ผลของความยาวสายโซ่แอลคิลต่อการเปลี่ยนสีตามอุณหภูมิ ของพอลิไดแอเซทิลีนที่มีเอไมด์สองหมู่

นางสาว ศศิกานต์ อัมพรพันธ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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EFFECTS OF ALKYL CHAIN LENGTH ON THERMOCHROMISM OF POLYDIACETYLENE CONTAINING TWO AMIDE GROUPS

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Field of Study Petrochemistry and Polymer Science
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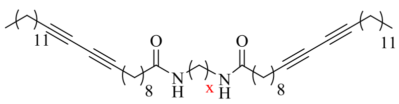
ศศิกานต์ อัมพรพันธ์ : ผลของความยาวสายโซ่แอลคิลต่อการเปลี่ยนสีตามอุณหภูมิของพอลิไดแอเซทิลีนที่มีเอไมด์สองหมู่ (EFFECTS OF ALKYL CHAIN LENGTH ON THERMOCHROMISM OF POLYDIACETYLENE CONTAINING TWO AMIDE GROUPS) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: อ.ดร.สัมฤทธิ์ วัชรสินธุ์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: รศ.ดร.มงคล สุขวัฒนาสินิทธิ์, 88 หน้า

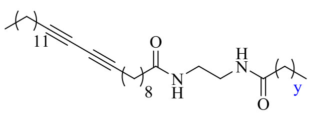
ได้เตรียมมอนอเมอร์ไดเอไมด์แบบสมมาตรห้าชนิด และไดเอไมด์แบบไม่สมมาตรหกชนิด และศึกษาสมบัติของการเปลี่ยนสีตามอุณหภูมิ เพื่อตรวจสอบผลกระทบของจำนวนของส่วนเชื่อมต่อเมทิลีน (x) และส่วนหางที่ไม่ชอบน้ำ (y) ต่อความสามารถในการผันกลับสีตามอุณหภูมิ มอนอเมอร์ที่เตรียมได้ทุกตัวสามารถกระจายตัวได้ในน้ำมิลลิคิวโดยอัลตราโซนิเคชัน และเปลี่ยนไปเป็นโซลสีน้ำเงินของพอลิไดแอเซทิลีนด้วยการฉายแสงยูวี ในส่วนของพอลิไดแอเซทิลีนที่เตรียมจากไดอายนออิกแอซิด ไดเอไมด์มอนอเมอร์แบบสมมาตร พบว่าเมื่อจำนวนหมู่เมทิลีนเป็นจำนวนคู่ ช่วงอุณหภูมิในการเปลี่ยนสี (CTT) อยู่ในช่วงที่สูง (70-80°C) และสีของมันสามารถผันกลับตามอุณหภูมิได้อย่างสมบูรณ์ (%DR = 88-93) อย่างไรก็ตามเมื่อจำนวนหมู่เมทิลีนเป็นจำนวนคี่กลับทำให้มีช่วงอุณหภูมิของการเปลี่ยนสี (CTT) ที่ต่ำลง (35-45°C) และยังผันกลับสีตามอุณหภูมิได้ไม่สมบูรณ์ (%DR = 20-65) สำหรับไดเอไมด์มอนอเมอร์แบบไม่สมมาตรนั้น ระดับความสามารถในการผันกลับสีตามอุณหภูมิ (%DR) ของพอลิไดแอเซทิลีนในกลุ่มนี้จะเพิ่มขึ้นเมื่อเพิ่มจำนวนของกลุ่มเมทิลีนในส่วนหางที่ไม่ชอบน้ำ (y) นั้นเพิ่มขึ้น ผลที่ได้จากการทดลองแสดงให้เห็นว่าจำนวนของเมทิลีนมีบทบาทสำคัญในการผันกลับของสีในกระบวนการเพิ่มและลดความร้อนของพอลิไดแอเซทิลีน ผลการทดลองนี้จะให้แนวทางสำหรับการออกแบบโมเลกุลพอลิไดแอเซทิลีนเพื่อพัฒนาใช้งานเป็นอุปกรณ์ตรวจวัดความร้อน

Symmetrical diyndiamides



P_x : x = 2, 3, 4, 5, 6

Unsymmetrical diyndiamides



S_y : y = 0, 1, 4, 8, 12, 16

สาขาวิชา....ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์....ลายมือชื่อนิสิต......................................

