พอลิไดอะเซทิลีนที่มีหมู่เอไมด์และสมบัติการเปลี่ยนสี

นายสุริยกมล มณฑา

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2551

POLYDIACETYLENE CONTAINING AMIDE GROUPS AND THEIR CHROMISM PROPERTIES

Mr.Suriyakamon Montha

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 2008

Thesis Title	POLYDIACETYLENE CONTAINING AMIDE GROUPS AND THEIR CHROMISM PROPERTIES
By	Mr.Suriyakamon Montha
Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Associate Professor Mongkol Sukwattanasinitt, Ph.D.
Thesis Co-Advisor	Sumrit Wacharasindhu, 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
(Assistant Professor Supot Hannongbua, Ph.D.)

THESIS COMMITTEE

……………………………………...Chairman
(Assistant Professor Warinthorn Chavasiri, Ph.D.)

………………………………………Thesis Advisor
(Associate Professor Mongkol Sukwattanasinitt, Ph.D.)

………………………………………Thesis Co-Advisor
(Sumrit Wacharasindhu, Ph.D.)

……………………………………….Examiner
(Assistant Professor Varawut Tangpasuthadol, Ph.D.)

……………………………………….External Examiner
(Assistant Professor Rakchart Traiphol, Ph.D.)

สุริยกมล มณฑา : พอลิไดอะเซทิลีนที่มีหมู่เอไมด์และสมบัติการเปลี่ยนสี.
(POLYDIACETYLENE CONTAINING AMIDE GROUPS AND THEIR
CHROMISM PROPERTIES) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร.มงคล สุขวัฒนาสินิทธิ์,
อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: อ.ดร.สัมฤทธิ์ วัชรสินธุ์, 66 หน้า.

ไดอะเซทิลีนลิปิดถูกเตรียมจากการควบแน่นระหว่าง 10, 12-pentacosadiynoic acid (PCDA) กับ สารประกอบไดเอมีนโดยใช้ 1-ethyl-3-(3′-dimethylamino)carbodiimide hydrochloride salt เป็นรีเอเจนต์ควบแน่น เมื่อใช้สารประกอบไดเอมีนมากเกินพอจะได้รับไดอะเซทิลีนที่มี 1 หมู่เอไมด์ในปริมาณผลผลิตปานกลาง (47-55 % ผลผลิต) เมื่อใช้ PCDA เป็น 2 เท่า ภายใต้ภาวะของปฏิกิริยาคล้ายกันจะได้รับอนุพันธ์ไดอะเซทิลีน ที่มี 2 หมู่เอไมด์ในปริมาณผลผลิตที่ดี (52-75% ผลผลิต) ไดอะเซทิลีนลิปิดที่สังเคราะห์ได้สามารถ กระจายตัวในน้ำได้โดยกระบวนการอัลตราโซนิเคชั่นได้คอลลอยด์โปร่งแสงซึ่งเมื่อได้รับแสงอัลตราไวโอเลต ลิปิดเกิดการโฟโตพอลิเมอไรซ์เป็นพอลิไดอะเซลิทิลีน (PDAs) ที่มีสีน้ำเงิน สมบัติการเปลี่ยนสีตามอุณหภูมิของ PDAs ศึกษาได้ด้วยเครื่อง UV-Vis สเปกโทรมิเตอร์และบันทึกด้วยภาพถ่าย ผลที่ได้แสดงให้เห็นว่าอุณหภูมิการเปลี่ยนสีและการผันกลับได้ของสีขึ้นอยู่กับโครงสร้างของไดอะเซทิลีนลิปิดคือ PDAs ที่เตรียมจากไดอะเซทิลีนที่มีตัวเชื่อมระหว่างหมู่เอไมด์ 2 หมู่ทั้งเป็นวงแหวนอะโรมาติก หรือสายโซ่อะลิฟาติกแสดงสมบัติการผันกลับได้ของสีน้ำเงิน-แดง ในขณะที่ PDAs ที่เตรียมจากไดอะเซทิลีนที่มีหมู่เอไมด์เพียง 1 หมู่แสดงการผันกลับได้เพียงบางส่วนหรือผันกลับไม่ได้เลย นอกจากนี้ไดอะเซทิลีนที่มี 2 หมู่เอไมด์ให้ PDAs ที่มีช่วงการเปลี่ยนสี (70-95 ^{o}C) ที่สูงกว่าเมื่อเทียบกับ PDAs ที่ได้จากไดอะเซทิลีนที่มี 1 หมู่เอไมด์ (65-75 ^{o}C) การเปลี่ยนสีตามอุณหภูมิของ PDAs ที่มีไซโคลเฮกเซนหรือบิส (โพรพิลีนออกไซด์เอทิลีนออกไซด์)เป็นตัวเชื่อมระหว่างเอไมด์ 2 หมู่เป็นแบบผันกลับไม่ได้และมีช่วงการเปลี่ยนสีที่อุณหภูมิต่ำ (25-60 ^{o}C) จากผลการทดลองแสดงว่าจำนวนพันธะไฮโดรเจนที่ดีอย่างน้อยที่สุด 2 พันธะจากหมู่เอไมด์จำเป็นสำหรับการผันกลับได้ของสีอย่างสมบูรณ์ตามอุณหภูมิ และวิทยานิพนธ์นี้ได้ ให้ข้อมูลเกี่ยวกับการออกแบบโครงสร้างควบคุมการผันกลับได้ของสีและการปรับอุณหภูมิการเปลี่ยนสีของพอลิไดอะเซทิลีน

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต...
ปีการศึกษา 2551 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก...............
ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม...............

4972545523: MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEYWORDS: POLYDIACETYLENE/ THERMOCHROMISM/ NANOVESICLES

SURIYAKAMON MONTHA: POLYDIACETYLENE CONTAINING AMIDE GROUPS AND THEIR CHROMISM PROPERTIES. THESIS ADVISOR: ASSOC. PROF. MONGKOL SUKWATTANASINITT, Ph.D., THESIS CO-ADVISOR: SUMRIT WACHARASINDHU, Ph.D., 66 pp.

Amidodiacetylene lipids are prepared from the condensation of 10, 12-pentacosadiynoic acid (PCDA) and diamine compounds in the presence of 1-ethyl-3-(3′-dimethylamino)carbodiimide hydrochloride salt as a coupling reagent. The monoamindodiacetylenes are obtained in moderate yields (47-55 % yield) when using excess amount of diamines. Using the similar reaction with two equivalents of PCDA, the diamidodiacetylene derivatives are obtained in good yields (52-75% yield). The synthesized amidodiacetylene lipids can be dispersed in water by ultrasonication, giving translucent sol. Upon exposure with UV light, the dispersed lipids undergo photopolymerization to generate the desired blue polydiacetylenes (PDAs). The thermochromic properties of the PDAs are observed by UV-Vis spectrometer and photograph recorder. The observation reveals the structural dependence of the color transition temperatures and their reversibility. The PDAs prepared from diamidodiacetylenes with either aromatic ring or aliphatic chain linkers exhibit complete reversibility of the blue-red color transition while those prepared from the corresponding monoamido derivatives display only partial or no reversibility. The diamidodiacetylenes also gave PDAs with higher color transition temperature (70-95 ^{o}C) comparing to the monoamido analogues (65-75 ^{o}C). The thermochromism of PDAs having cyclohexyl or bis(propylenoxide ethylenoxide) as linkers between the diamide groups is virtually irreversible and has low color transition temperature (25-60 ^{o}C). The results suggest that at least two well-developed hydrogen bonds from amide groups are required for complete thermochromic reversibility. This thesis provides useful structural design for controlling color reversibility and tuning color transition temperature of PDAs.

Field of Study: Petrochemistry and Polymer Science	Student's Signature: ………………
Academic Year: 2008	Advisor's Signature: ………………
	Co-Advisor's Signature: …………..

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my advisor, Associate Professor Mongkol Sukwattanasinitt, Ph.D., and my Co-Advisor Sumrit Wacharasindhu, Ph.D., for his invaluable guidance, excellent and kind supervision, and helpful suggestion throughout this research. This thesis research would not be completed without his advice and guidance.

My appreciation is also given to Assistant Professor Warinthorn Chavasiri, Ph.D.and Assistant Professor Varawut Tangpasuthadol, Ph.D., thesis defense committee, for their kind attention, valuable suggestion and recommendations. I also would like to thank Associate Professor Tirayut Vilaivan, Ph.D., for permission to use UV-Vis spectrophotometer throughout this research.

I would like to thank Assistant Professor Rakchart Traiphol, Ph.D., thesis defense committee from Naresuan University for suggestions.

Furthermore, I gratefully thank to my friends at dormitory for their genuine, help, and friendship and everyone in MS-group, especially Anupat, Chantana, Jasuma, Sansanee and Theodtoon for their educated, suggestion and big help in everything. Moreover, I express my appreciation to Warathip, Sulaleewan, Nakorn, Thirawat, Chaiwat, Yamonphon and for spirit, smile, good wish and their helps in everything.

I would like to thank National Nanotechnology Center and The 90th Anniversary of Chulalongkorn University Fund (Ratchadaphiseksomphot Endowment Fund) for the financial support of this work.

Finally, I would like to express thankfulness to my family for their love, care, encouragement and support throughout my study.

CONTENTS

Page

LIST OF TABLES

Table **Page**

LIST OF FIGURES

Figure **Page**

Figure **Page**

Figure **Page**

LIST OF SCHEMES

Scheme **Page**

LIST OF ABBREVIATIONS

PDA	Polydiacetylene
PCDA	10,12-pentacosadiynoic acid
o-PA-1DA	N, N’-(1, 2-phenylene) dipentacosa-10, 12-diynamide
m-PA-1DA	N, N’-(1, 3-phenylene) dipentacosa-10, 12-diynamide
p-PA-1DA	N,N’-(4-aminophenyl) pentacosa-10, 12-diynamide
o-PA-2DA	N, N’-(1, 2-phenylene) dipentacosa-10, 12-diynamide
m-PA-2DA	N, N’-(1, 3-phenylene) dipentacosa-10, 12-diynamide
p-PA-2DA	N, N’-(1, 4-phenylene) dipentacosa-10, 12-diynamide
c-CA-2DA	N,N'-(1S,2R)-cyclohexane-1,2-diyl)dipentacosa-10,12-diynamide
t-CA-2DA	N,N'-(1R,2R)-cyclohexane-1,2-diyl)dipentacosa-10,12-diynamide
BA-2DA	N, N’-(butane-1, 4-diyl) dipentacosa-10, 12-diynamide
HA-2DA	N, N’-(hexane-1, 6-diyl) dipentacosa-10, 12-diynamide
APOEO-2DA	N,N'-(3,3'-(2,2'-oxybis(ethane-2,1-diyl)bis(oxy))bis(propane-3,1-diyl))dipentacosa-10,12-diynamide
CTT	Color transition temperature
CR	Colorimetric response
NMR	Nuclear magnetic resonance spectroscopy
AFM	Atomic force microscopy
DLS	Dynamic light scattering
°C	Degree celsius
g	Gram
mL	Millilitre
mM	Millimolar
nm	Nanometre
min	Minute
%	Percent

CHAPTER I

INTRODUCTION AND THEORY

1.1 Overview

Temperature is one the most important physical parameters affecting quality of various sensitive products such as foods, beverages, medicines and chemicals. The most popular material used as temperature indicator is one of the earliest known element, mercury. It is a toxic liquid that limits it used within a close system not in any direct contact with human and environment. Liquid crystals and leuco dyes, the more recently developed temperature sensing materials, required encapsulation for stability and safety purposes [1]. Novel heat sensitive materials which can be used safely and economically as temperature indictors remains to be sought after.

Among sensing materials derived from organic compounds, conjugated polymers have received much attention. The sensing properties of the polymers associate with the electronic states of the extensively delocalized π-conjugated system of the polymer backbone. External stimuli generally disturb the electronic states of the delocalized π-system that induces changes in their absorption, emission and redox properties. Furthermore, conjugated polymer-based sensors have also been demonstrated to offer signal amplification comparing to their small molecular coumpounds [2].

One of the best known conjugated polymers possessing temperature sensing property is polydiacetylene (PDA). PDAs are prepared by 1,4-addition polymerization initiated by heat, UV or γ-irradiation of the corresponding diacetylene monomers. The polymerization can proceed effectively only when the diyne units orderly arrange and tilt with appropriate interatomic distance and angle. Thus, only certain forms of supramolecular assemblies *e.g.* crystals, monolayer or multilayer films and nanostructure in host matrices, can be polymerized. The polymerization requiring strict molecular arrangement of type is called “topopolymerization” [3]. The most unique and interesting property of PDAs is in connection with their color changing under various external perturbations such as heat (Thermochromism), pH, solvent (solvatochromism), mechanical stress (mechanochromism) and ligand-receptor interactions (affinochromism) [4-11].

Thermochromism is probably one of the most widely investigated for structure and property relationships as well as its 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 [12-14]. Variation of the total chain length and the position of the diyne unit within the chain can provide diverse colorimetric responses to temperature [15]. However, the early study limited to intractable PDAs that the spectroscopic characterization and the fabrication for applications were not possible.

Recently, diacetylene monomers having a lipid like structure containing a long hydrophobic tail and a hydrophilic head group have attracted much attention. The molecules of this type of diacetylene lipid can self-assemble into vesicular structures which can be homogeneously dispersed in water. One of the diacetylene lipids most commonly used in the preparation of vesicles is 10,12-pentacosadiynoic acid (PCDA) that gives intense blue-colored homogeneous sol of poly(PCDA) vesicles upon photopolymerization [16]. Poly(PCDA) sol exhibits irreversible color transition from blue to red upon heating, increasing pH and adding less polar solvent like ethanol [17]. The color transition behaviors of the solution like poly(PCDA) sol are favorably studied by means of electronic absorption spectroscopy. PCDA and their derivatives have also been utilized in the construction of biosensors for naked eye detection of influenza virus, cholera toxin, Escherichia coli, glucose and cyclodextrin [18-22].

Spectroscopic investigations of thermochromic behaviors have been conducted mostly on PDAs derived from diacetylene lipids possessing acid head group. There have been only little information available for diacetylene lipids having other head groups such as amide. In this work, the diacetylene monomeric lipids being studied are designed to portray the effects of amide head groups on the thermochromic behaviors of the resulting

PDAs. The amide head groups described here are appealing for two features: (1) the amides can develop strong hydrogen bonds between the heads group and (2) one bond of N atom in the amide can be attached to a linker unit without losing all the hydrogen bond forming ability. A series of diacetylene monomeric lipids containing either one or two amide with various linkers were synthesized in this work. The monomeric lipids were then dispersed in water and photopolymerized to form PDA vesicle 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 amide groups and the linkers influence the thermochromic properties of the PDAs. The results from this investigation increased the assortment of safe and economical temperature sensing materials as well as guidelines for designing new PDAs for universal temperature indicators.

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. PDAs can be prepared 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 [2].

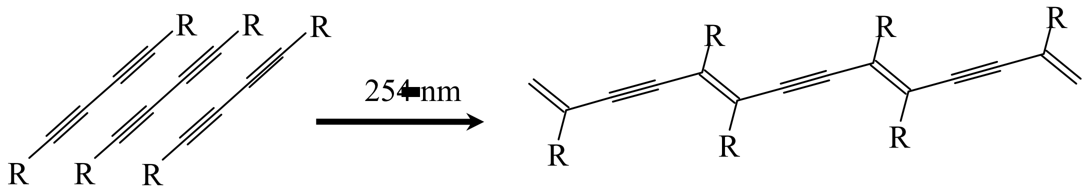


Figure 1.1 Polymerization of diacetylene monomers by irradiation with UV light.

The topopolymerized diacetylene crystals are nearly perfectly ordered crystals which cannot be achieved by solution polymerization or recrystallization of a preformed polymer from solution or melt [14, 23]. Some PDAs, if generated under optimized conditions, appear as an intense blue color. In general, blue PDAs show a strong absorption band in the visible range with maximum absorption wavelength (λ_{max}) around 630 nm. With a suitable stimulation, this blue form of PDAs can undergoes color transition to a red form concomitantly with a shift of λ_{max} to around 540 nm. Owing to these color changing properties, several PDA-based sensors have been prepared in a wide range of organized structures such as single crystals, thin films on solid supports using Langmuir-Blodgett or Langmuir-Schaefer techniques, self-assembled monolayers, liposome or vesicles in water.

Diacetylene lipids are known to spontaneously arrange into vesicular structures 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). Possessing both carboxylic group and long hydrocarbon chain, PCDA can assemble in the form of lipid bilayer vesicles in water which are able to polymerized by irradiation with UV light (Figure 1.2).

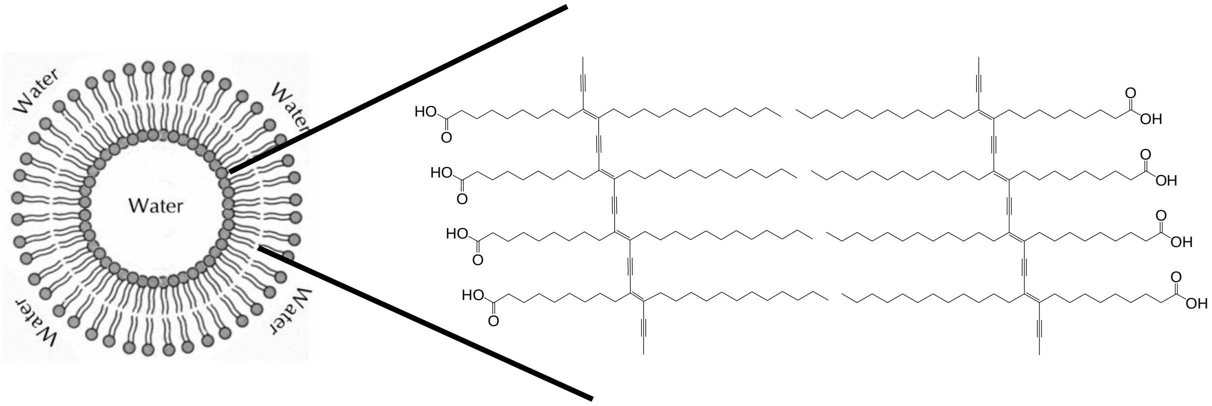


Figure 1.2 Illustration of poly(PCDA) vesicle.

1.2.2 Electronic transition of polydiacetylenes

Optical absorption in polydiacetylenes occurs *via* $\pi \rightarrow \pi^*$ excitation within the linear π-conjugated polymer backbone. Upon polymerization, frequently the first chromogenically interesting form of PDA appears blue in color. The exposure of PDA to environmental perturbations such as heat (thermochromism), mechanical stress (mechanochromism), or solvent (solvatochromism) involve a significant shift in absorption from low to high energy bands of the visible spectrum, so the polydiacetylene transforms from blue to red color. Even though detail mechanism of the color transiton of each PDA is still puzzling and some parts remain controversial, many believe that it is caused by strain and torsion imposed onto the conjugated backbone by order-disorder transitions in the side chains. This causes the reduction of effective conjugation length, thus changing the electronic states and the corresponding optical absorption that leads to the chromic transition [24-25].The color transition of the polymerized vesicles was monitored by measuring the absorbance differences between the vesicles before and after stimulation. The spectroscopic information is often converted to a percentage, termed the Colorimetric Response (CR) [26].

1.2.3 Colorimetric response (CR)

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

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

where $PB = A_{blue}/(A_{blue}+A_{red})$, A_{blue} and A_{red} are the absorbance at the λ_{max} of the blue and the red phases, typically at 630 and 540 nm, respectively. PB_0 is the initial percent blue before the PDAs are subjected to a concerned perturbation. The visible absorbance is measured by a UV-Vis spectrometer.

1.2.4 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. The color change from blue to red corresponds to the increase of energy gap between the HOMO and LUMO level. This change of energy gap has been proposed to arise from the movement of the side chains inducing either the conformational changes of the conjugated backbone from planar to non-planar [15] or the release of backbone strain in the ene-yne conjugation [27].

For polydiacetylene vesicles, hydrogen bonding between the head groups of the lipid monomers is usually responsible for keeping the conjugated backbone in long range planarity and bond strain. Thermal energy can break or weaken the hydrogen bonding between the head groups resulting in some movement of the side chains that shorten the planarity range and release the strain within the backbone. The reduction in planarity or the average π-conjugation length is theoretically established as the lower HOMO and higher LUMO [28] while the release of bond strain in the backbone has been coupled mainly to the lower HOMO with little or no change of the LUMO level [29].

1.3 Literature survey

The colorimetric reversibility of PDA upon heating stimuli was first reported in 1986 by Singh and Coworker [30]. Polymerized diacetylene obtained from bisdiacetylenic phossphorylcholine (figure 1.3) was prepared in aqueous solution. The blue to red colorimetric reversibility of this compound was found in the range of 10 -60 °C.

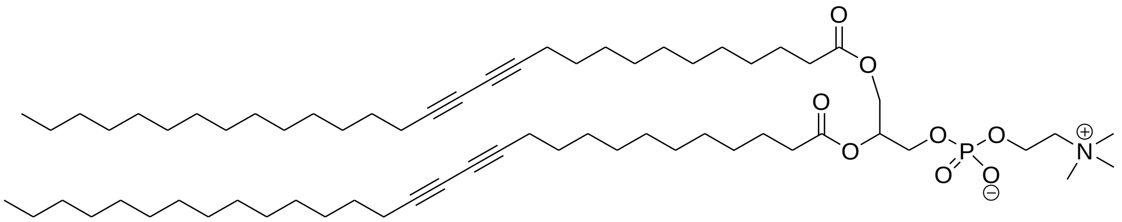


Figure 1.3 The structure of the diacetylene obtained from bisdiacetylenic phossphorylcholine

In 2003, Ahn *et al.* [12] synthesized derivatives of 10,12-pentacosadiynoic acid having an anilide and carboxylanilides (ortho-, meta-, and para-) (Figure 1.4).

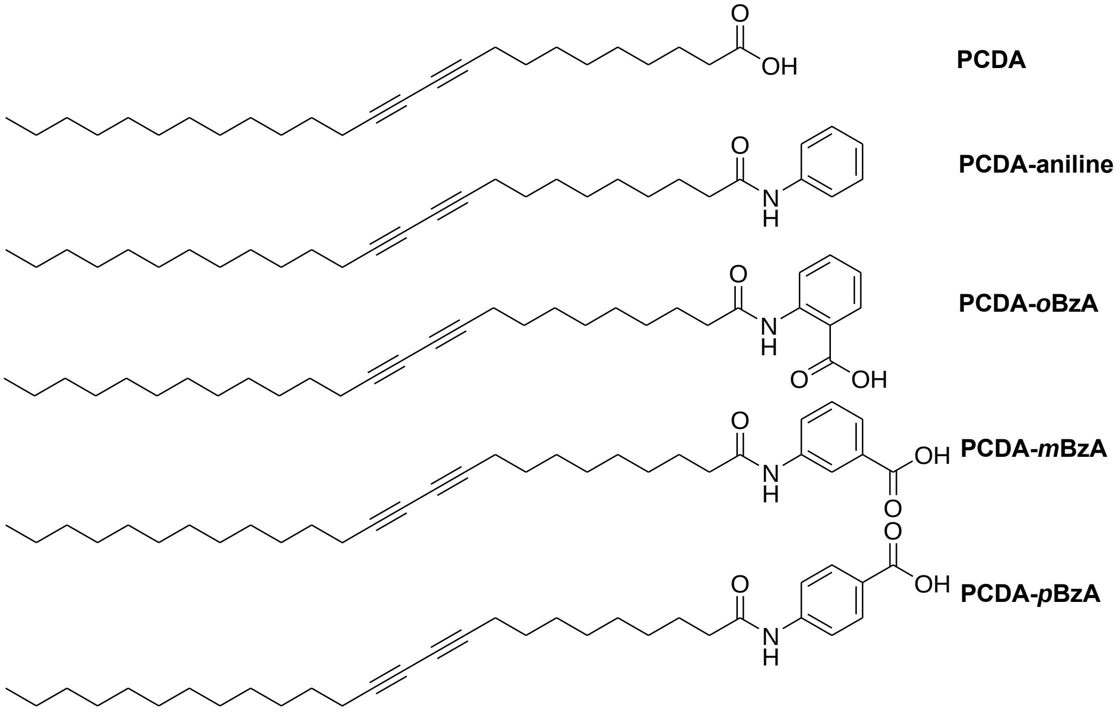


Figure 1.4 Structure of diacetylene monomers used in investigations of reversible thermochromism in Langmuir-Schaefer films.

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.

