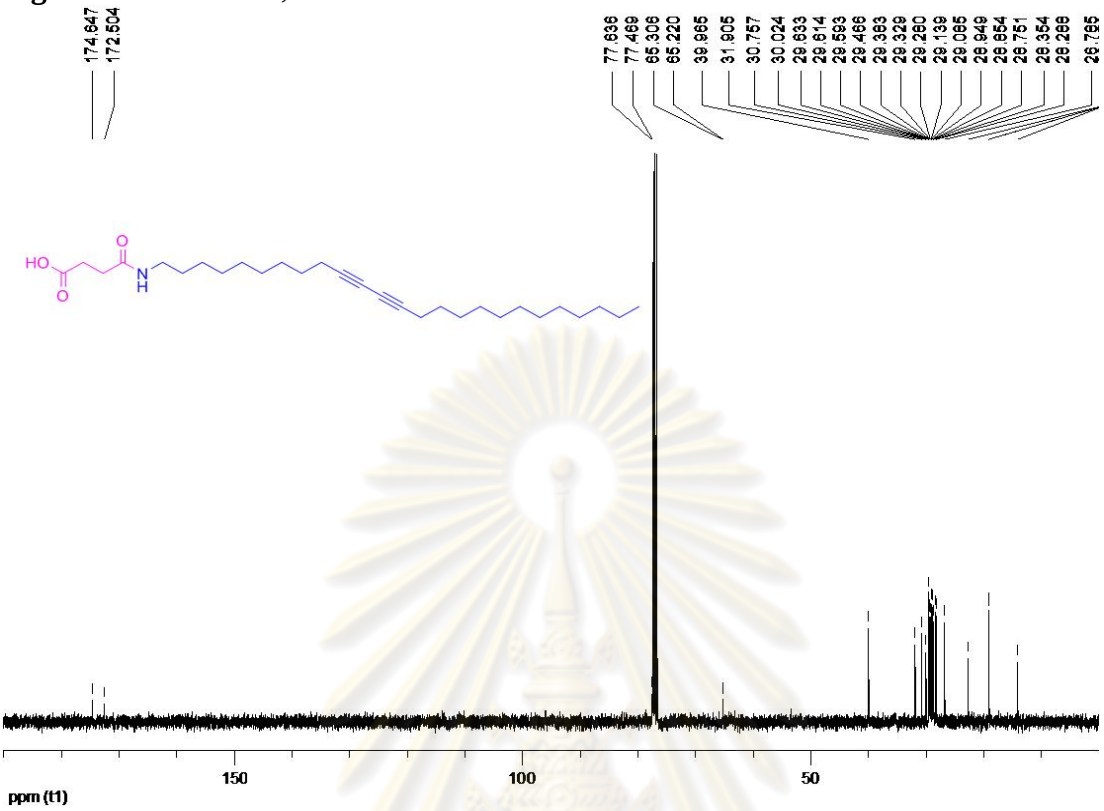


Figure A10: ^{13}C NMR; PCDAG

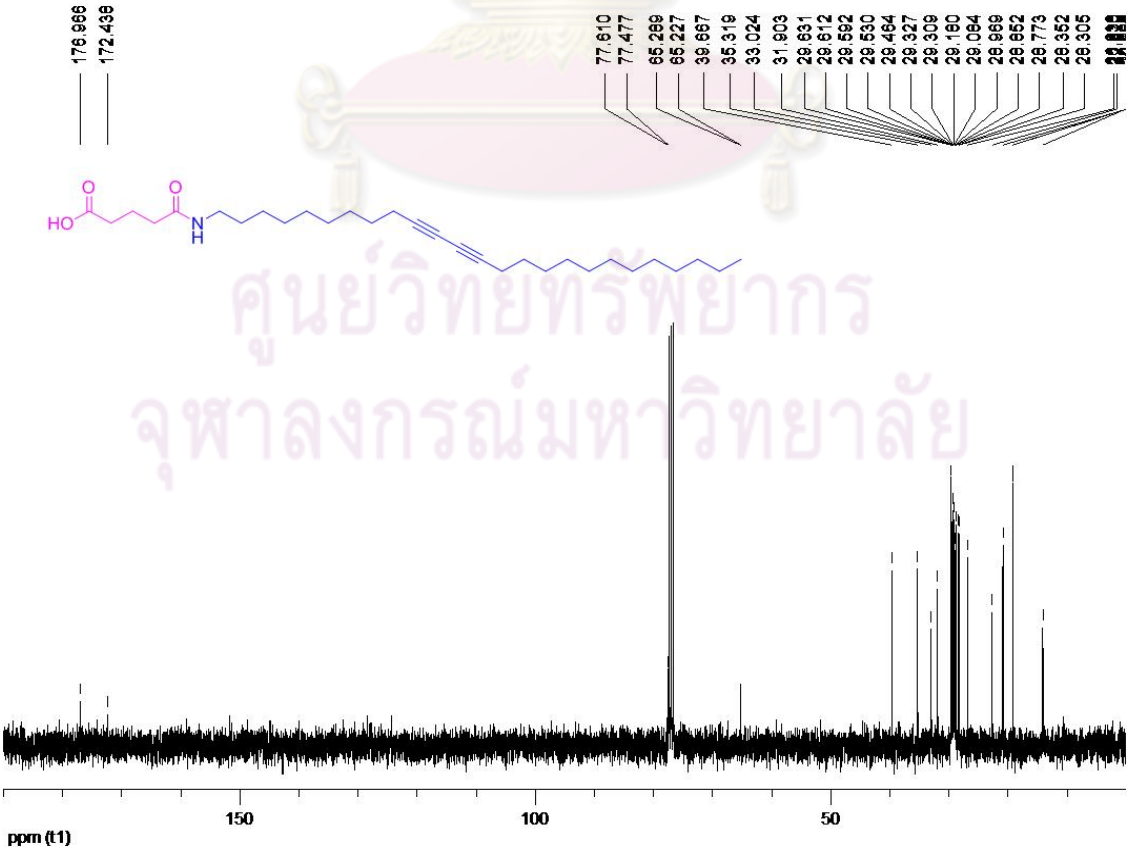


Figure A11: ^{13}C NMR; PCDAA

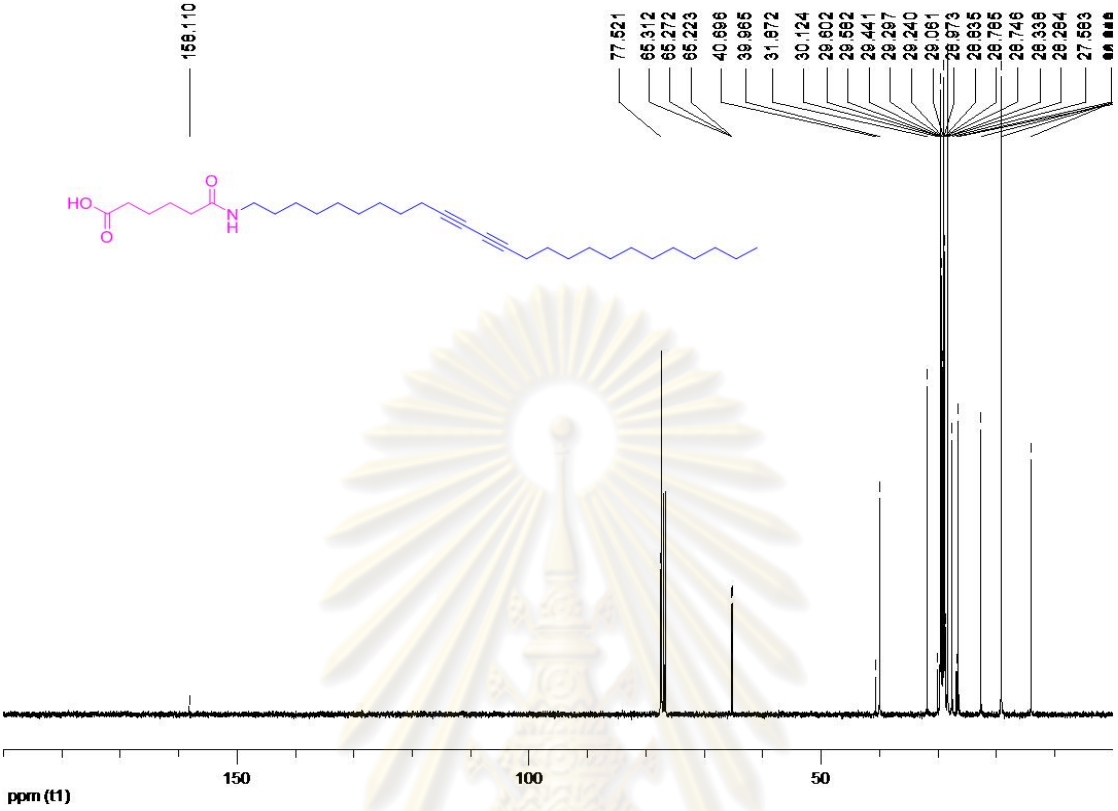