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

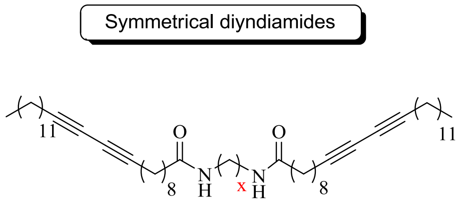
ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม......................................

5172466123: MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

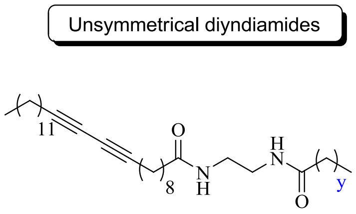
KEYWORDS: POLYDIACETYLENE/ ODD-EVEN EFFECT/ METHYLENE CHAIN LENGTH/ THERMOCHROMIC REVERSIBLE

SASIKARN AMPORNPUN: EFFECTS OF ALKYL CHAIN LENGTH ON THERMOCHROMISM OF POLYDIACETYLENE CONTAINING TWO AMIDE GROUPS. ADVISOR: SUMRIT WACHARASINDHU, Ph.D., CO-ADVISOR: ASSOC.PROF. MONGKOL SUKWATTANASINITT, Ph.D., 88 pp.

Five symmetrical and six unsymmetrical diyndiamide monomers were prepared. Their thermochromic properties were investigated in order to probe the effects of methylene units within the linker (x) and hydrophobic tail (y) on thermochromic reversibility. All synthesized monomers were dispersed well in Milli-Q water by ultrasonication. The dispersion could be converted to blue sols of polydiacetylenes (PDA) via UV irradiation. In case of PDA derived from symmetrical diyndiamides, high color transition temperature (CTT) (70-80 °C) and high degree of color reversibility (%DR = 88-93) were observed with PDAs containing even methylene linkers while the PDAs with odd methylene linkers showed low CTT (35-45 °C) and low degree of color reversibility (%DR = 20-65). For the PDAs derived from unsymmetrical diyndiamide, %DR of the PDAs increased upon raising the number of methylene units within the hydrophobic tail (y). The results indicate that the number of methylene units play an important role in thermochromic reversibility providing the strategy in molecular design for thermal sensor development.



P_x : x = 2, 3, 4, 5, 6



S_y : y = 0, 1, 4, 8, 12, 16

Field of Study: Petrochemistry and Polymer Science Student's Signature……………..
Academic year: 2010 Advisor's Signature…………….
Co-advisor's Signature…………

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LIST OF ABBREVIATIONS

DA	Diacetylene
PDA	Polydiacetylene
PCDA	10,12-pentacosadiynoic acid
AEPCDA	*N*-(2-aminoethyl)pentacosa-10,12-diyndiamide
P_2	*N,N′*-ethylenebispentacosa-10,12-diyndiamide
P_3	*N,N′*-propylenebispentacosa-10,12-diyndiamide
P_4	*N,N′*-butylenebispentacosa-10,12-diyndiamide
P_5	*N,N′*-pentylenebispentacosa-10,12-diyndiamide
P_6	*N,N′*-hexamethylenebispentacosa-10,12-diyndiamide
S_0	*N*-(2-acetamidoethyl)pentacosa-10,12-diyndiamide
S_1	*N*-(2-propionamidoethyl)pentacosa-10,12-diyndiamide
S_4	*N*-(2-hexanamidoethyl)pentacosa-10,12-diyndiamide
S_8	*N*-(2-decanamidoethyl)pentacosa-10,12-diyndiamide
S_{12}	*N*-(2-myristamidoethyl)pentacosa-10,12-diyndiamide
S_{16}	*N*-(2-stearamidoethyl)pentacosa-10,12-diyndiamide
AFM	Atomic force microscopy
NMR	Nuclear magnetic resonance
DLS	Dynamic light scattering
UV/vis	Ultra violet-visible
FTIR	Fourier transform infrared spectroscopy
^{13}C NMR	Carbon nuclear magnetic resonance
^{1}H NMR	Proton nuclear magnetic resonance
%CR	% Colorimetric response
%DR	Degree of reversibility
CTT	Color transition temperature
$CDCl_3$	Deuterated chloroform
$CHCl_3$	Chloroform
CH_2Cl_2	Dichloromethane
EtOAc	Ethyl acetate
MeOH	Methanol