In 2004, Yuan and coworkers prepared a new reversible themochromic PDA [31]. Diacetylene monomer derived form the bisdiacetylene-substituted terephthalic acid (Figure 1.5) was polymerized in thin film using spin coated technique. The Film showed a complete colorimetric reversibility under heating and cooling process. The authors claim that H-bonding from dicarboxylic facilitates in restoration of the original conformation resulting in the colorimetrical reversibility.

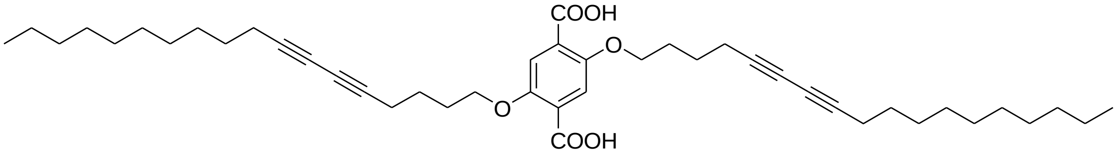


Figure 1.5 The structure of the diacetylene monomer derived form the bisdiacetylene-substituted terephthalic acid.

In 2005, Kim *et al.* expanded their previous works [2]. To evaluate the structural effect on thermochrmisn of polydiacetylenes, 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 1.6. 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 polydaicetylenes.

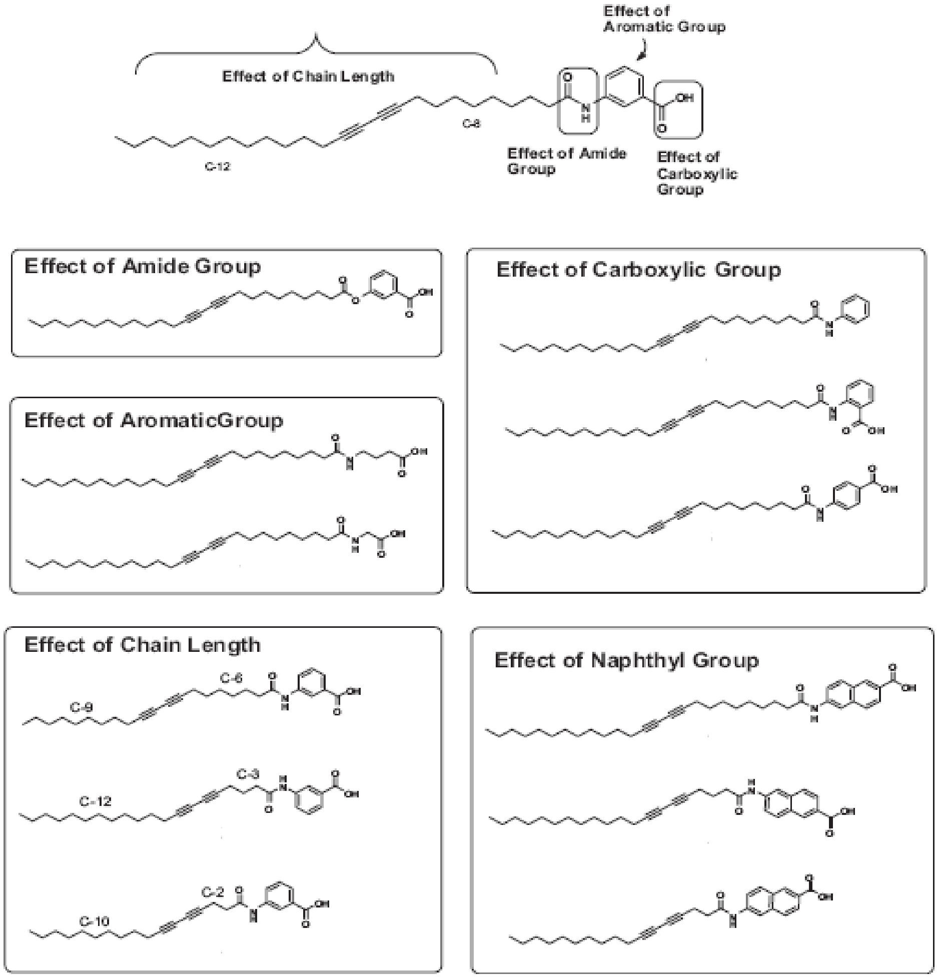


Figure 1.6 Structure of diacetylene monomers used in investigations of reversible thermochromism in aqueous solution.

In 2007, Lim and coworkers generated PCDA which is immobilized and molecularly assembled on Ag surface [32]. Rewarding, an irreversible PCDA were transforming into completely reversible one. These PCDA shows blue to red color change and *vice versa* during heating and cooling process. Later, the similar approach was reported by Gu and coworkers [33]. Mixing between PCDA and PVP (polyvivylpyrolidine), the colorimetrically reversible thromochrmism was achieved in temperature rage of 20-85 ^{o}C. The authors proposed “brick and motar” structure in PVP/PCDA nanoaggregates was generated due to intramolecular hydrogen bonding between carboxylic of PCDA with pyrolidine (Figure 1.7). These arrangements cause the color reversibility of the blending product during the thermal cycle.

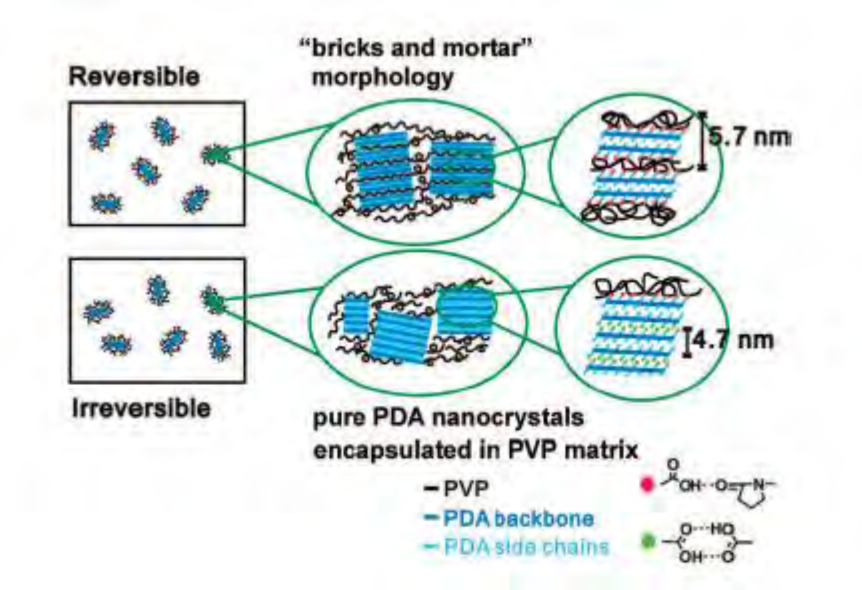


Figure 1.7 Schematic Illustration of the "Bricks and Mortar" Morphology and Pure PDA Nanocrystals

Moreover, Peng and co-worker reported the colorimetrically reversible PDA-silica nanocomposites. [34, 35]. The studied polydiacetylene was derived from the ethoxysilane-containing diacetylene monomer (Figure 1.8). It has been suggested that ethoxysilane side chin of PDA attached covalently to inorganic frame work are responsible of reversible color transition. This stable and strong interaction should sufficiently enough to regain the original conformation when temperature was decreased to stating point.

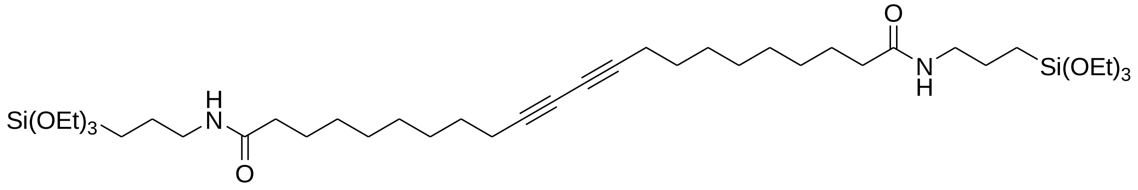


Figure 1.8 Molecular Structure of a Diacetylene-Bridged Silsesquioxane

Recently, Anupat Potisatityuenyong and co worker conduced extensively investigation poly-10,12-pentacosadiynoic acid (poly(PCDA)) vesicle solution in the aspect of thermochromism, solvatochromism and alkalinochromism [17]. 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. Thermochromism, however, the different phenomena was observed. The steady hypsochromic shift and color reversibility of solution at low temperature were found, indicating calorimetrically reversibility. On the other hands, higher temperature was not resulted in the recovery of the color when heating over 75 ^{o}C. The author proposed the mechanism of color transition of PCDA as shown in Figure 1.9.

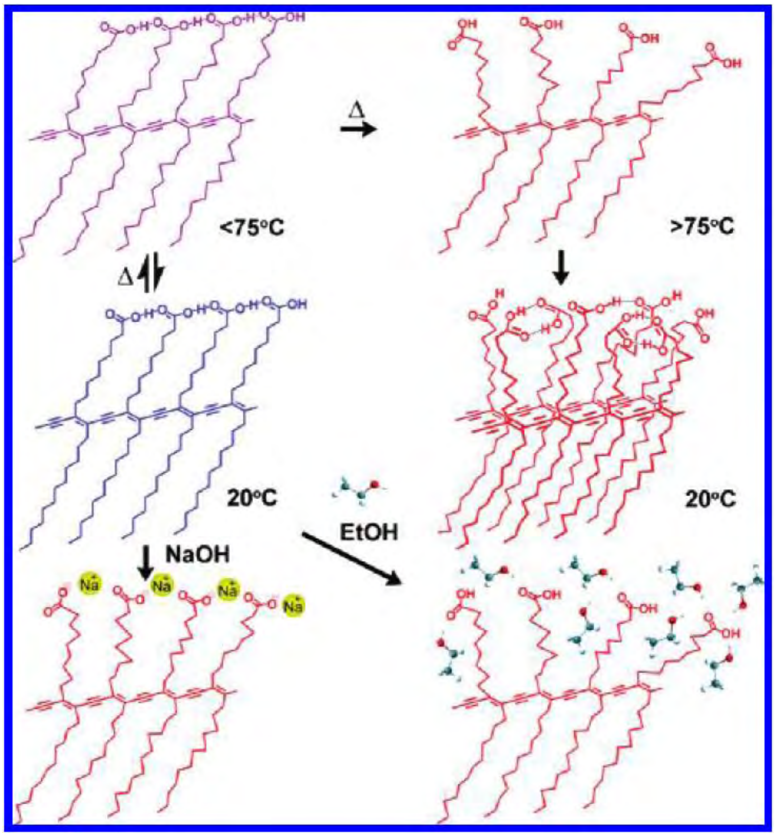


Figure 1.9 Proposed side-chain movement in the chromic transitions of poly(PCDA) vesicles.

At lower 75 ^{o}C, the side-chain movement takes place initially generating blue color without disturbing the hydrogen bond. At 75 ^{o}C and higher, thermal energy is enough to break hydrogen bond generated red vesicle. At this stage, the color of vesicle is not able to recover upon decreasing the temperature. Solvatochromism and alkalinochromism involve hydrogen bond breaking turning the blue vesicle into red color.

From the above review, polar head group in diacetylene is a crucial factor in controlling thermochromism of polydiacetylene. We believe that functional group manipulation on head part of diacetylene will give us the opportunity to control colorimetric reversibility and color transition temperature of polydiacetylene. This will enhance and expand the scope where polydiacetylene-based material can be recognized and applied as sensor, actuator and other device purposes.

1.4 Objective and scope of the research

The objective of work is to study thermochomism of polydiacetylene containing amido group(s). To achieve the objective, the work scope includes 1) synthesis of diacetylene monomers derived form 12-pentacosadiynoic acid (PCDA). Those will contain either one or two amide functional group with various kind of liker. 2) Preparation of polydiacetylene vesicles from its derivatives, 3) characterization of the prepared vesicles by AFM and dynamic light scattering for morphology and particle sizes. 4) Study of thermochromic properties of the prepared vesicle solutions monitoring by UV-vis spectrometer.

CHAPTER II

EXPERIMENTAL

2.1 General Information

All reagents were purchased from Sigma-Aldrich and Fluka. 10,12-pentacosadiynoic acid (PCDA) was purchase from GFS company. Analytical grade solvent such as chloroform and methylene chloride were used without further purification. Analytical thin layer chromatography was performed on glass-blacked silica gel plates with F_{254} indicator. Compounds were visualized under UV lamp or by developing in iodine, vanillin, phosphomolybdic acid solution or with a potassium permanganate solution followed by heating on a hot plate to approximately 350 ^{o}C. Flash chromatography was performed on 70-230 mesh silica gel with commercial grade solvents that were distilled prior to use.

^{1}H NMR spectra were recorded on a Varian Mercury 400 MHz NMR spectrometry as $CDCl_3$ solutions with tetramethylsilane (δ = 0 ppm) as the internal standard. Chemical shifts (δ) are reported in parts per million (ppm). Multiplicites are reported as s (singlet), br (broad), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), etc. UV/vis spectra were record were measured with dilute aqueous solution in a 10 mm thick quartz using Varian Cary 100 Bio UV-Visible spectrophotometer. AFM image were recorded on SPA 400 atomic force microscope (Seiko, Japan). The particle size measurements were made by a dynamic light scattering using a Nanosizer (Malvern instrument). Sonication was performed by ultrasonicator Transinic T570/S (Elama, Germany).

2.2 Procedures for synthesis of diacetylene lipid monomers

2.2.1 General procedure for synthesis of monoamido diacetylene lipid monomers *o*-PA-1DA, *m*-PA-1DA and *p*-PA-1DA:

1-ehtyl-3-(3’-dimethylamino)carbodiimide HCl salt (EDCI) (230.04 mg, 1.2 mmol) in chloroform (4 mL) was added dropwise into a solution of 10,12-

pentacosadiynoic acid (374.61 mg, 1.0 mmol) in chloroform (5 mL). The mixture was stirred for 1 hour at 0 ^{o}C and was then added drop wise into corresponding diamine (1,2-phenylenediamine, 162.21 mg, 1.5 mmol) in chloroform (4 mL) at 0 ^{o}C. The reaction mixture was stirred for overnight at room temperature and the white precipitate was clearly observed. The reaction mixture was concentrated under reduced pressure to yield the crude product as a white solid. Purification was accomplished by column chromatography on silica gel eluting with the mixture of hexane and EtOAc (50:50) to give *o*-PA-1DA (386 mg, 47%) as a white solid: mp. 82-84 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.07 (1H, s, NH=CO), 7.11 (1H, d, *J* = 7.82 Hz, CH), 6.86 (1H, t, *J* = 7.05 Hz, CH), 6.68 (1H, d, *J* = 7.96 Hz, CH), 6.51 (1H, t, *J* = 7.51 Hz, CH), 4.78 (2H, s, NH_2), 2.41-2.06 (6H, m, CH_2), 1.65-1.03 (32H, m, CH_2), 0.83 (3H, t, *J* = 6.69 Hz, CH_3); HMRS calcd for $C_{31}H_{48}N_2ONa$ $[M+Na]^+$: 488.73 ; Found 487.72.

m-PA-1DA (427 mg, 52%): mp. 76-78 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.51 (1 H, s, NH=CO), 6.88 (2 H, dd, *J* = 17.99, 10.04 Hz, CH), 6.64 (1 H, d, *J* = 8.03 Hz, CH), 6.21 (1 H, d, *J* = 6.75 Hz, CH), 5.00 (2 H, s, NH_2), 2.24 (6 H, td, *J* = 14.06, 7.10 Hz, CH_2), 1.65-1.15 (32 H, m, CH_2), 0.84 (3 H, t, *J* = 6.76 Hz, CH_3); HMRS calcd for $C_{31}H_{49}N_2O$ $[M+H]^+$: 465.38 ; Found 465.47.

p-PA-1DA (452mg, 55%) : mp. 101-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.42 (1 H, s, NH=CO), 7.19 (2 H, d, *J* = 8.71 Hz, CH), 6.48 (2 H, d, *J* = 8.67 Hz, CH), 4.86 (2 H, s, NH_2), 2.23 (6 H, td, *J* = 14.77, 7.13 Hz, CH_2), 1.65-1.04 (32 H, m, CH_2), 0.85 (3 H, t, *J* = 6.70 Hz, CH_3); HMRS calcd for $C_{31}H_{48}N_2ONa$ $[M+Na]^+$: 488.73 ; Found 487.37.

2.2.2 General procedure for synthesis of diamido diacetylene lipid monomers *o*-PA-2DA, *m*-PA-2DA, *p*-PA-2DA, *c*-CA-2DA, *t*-CA-2DA, BA-2DA, HA-2DA and APOEO-2DA:

1-ehtyl-3-(3’-dimethylamino)carbodiimide HCl salt (EDCI) (383.4 mg, 2 mmol) in chloroform (2 mL) was added dropwise into a solution of 10,12-pentacosadiynoic acid (637 mg, 1.7 mmol) in chloroform (2 mL). After stirring for an hour the corresponding diamine (1,2-phenylenediamine, 81 mg , 0.75 mmol) in chloroform (10 mL) was then added dropwise and kept stirring for overnight. The reaction mixture was concentrated under reduced pressure to yield the crude product as a white solid. The crude product was then recrystallization with methanol to afford

o-PA-2DA (370 mg, 60%): mp 112-114°C. ^{1}H NMR (400 MHz, $CDCl_3$). δ = 8.05-7.98 (2 H, br, NH=CO), 7.42-7.36 (2 H, m, CH), 7.22-7.17 (2 H, m, CH), 2.36 (4 H, t, *J* = 7.51 Hz, CH_2), 2.24 (8 H, dd, *J* = 8.75, 4.52 Hz, CH_2), 1.78-1.18 (64 H, m, CH_2), 0.88 (6 H, t, *J* = 6.79 Hz, CH_3); HMRS calcd for $C_{56}H_{88}N_2O_2Na$ $[M+Na]^+$: 844.68 ; Found 843.74.

m-PA-2DA (320 mg, 52%) : mp 103-105 °C.^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.86-7.79 (2 H, br, NH=CO), 7.30-7.16 (4 H, m, CH), 2.33 (4 H, t, *J* = 7.47 Hz, CH_2), 2.24 (8 H, t, *J* = 6.80 Hz, CH_2), 1.76-1.18 (64 H, m, CH_2), 0.88 (6 H, t, *J* = 6.69 Hz, CH_3); HMRS calcd for $C_{56}H_{88}N_2O_2Na$ $[M+Na]^+$: 844.68 ; Found 844.16.

p-PA-2DA (363 mg, 59 %): mp 167-169 °C. ^{1}H NMR (400 MHz, $CDCl_3$); δ = 7.47 (4 H, s, CH), 7.07 (2 H, br, NH=CO), 2.33 (4 H, t, *J* = 7.24 Hz, CH_2), 2.24 (8 H, t, *J* = 6.90 Hz, CH_2), 1.78-1.18 (64 H, m, CH_2), 0.88 (6 H, t, *J* = 6.59 Hz, CH_3); HMRS calcd for $C_{56}H_{87}N_2O_2$ $[M-H]^-$: 819.68 ; Found 819.83.

c-CA-2DA (323 mg, 52%),: mp 62-64 °C. ^{1}H NMR (400 MHz, $CDCl_3$); δ 6.28 (2 H, br, NH=CO), 3.95-4.00 (2 H, m, CH), 2.21 (12 H, td, *J* = 15.16, 7.19 Hz, CH_2), 1.89 (4H, d, *J* = 1.56 Hz, CH_2), 1.70-1.13 (68 H, m, CH_2), 0.88 (6 H, t, *J* = 6.44 Hz, CH_3); HMRS calcd for $C_{56}H_{94}N_2O_2Na$ $[M+Na]^+$: 849.73 ; Found 850.27.

t-CA-2DA (379 mg, 61%): mp 62-64 °C. ^{1}H NMR (400 MHz, $CDCl_3$); δ = 5.87 (2 H, br, NH=CO), 3.74-3.56 (2 H, CH), 2.49-1.97 (16 H, m, CH_2), 1.82-1.15 (68 H, m, CH_2), 0.88 (6 H, t, *J* = 6.75 Hz, CH_3)

BA-2DA (451 mg, 75%): mp 117-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$); δ = 6.34 (2 H, br, NH=CO), 3.28 (4 H, m, CH_2), 2.22 (12 H, t, *J* = 6.89 Hz, CH_2), 1.68-1.15 (66 H, m, CH_2), 0.86 (6 H, t, *J* = 6.74 Hz, CH_3); HMRS calcd for $C_{37}H_{75}N_2O_2$ $[M- C_{17}H_{27}]^+$: 570.51 ; Found 569.72.

HA-2DA (404 mg, 65%): mp 122-125 °C. ^{1}H NMR (400 MHz, $CDCl_3$); δ = 5.56 (2 H, t, *J* = 5.11 Hz, NH=CO), 3.24 (4 H, q, *J* = 6.73 Hz, CH_2), 2.20 (12 H, td, *J* = 15.17, 7.37 Hz, CH_2), 1.71-1.13 (72 H, m, CH_2), 0.88 (6 H, t, *J* = 6.81 Hz, CH_3); HMRS calcd for $C_{56}H_{96}N_2O_2Na$ $[M+Na]^+$: 852.75 ; Found 850.27.

APOEO-2DA (504 mg, 72%): mp. 77-80°C; ^{1}H NMR (400 MHz, $CDCl_3$); δ =

6.17 (2 H, br, NH=CO), 3.71-3.49 (16 H, m, CH_2), 3.35 (4 H, q, *J* = 6.13 Hz, CH_2), 2.18 (12 H, td, *J* = 15.21, 7.32 Hz, CH_2), 1.83-1.17 (64 H, m, CH_2), 0.87 (6 H, t, *J* = 6.69 Hz, CH_3).

2.3 Typical Method for preparation of polydiacetylene vesicles

Monomers were dissolved in chloroform (0.5 mL) in a test tube and the solvent was removed under reduced pressure. A volume of milli-Q water was added to provide the lipid concentration of 0.25 mM. The suspensions were heated to 75-85 ºC, followed by sonication in an ultrasonicating bath for 30-40 minutes forming a semitransparent or transparent vesicle solution. Then solution was kept at 4 ºC for overnight. The vesicle solution was irradiated with UV light (254 nm) for 5 minutes at room temperature and filtered through a filter paper (No.1) to give a clear intense blue-colored vesicle solution.

2.4 Characterization of polydiacetylene vesicles

2.4.1 Atomic force microscopy (AFM)

Vesicles were deposited on a freshly cleaved mica plate and dried at room temperature in desiccators for 4 hours. Seiko SPA 400 (SII Nanotechnology Inc.) operating in non contact mode using a SI-DF20 cantilever was used to observe the morphology and particle size of the deposited vesicles. The image of the vesicles was measured on an air-dried sample of vesicles were prepared from a drop of solution on a freshy cleaved on mica plate.

2.4.2 Dynamic light scattering (DLS)

The mean size of vesicles and the size distribution were determined by nanosizer (zeta sizer Nano ZS Malvern Instruments). The samples were sonicated for 1 min before measurement and vesicle solutions was taken in a plastic cuvette with 2 cm. Each measurement was repeated 3 times in order to acquire an average data. Analysis and report by using intensity statistics mode to plot range of particle size graph.

2.5 Thermochromism Properties

2.5.1 UV-Visible spectroscopy

The visible absorption of vesicle solutions was taken in a quartz cuvette with 1 cm. optical path length on a temperature controlled UV-Vis spectrometer. The spectra were collected from 850 to 400 nm with the zero absorbance set at 850 nm. The λ_{max} of the blue and red phases of each sample was determined at 25 and 95°C except poly (*c*-CA-2DA) and poly(*t*-CA-2DA) were determined at 10 and 95°C. The correlation between the absorbance at the λ_{max} and adjust the initial absorbance in the range of 0.4 – 0.6.

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

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

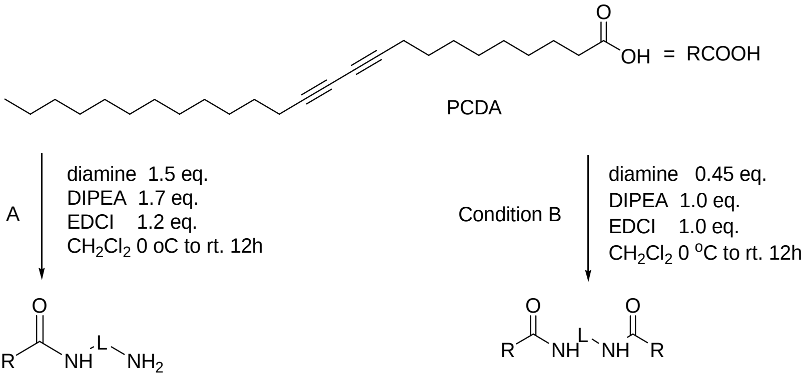
Where $PB = A_{blue}/(A_{blue}+A_{red})$, A_{blue} and A_{red} are the absorbance of the blue and the red phase at 630 and 540 nm, respectively. The visible absorbance was measured by a temperature controlled UV-*vis* spectrometer. PB_0 is the initial percent blue of the vesicle solution and film before heated. All blue-colored PDA vesicle solution and film samples were heated from 25 to 90 °C.