Figure A12: ^{13}C NMR; diPCDAS

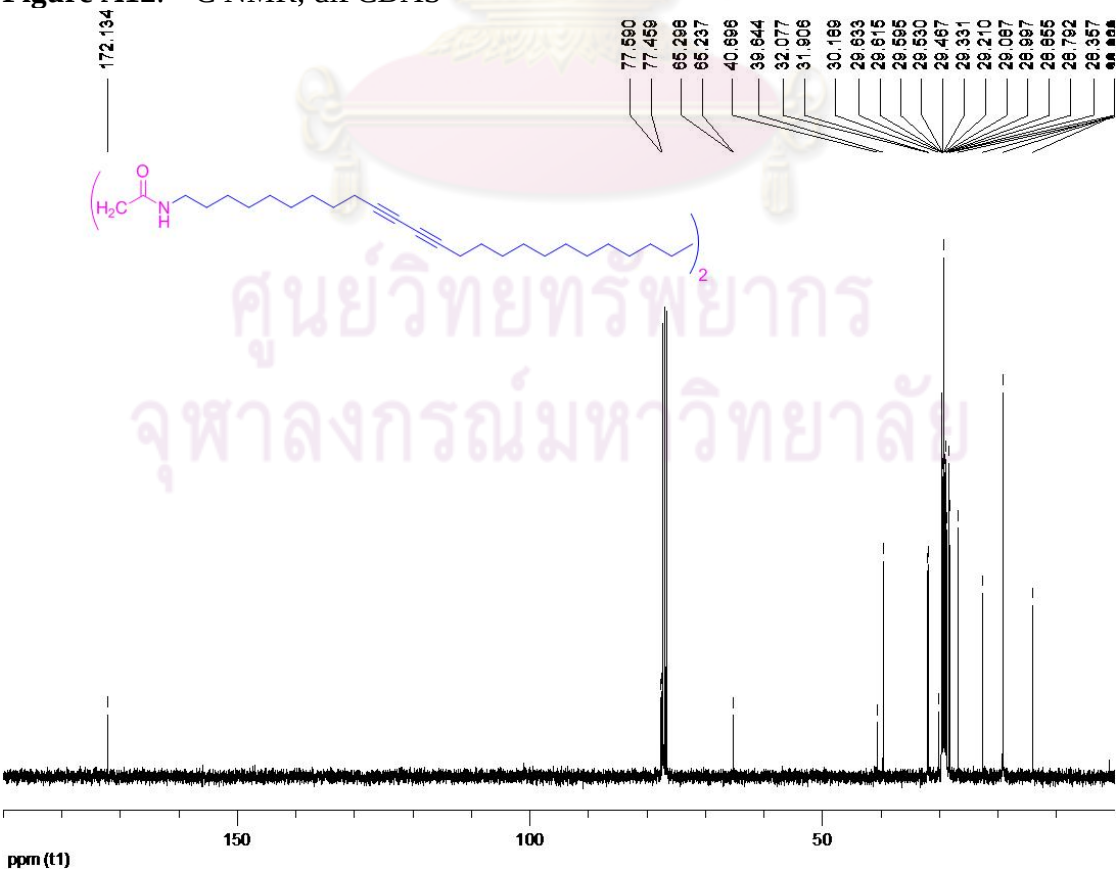


Figure A13: ^{13}C NMR; diPCDAG

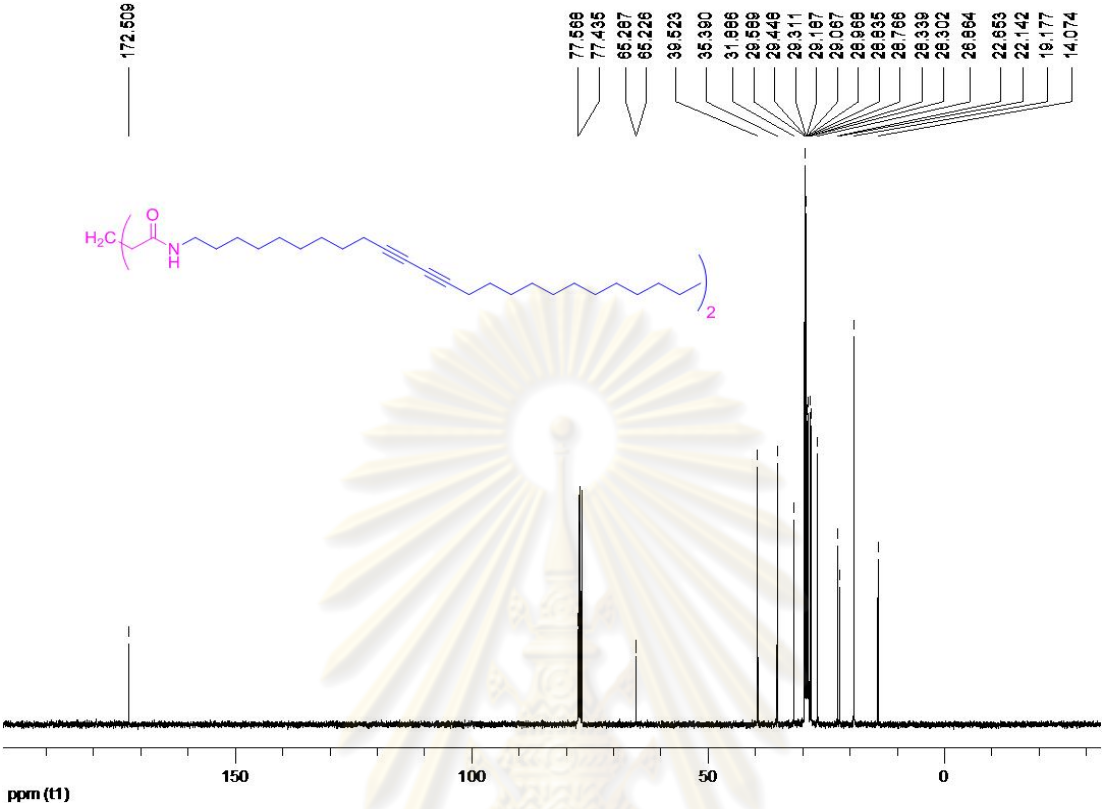
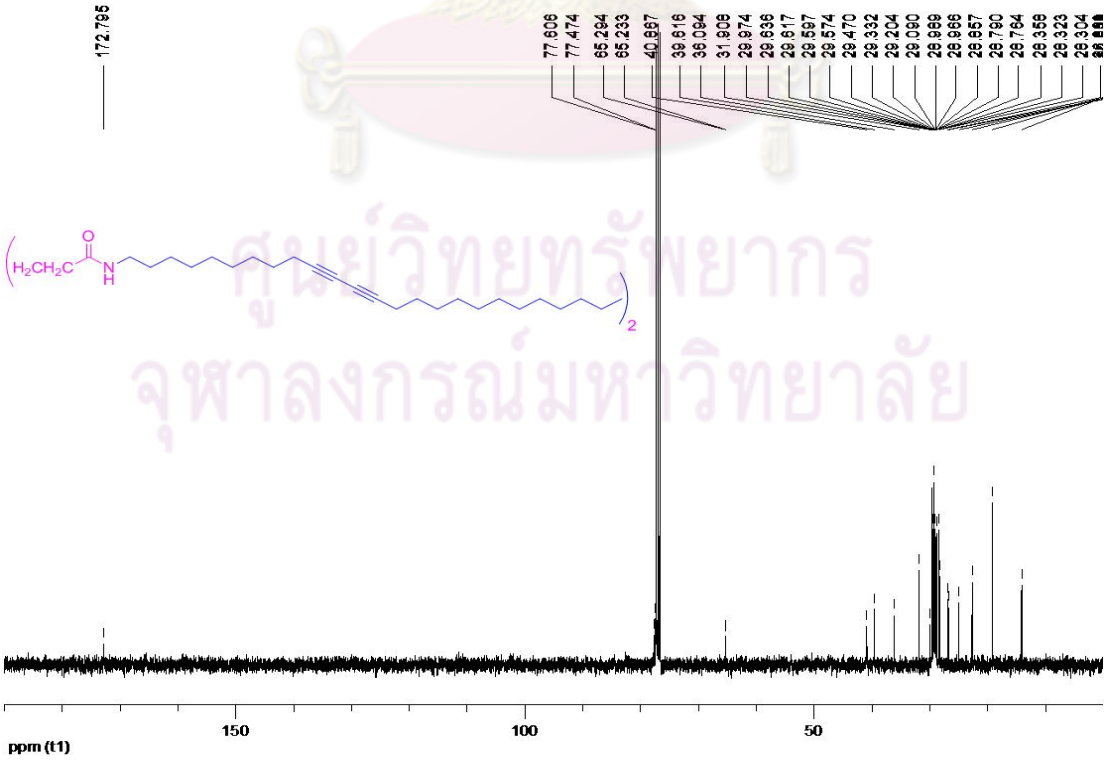