v/v	Volume by volume
δ	Chemical shift
°C	Degree Celsius
g	Gram (s)
Hz	Hertz
h	Hour
mg	Milligram (s)
mL	Milliliter (s)
min	Minute (s)
µm	Micrometer (s)
%	Percent
λ	Wavelength
mM	Millimolar
Å	Angstrom
J	Coupling constant
Abs	Absorbance

CHAPTER I

INTRODUCTION

1.1 Overview

Thermochromism is the ability of substance to change color due to a change in temperature. Generally, there are two types of thermochromic materials: irreversible and reversible, depending on the behavior of the color change. Irreversible thermochromism is occurrence of thermochromic material that can change color permanently when the temperature is changed. The original color cannot be recovered even after the temperature is back to the starting point. Reversible thermochromism is incident that the original color of thermochromic material can be regained after the temperature is reversed back to the starting point. Both commercial thermochromic materials are based on liquid crystals and leuco dyes. Liquid crystals are used in precision applications, as their responses can be engineered to accurate temperatures, but their color range is limited by their principle of operation. Leuco dyes allow wider range of colors to be used, but their response temperatures are more difficult to set with accuracy. Although thermochromic liquid crystal and leuco dye are useful in wide range of applications, both of them still have some problems and limitations for example, they are toxic substances and generally require microencapsulation to improve stability and safety before use.

Recently, polydiacetylene (PDA) has been extensively studied as a new material for universal indicator. PDAs are conjugated polymer that possesses useful sensing properties. Most important, as a sensing material, the typical color change from blue to red for PDA under external stimuli can be directly observed by the naked eye [1]. Among the external stimuli, thermochromism or color changes in response to variation in temperature, which mostly appear as blue to red color transition, has been most extensively studied. However, after increasing the temperature, the red PDA may or may not return to the original blue color after being cooled down to room temperature. As reported by Sukwatanasinitt and coworkers, thermochromic reversibility can be classified into three types: irreversible, partially reversible, and fully reversible, as indicated by the degree of reversibility (% DR) [2]. PDA with variable themochromic reversible property can be used as a universal temperature sensor. For example, irreversible PDAs can indicate, by a color change, whether the labeled product been exposed to a temperature higher than a predetermined one. On the other hand, fully reversible PDAs can be used to monitor changes in temperature via color transition. To date, the mechanism of thermochromic reversibility of PDA remains unclear. To adjust the thermochromic reversibility, previous studies focused on adjusting the structure of diacetylene monomers to fine tune sensitivity of resulting PDA materials in sensor application. Structurally, in order to adjust the thermochromic reversibility of PDAs, most strategies deal with the modification of diacetylene lipid monomer side chain by either enrichment of hydrogen bond [3-6] or incooperation of conjugated organic group at the polar head group, [3-4, 7] which results in the formation of a strong interaction between polymer side chains. For examples, PDA with completely thermochromic reversibility were first introduced by Kim and co-worker [3, 7], wherein hydrogen bonding between the carboxylic acid head groups as well as the interactions between aromatic moiety in lipid assemblies have been proven to be essential for the complete reversibility of PDAs thermochromism [7]. Later by Zou and others, [8-11] PDA containing azobenzenechromophore with full thermochromic reversibility when subjected to heating and cooling cycle between 25 to 105 °C was described. However, the hydrophobicity effect to thermochmic reversibility of PDA supramolecular contributed by number of methylene unit has been less investigated. To the best of our knowledge, no work has reported on the effect of the number of methylene on thermochromic reversibility although several works described that odd/even effect of alkylene spacer length on photopolymerizability of PDAs [12-13] contributed to the chain packing of diacetylene monomer.