CHAPTER III

RESULTS AND DISCUSSION

3.1 Preparation of diacetylene monomers

In this study, the diacetylene lipid monomers were synthesized via amide bond formation of commercially available 10,12-pentacosadiynoic acid) PCDA) with an appropriate diamine shown in Scheme 3.1. Condition **A** represents the synthetic method for the preparation of monoamido derivatives while the synthesis of diamido diacetylenes is described as condition **B.**



Name(Yield), L=Linker

o-PA-1DA(47%), L= *o*-(-C_6H_4-)

m-PA-1DA(52%), L= *m*-(-C_6H_4-)

p-PA-1DA(55%), L= *p*-(-C_6H_4-)

Name(Yield), L=Linker

o-PA-2DA(60%), L= *o*-(-C_6H_4-)

m-PA-2DA(52%), L= *m*-(-C_6H_4-)

p-PA-2DA(59%), L= *p*-(-C_6H_4-)

t-CA-2DA(61%), L= 1,2-*t*-(-C_6H_{10}-)

c-CA-2DA(52%), L= 1,2-*c*-(-C_6H_{10}-)

BA-2DA(75%), L= *1,4*-(-$(CH_2)_4$-)

HA-2DA(65%), L=1,6-(-$(CH_2)_6$-)

APOEO-2DA(72%), L= (-$(CH_2)_3$-O-$(CH_2)_2)_2$-O

Scheme 3.1: Synthesis of diacetylene lipid monomers

Initially, PCDA was reacted with 1.5 equivalents of the diamine *i.e.* 1,2-phenylenediamine, 1,3-phenylenediamine, 1,4-phenylenediamine in the presence of 1-ehtyl-3-(3´-dimethylamino)carbodiimide HCl salt (EDCI) as a coupling reagent to obtain monoamidodiacetylene derivative. *N*-(2-aminophenyl)pentacosa-10,12-diynamide (*o*-PA-1DA), *N*-(3-aminophenyl)pentacosa-10,12-diynamide (*m*-PA-1DA), *N*-(4-aminophenyl)pentacosa-10,12-diynamide (*p*-PA-1DA) were isolated as a white solid after column purification in low to moderate yield (29-61%). Low isolated yield was caused by the formation of the diamido compounds (ca. 10%) that led to some losses during the column purification.

In the synthesis of diamidodiacetylenes, 2 equivalents of PCDA was reacted with the diamines to afford the desired product; *N,N′*-(1,2-phenylene)dipentacosa-10,12-diynamide (*o*-PA-2DA), *N,N′*-(1,3-phenylene)dipentacosa-10,12-diynamide (*m*-PA-2DA) and *N,N′*-(1,4-phenylene)dipentacosa-10,12-diynamide (*p*-PA-2DA) in 60, 52 and 59% yield, respectively, after recrystallization of crude product with MeOH (Scheme 3.1, Condition B). Besides phenylenediamine, 1,4-butylenediamine, 1,6-hexylenediamine 1,2-*cis*-diaminocyclohexane, 1,2-*trans*-diaminocyclohexane, and bis((3-aminopropyloxy)ethylenoxide) were also used to react with 2 equivalents of PCDA to generate BA-2DA, HA-2DA, *c*-CA-2DA, *t*-CA-2DA and APOEO-2DA in moderate to good yields (52-75%).

^{1}H NMR spectra of *o*-PA-1DA, *m*-PA-1DA and *p*-PA-1DA are shown along with the spectrum of PCDA in Figure 3.1.

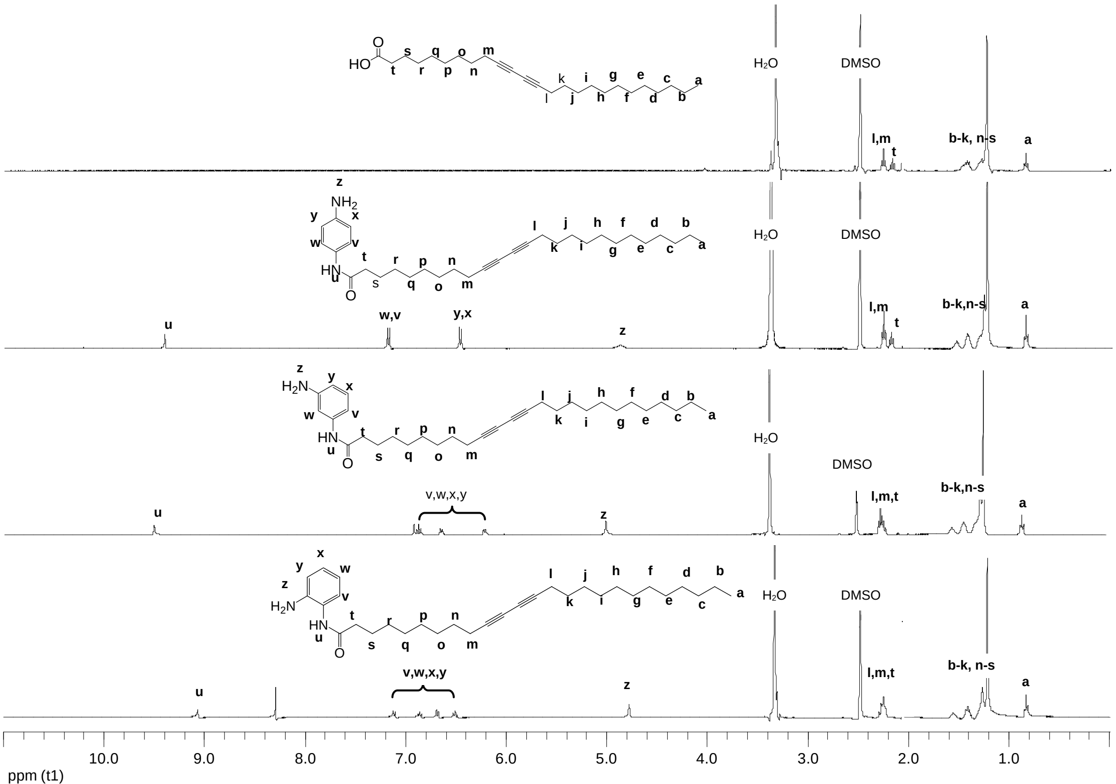


Figure 3.1 ^{1}H NMR spectra of PCDA, *p*-PA-1DA, *m*-PA-1DA and *o*-PA-1DA lipids in DMSO.

The spectra of the products show the signals of N-H protons in the chemical shift range of 4.8-5.0 ppm. The extra singlet signals in the 9.0-9.5 ppm range belong to the amido N-H protons. The aromatic protons of the phenylene unit are observed in the range of 6.2 to 7.8 ppm. Moreover, the signals of the methylene protons next to the carboxylic carbonyl group in PCDA shifted slightly up field from 2.3 to 2.1 ppm upon the conversion to the amido groups. Due to their greater symmetry, bis(PCDA) phenylenediamide derivatives (*o*-PA-2DA, *m*-PA-2DA and *p*-PA-2DA, showed less aromatic proton signals between δ 7.1-7.4 ppm comparing to those of the corresponding monoamide compounds (Figure 3.2). The diamides also showed the signals of amido N-H protons at the higher field of 7.0-8.0 ppm comparing to the monoamides. Inadvertently, the methylene protons connected to the amide group remained at relatively the same chemical shift of the methylene protons connected to the carboxylic group of the parent PCDA.

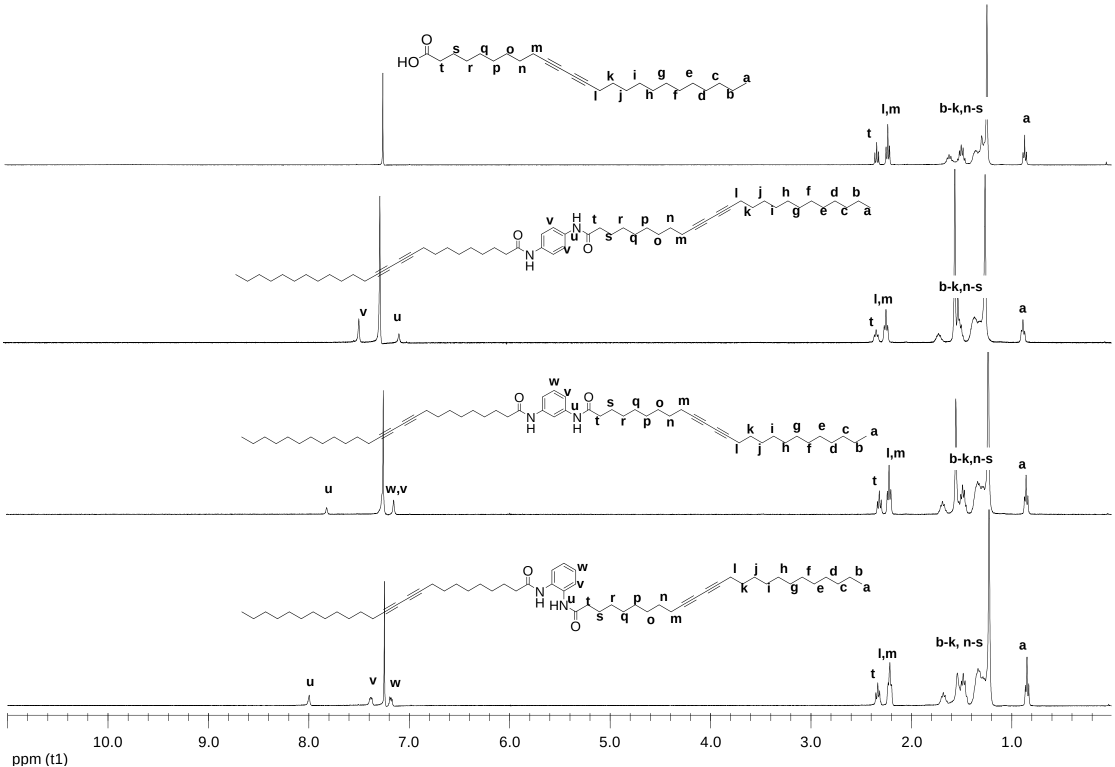


Figure 3.2 ^{1}H NMR spectra of PCDA, *p*-PA-2DA, *m*-PA-2DA and *o*-PA-2DA lipids in $CDCl_3$.

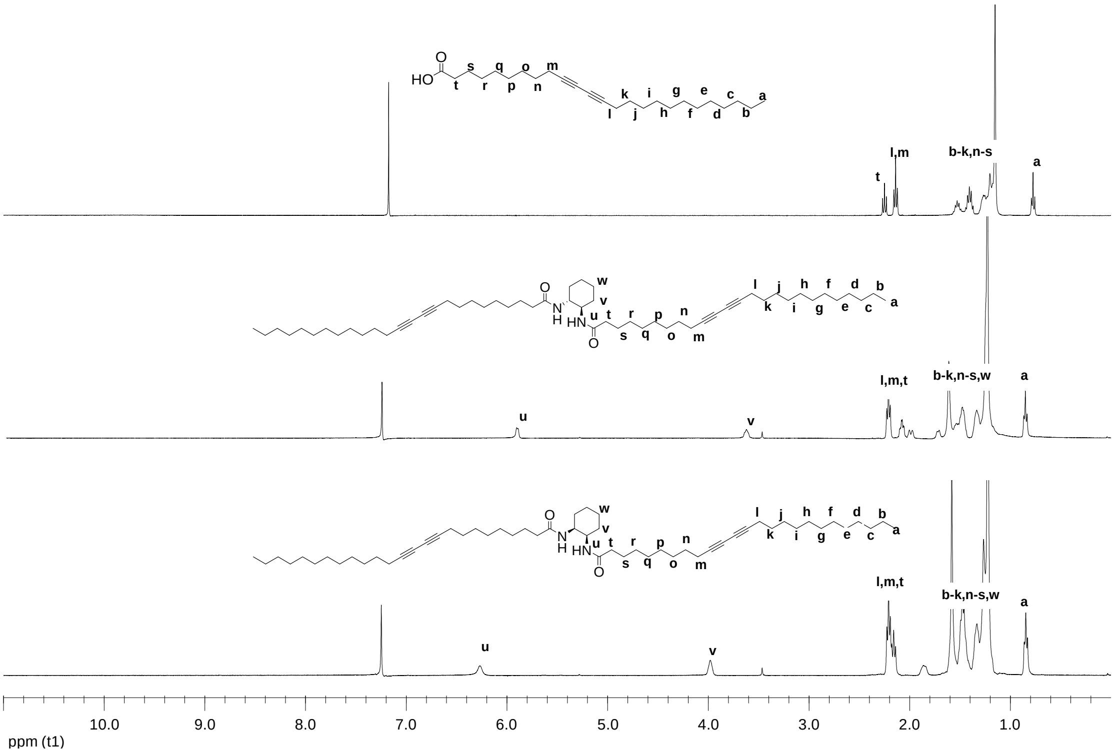


Figure 3.3 ^{1}H NMR spectra of PCDA, *c*-CA-2DA and *t*-CA-2DA lipids in $CDCl_3$.

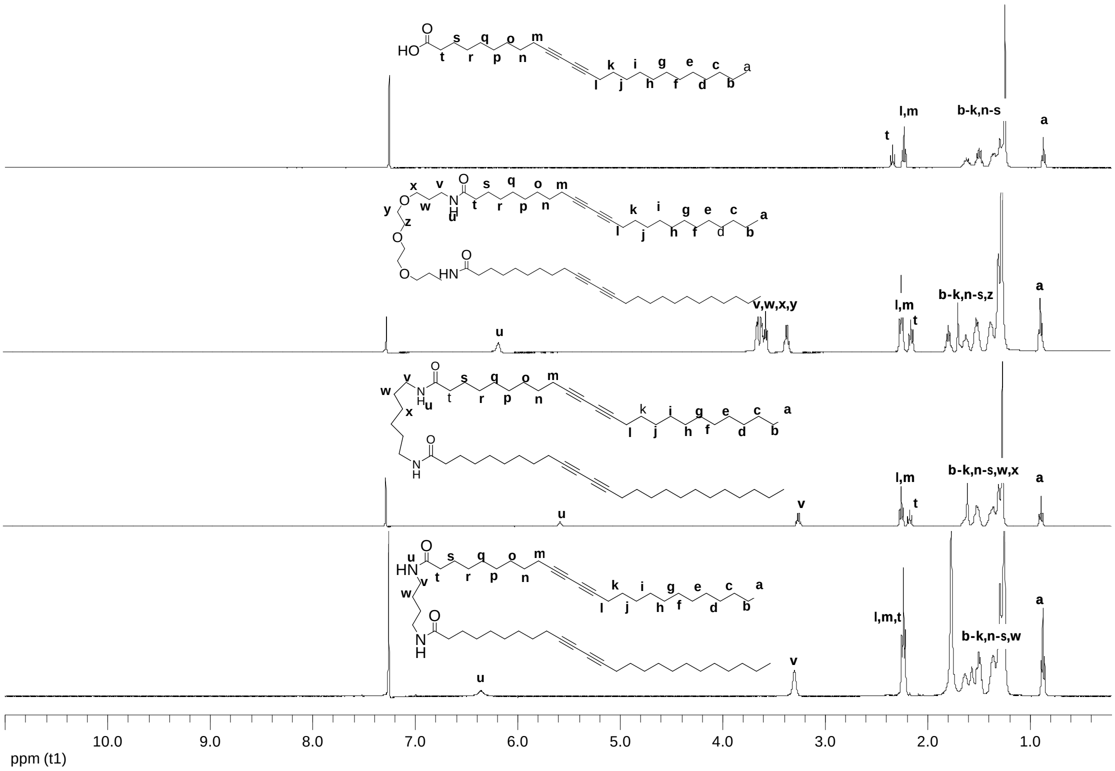


Figure 3.4 ^{1}H NMR spectra of PCDA, POEA-2DA, HA-2DA and BA-2DA lipids in $CDCl_3$.

For *c*-CA-2DA and *t*-CA-2DA, that possess 1,2-*cis*-diaminocyclohexane and 1,2-*cis*-diaminocyclohexane as the liker, the signal of C-H cyclohexane ring connecting to the amido groups appeared at δ 4.0 and 3.7 ppm, respectively, in addition to the amide N-H signal in the range of 6.0–6.4 ppm (Figure 3.3). The last series of the synthesized diacetylene lipid is the diamido derivatives containing the alkyl chain linker. The spectra of HA-2DA and BA-2DA lipids exhibit the signals of amido N-H proton at δ 5.5 and 6.3 ppm, respectively (Figure 3.4). The signals of N-CH_2 protons appeared at 3.24 and 3.28 ppm for HA-2DA and BA-2DA, respectively. The spectra of APOEO-2DA were quite similar to the spectra of HA-2DA and BA-2DA except for that there were extra signals around 3.5-3.8 ppm corresponding to the protons of propylene and ethylene oxide liker.

3.2 Preparation of polydiacetylene (PDA) sols and characterization

The synthesized monomers were transformed into aqueous polydiacetylene (PDA) sols. The vesicles were prepared by sonication of lipid monomer in milli-Q water followed by irradiation with 254 nm UV-light. The ability to be hydrated and the color of polymerized diacetylenes are presented in Table 3.1. All monoamide monomers, *o*-PA-1DA, *m*-PA-1DA and *p*-PA-1DA, are able to be hydrated to give colorless solution prior to UV light irradiation. On the other hands, diamido diacetylene such as *o*-PA-2DA, *m*-PA-2DA, *p*-PA-2DA, *t*-CA-2DA, *c*-CA-2DA, BA-2DA, HA-2DA and POEA-2DA gave poor dispersion after normal sonication condition due to their high melting points (90-128^{o}C). However, the dispersion can be improved by repeating the heating and the sonicating process until the translucent sols were obtained. The dispersed monomers were subsequently irradiated with 254 nm light at 500 μW/cm^2 for 4 min. After UV exposure, the colorless sols of *o*-PA-1DA, *m*-PA-1DA and *p*-PA-1DA diacetylene lipids readily turned to distinct blue sols signifying the polymerization of diacetylene monomers to form ene-yne conjugated PDAs. These results also support the formation of ordered diacetylene monomer assembly before the polymerization step. The sols of poly(*o*-PA-1DA), poly(*m*-PA-1DA) and poly(*p*-PA-1DA) showed the electronic absorption maximum at 631, 623 and 629 nm, respectively. The similar blue sols were also obtained from the irradiation of *m*-AP-2DA and *p*-AP-2DA sols. Nevertheless, *o*-AP-2DA rapidly formed blue aggregates upon irradiation. This observation may be associated with the possibility to form intramolecular hydrogen bonding between amino hydrogen and amido carbonyl moieties in the *ortho*-position which reduces the possibility to form intermolecular hydrogen bonding among diacetylene molecules. Interestingly, *t*-CA-2DA and *c*-CA-2DA produced reddish purple sols upon exposure to UV at room temperature.

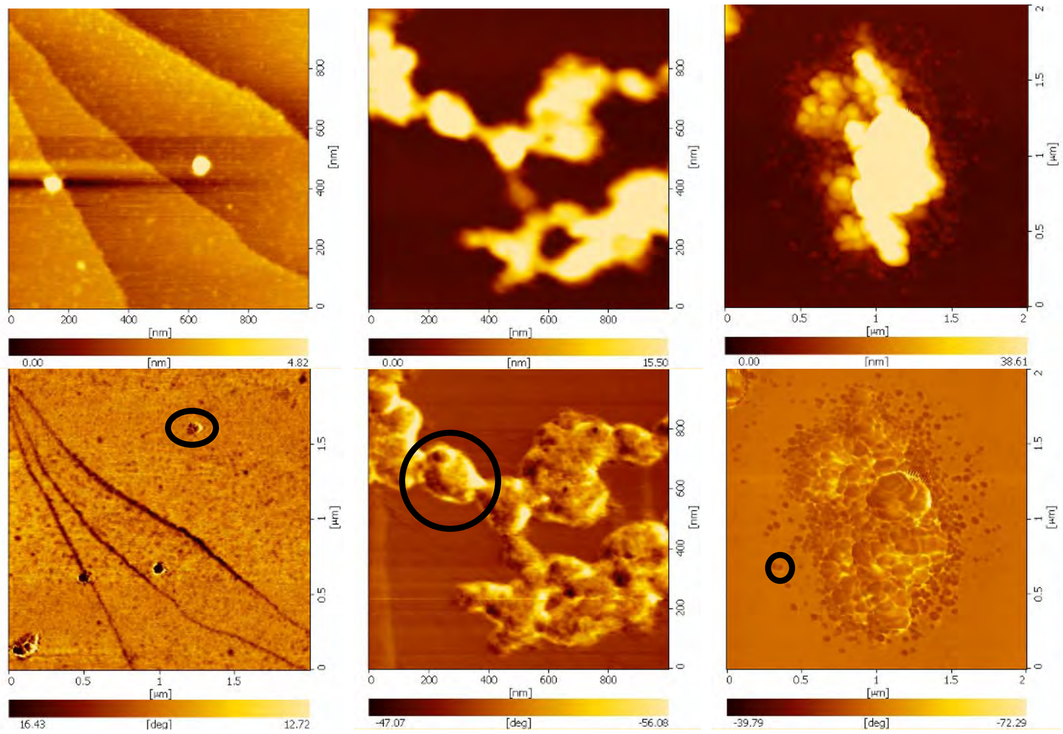
Table 3.1 Properties of prepared PDA.

Polydiacetylene	Linker	Vesicle formation (λ_{max},nm)	Color	Vesicle size [a]
Poly(*o*-PA-1DA)	*o*-(-C_6H_4-)	Yes(631)		ND
Poly(*m*-PA-1DA)	*m*-(-C_6H_4-)	Yes(623)		139 nm
Poly(*p*-PA-1DA)	*p*-(-C_6H_4-)	Yes(629)		ND
Poly(*o*-PA-2DA)	*o*-(-C_6H_4-)	AG	-	-
Poly(*m*-PA-2DA)	*m*-(-C_6H_4-)	Yes(641)		169 nm
Poly(*p*-PA-2DA)	*p*-(-C_6H_4-)	Yes(633)		ND
Poly(*t*-CA-2DA)	1,2-*t*-(-C_6H_{10}-)	Yes(640)		ND
Poly(*c*-CA-2DA)	1,2-*c*-(-C_6H_{10}-)	Yes(629)		ND
Poly(BA-2DA)	1,4-(-$(CH_2)_4$-)	Yes(675)		ND
Poly(HA-2DA)	1,6-(-$(CH_2)_6$-)	Yes(677)		157 nm
Poly(POEA-2DA)	(-$(CH_2)_3$-O-(CH_2)-$)_2$-O	Yes(633)		ND

AG = aggregate, ND= not determine

In an attempt to generate the blue sol of poly(*t*-CA-2DA) and poly(*c*-CA-2DA), the irradiation was thus conducted at 5 °C in an ice batch. Clear blue sol could be produced in the case of *t*-CA-2DA but *c*-CA-2DA still gave the purple sols. The results suggest that the dihedral angles, 60° for the diequatorial *trans*-isomer and 120° for the axial-equatorial *cis*-isomer, between the 1,2-cyclohexylene bonds connecting to amido N atoms may not allow good chain packing between the diactylene units. Among the PDA sols prepared from the synthesized lipids, poly(BA-2DA) and poly(HA-2DA) showed the absorption maximum (675 and 677 nm, respectively) at the unusually long wavelength and two additional peaks were observed at 560 and 635 nm. It is also important to note here that with the same starting concentration of the monomeric lipids, the preparation of poly(BA-2DA) and poly(HA-2DA) showed the deepest blue color. The results suggested that the polymerization of BA-2DA and HA-2DA yielded more extensive π-conjugation PDAs than the other diacetylene lipids. Replacing aliphatic alkyl chain linker with triethylene glycol, poly(APOEO-2DA) showed typical main absorption peak at 633 nm suggesting that the repulsion between lone pair electron of the O atoms has reduced the packing between the lipid chains comparing to the normal alkyl chain.