Figure A14: ^{13}C NMR; diPCDAA



Appendix B

Appendix B: ESI mass spectra of synthesized diacetylene monomers

Figure B1 : ESI mass spectra of PCDAmide

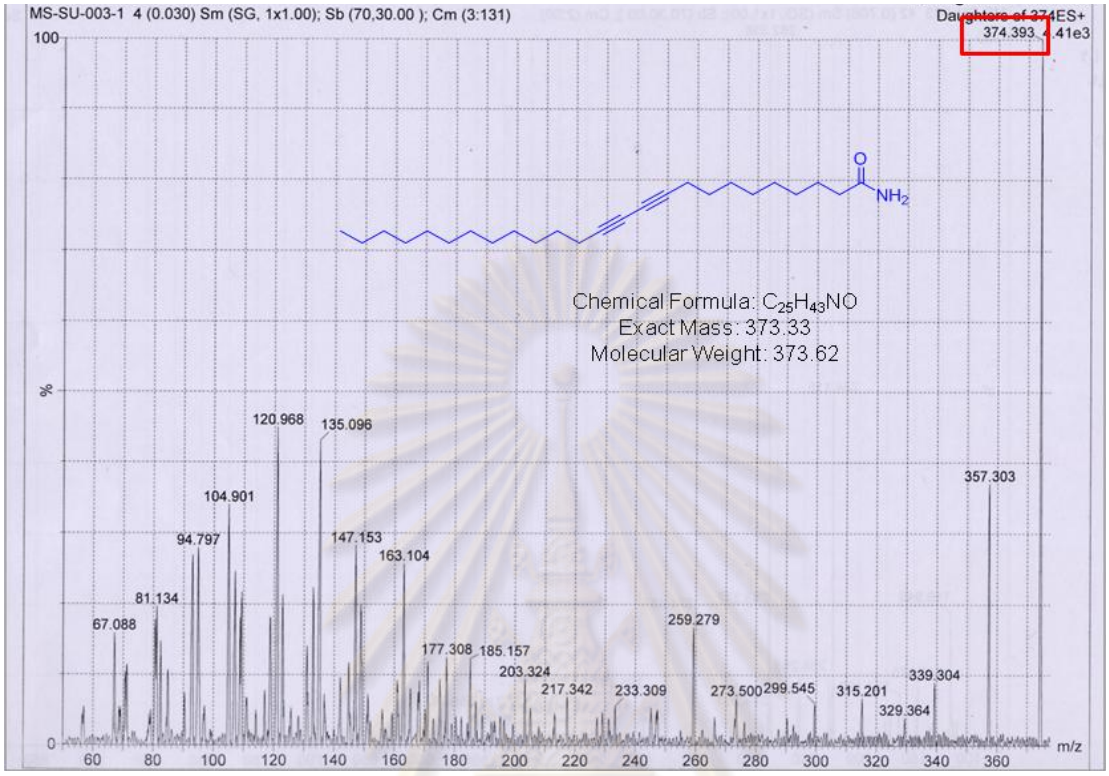


Figure B2 : ESI mass spectra of PCDAmine

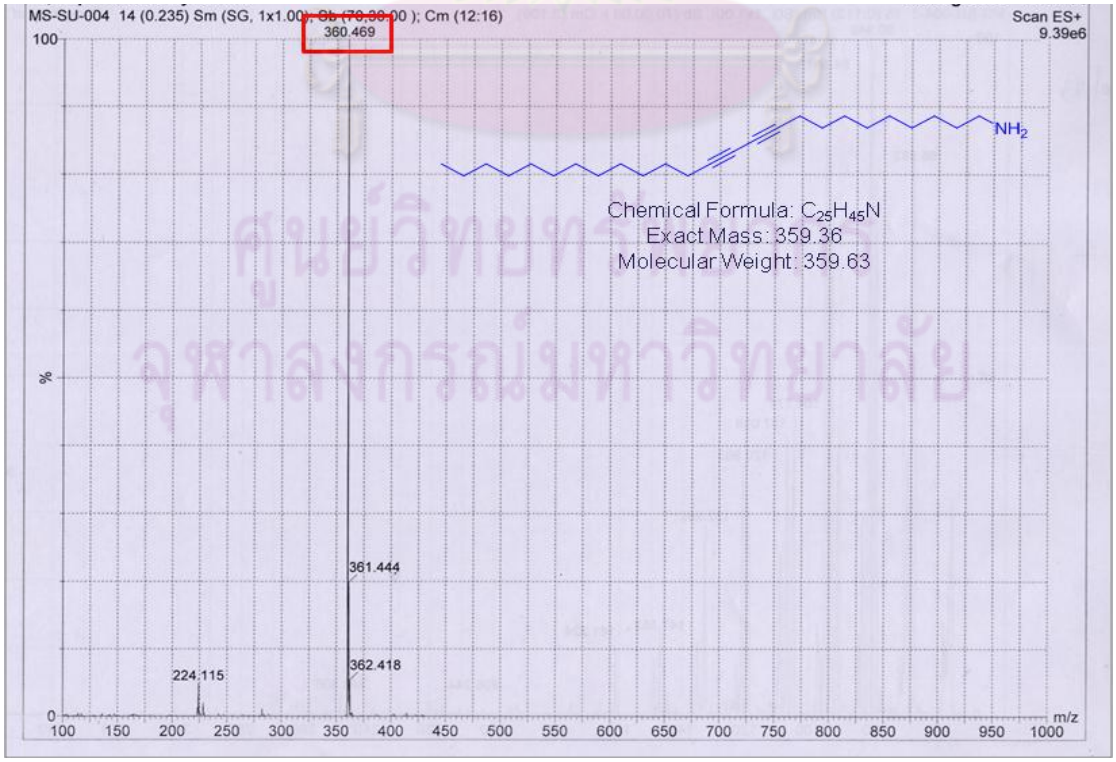


Figure B3 : ESI mass spectra of PCDAS

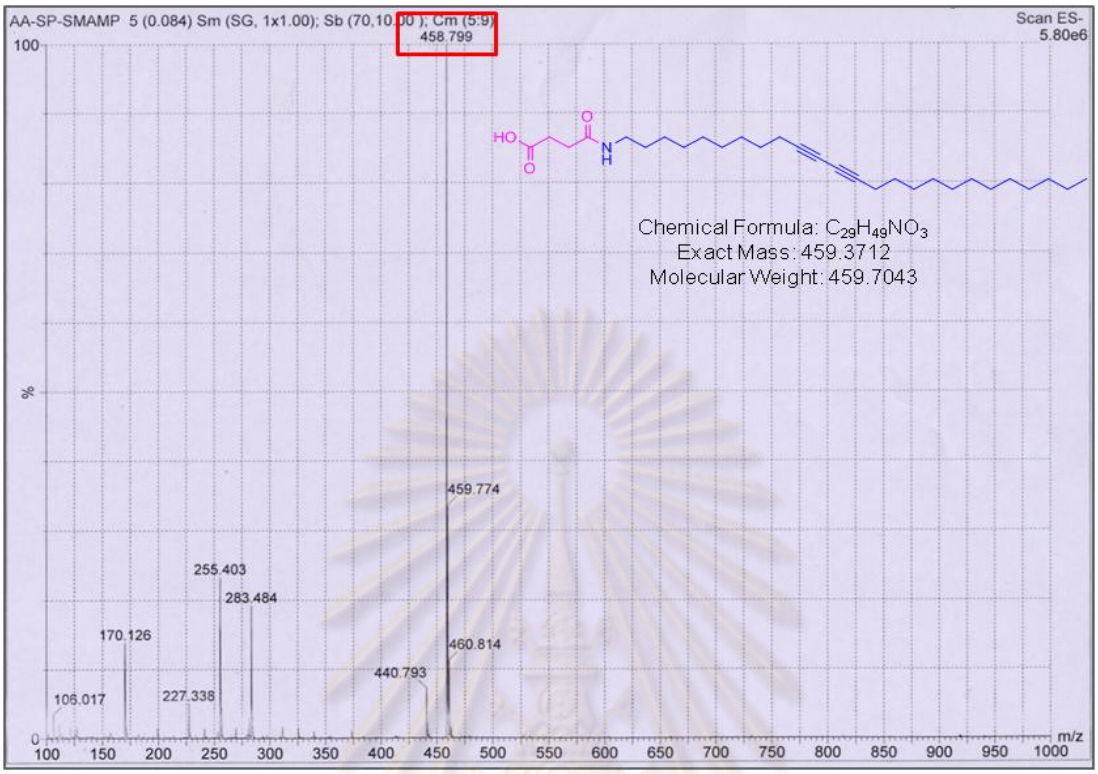