On continuing attempt to fine tune themochromic properties of PDA, Sukwatanasinitt and coworkers recently synthesized a novel class of PDAs having two amido groups with two diacetylene units in two symmetric side chain. Our PDAs showed full colorimetric reversibility. The author hypothesized that by varying the number of methylene spacer between amido groups, the chain packing of polymer backbones would be affected. This would then cause the change in thermochromic properties of PDAs. To expand the work on PDA with diamido moeties, symmetrical diyndiamide monomers with various number of methylene spacer were synthesized and investigated for their thermochromism. In addition two questions were addressed.

Firstly, was the existence of two diacetylene units on the monomer necessary for the thermochromic reversibility of PDA molecules? Secondly, could the thermochromic reversibility be controlled by replacing a diacetylene unit with a simple straight alkyl chain containing varying number of methylene units? To answer these questions, PDAs from unsymmetrical diyndiamide monomers with varying degree of alkyl side chain hydrophobicity were synthesized. Number of methylene units in the tail group was altered to investigate the relationship between their structure and thermochromic reversibility. The outcome of this investigation should provide a solution to structural design and increase the assortment of PDAs available for constructing universal temperature sensing materials.

1.2 Theory

1.2.1 Self-assembly of lipids

Spontaneous assembly of lipids is mainly driven by the hydrophobic effect organizing amphiphilic lipid molecules so as to minimize entropically unfavorable interactions between hydrophobic alkyl chains with surrounding water and is further fine-tuned by various intermolecular forces such as electrostatic interactions, hydrogen bonding, as well as van der Waals and dispersion forces. Lipid packing into small scale 3-D structures is governed by effective shape of the lipid that is determined by van der Waals volume and geometry of the molecule as well as hydration shell, conformation and intermolecular forces acting on a molecule. This relationship is generally described by packing parameter p defined as

$$p = v/al$$

where v is the volume of hydrocarbon chain(s), a is the area occupied by headgroup, and l is the maximum length of hydrocarbon chains. Accordingly, conventional spherical micelles are formed when molecule preferentially adopts conical shape, i.e. $p < 1/3$, and non-spherical (e.g. rod-like or discoidal) micelles form when molecular geometry resembles truncated cone with $1/3 < p < 1/2$ (Figure 1.1). Alternatively, very large head group area compared to area occupied by acyl chains can drive bilayer into chain interdigitated phase as the energetic penalty of exposing acyl chains to aqueous phase is counterbalanced by increased separation of bulky headgroups. Biologically most important mode of lipid packing, lipid bilayer, requires nearly cylindrical molecular shape with $1/2 < p < 1$. If $p > 1$, inverted structures with negative spontaneous curvature (e.g. inverted micelles or inverted hexagonal phase) can be formed. [14, 41-42]