Atomic force microscopy (AFM) was utilized to observe the shape and size of the air-dried PDA sols. The AFM images showed spherical structures of PDA sols (Figure 3.5). The AFM results of poly(*m*-PA-1DA) were in good agreement with the DLS results. The typical particle sizes of non-aggregated poly(*m*-PA-1DA) observed in the AFM images are 80-100 nm. The AFM image of poly(*m*-PA-2DA) and poly(HA-2DA) sols shows extensive aggregation of the vesicles which may explain a relatively bigger particle size measured by DLS.



Poly(*m*-PA-1DA) **Poly(*m*-PA-2DA)** **Poly(HA-2DA)**

Figure 3.5 Morphology (top row) and phase (bottom row) AFM images of dry Poly(*m*-PA-1DA), Poly(*m*-PA-2DA) and Poly(HA-2DA) vesicles.

3.3 Thermochromic properties of PDA sols

Having prepared PDA sols, the next stage of investigation focused on thermochromic properties. Initially, they were filtered and subjected to the stepwise heating from 25 to 90 °C within the heating cell of variable temperature UV-Vis spectrometer. Figure 3.6 illustrates the annealing temperature dependence of UV-Vis absorption spectrum along with photographs of PDAs. As mentioned above, the blue sols prepared from monoamidodiacetylene such as *o*-PA-1DA, *m*-PA-1DA and *p*-PA-1DA possess a maximum wavelength around 630 nm with the phonon side band approximately at 580 nm. Upon increasing temperature, the absorbance band is decreased and shifted to shorter wavelength. At 95 °C, the red solution of poly(*o*-PA-1DA), poly(*m*-PA-1DA) and poly(*p*-PA-1DA) showed the maximum absorption at 539, 537 and 540 nm, respectively, indicating the larger band gap between the ground and excited states. As shown by the color photograph, the color changes from blue to red of these sols took place in the range of 65-75 °C.

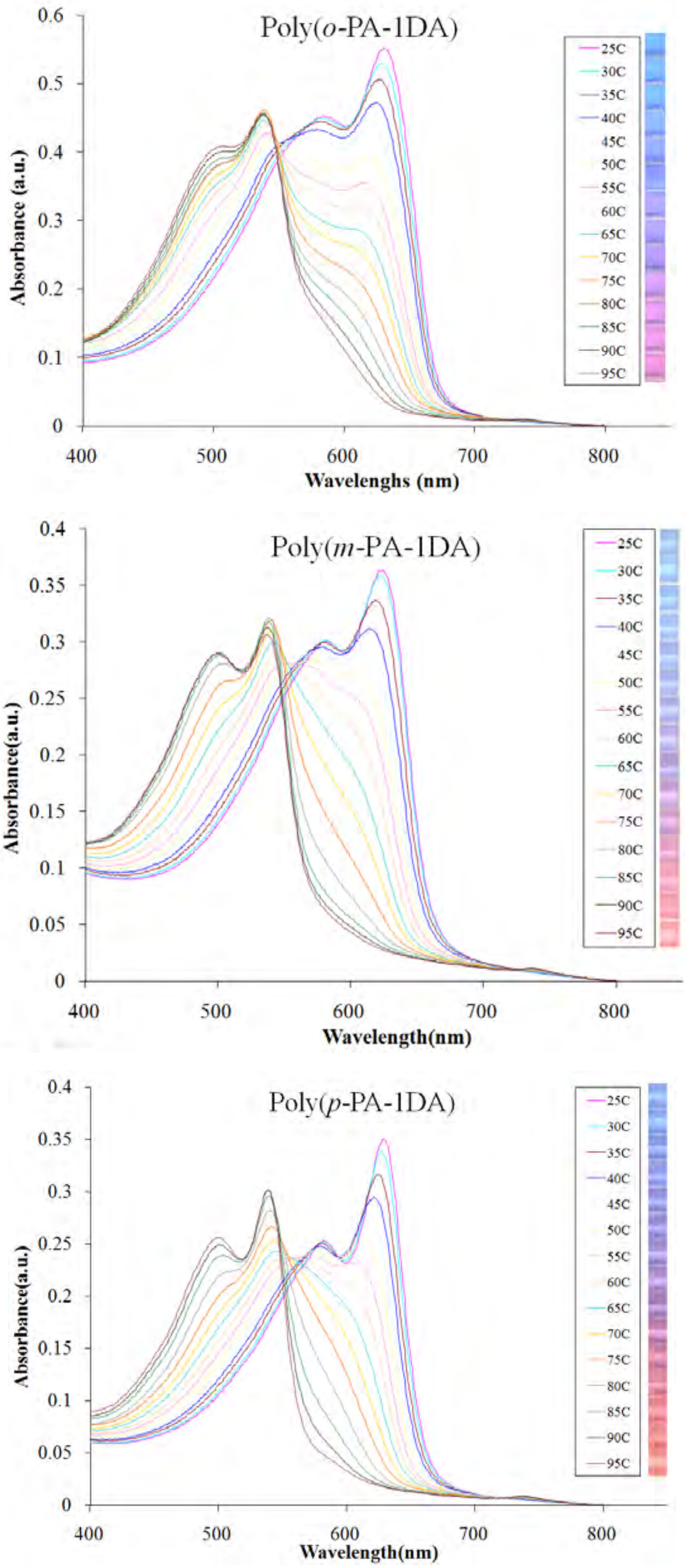


Figure 3.6 UV-spectra and samples of color photographs of poly(*o*-PA-1DA), poly(*m*-PA-1DA) and poly(*p*-PA-1DA) sols upon stepwise heating to various temperatures.

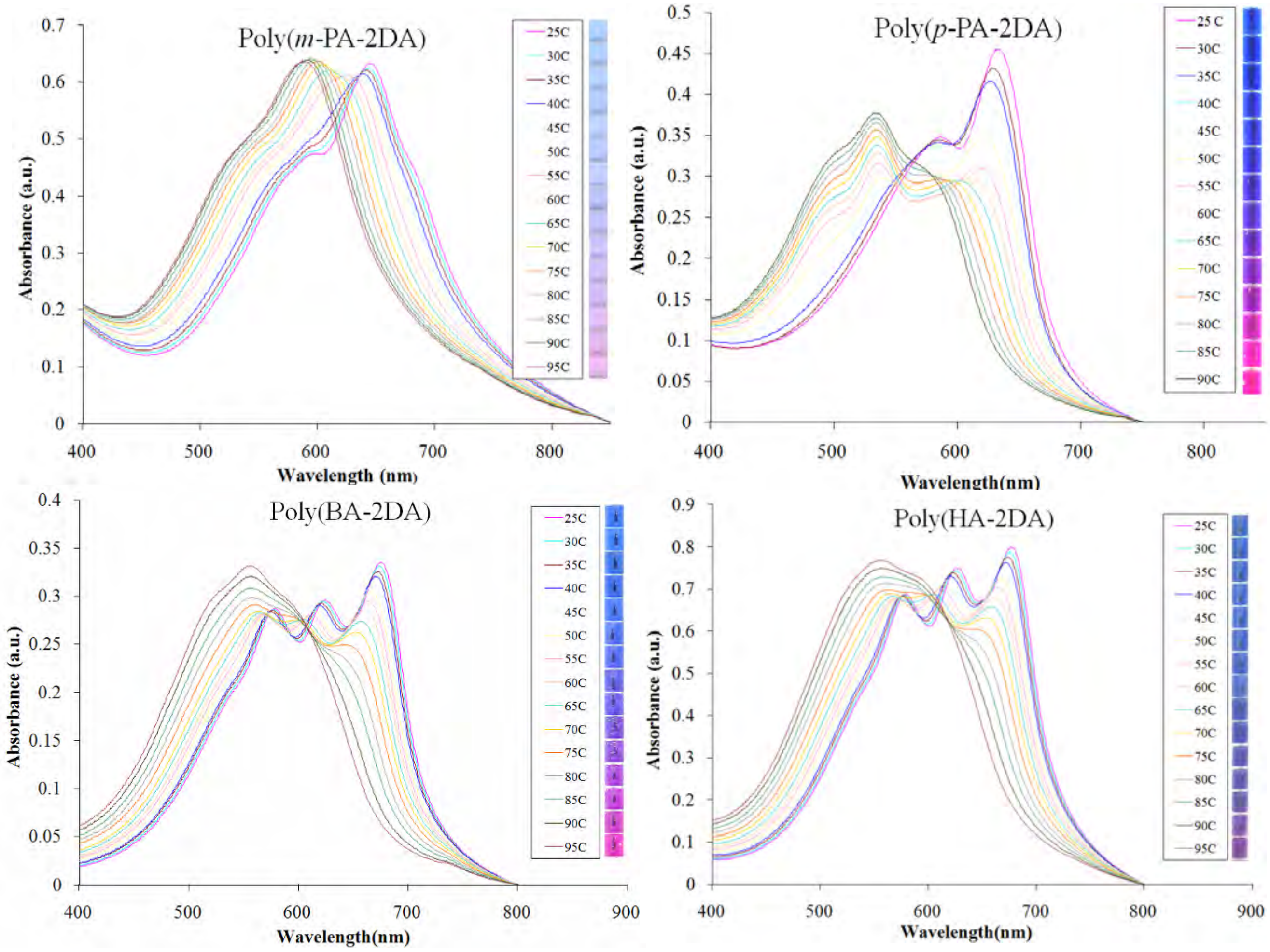


Figure 3.7 UV-spectra and samples of the color photographs of poly(*m*-PA-2DA), poly(*p*-PA-2DA), poly(BA-2DA) and poly(HA-2DA) sols upon stepwise heating to various temperatures.

Similarly, the PDA derived from the diamidodiacetylene monomer demonstrated the same phenomena. The blue sols of poly(*m*-PA-2DA) and poly(*p*-PA-2DA) turned to red around 80-90 °C and 70-80 °C, respectively, and the absorption bands were shifted to shorter wavelength from λ_{max} ~640 nm to ~550 nm (Figure 3.7). The deep blue sols of poly(BA-2DA) turned to red around 85-95 °C while the color transition of poly(HA-2DA) did not reach red even at 95 °C. These again occurred along with blue to red color change.

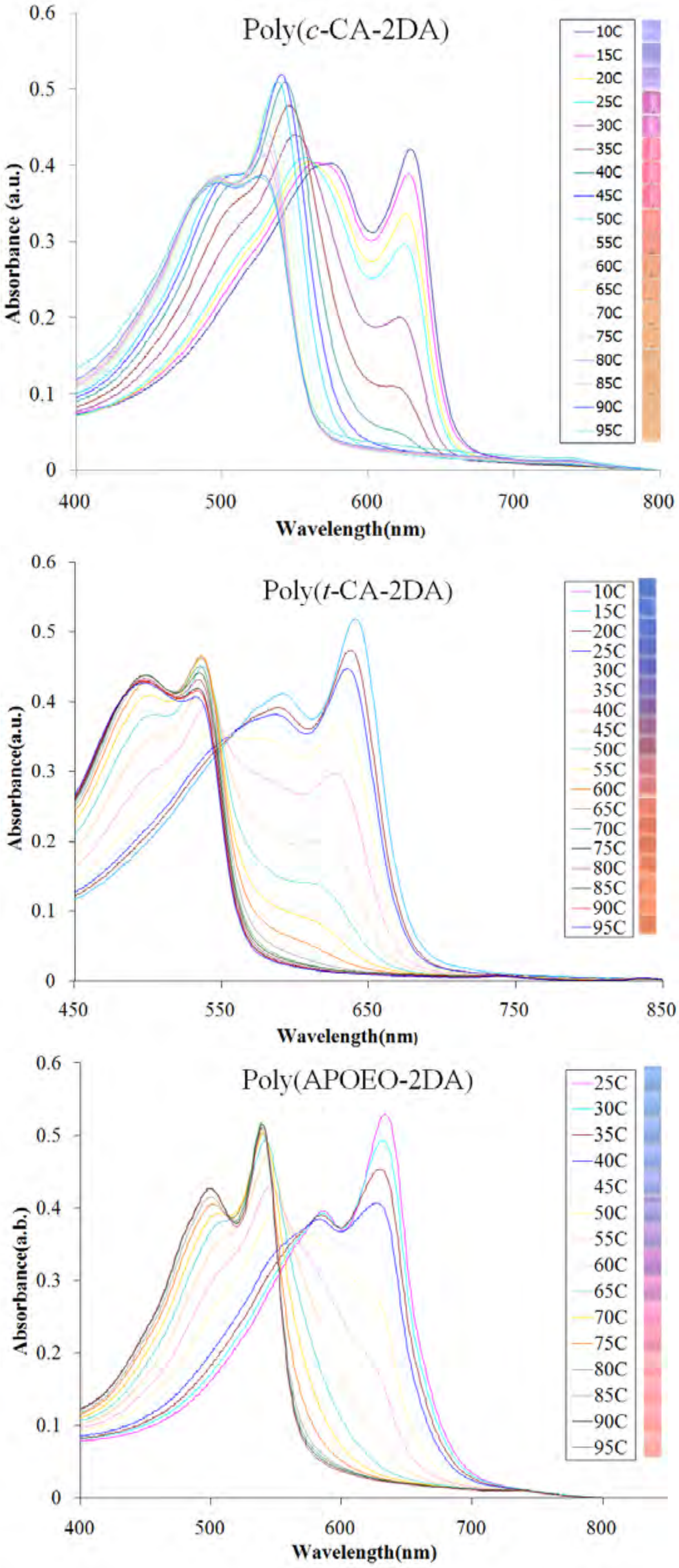


Figure 3.8 UV-spectra and samples of the color photographs of poly(*c*-CA-2DA), poly(*t*-CA-2DA), and poly(APOEO-2DA) sols upon stepwise heating to various temperatures.

The other groups of PDAs, poly(*c*-CA-2DA), poly(*t*-CA-2DA) and poly(APOEO-2DA), showed relatively lower color transition temperatures around 25-30, 45-55 and 50-60 °C, respectively (Figure 3.8). The lower color transition temperature of poly(*t*-CA-2DA), poly(*c*-CA-2DA) and poly(APOEO-2DA) in comparison to poly(*m*-PA-2DA) and poly(*p*-PA-2DA) confirmed the weaker attractive interactions, hydrogen bonding and hydrophobic interaction, due to the poor packing among the side chains in these diacetylene lipids. It is also interesting to note that the *trans*-geometry, exhibited higher color transition temperature comparing to the *cis*-geometry. The observation suggested that the diequatorial arrangement of the diamide side chain allowed better packing than the axial-equatorial orientation.

According to results described above, the color transition temperature observed by eye were in the following order: poly(HA-2DA) > poly(BA-2DA) > poly(*m*-PA-2DA) > poly(*p*-PA-2DA) > poly(*o*-PA-1DA) > poly(*m*-PA-1DA) > poly(*p*-PA-1DA) > poly(APOEO-2DA) > poly(*t*-CA-2DA) > poly(*c*-CA-2DA). This order indicates the importance of the number of amide groups, the geometry or dihedral angle of the linkers as well as the lone pair electron presence in the linkers. Greater number of amide groups can lead to higher color transition temperature (poly(*m*-PA-2DA), poly(*p*-PA-2DA) > poly(*o*-PA-1DA), poly(*m*-PA-1DA), poly(*p*-PA-1DA). The planar geometry of the linker connecting the two amides groups (poly(HA-2DA), poly(BA-2DA), poly(*m*-PA-2DA) and poly(*p*-PA-2DA) give higher color transition temperature than those of non planar geometry (poly(*t*-CA-2DA) and poly(*c*-CA-2DA)). The lone electron pairs within the linker can reduce the color transition temperature (poly(APOEO-2DA) < poly(HA-2DA) and poly(BA-2DA)).

To evaluate the color transition from the UV-visible absorption spectra of all prepared PDA sols were translated into colorimetric response (%CR). The %CR is defined as percent change in the maximum absorption of the blue phase with the respect to the total absorption at both red and blue phases. The plot of %CR against the temperature of all PDA studied yielded sigmoidal curves as a result of blue to red transition upon raising temperature (Figure 3.9).

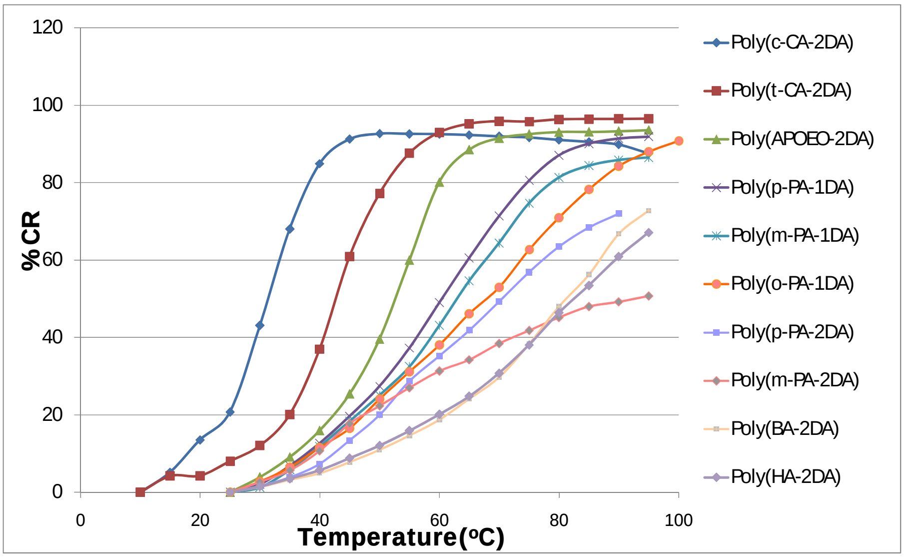


Figure 3.9 Colorimetric responses to temperature of PDAs containing one and two amide groups.

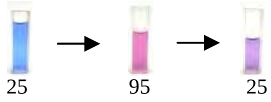
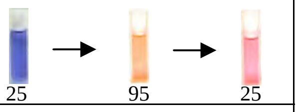
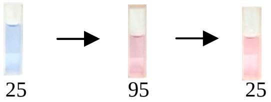
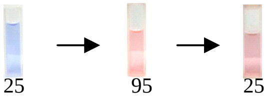
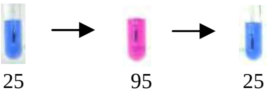
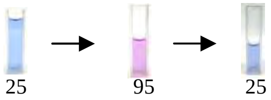
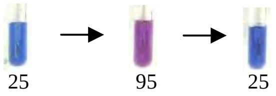
Comparison between photographic observation and colorimetric response plot of PDA sols upon heating indicates similar apparent tendency. The order of CTT assessed from %CR is found in the following order: poly(HA-2DA) > poly(BA-2DA) = poly(*m*-PA-2DA) > poly(*p*-PA-2DA) > poly(*o*-PA-1DA) > poly(*m*-PA-1DA) > poly(*p*-PA-1DA) > poly(APOEO-2DA) > poly(*t*-CA-2DA) > poly(*c*-CA-2DA). This order of CTT of PDA observed from %CR is in good agreement with those observed from photographic recording. The %CR plots also provided valuable information. Evidently, PDAs derived from *c*-CA-2DA, *t*-CA-2DA and APOEO-2DA exhibited rather steep sigmoidal %CR plots meaning that they undergo sharp color transition within narrow ranges of temperature. The %CR PDAs of these PDAs increased from 20% to 60% within the temperature range of no more than 10 °C. On the other hands, poly(*o*-PA-1DA), poly(*m*-PA-1DA) and poly(*p*-PA-1DA) showed more gradual change in %CR upon heating. It generally required the temperature increase of 20-25 °C, to have the %CR raised from 20% to 60% for this PDA series. The PDAs derived from the monomers such as *m*-PA-2DA, *p*-PA-2DA, BA-2DA and HA-2DA showed even slower blue to red color transition that usually requires the increase of the temperature of more than 25 °C to attain the 20% to 60% level of the %CR change.

The steep and gradual responses of PDA to the temperature induced color transition are very interesting and would increase the selections of PDAs to be applied as thermal sensor for various applications providing that the relationships between this property and the structure is well understood. The most notable trend described above is that the lower the CTT the sharper the temperature induced colorimetric response. The hydrogen bonding is again likely to be the main contribution governing this trend. The blue-to-red color transition is associated with the movement of the side chains that results in the release of backbone strain and disturbing the ene-yne planarity upon thermal stimulation [28]. The side chain movement will be sluggish and will require more energy if the hydrophobic interaction between the side chains and the hydrogen bonding between the head groups are strong. Since all diacetylene monomers investigated contains the same C_{25} aliphatic structure. It is thus the two hydrogen forming points between the head groups of poly(HA-2DA), poly(BA-2DA), poly(*m*-PA-2DA) and poly(*p*-PA-2DA) that attributes to both broad temperature induced colorimetric response and high CTT. Although *c*-CA-2DA, *t*-CA-2DA and APOEO-2DA also have two hydrogen forming points, they give PDAs with lower CTT and sharper colorimetric response even when compared with the monoamide lipids like *o*-PA-1DA, *m*-PA-1DA and *p*-PA-1DA. The results reiterate the importance of the geometry and the electron lone pair repulsion on the O atoms of the linkers between the diamide. An interesting question to be answered is if it is possible to design a new PDA with sharp thermochromic response at high CTT that shall be the subject of future work.

3.4 Reversibility of the color transition

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 95 °C and cooled back to 25 °C, the recorded color photographs before heating, after heating and after cooling provided an approximate idea about the reversibility of these PDAs (Table 3.2).

Table 3.2 Color photographs showing approximate degrees of reversibility of the color transition of the PDA sols observed by eyes.

Polydiacetylene	**Reversibility** (°C)	**Polydiacetylene**	**Reversibility** (°C)
Poly(*o*-PA-1DA)		Poly(*t*-CA-2DA)	
Poly(*m*-PA-1DA)		Poly(*c*-CA-2DA)	
Poly(*p*-PA-1DA)		Poly(BA-2DA)	
Poly(*m*-PA-2DA)		Poly(HA-2DA)	
Poly(*p*-PA-2DA)		Poly(APOEO-2DA)	

*Note AG = aggregated

The PDAs possessing one amide head group such as poly(*o*-PA-1DA), poly(*m*-PA-1DA) and poly(*p*-PA-1DA) exhibited none to little reversibility of the color transition. On the other hand, the corresponding PDAs having two amide head groups, poly(*m*-PA-2DA), poly(*p*-PA-2DA), and alkyl linked diamide like poly(BA-2DA) and poly(HA-2DA) displayed complete reversibility of the color transition suggesting that the two amide head groups are necessary for complete reversibility. Poly(*c*-CA-2DA), poly(*t*-CA-2DA) and poly(APOEO-2DA) however displayed very little reversibility of the color transition despite having two amide head groups. This result implies that the amide head groups in poly(*c*-CA-2DA), poly(*t*-CA-2DA) and poly(APOEO-2DA) cannot form strong hydrogen bonds among them.

To assess the degree of thermochromic reversibility of the PDAs, the blue absorbance, defined as the absorbance at the λ_{max} of “blue from”, was monitored for 9 cycles of heating and cooling between 95 and 25 °C. The plots between the absorbance and the cycle numbers of poly(*m*-PA-2DA), poly(*p*-PA-2DA), poly(BA-2DA) and poly(HA-2DA) displayed a zigzag pattern with virtually full recovery of the initial absorbance in every cycles (Figure 3.10), indicating the complete thermochromic reversibility of these PDAs. Again, the two hydrogen bond forming head groups, amide groups, probably play the most important roles to this reversibility. As expected, the rest of the PDAs did not show the full reversibility as the blue absorbance dropped dramatically after the first heating-cooling cycle. Interestingly, all of these PDAs, except poly(*c*-CA-2DA), however showed certain degrees of consistent reversibility from the second heating-cooling cycle. The ability to regain the intensity of the initial blue absorbance is diverse among them. For comparison, the most studied PDA, poly(PCDA), was studied in the same manner and the plot between the blue absorbance and the number cycles also showed a low degree but consistent recovery of the absorbance after the second heating-cooling cycle. Some PDAs such as poly(*o*-PA-1DA) and poly(*p*-PA-1DA) can recover the blue absorbance significantly greater than poly(PCDA).

To obtain a quantitative value of the degree of reversibility, the recovery of color (% RC) is determined according to the following equation. %RC = 100 × A_{avg}/A_i where A_{avg}, the average $A_{25\text{-}95°C}$ of blue from the 2nd to 10th cycle of heat and A_i is $A_{25\text{-}95°C}$ of blue of 1st cycle of heat. According to the degree of reversibility presented in Table 3.3, it is quite convenient to classify the PDAs investigated in this work into three categories *i.e.* 1) fully reversible PDA (%RC > 90%), partially reversible PDA (10 < %RC < 90%) and irreversible PDA (%RC < 10%).