Figure B4 : ESI mass spectra of PCDAG

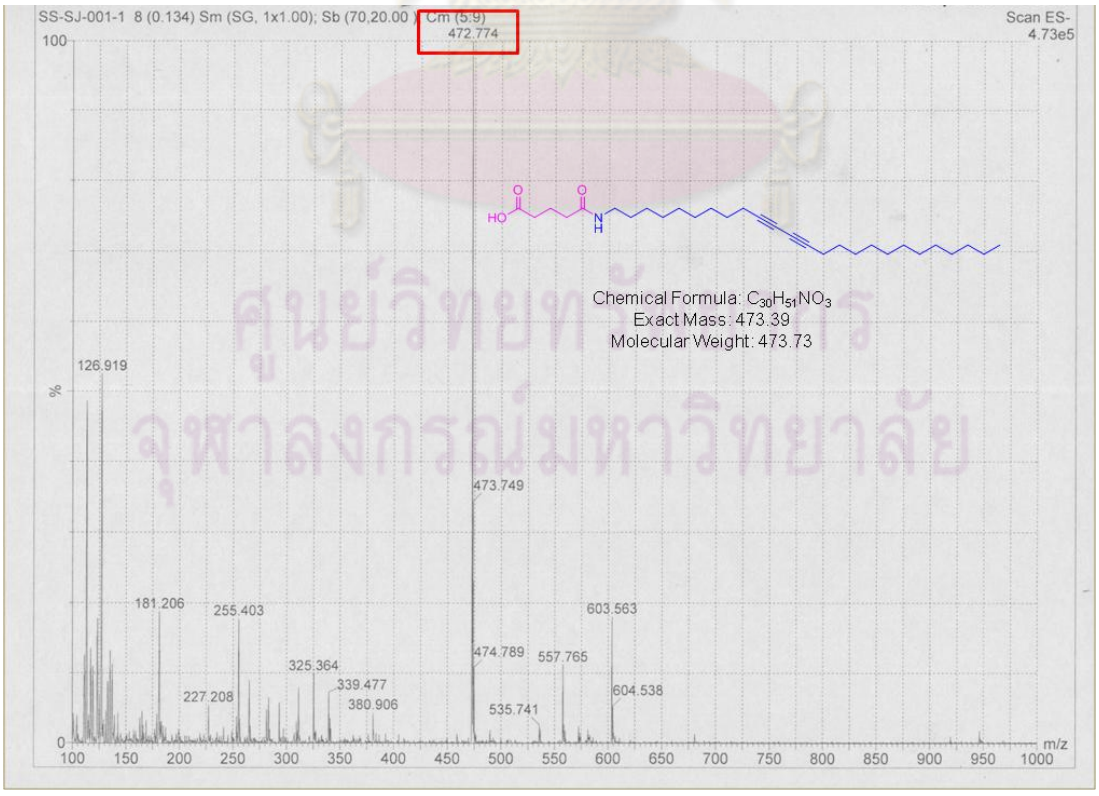


Figure B5 : ESI mass spectra of PCDAA

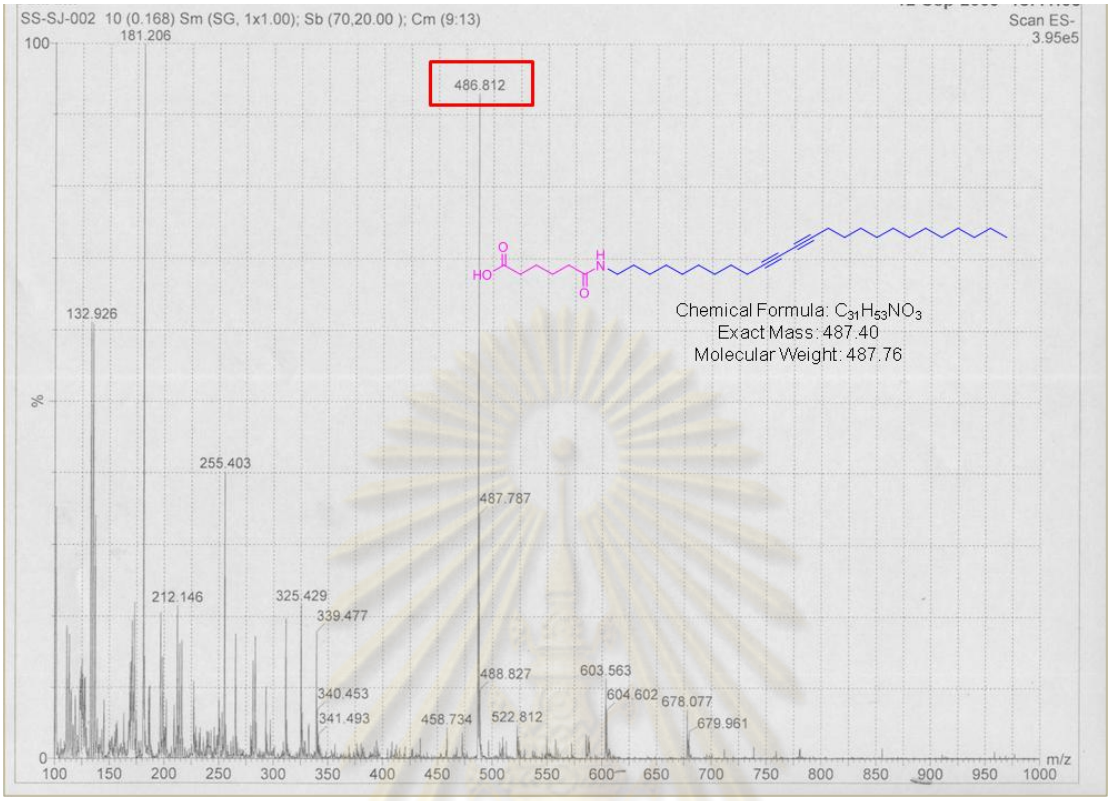


Figure B6 : ESI mass spectra of diPCDAS

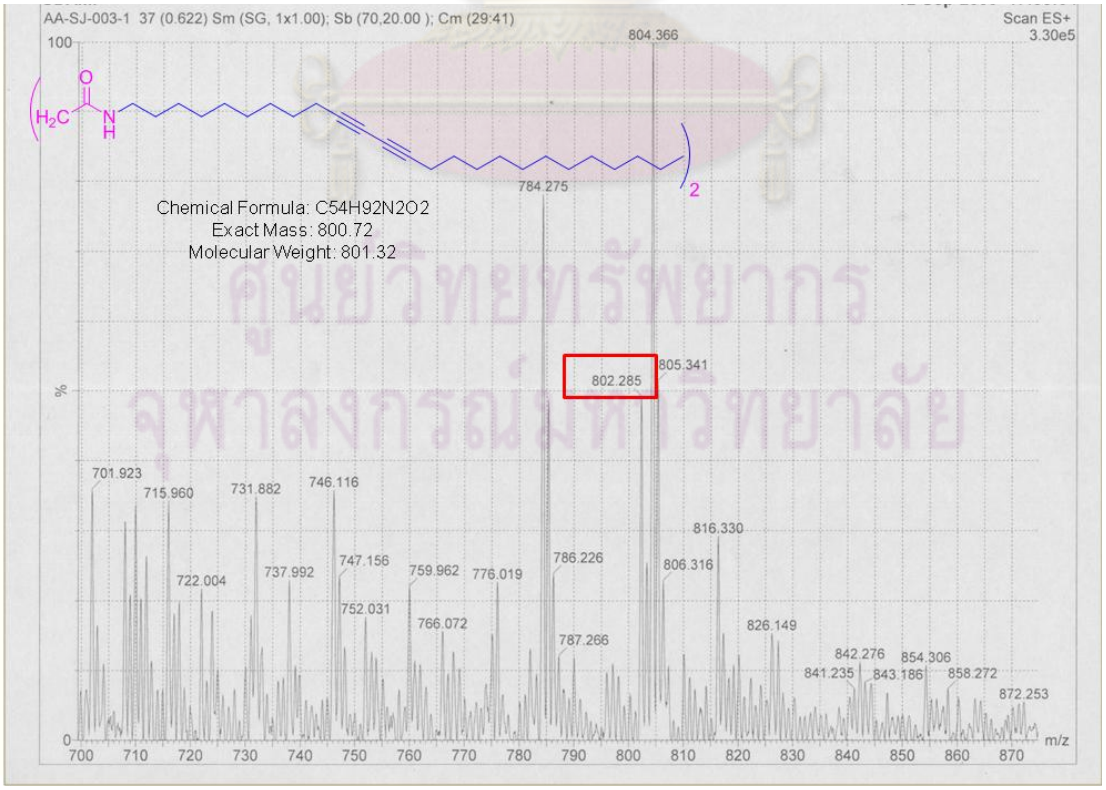


Figure B7 : ESI mass spectra of diPCDAG

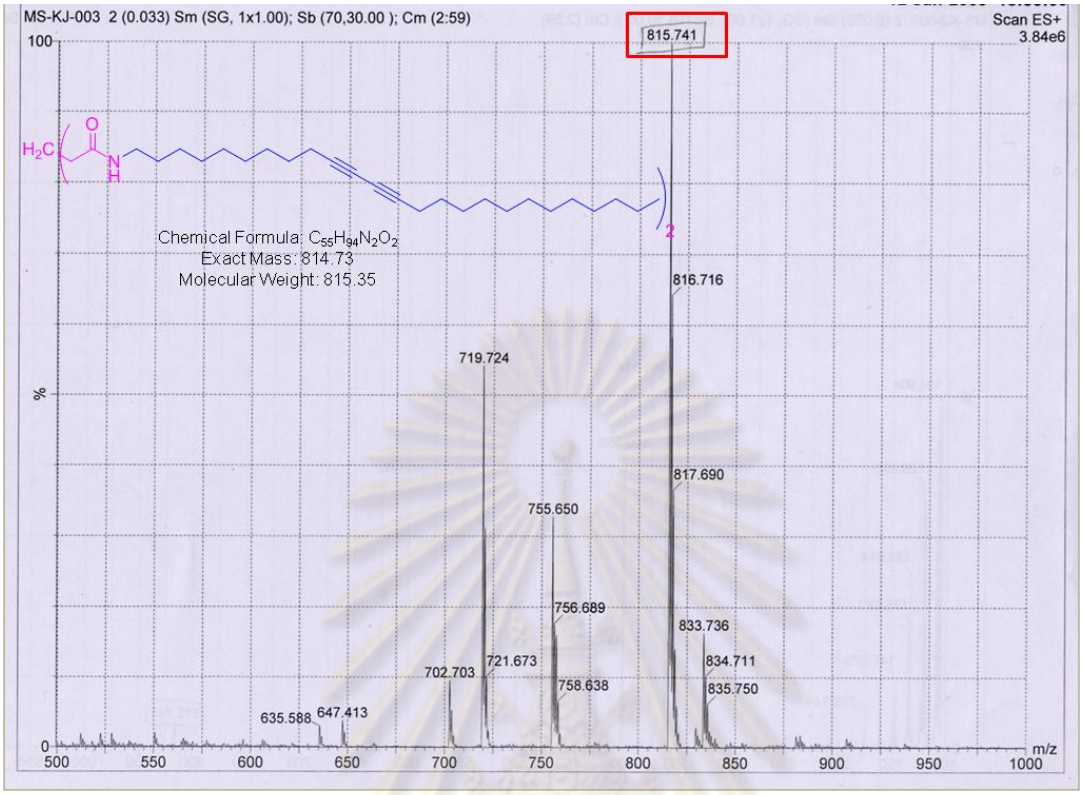
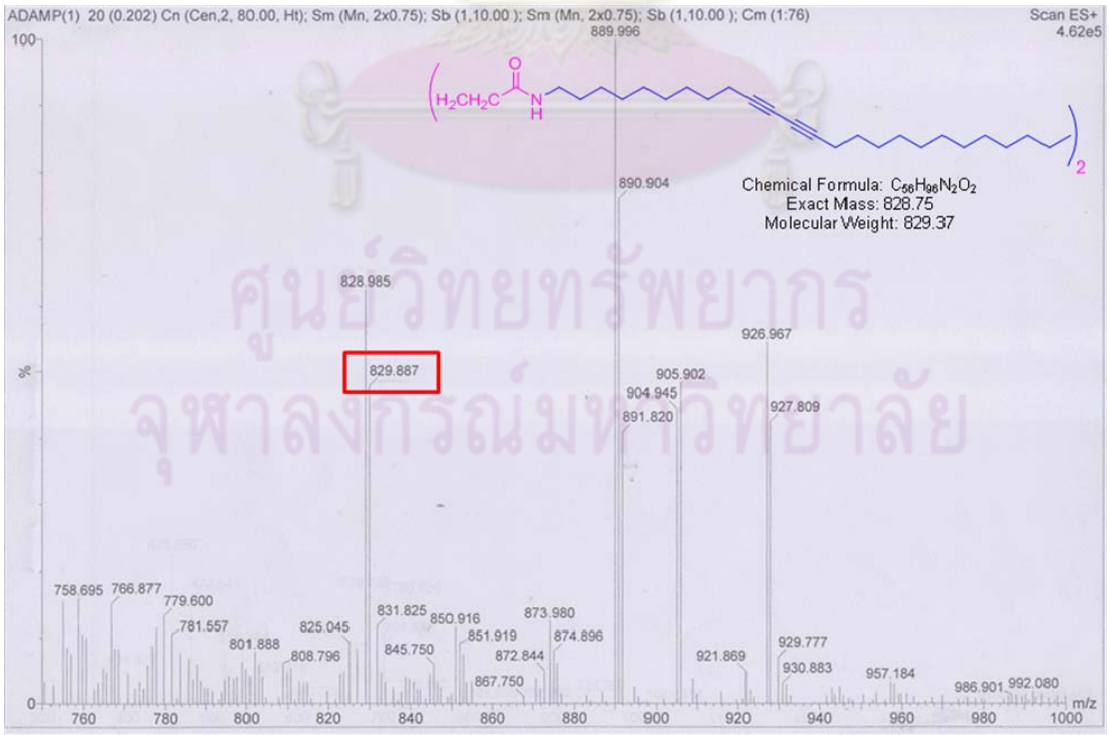


Figure B8 : ESI mass spectra of diPCDAA



Appendix C

Appendix C: Dynamic Light Scattering (DLS) of synthesized diacetylene monomers

Figure C1 : DLS of PCDAS

			Diam. (nm)	% Intensity	Width (nm)
Z-Average (r.nm):	136.2	Peak 1:	136.5	100.0	26.36
PdI:	0.101	Peak 2:	0.000	0.0	0.000
Intercept:	0.917	Peak 3:	0.000	0.0	0.000
Result quality :	Good				