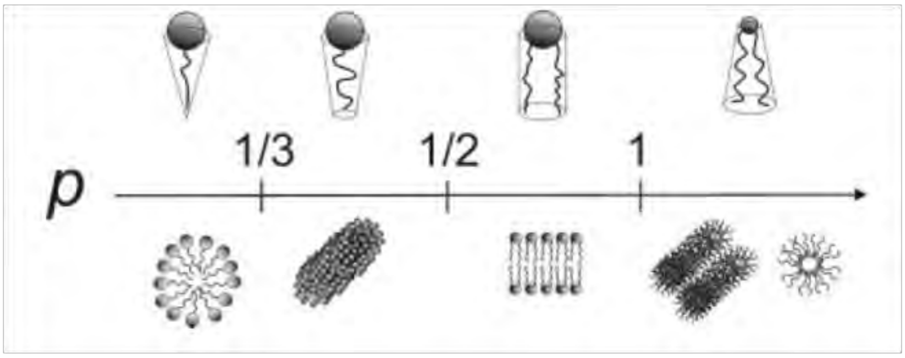


Figure 1.1 Schematic illustration of the impact of packing parameter (p) on lipid assemblies formed in aqueous solution

1.2.2 Polydiacetylene

Polydiacetylene (PDA) is one of the most intriguing classes of conjugated polymers as it possesses unique chromism properties that can be developed into practical colorimetric transducers in biological [15-17] and chemical sensors [18-23]. PDA is an ene-yne π-conjugated polymer which is generally prepared from the topological polymerization of a diacetylene monomer under UV light or γ-ray irradiation. Its π-conjugated backbone which is the chromophore of this polymer can be disturbed by various external stimuli to cause changes in its backbone that affects electronic absorption and color.

1.2.3 Polydiacetylene self-assembly

Diacetylene polymerization occurs only when it is in a highly ordered state (i.e. topochemical or solid-state polymerization). It requires an optimal packing of the diacetylene units to allow propagation of the linear chain through the organized phase. When the system is extremely well-ordered and extent of polymerization is high, the potential for application is enhanced because polymerization does not alter the morphology. The packing of monomers are determined by the side groups attached to the diacetylene units, thus it can be tailored by choosing the appropriate substituents or head groups. The key structural factors for a diacetylene lipid system include the total chain length, the position of the diacetylene unit within the chain and the chemical nature of the head group. Interactions between neighboring molecules via head groups are especially important for the propagation of induced with one-dimensional ordered nanostructures. When diacetylene polymerization occurs in the middle of an alkyl chain, highly arranged self-assembled systems in which the diacetylene groups are aligned as a band form. Unlike polydiacetylene itself, these materials are rather tractable, especially if a linear superstructure is required. Many one-dimensional ordered nanostructures have been constructed from the polymerization of diacetylene in the past decade such as nanorods, nanowires, nanoplanes, helical ribbons and vesicles. The general explanations suggested for the driving force of the self-assembly and the mechanisms of the aggregation process are hydrogen bonding, hydrophobic interactions and π-π stacking [24].

Topological polymerization is a polymerization which requires precise prealignment of the monomer molecules that usually observe in solid state crystal [25]. Topological polymerizations of diacetylene monomers were first reported by Wegner in 1969 [26]. The mechanism of this kind of polymerization is quite different from that of other polymerization systems which usually take place in solution or liquid state while diacetylene monomers normally polymerized in crystal state. Similar to all topological reactions, this type of polymerization requires precise pre alignment of the reactant molecules within a suitable position for example in crystal state. Diacetylene monomers are polymerized via a 1,4-addition mechanism where the ideal packing parameters can be achieved. The suitable distance between reacting carbons (r) should be around 4 Å and the inclination angle between the diacetylene moiety and stacking axis of diacetylene (θ) should be around 45° (Figure 1.2) [27,28].