Using the classification mentioned above, poly(*m*-PA-1DA), poly(*c*-CA-2DA) poly(APOEO-2DA) and poly(PCDA) possess irreversible thermochromic property. After the 2nd heating-cooling cycle, these polymers appeared as red color at both 95 and 25 (Table 3.3). The small percent recovery (1-10%) maybe caused by either the small recovery of planarity of the ene-yne conjugated system or the altering of the population in vibronic states at different temperatures.

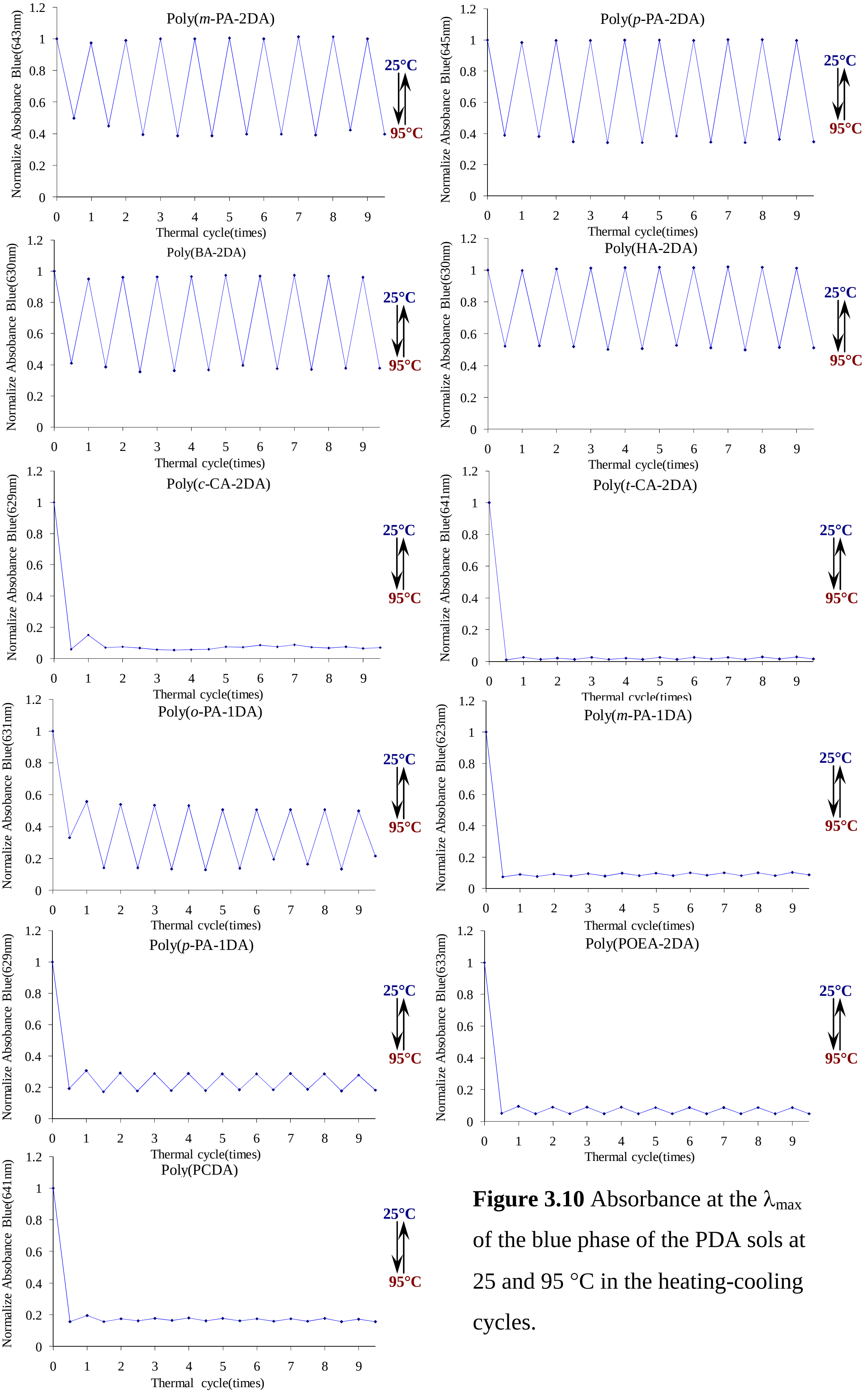


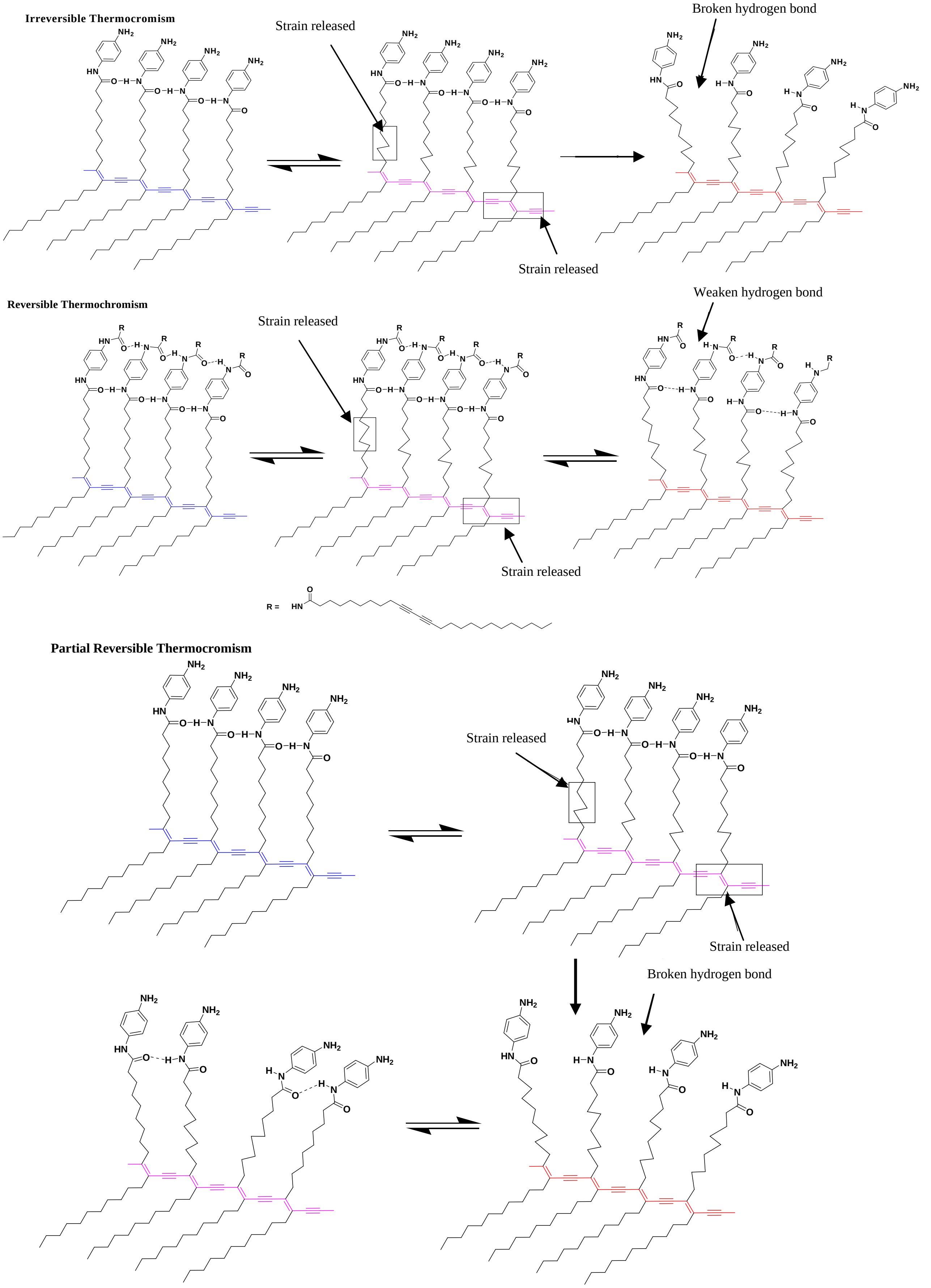
Figure 3.10 Absorbance at the λ_{max} of the blue phase of the PDA sols at 25 and 95 °C in the heating-cooling cycles.

Table 3.3 Degree of reversibility of the PDAs and their simple classification

PDA	**% RC**	**Classification of PDA**
Poly(PCDA)	2.2%	irreversible
Poly(*m*-PA-1DA)	1.7%	irreversible
Poly(*c*-CA-2DA)	1.2%	irreversible
Poly(*t*-CA-2DA)	1.2%	irreversible
Poly(APOEO-2DA)	4.3%	irreversible
Poly(*o*-PA-1DA)	54.7%	partially reversible
Poly(*p*-PA-1DA)	13.3%	partially reversible
Poly(*m*-PA-2DA)	119.0%	fully reversible
Poly(*p*-PA-2DA)	104.7%	fully reversible
Poly(EA-2DA)	99.7%	fully reversible
Poly(BA-2DA)	100.3%	fully reversible
Poly(HA-2DA)	104.9%	fully reversible

It may be useful to introduce the thermodynamic terms contributing to the free energy change (ΔG) of the color transition process. From $\Delta G = \Delta H - T\Delta S$, it is obvious that the positive entropy term (ΔS) is favored by high temperature. It is thus reasonable to assume that PDAs is in less ordered form at high temperature (95 °C). The red form is thus a less ordered form comparing to the blue form (see references 37 for support and references 38-40 for argument to this statement). The enthalpy term (ΔH) is more complicated to analyze as it is a sum of several parts contributed by various energy related factors *i.e.* hydrogen bonding between the head groups (ΔH_H), interaction among the hydrophobic side chains (ΔH_i), conformation of individual side chain (ΔH_c), delocalization energy within the conjugated system (ΔH_d) and strain within the conjugated backbone (ΔH_s). Thus, $\Delta H = \Delta H_H + \Delta H_i + \Delta H_c + \Delta H_d + \Delta H_s$. Upon heating, ΔH_H, ΔH_i and ΔH_d are positive while ΔH_s is negative providing that the hydrogen bonding, hydrophobic interaction, delocalization energy and backbone strain presents in the original blue form in greater deals comparing to the red form. Some literature works have reported that the blue from contains more guach conformation while the red form has more anti conformation of the side chains suggesting that ΔH_c is negative upon heating [29]. For the process to be irreversible, ΔH must be less than $T\Delta S$ implying that the positive enthalpy changes (ΔH_H, ΔH_i and ΔH_d) are either less or comparable to the negative enthalpy changes (ΔH_c and ΔH_s). In the other words, the sum of the hydrogen bonding, hydrophobic interaction in the original and the gain in delocalization energy in the blue form are not enough to overcome the original conformational and backbone strains as well as the entropy lost after heating and cooling back these PDAs (Scheme 3.2) [17].

The partially reversible thermochromism observed for poly(*o*-AP-1DA), poly(*p*-AP-1DA) and poly(*t*-CA-2DA) exhibiting %RC of 10-40% indicates that there are two more forms of the PDAs besides the blue form after heating, red form at 95 °C and purple form at 25 °C (see Table 3.2 for the appearing color). In these polymers, the red form is a metastable form present only at high temperature and the purple form is a stable form that exists after the PDAs are cooled back to room temperature. As the entropy term become less important after cooling, the hydrogen bonding, the hydrophobic interaction as well as partial gain in delocalization energy can probably restore some order and planarity of the conjugated backbone back. The backbone strain and the conformational relaxation of the side chains are probably the main factors preventing the PDAs to return to their original blue form even after cooling back to room temperature (see Scheme 3.2 for illustrative mechanism). The consistent recovery of the blue absorbance for a number of cycles suggests that the side chains retain certain degree of order even at the temperature above their CTT where the polymer is already in the red form.



Scheme 3.2 Schematics representation of the mechanisms of irreversible, partially reversible and fully reversible thermochromism of the PDAs.

The complete reversibility observed for poly(*m*-AP-2DA), poly(*p*-AP-2DA), poly(BA-2DA) and poly(HA-2DA) have been discussed previously, in various sections, to be the results of two hydrogen bond forming points of the side chain head groups. These two hydrogen bond forming points are importance for both keeping the head groups of the side chains to be in place at all time during heating and reinstall the original packing of the side chains as well as the backbone strain. It is likely that at least one of the hydrogen bonds per head group remained strongly present up to 95 °C (Scheme 3.2). Thermodynamically, ΔS and ΔH_c are probably small in these PDAs as less movement of the side chains are allowed with the head group locked in the position. The reversibility process is thus likely to associate with the sum of ΔH_H, ΔH_i and ΔH_d being appreciably greater than ΔH_s that makes the blue form being the stable form and the red form being the metastable form which present only at high temperature where the term $T\Delta S$ becomes more significant.

CHAPTER IV

CONCLUSION

4.1 Conclusion

In conclusion, we have demonstrated how the numbers of amide groups affect the thermochromic properties of polydiacetylenes (PDAs) obtained from the diacetylene lipids in the form of aqueous sols. The color transition temperature and the reversibility properties of polydiacetylene sols were found to be associated with the number of the possible hydrogen bond forming amide groups and the geometry of the linker between the amide groups. The PDAs carrying two amide groups with aromatic and aliphatic chain linker showed complete color transition reversibility along with higher color transition in comparison with the corresponding monoamide. On the other hands, the diamide having cyclohexane or bis(propylenoxide ehthylenoxide) linkers gave irreversible PDAs with lower color transition temperature. The results suggested that the heteroatom and the non-planar geometry of the linker may prevent the formation of two strong hydrogen bonds despite having two amide groups. This observation should provide guidelines for design polydiacetylenes with desired thermochromic properties for various applications as thermal indicators.

REFERENCE

[1] Paula T. H., and Michael F. R. Thermochromism in Liquid Crystalline Polydiacetylenes. *Macromolecules*. 30(1997) : 5773.

[2] Kim, J.M.; Lee, J.S.; Choi, H.; Sohn, D., and Ahn, D.J. Rational design and in-situ FTIR analyses of colorimetrically reversibe polydiacetylene supramolecules. *Macromolecules*. 38(2005) : 9366.

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

[4] Ji, E.K.; Ahn, D.J., and Kim, J.M. The fluorescent polydiacetylene liposome. *Bull. Korean Chem. Soc.* 23(2003) : 667.

[5] Simon, J.K., and Elizabeth, A.H.H. pH response of carboxy-terminated colorimetric polydiacetylene vesicles. *Anal. Chem.* 78(2006) : 2231.

[6] Carpick, R.W.; Sasaki, D.Y., and Burns, A.R., First observation of mechanochromism at the nanometer scale. *Langmuir*. 16(2000) : 1270.

[7] Wenzel, M., and Atkinson, G.H. Chromatic properties of polydiacetylene films. *J. Am. Chem. Soc.* 111(1989) : 6123.

[8] Beckham, G.H., and Rubner, M.F. On the origin of thermochromism in cross-polymerized diacetylene-functionalized polyamides. *Macromolecules*. 26(1993) : 5198.

[9] Lee, D.C.; Sahoo, S.K.; Cholli, A.L., and Sandman, D.J. Structural aspects of the thermochromic transition in urethane-substituted polydiacetylenes. *Macromolecules.* 35(2002) : 4347.

[10] Nallicheri, R.A., and Rubner, M.F. Investigations of the mechanochromic behavior of poly(urethane-diacetylene) segmented copolymers. *Macromolecules.* 24(1991) : 517.

[11] Reichert, A.; Nagy, J.O.; Spevak, W., and Charych, D. Polydiacetylene liposomes functionalized with sialic acid bind and colorimetrically detect influza virus. *J. Am. Chem. Soc.* 117(1995) : 829.

[12] Ahn, D.J.; Chae, E.H.; Lee, G.S.; Shim, H.Y.; Chang, T.E.; Ahn, K.D., and Kim, J.M. Colorimetric reversibility of polydiacetylene supramolecules having enhanced hydrogen-bonding under thermal and pH stimuli. *J.* Am. Chem. Soc. 125(2003) : 8976.

[13] Tachibana, H.; Hosaka, N., and Tokura, Y. Effect of alkyl chain length on thermochromic phase transition in urethane-substituted polydiacetylene crystals. *Polym. Commun.* 42(2001) : 8311.

[14] 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.

[15] Okada, S.; Peng, S.; Spevak, W., and Charych, D. Color and Chromism of Polydiacetylene Vesicles. *Acc. Chem. Res.* 31(1998) : 229.

[16] Ji, E.K.; Ahn, D.J., and Kim, J.M. The Fluorescent Polydiacetylene Liposome. *Bull. Korean Chem. Soc.* 23(2003) : 667.

[17] Anupat Potisatityuenyong, Rojrit Rojanathanes, Gamolwan Tumcharern, and Mongkol Sukwattanasinitt. Electronic absorbtion spectroscopy probed side-chain movement in chromic transitions of polydiacetylene vesicles. *Langmuir*. 24(2008) : 4461.

[18] Shim, H.Y.; Lee, S.H.; Ahn, D.J.; Ahn, K.D., and Kim J.M. Micropatterning of diacetylenic liposomes on glass surfaces. *Mater Sci. Eng. C*.24(2004) : 157.

[19] Su, Y.L.; Li, J.R.; Jiang, L., and Cao, J. Biosensor signal amplification of vesicles functionalized with glycolipid for colorimetric detection of Escherichia coli. *J. Colloids Interface Sci*. 284(2005) : 114.

[20] Volinsky R.; Kliger M.; Sheynis T.; Kolusheva S., and Jelinek R. Glass-supported lipid/polydiacetylene films for colour sensing of membrane-active compounds. *Biosens. Bioelectron.* 22(2007) : 3247.

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

[22] Silbert, L.; Shlush, I. B.; Israel E.; Porgador, A.; Kolusheva, S., and Jelinek R. Rapid chromatic detection of bacteria by use of a new biomimetic polymer sensor. *Appl. Environ. Microbiol.* 72(2006) : 7339.

[23] Morigaki, K.; Buamgart, T.; Jonas, U.; Offenhausser, A., and Knoll, W. Photopolymerization of diacetylene lipid bilayers and its application to the construction of micropatterned biomimetic membranes. *Langmuir*. 18(2002) : 4082.

[24] Shibata, M.; Kaneko, F.; Aketagawa, M., and Kobayashi, S. Reversible color phase transitions and annealing properties of Langmuir-Blodgett polydiacetylene films. *Thin solid films*. 179(1989) : 433.

[25] Huo, Q.; Russell, K.C., and Leblanc, R.M. Chromatic studied of a polymerizable diacetylene hydrogen bonding self - assembly: a self-folding process to explain the chromatic changes of polydiacetylenes. *Langmuir*. 15(1999) : 3972.

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

[27] Ahn, D. J.; Lee, S., and Kim J. M. Rational Design of Conjugated Polymer Supramolecules with Tunable Colorimetric Responses. *Adv. Funct. Mater.* 18(2008) : 1.

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

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

[30] Singh, A.; Thompson, R. B. and Schnur, J. M. Reversible thermochromism in photopolymerized phosphatidylcholine vesicles. *J. Am. Chem. Soc.* 108(1986) : 2785.

[31] Yuan, Z.; Lee, C.W. and Lee, S.H. Reversible Thermochromism in Hydrogen-Bonded Polymers Containing Polydiacetylenes. *Angew. Chem. Int. Ed.* 43(2004) : 4197.

[32] Lim, J. K.; Lee, Y.; Lee, K.; Gong, M. and Joo, S.W. Reversible Thermochromic Change of Molecular Architecture for a Diacetylene Derivative 10,12-Pentacosadiynoic Acid Self-assembled Thin Films on Ag Surfaces. *Chem. Lett.* 36(2007) : 1226.

[33] Gu, Y.; Cao, W.; Zhu, L.; Chen, D. and Jiang, M. Polymer Mortar Assisted Self-Assembly of Nanocrystalline Polydiacetylene Bricks Showing Reversible Thermochromism. *Macromolecules* 41(2008) : 2299.

[34] Peng, H.; Tang, J.; Pang, J.; Chen, D.; Yang, L.; Ashbaugh, H. S.; Brinker,C. J.; Yang, Z. and Lu, Y. Polydiacetylene/Silica Nanocomposites with Tunable Mesostructure and Thermochromatism from Diacetylenic Assembling Molecules. *J. Am. Chem. Soc.* 127(2005) : 12782.

[35] Peng, H.; Tang, J.; Yang, L.; Pang, J.; Ashbaugh, H. S.; Brinker, C. J.; Yang, Z. and Lu, Y. Responsive Periodic Mesoporous Polydiacetylene/Silica Nanocomposites. *J. Am. Chem. Soc.* 128(2006) : 5304.

[36] Nagasawa, J.; Kudo, M.; Hayashi, S., and Tamaoki, N. Organogelation of Diacetylene Cholesteryl Esters Having Two Urethane Linkages and Their Photopolymerization in the Gel State. *Langmuir*. 20(2004) : 7907.

[37] Schott, M. The Color of polydiacetylenes : a *Commentary. J. Phys. Chem. B.* 110(2006) : 15864.

[38] Schott, M. *Optical Properties of Single Conjugated Polymer Chains*, In *Photophysics of Molecular Materials*; Lanzani G., Ed.; Wiley-VCH: Berlin, 2006 : 49.

[39] Fujimori, A.; Ishitsuka, M.; Nakahara, H.; Ito, E.; Hara, M.; Kanai, K.; Ouchi Y., and Seki, K. Formation of the Newly Greenish Organized Molecular Film of Long-Chain Diynoic Acid Derivatives by Photopolymerization and Its Structural Study Using Near-Edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy *J. Phys. Chem. B* 108(2004) : 13153.

[40] Lio, A.; Reichert, A.; Ahn, D. J.; Nagy, J. O.; Salmeron R., and Charych D. H. Molecular Imaging of Thermochromic Carbohydrate-Modified Polydiacetylene Thin Films. *Langmuir.* 13(1997) : 6524.