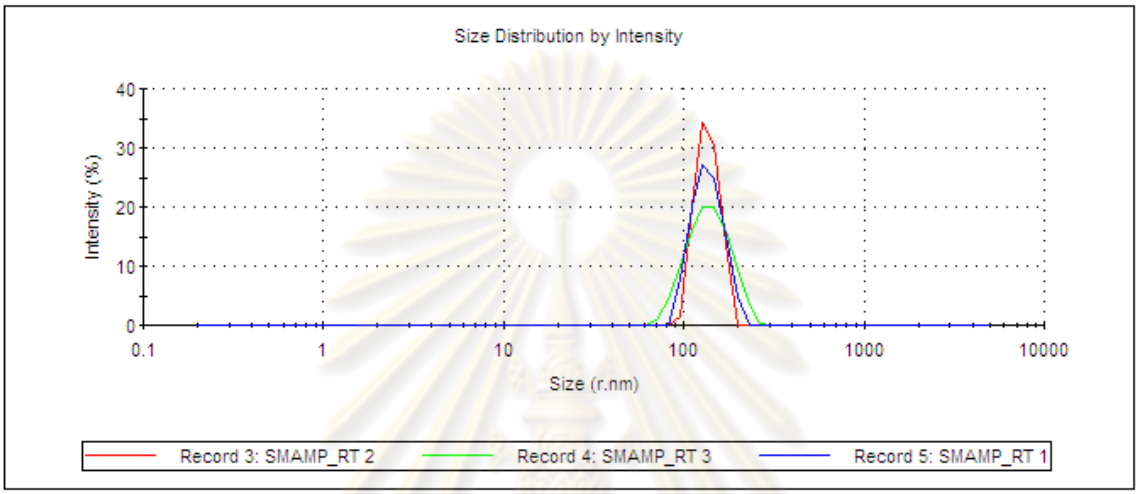


Figure C2 : DLS of PCDAG

			Diam. (nm)	% Intensity	Width (nm)
Z-Average (r.nm):	395.0	Peak 1:	353.2	100.0	46.14
PdI:	0.221	Peak 2:	0.000	0.0	0.000
Intercept:	0.863	Peak 3:	0.000	0.0	0.000
Result quality :	Good				

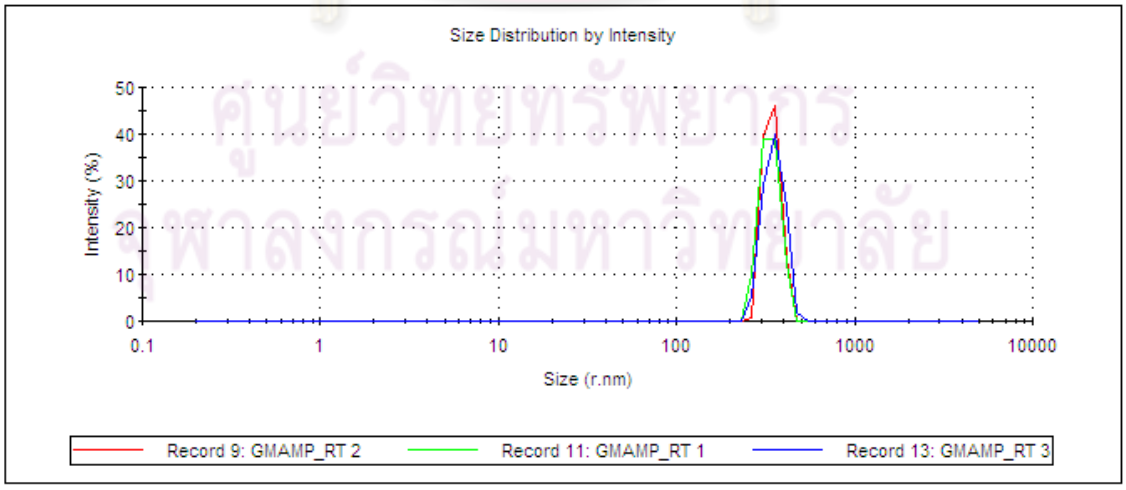


Figure C3 : DLS of PCDAA

		Diam. (nm)	% Intensity	Width (nm)
Z-Average (r.nm): 57.61	Peak 1:	73.24	90.5	26.46
PdI: 0.330	Peak 2:	17.22	9.5	2.392
Intercept: 0.931	Peak 3:	0.000	0.0	0.000
Result quality : Good				

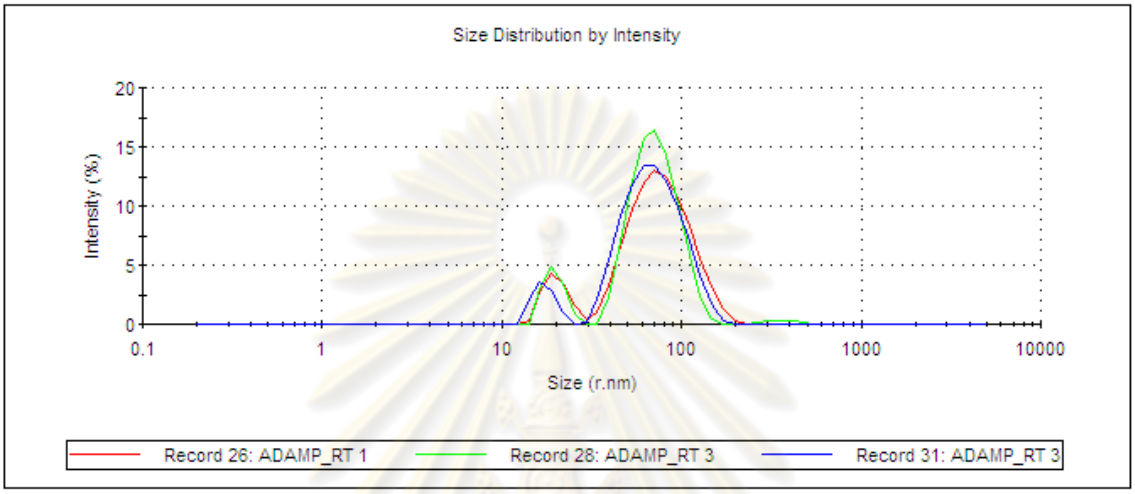


Figure C4 : DLS of diPCDAS

		Diam. (nm)	% Intensity	Width (nm)
Z-Average (r.nm): 98.52	Peak 1:	172.9	57.1	51.76
PdI: 0.343	Peak 2:	64.72	42.9	15.84
Intercept: 0.928	Peak 3:	0.000	0.0	0.000
Result quality : Good				

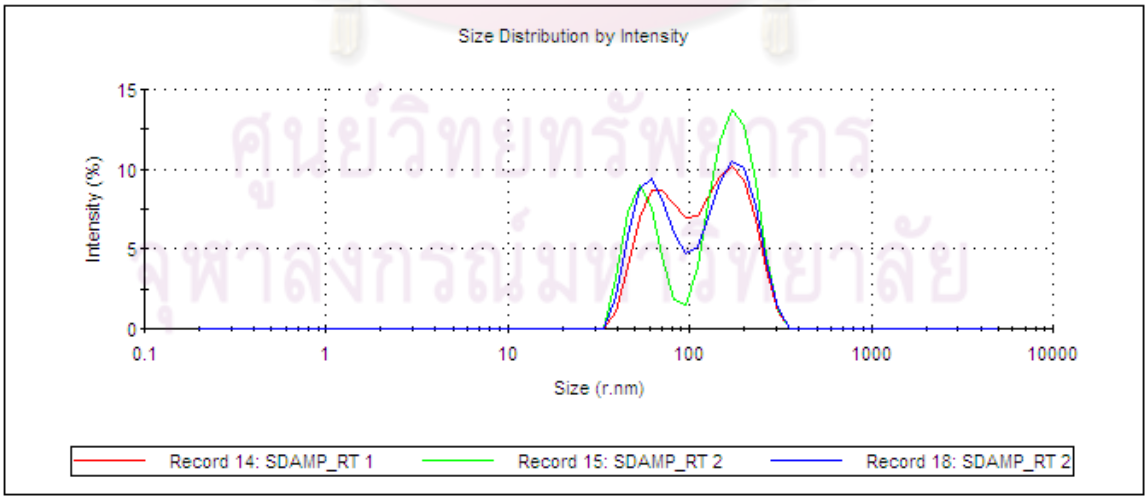


Figure C5 : DLS of diPCDAG

		Diam. (nm)	% Intensity	Width (nm)
Z-Average (r.nm): 54.69	Peak 1:	85.49	82.5	22.12
PdI: 0.391	Peak 2:	19.06	17.5	3.183
Intercept: 0.893	Peak 3:	0.000	0.0	0.000
Result quality : Good				