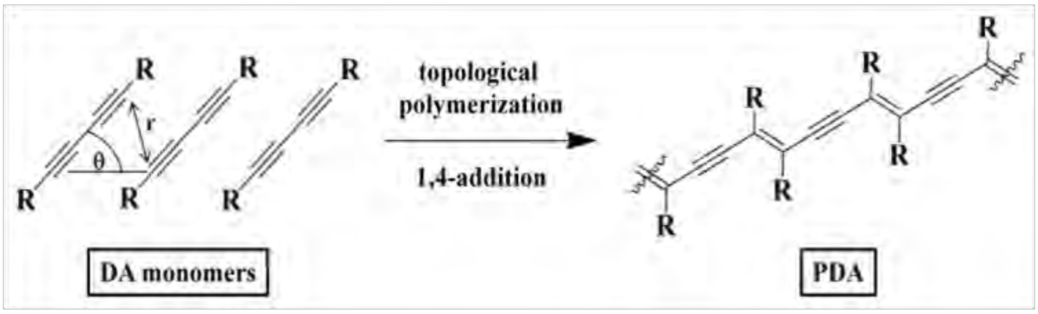


Figure 1.2 Packing parameters, r = ~4 Å and θ = ~45° are required for the topological polymerization of a diacetylene monomer

1.2.4 Polydiacetylene sols

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 1.3).

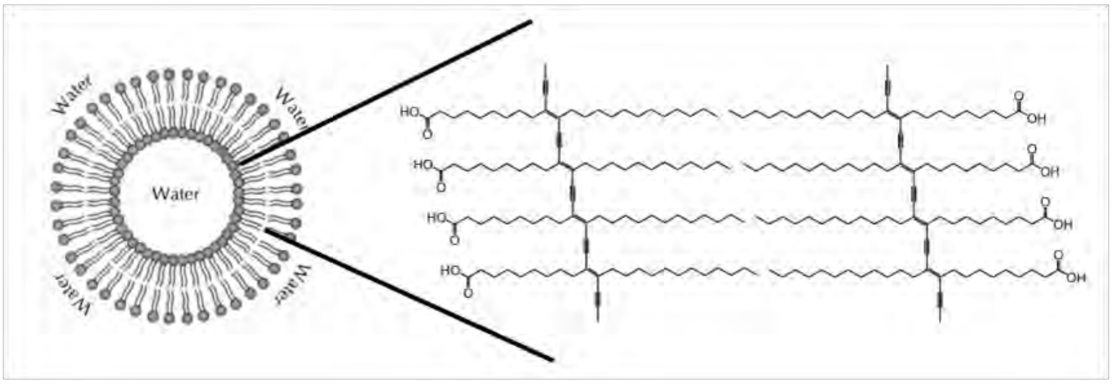


Figure 1.3 Illustration of poly(PCDA) vesicle

1.2.5 Electronic transition of polydiacetylenes

Optical absorption in polydiacetylene occurs via π→π* absorption within the linear π-conjugated polymer backbone. Upon polymerization, frequently the first chromogenic state of PDA appeared blue in color. The exposure of PDA to environmental perturbations such as heat (thermochromism), mechanical stress (mechanochromism), or solvent (solvatochromism) cause 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 [29]. The color transition of the polymerized vesicles was monitored by measuring the absorbance differences between the vesicles before and after stimulation. This information is often converted to a percentage, termed the Colorimetric Response (CR) [30].

1.2.6 Chromism

One of the most intriguing properties of PDA is its ability to change the color upon its exposure to external stimuli such as heat (thermochromism) [3], organic solvent (solvatochromism) [29] and mechanical stress [31]. The color change induced by heat is called thermochromism which always causes the electronic absorption of

PDA shifted to shorter wavelength resulting in the color change from blue to red or from red to yellow. The blue phase of PDA can be changed to the red phase when the PDA is exposed to an external stimulus. The external stimulus may release backbone strain or disturb the backbone conformation by the change of packing, ordering, and orientation of the side chain. In the case of released backbone strain concept, there are evidences from early literatures which have reported that the side chains in the blue phase contain more gauche conformation than those in the red phase [32-33], supporting that the conformational strain is decrease upon disturbing of PDA. In the case of the conformation change concept, disturbing of PDA by external stimuli can cause the twisting of the structure and the decreasing in the length of conjugated system which concerns the interaction between side chains of PDA. In addition, the C-C bond rotation in the polymer backbone may influence the overlap of the PDA molecular orbitals and consequently leading to the change in energy level. The red PDA may consist of a non-planar backbone configuration in combination with the alkyl side chains rotation and distortion (Figure 1.4) [34]. Both released backbone strain and conformational change concepts are thus changing the electronic states and the corresponding optical absorption [30, 35]. Generally, visible absorption in PDA occurs via π→π* absorption within the linear π-conjugated polymer backbone. A significant shift in the visible absorption spectrum from low to high energy band is a result of the change of light absorbed by π electron of conjugate system in a polymer main chain.