APPENDICES

Appendix A

Appendix A: ^{1}H NMR spectra of synthesized monomers

Figure A1: ^{1}H NMR; N, N'-(1, 2-phenylene) dipentacosa-10, 12-diynamide (*o*-AP-1DA) in DMSO

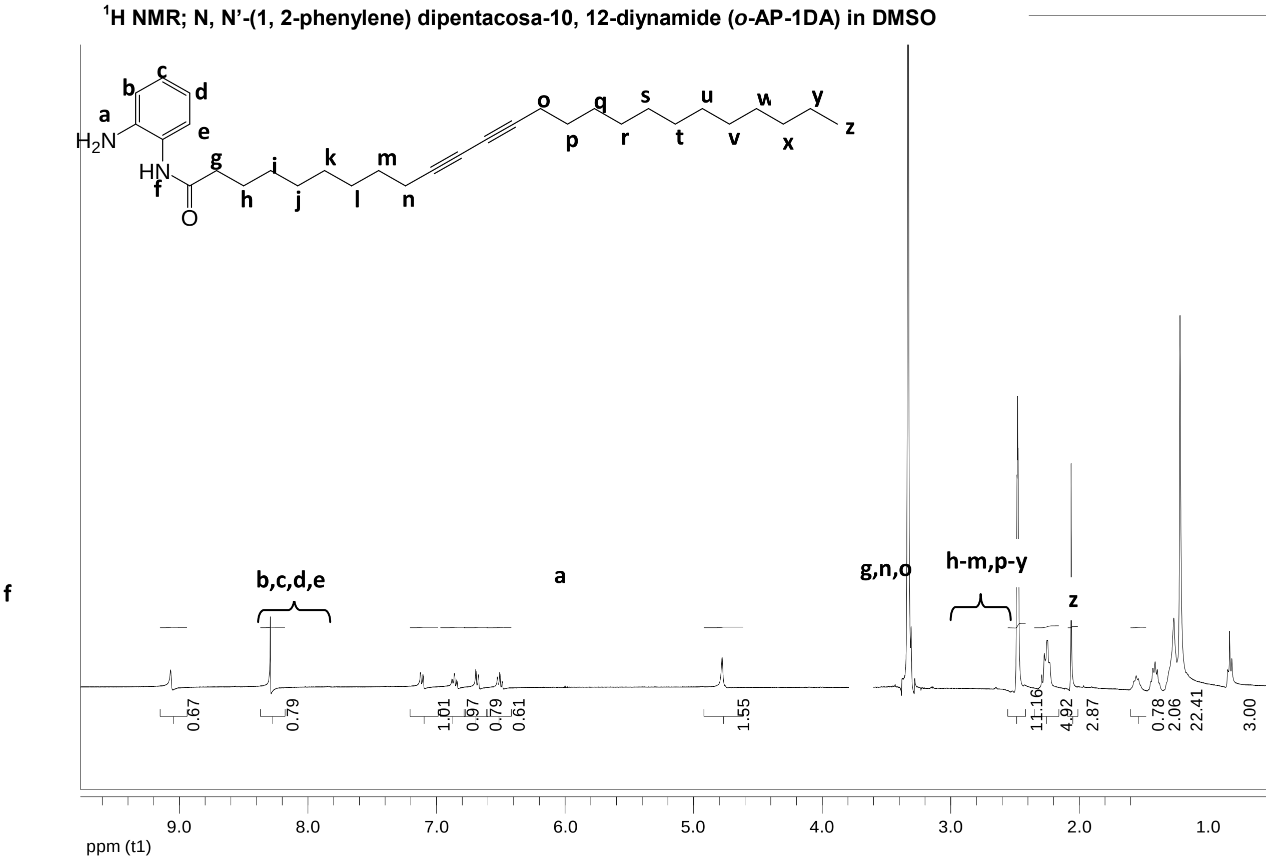


Figure A2: ^{1}H NMR; N, N'-(1, 3-phenylene) dipentacosa-10, 12-diynamide (*m*-AP-1DA) in DMSO

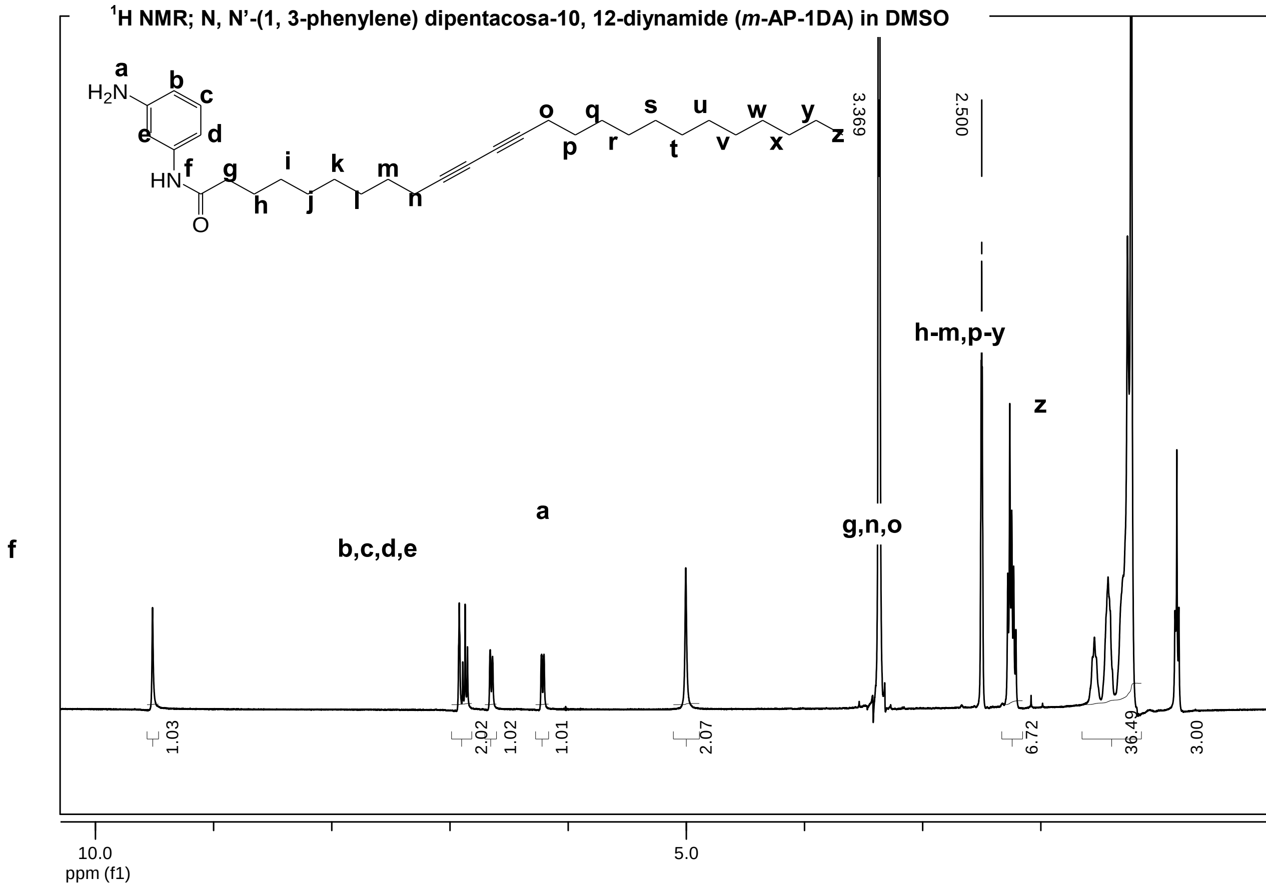


Figure A3: ^{1}H NMR; N,N'-(4-aminophenyl) pentacosa-10, 12-diynamide (*p*-AP-1DA) in DMSO

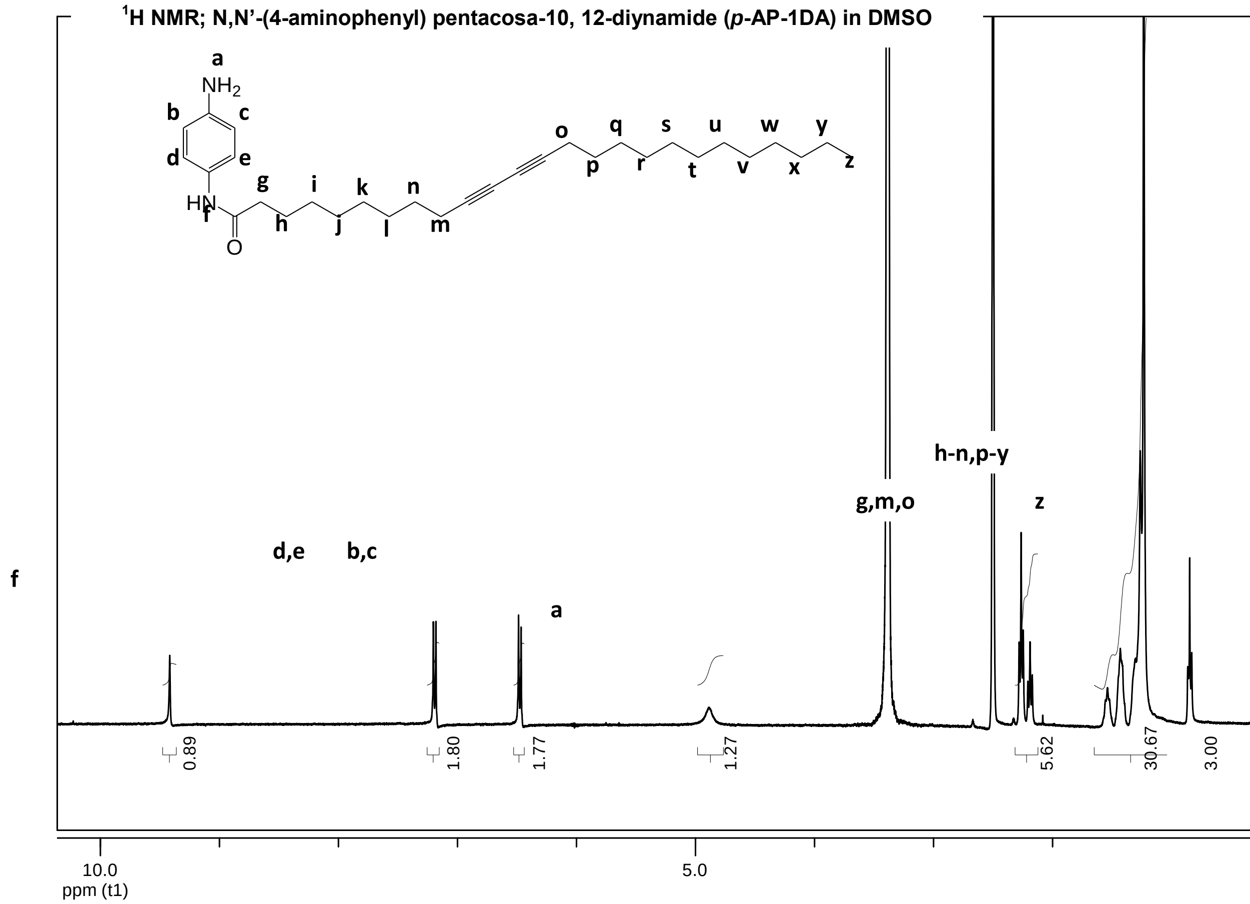


Figure A4: ^{1}H NMR; N, N’-(1, 2-phenylene) dipentacosa-10, 12-diynamide (*o*-AP-2DA) in CDCl$_3$

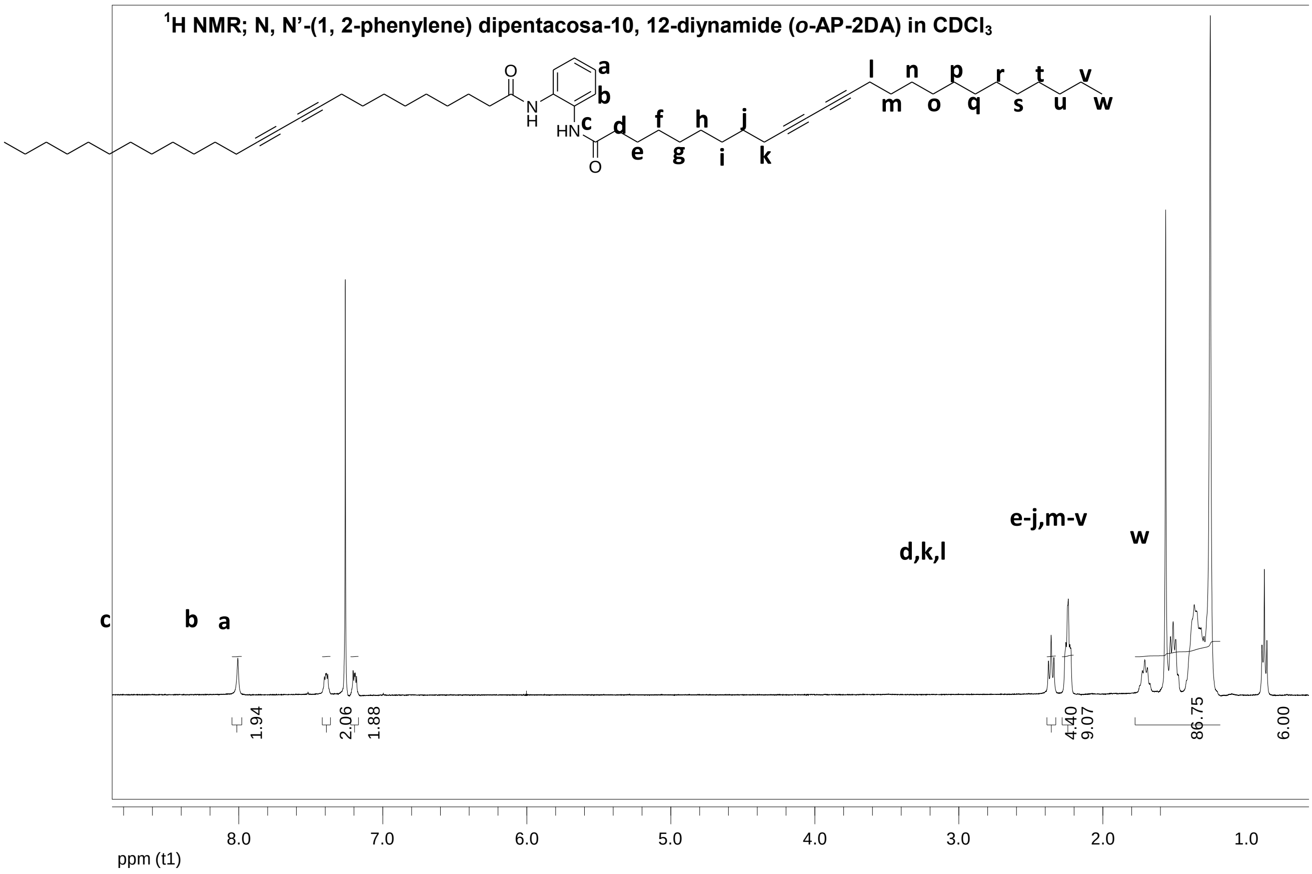


Figure A5: ^{1}H NMR; N, N’-(1, 3-phenylene) dipentacosa-10, 12-diynamide (*m*-AP-2DA) in CDCl$_3$

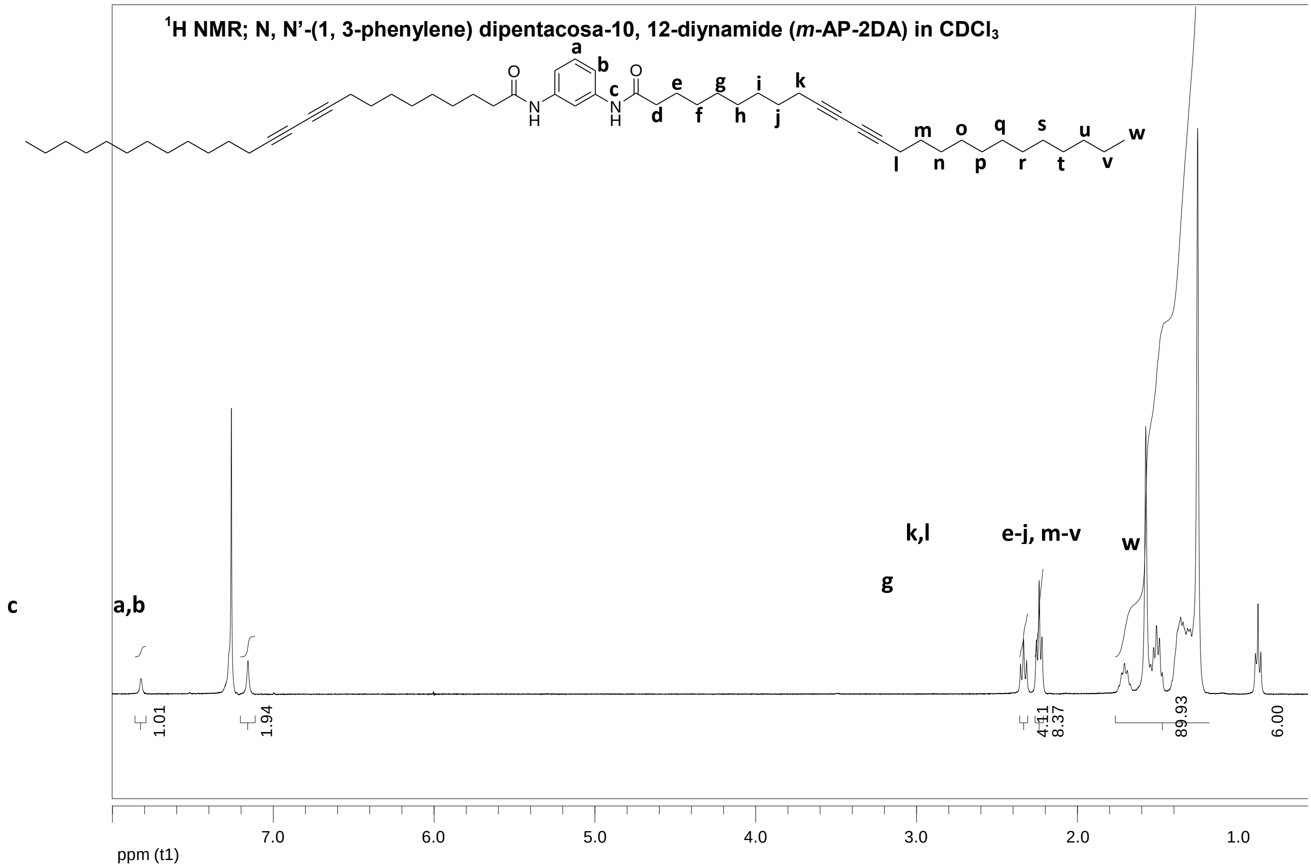


Figure A6: ^{1}H NMR; N, N'-(1, 4-phenylene) dipentacosa-10, 12-diynamide (*p*-AP-2DA) in $CDCl_3$

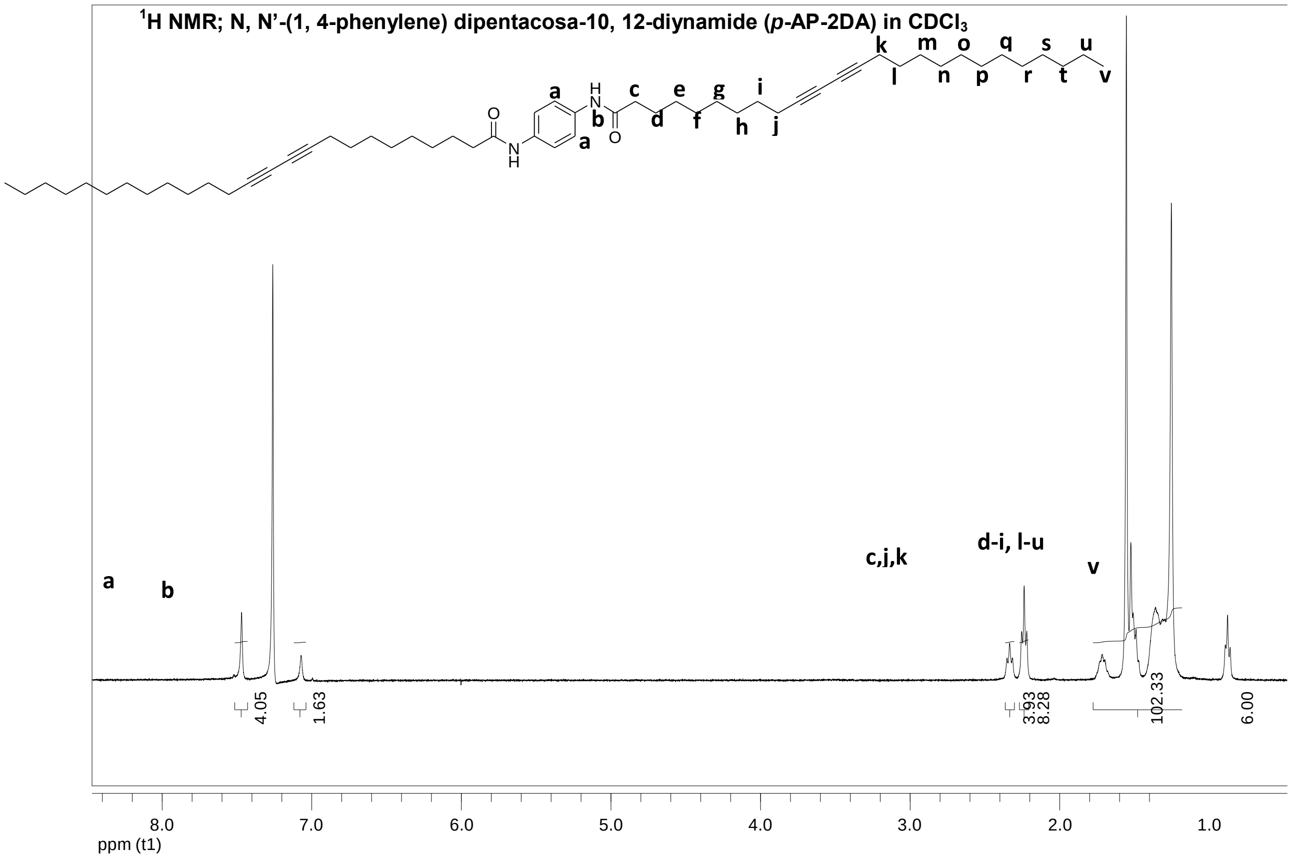


Figure A7: ^{1}H NMR; N,N'-(1R,2R)-cyclohexane-1,2-diyl)dipentacosa-10,12-diynamide (*c*-CA-2DA) in $CDCl_3$

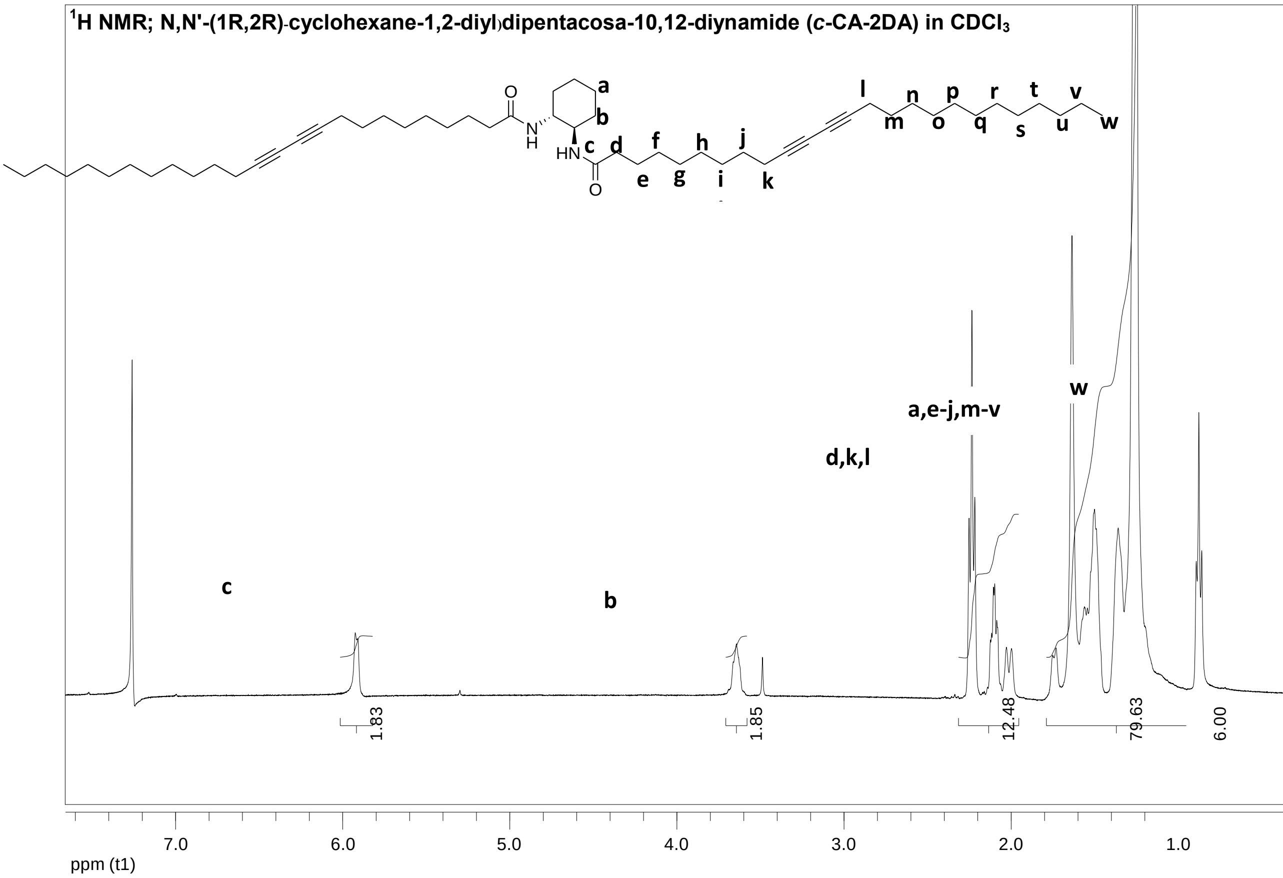


Figure A8: ^{1}H NMR; N,N'-(1R,2R)-cyclohexane-1,2-diyl)dipentacosa-10,12-diynamide (*t*-CA-2DA) in $CDCl_3$