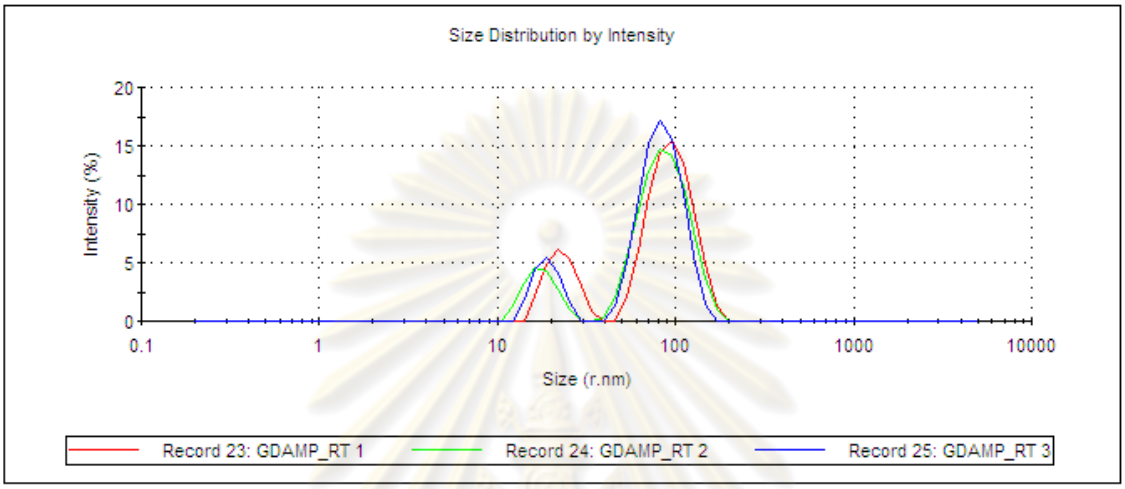
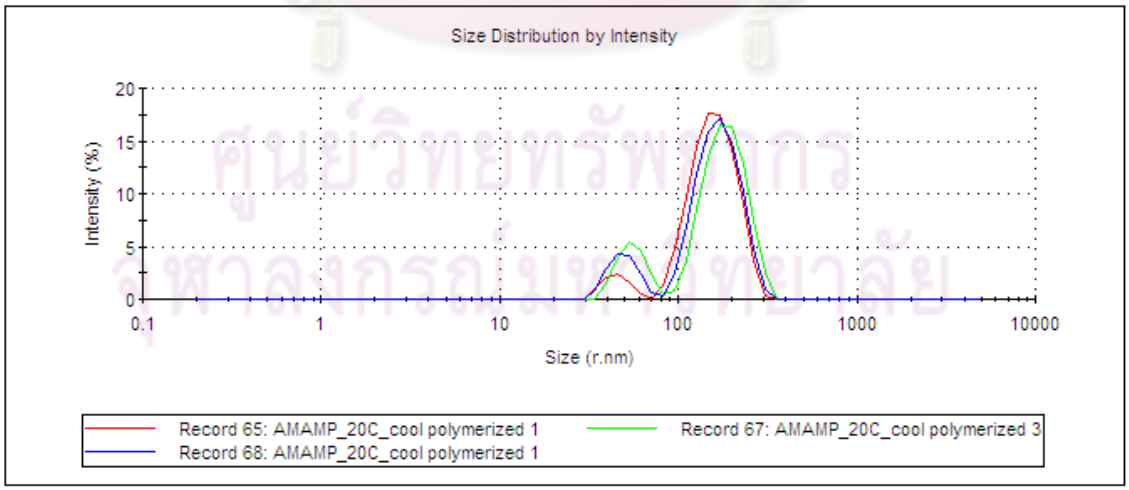


Figure C6 : DLS of diPCDAA

		Diam. (nm)	% Intensity	Width (nm)
Z-Average (r.nm): 127.8	Peak 1:	171.9	84.8	45.79
PdI: 0.258	Peak 2:	49.88	15.2	9.869
Intercept: 0.890	Peak 3:	0.000	0.0	0.000
Result quality : Good				



Appendix D

Appendix D: UV-vis Spectra of of synthesized diacetylene monomers

Figure D1 : Preparation of PDA sols

pH	PDAs		
	PCDAmine	PCDAS	PCDAG
Normal(6.2-6.8)			
2		ND	ND
3		ND	ND
4		ND	ND
5		ND	ND
6		ND	ND
8	ND		
9	ND		
10	ND		

Figure D2 : UV-vis spectra of poly(PCDAmine) (pH2)

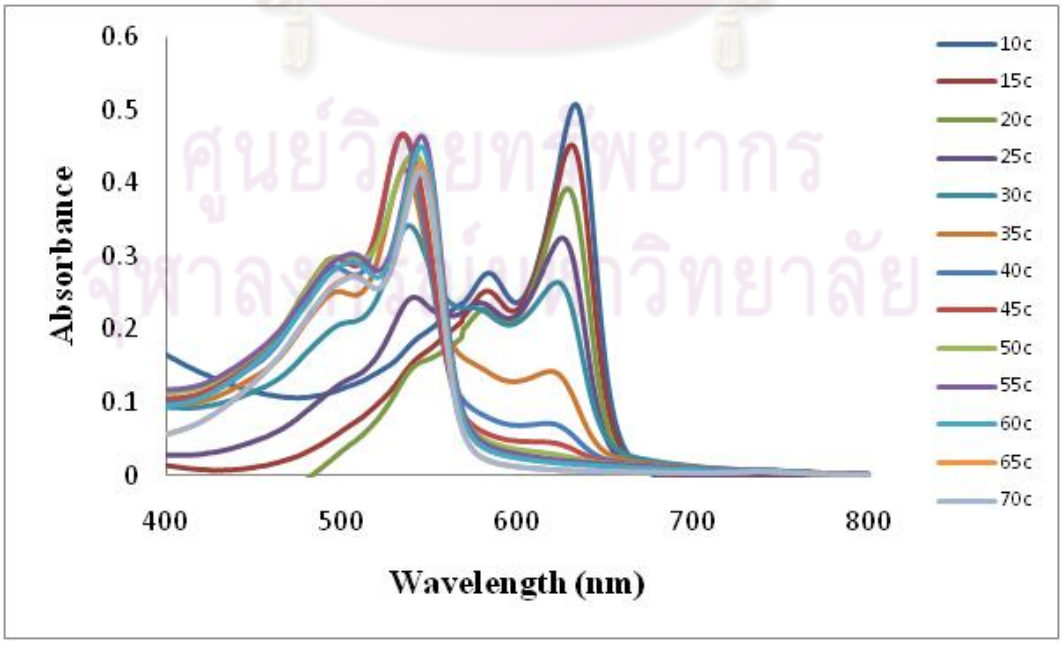
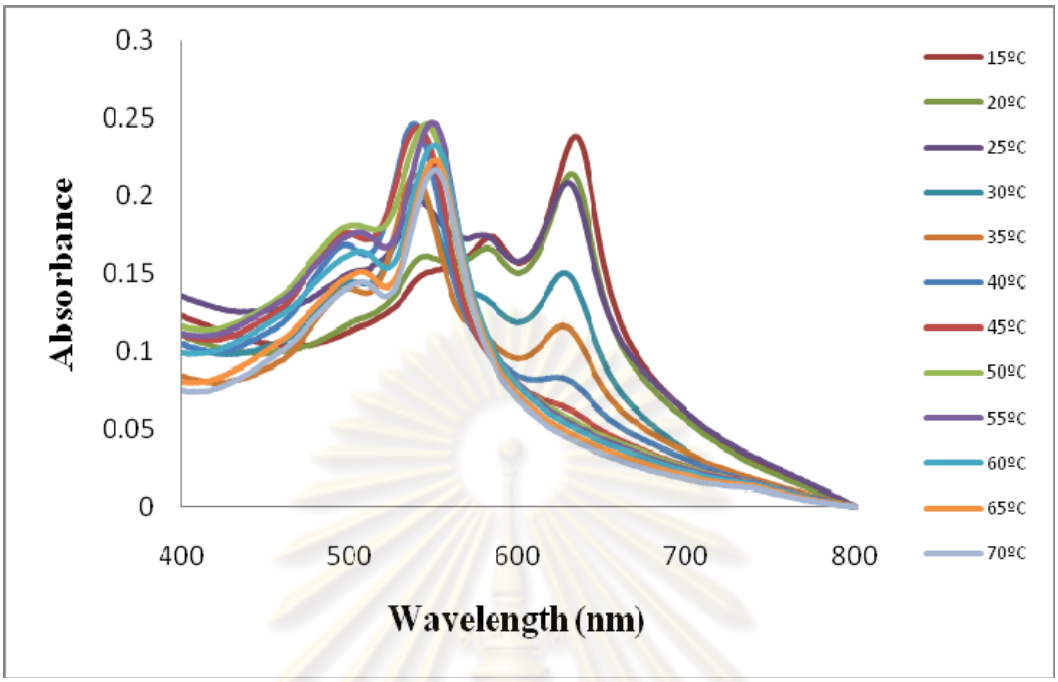


Figure D3 : UV-vis spectra of poly(PCDAmine) (pH4)



Appendix E

Figure E1 : Metal sensing of PDAs

PDAs monomer concentration 0.5% w/v in THF, Polymerized time 2 min, Deeping time 5 min, Metal ion concentration 1mM

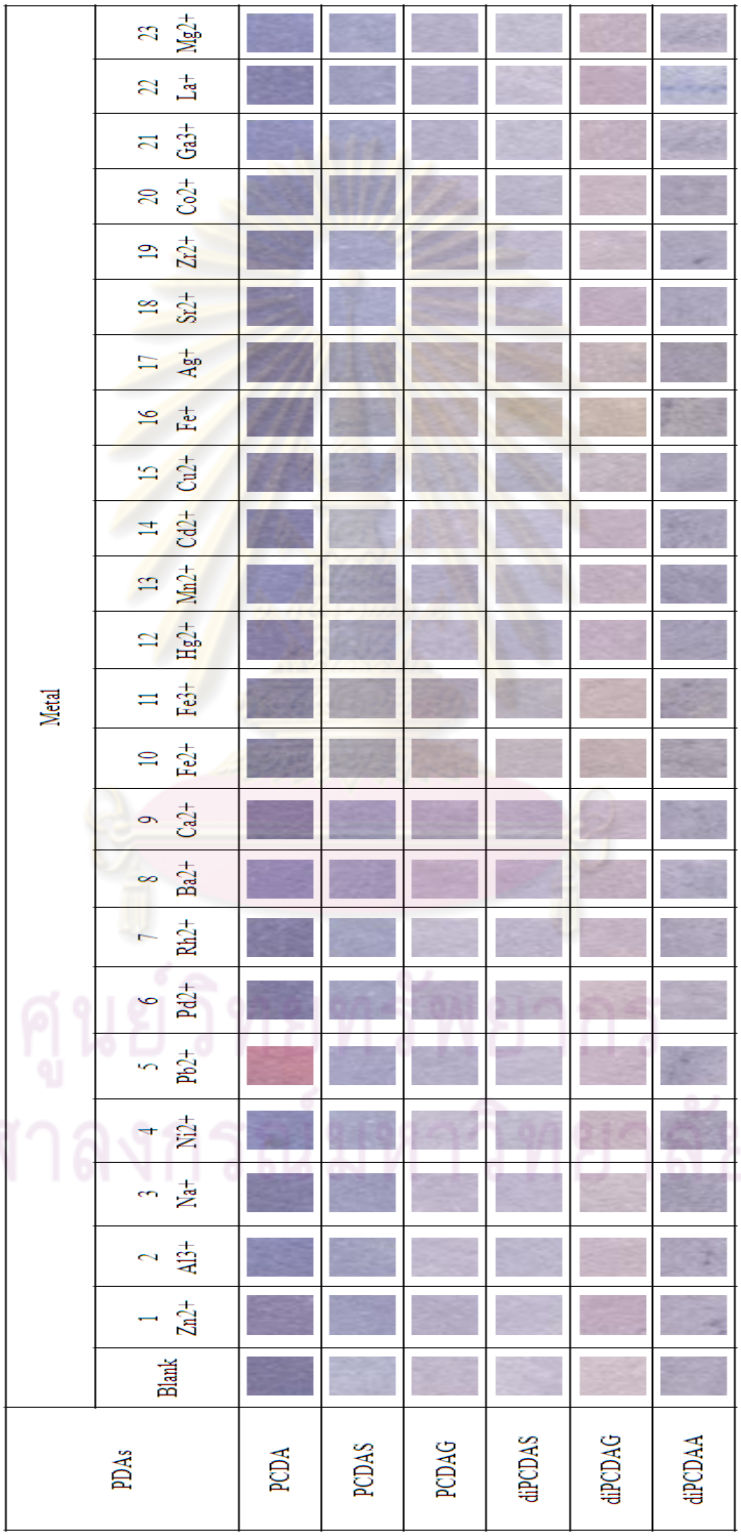


Figure E2 : Solvent sensing of PDAs

PDAs monomer concentration 2.0% w/v in THF, Polymerized time 2 min, Deeping time 5 min

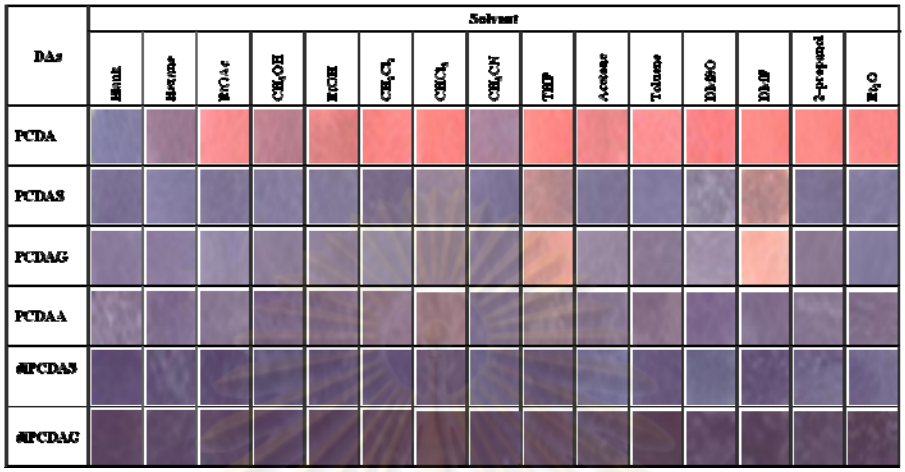
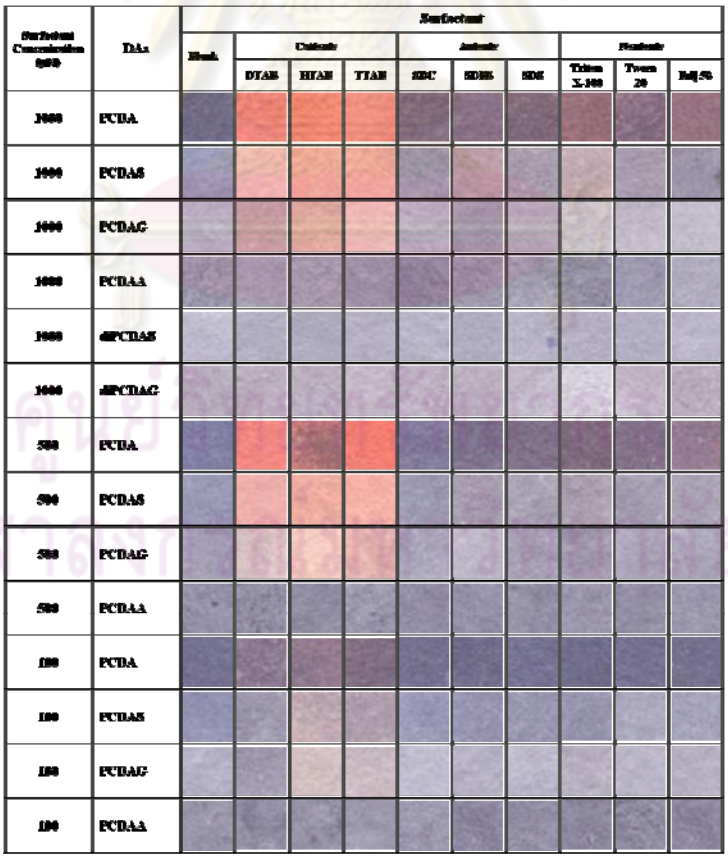


Figure E3 : Surfactant sensing of PDAs

PDAs monomer concentration 0.25% w/v in THF, Polymerized time 2 min, Deeping time 5 min



VITAE

Suricha Pumtang was born on June 14th, 1984 in Sukhothai, Thailand. She received a Bachelor's Degree of Science, majoring in Chemistry from Faculty of Science, Naresuan University in 2006. Since 2007, she has been a graduate student studying Petrochemistry and Polymer Science as her major course from Faculty of Science, Chulalongkorn University and completed the program in academic year of 2010.

Her present address is 9 M.5, Samraun, Srisumrong, Sukhothai, Thailand 64120.