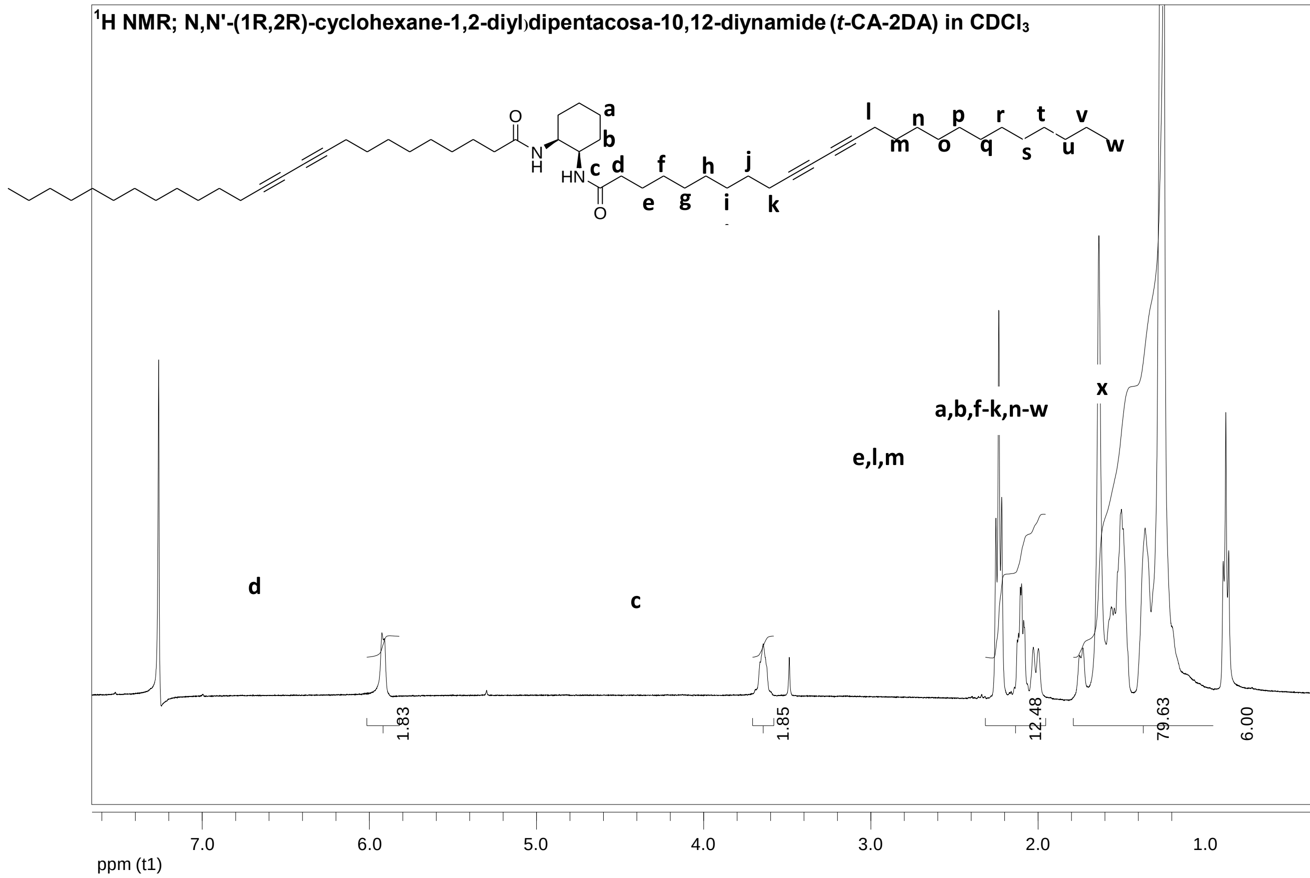
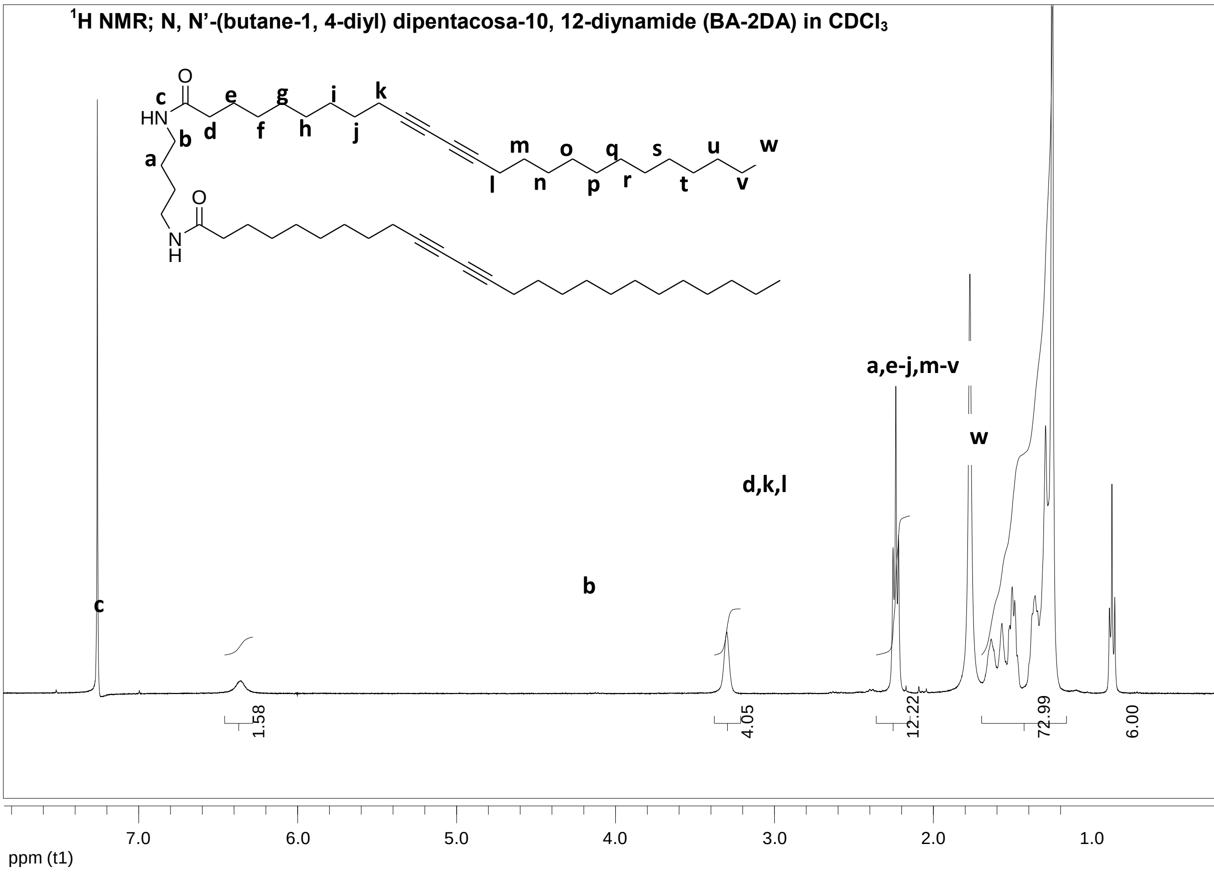


Figure A9: ^{1}H NMR; N, N'-(butane-1, 4-diyl) dipentacosa-10, 12-diynamide (BA-2DA) in $CDCl_3$



^{1}H NMR; N, N'-(butane-1, 4-diyl) dipentacosa-10, 12-diynamide (BA-2DA) in $CDCl_3$

Figure A10: ^{1}H NMR; N, N'-(hexane-1, 6-diyl) dipentacosa-10, 12-diynamide (HA-2DA) in CDCl$_3$

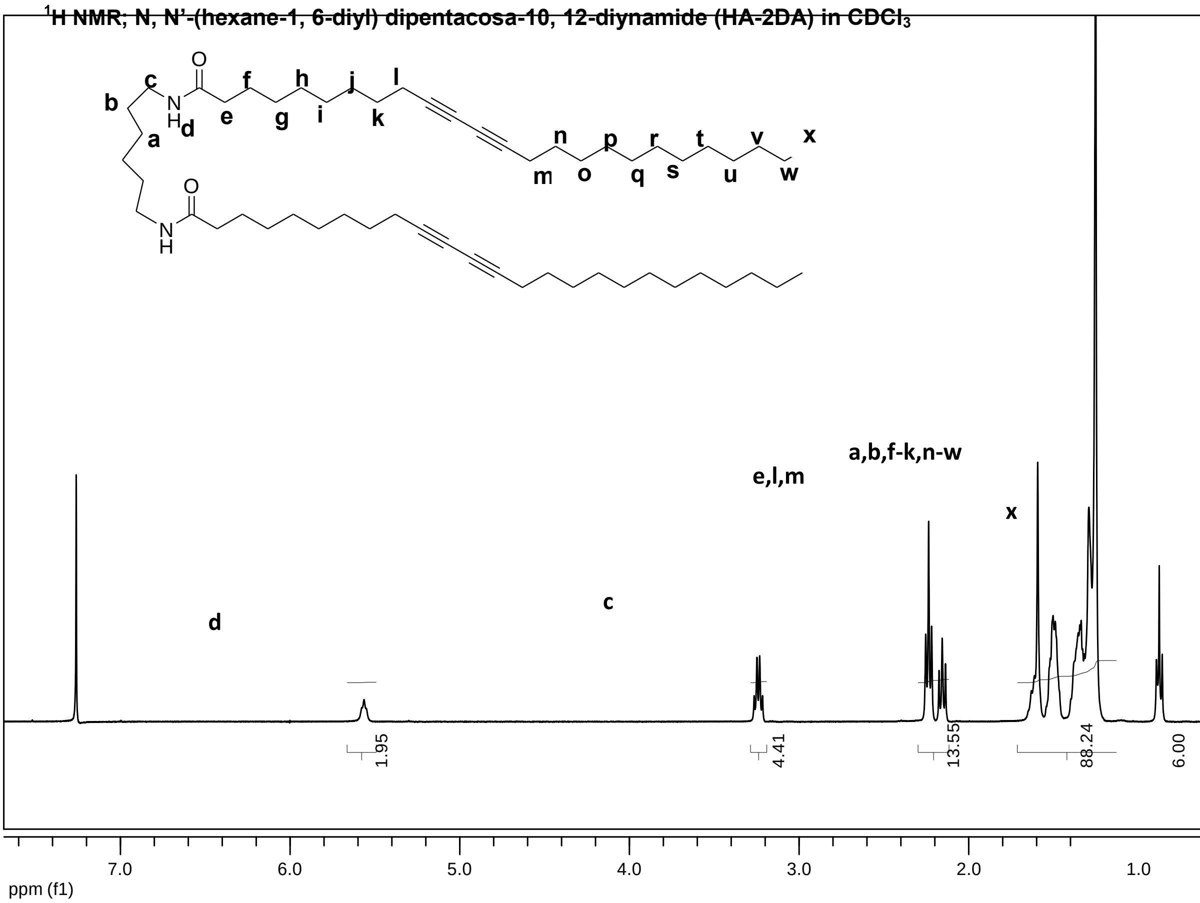
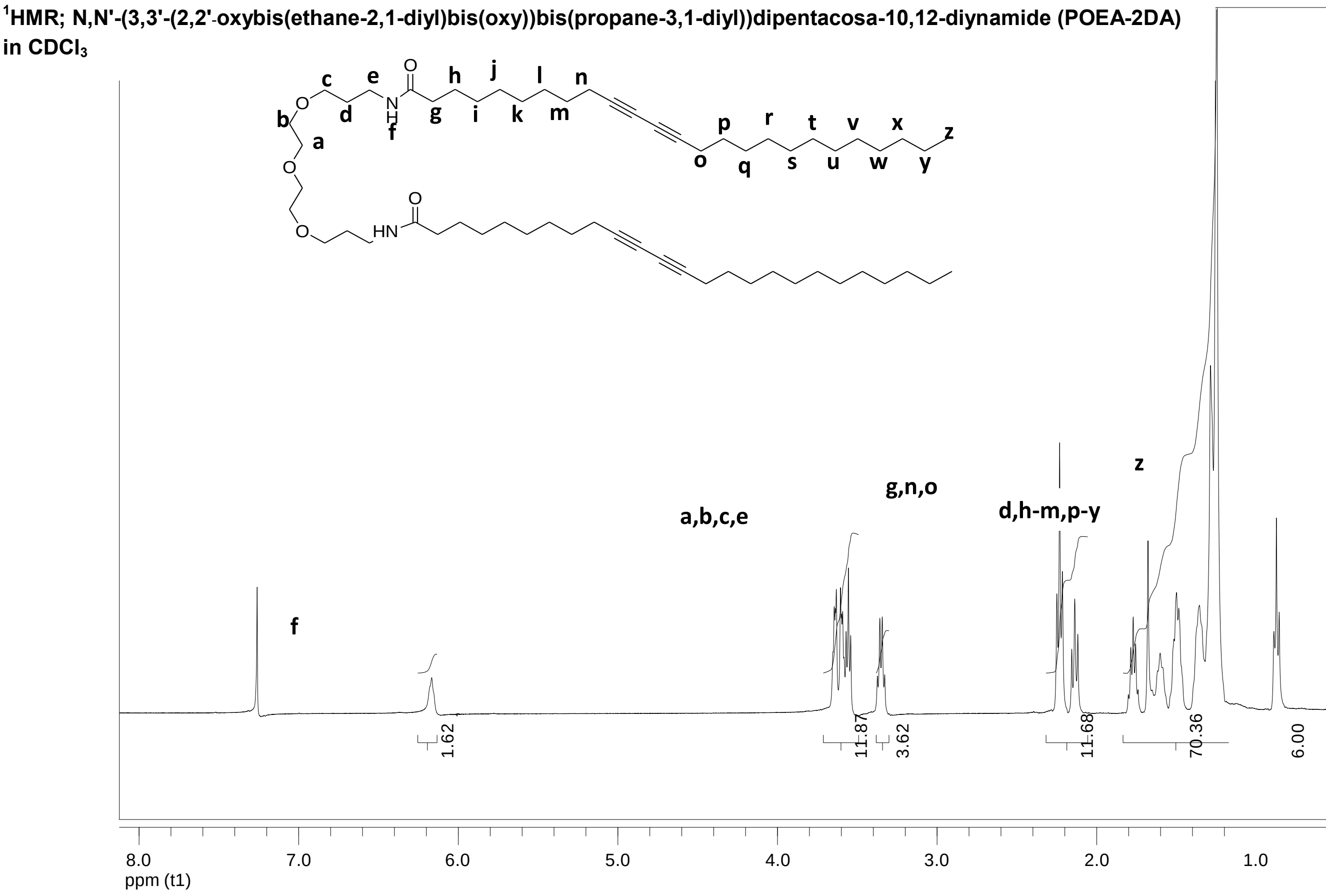


Figure A11: ^{1}HMR: N,N'-(3,3'-(2,2'-oxybis(ethane-2,1-diyl)bis(oxy))bis(propane-3,1-diyl))dipentacosa-10,12-diynamide (POEA-2DA) in $CDCl_3$



Appendix B

Appendix B: ESI mass spectra of synthesized monomers

Figure B1 : ESI mass spectra of *o*-AP-1DA

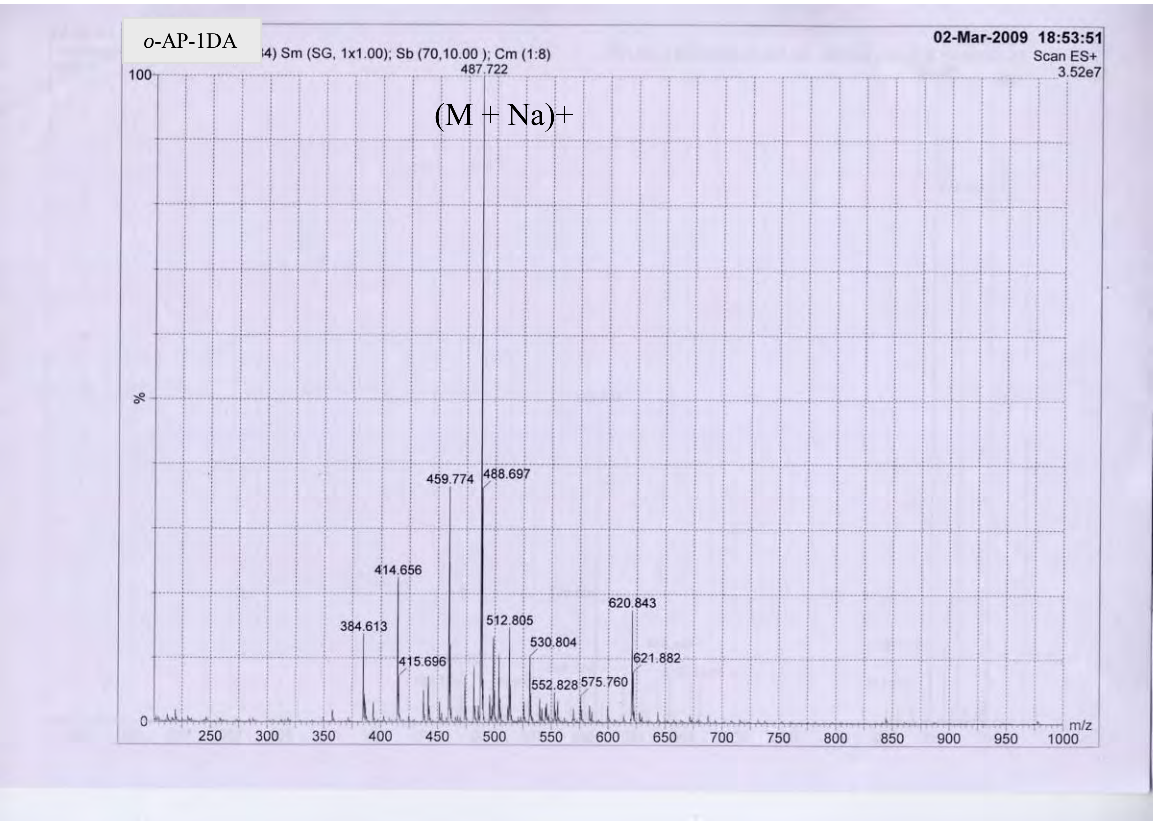


Figure B2 : ESI mass spectra of *m*-AP-1DA

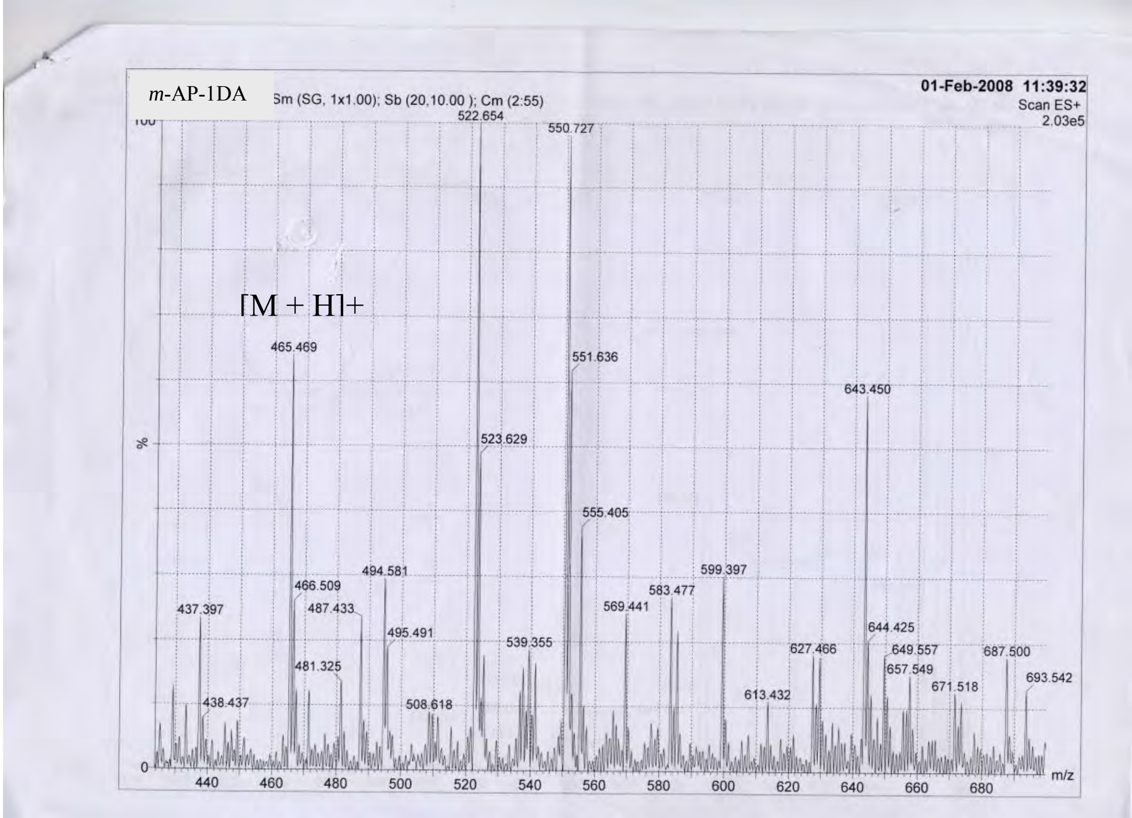


Figure B3 : ESI mass spectra of *p*-AP-1DA

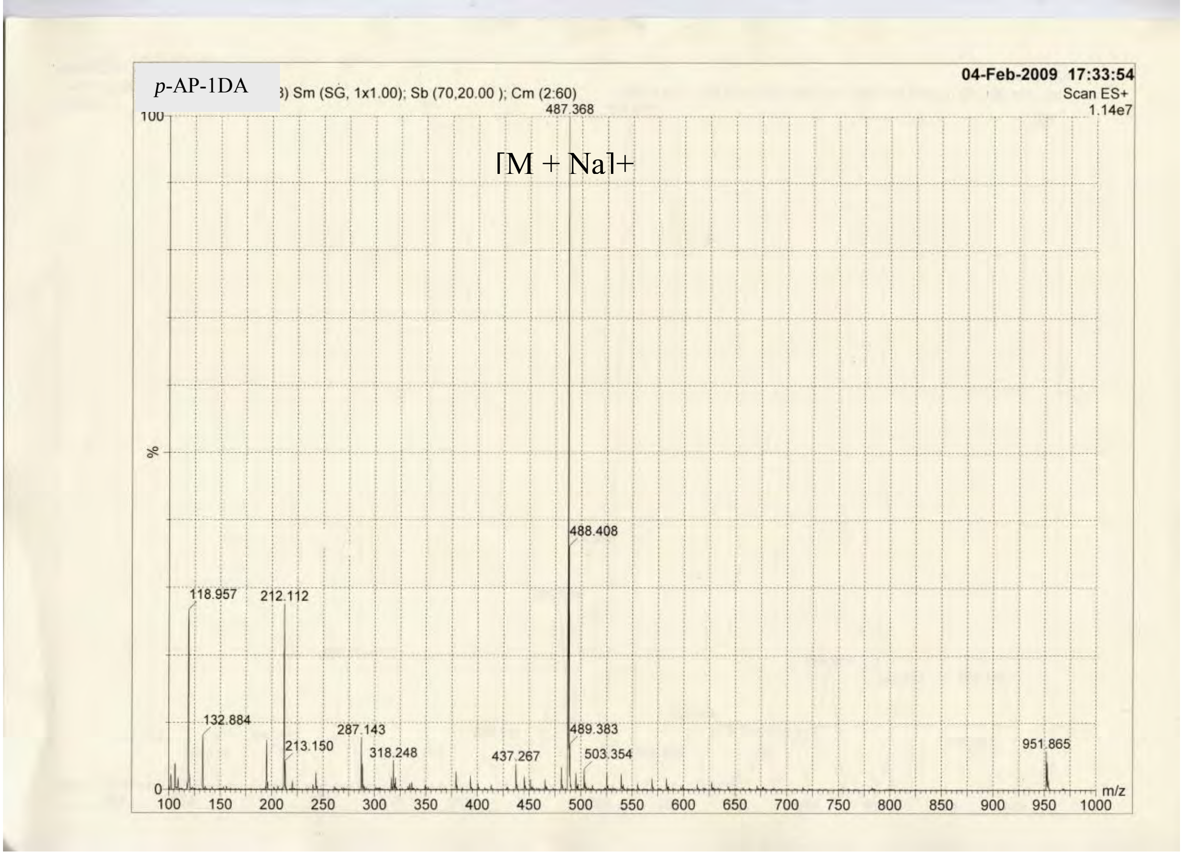


Figure B4 : ESI mass spectra of *o*-AP-2DA

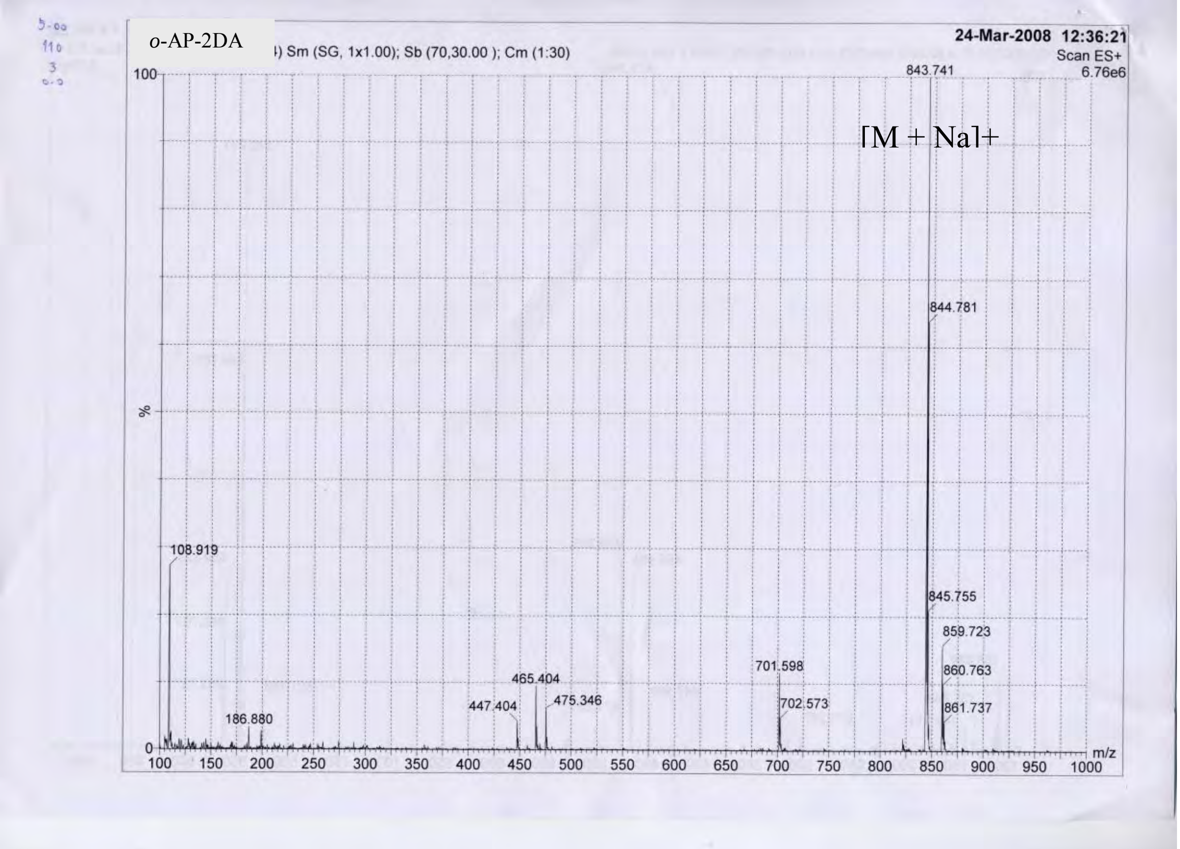


Figure B5 : ESI mass spectra of *m*-AP-2DA

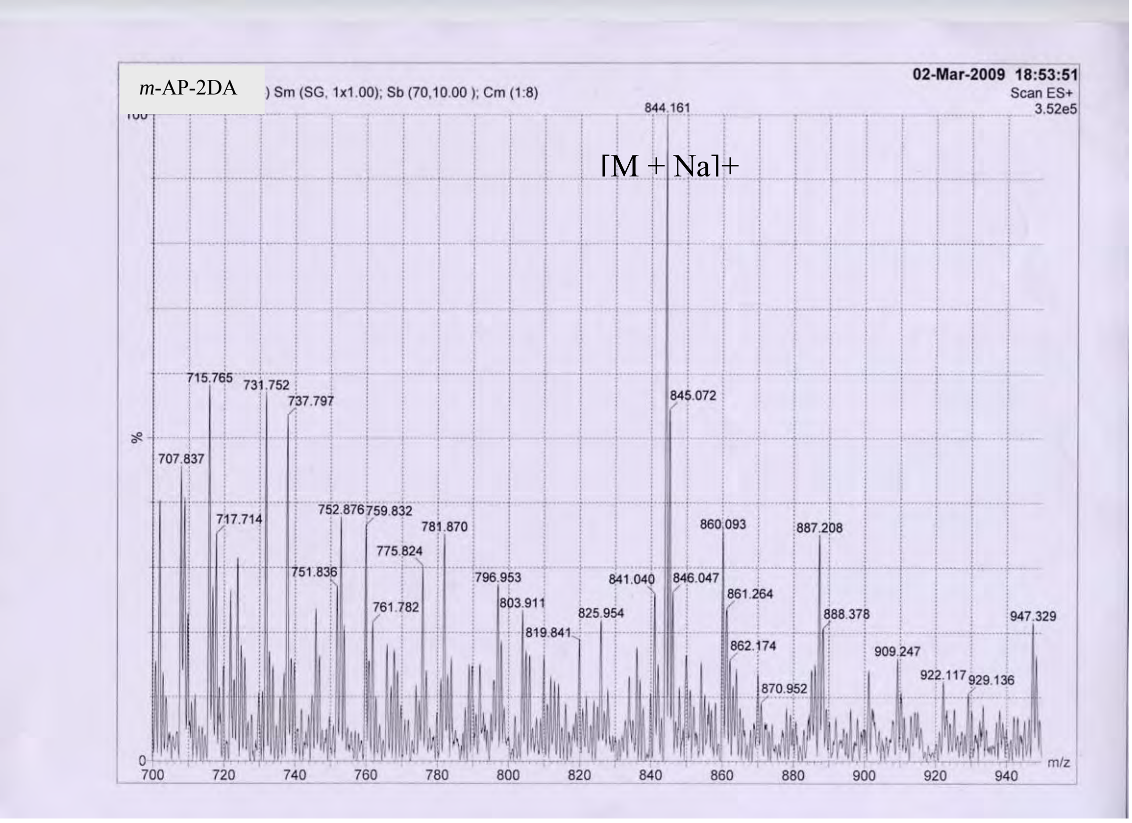


Figure B6 : ESI mass spectra of *p*-AP-2DA

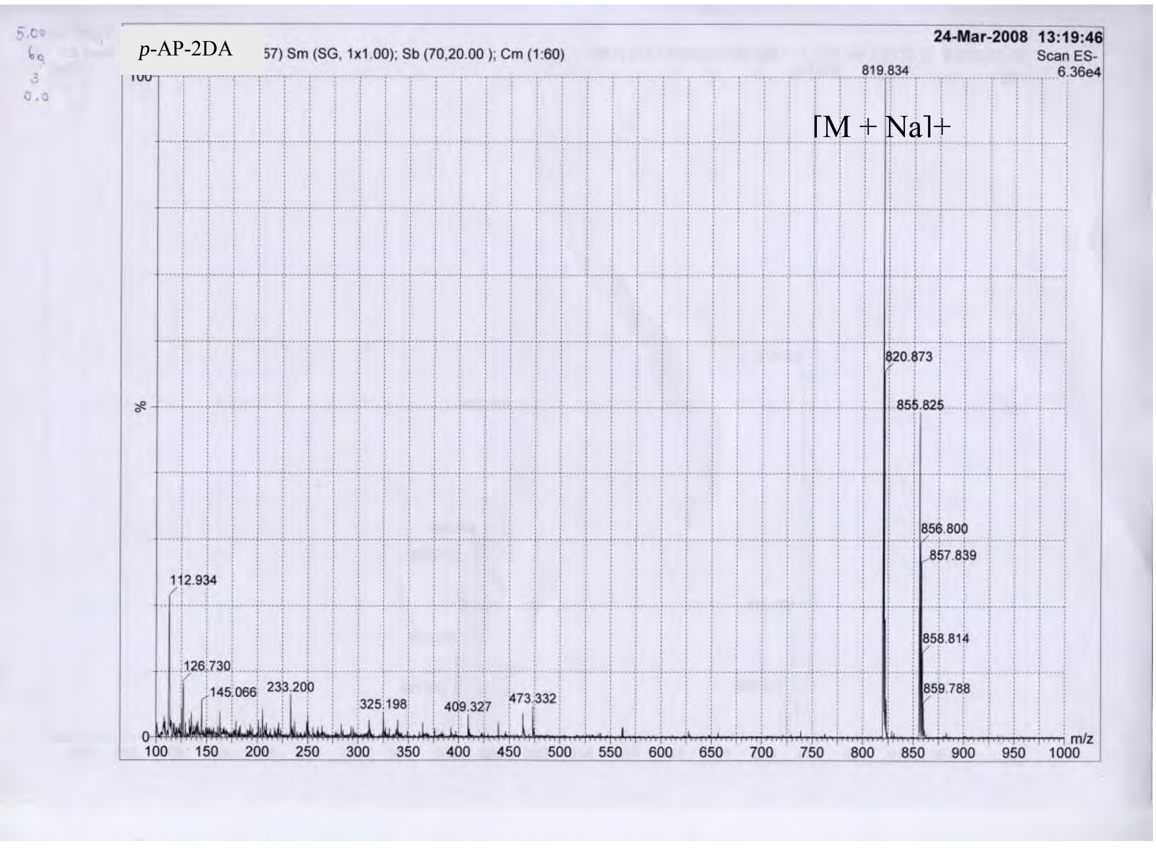


Figure B7 : ESI mass spectra of *c*-CA-2DA

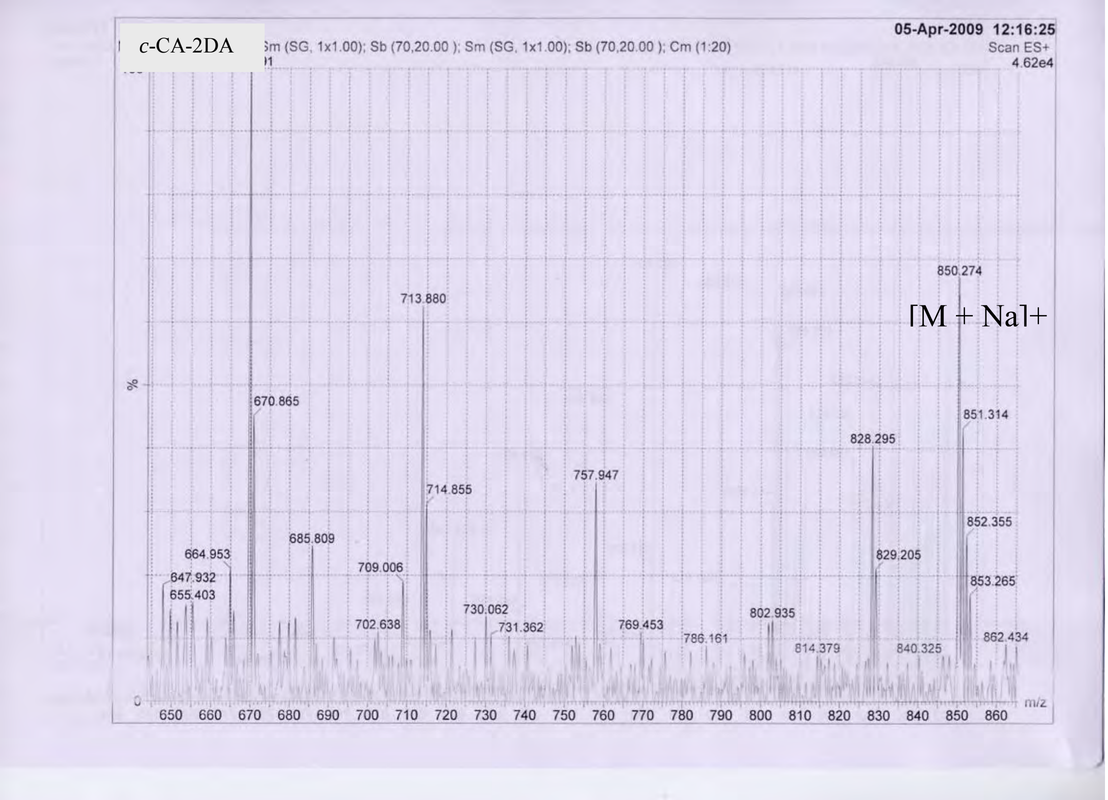


Figure B8 : ESI mass spectra of BA-2DA

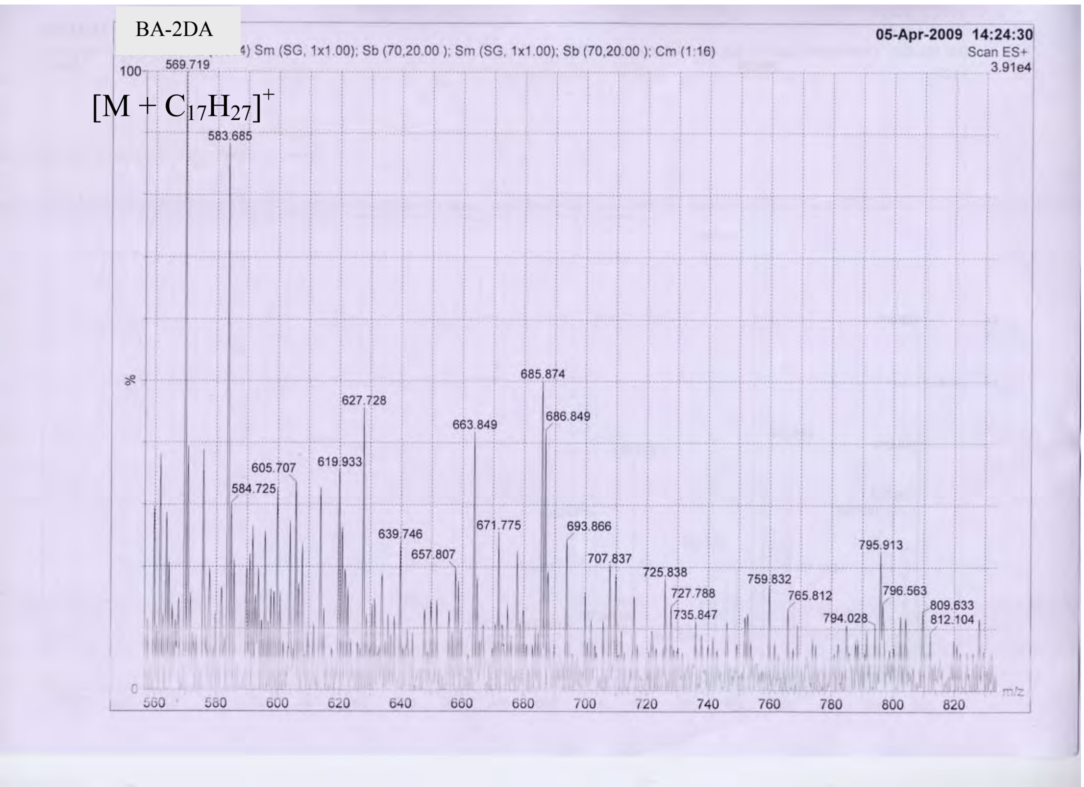
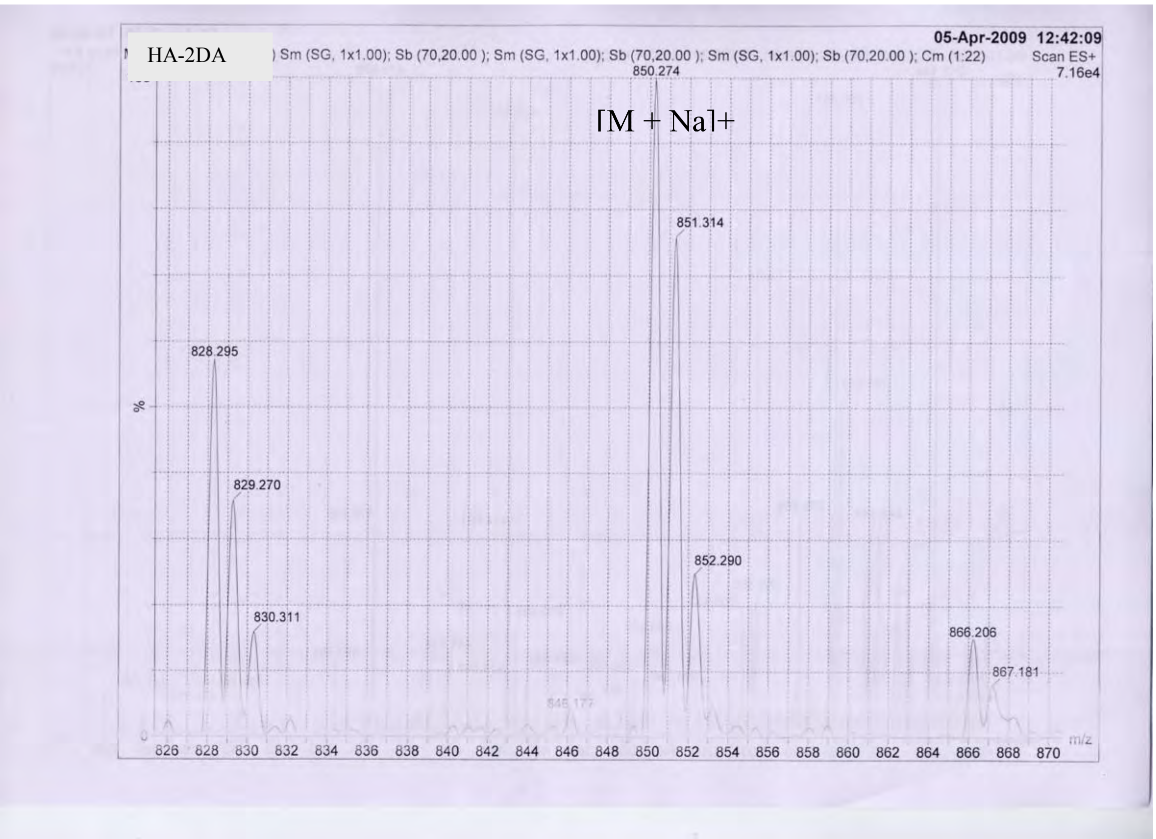


Figure B9 : ESI mass spectra of HA-2DA



Appendix C

Appendix C: DSL of synthesized monomers

Figure C1 : DSL of *m*-AP-1DA

			Diam. (nm)	% Intensity	Width (nm)
Z-Average (d.nm):	139	Peak 1:	155	100.0	37.5
PdI:	0.181	Peak 2:	0.00	0.0	0.00
Intercept:	0.925	Peak 3:	0.00	0.0	0.00

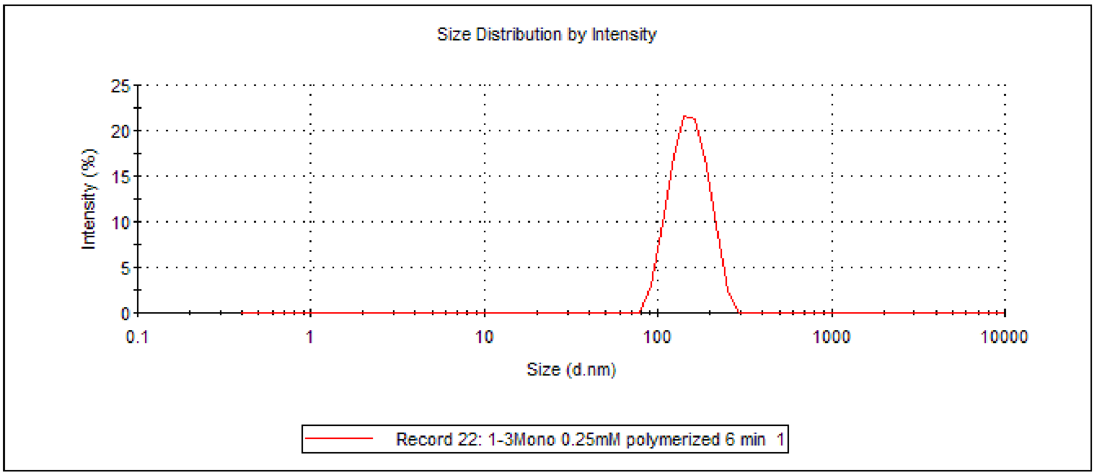


Figure C2 : DSL of *m*-AP-2DA

			Diam. (nm)	% Intensity	Width (nm)
Z-Average (d.nm):	169	Peak 1:	218	87.9	57.5
PdI:	0.277	Peak 2:	51.3	12.1	9.08
Intercept:	0.921	Peak 3:	0.00	0.0	0.00

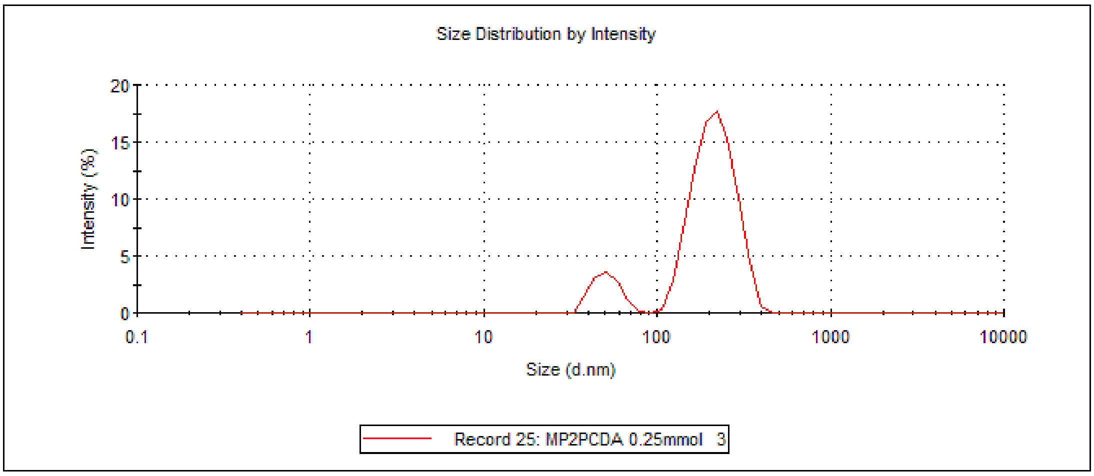
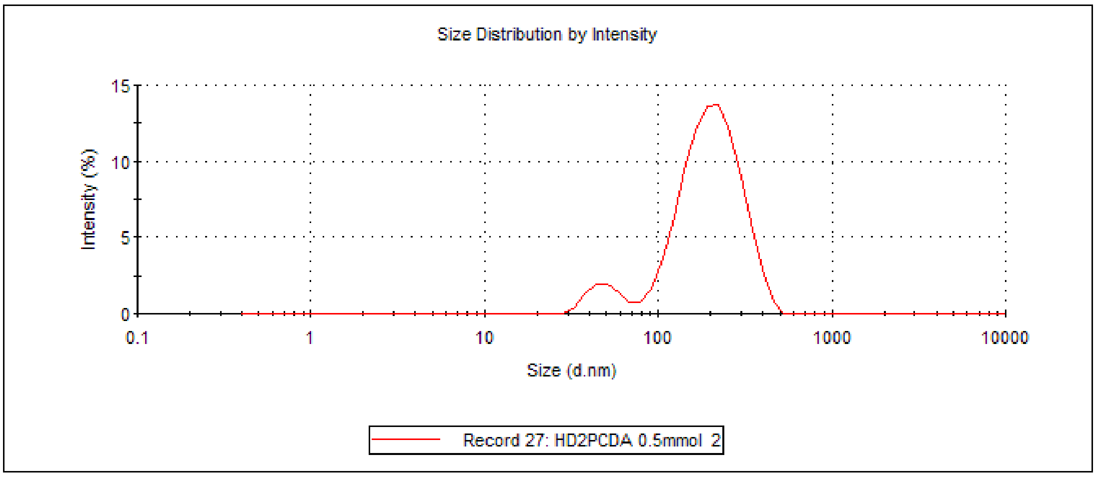


Figure C3 : DSL of HA-2DA

			Diam. (nm)	% Intensity	Width (nm)
Z-Average (d.nm):	157	Peak 1:	213	91.5	76.7
PdI:	0.277	Peak 2:	51.6	8.5	12.7
Intercept:	0.833	Peak 3:	0.00	0.0	0.00



VITAE

Suriyakamon Montha was born on December 30st, 1983 in Bangkok, Thailand. He received a Bachelor's Degree of Science, majoring in Medical Technology from Faculty of Allied Health Science, Chulalongkorn University in 2004. Since 2006, he has been a graduate student studying Petrochemistry and Polymer Science as his major course from Faculty of Science, Chulalongkorn University and completed the program in academic year of 2008.

His present address is 12 M.6, Hauykord, Sankaburi, Chainat, Thailand 17140.