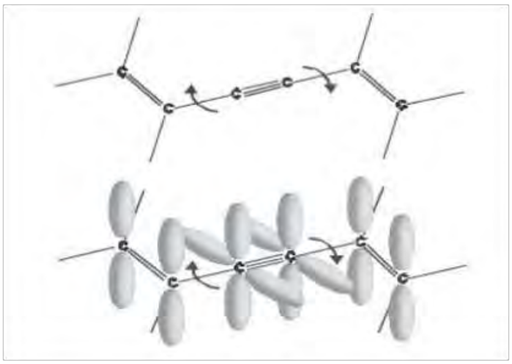


Figure 1.4 Molecular orbitals in the π-conjugated PDA backbone in the planar configuration

1.2.7 Thermochromism of polydiacetylene sols

Thermochromism, the color transition upon the rise of temperature, is one of the most 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 [30]. 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 [34].

The most notable thermochromism involves the color change from blue to red that have been developed for various colorimetric and fluorescence sensing applications. The thermochromic PDA can be either reversible or irreversible depending on the interaction between the side chain substituents and side chain head groups. There are many dedicated r to elucidate the mechanisms of color change in PDA materials which is still not fully understood. It is likely that more than one mechanism causes thermochromic change depending on the nature of the polymers. The report has shown that both side chain order and head group hydrogen bonding affect the chromic state [3].

1.3 Tuning thermochromic reversibility of PDA

In 2000, Evans and co-workers [12] reported the effect of odd/even methylene spacer on photopolymerization. Odd-numbered methylene spacers between the surface and the polymer backbone lead to the longer conjugation length blue form, whereas even-numbered spacers yield the shorter conjugation length red phase as shown in Figure 1.5. Polymerization kinetics exhibited a significant dependence on the methylene spacer length, with longer chains resulting in faster polymerization kinetics.

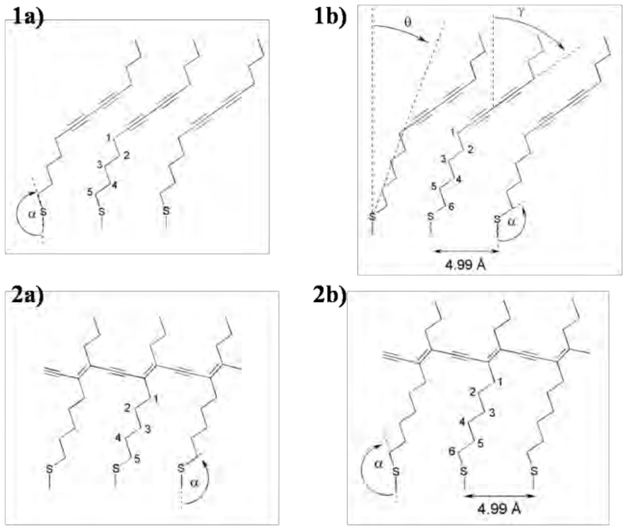


Figure 1.5 Schematic representation of the structure of unpolymerized diacetylene (1) and structure of polymerized diacetylenes (2) for odd methylene (a) and even methylene (b) spacers

In 2001, Tachibana and co-worker [36] synthesized a series of urethane-substituted diacetylene monomers (DA-mUPh) with different alkyl chain length (m=4, 5, and 6) in side-chain substituents of $(CH_2)_mOCONHC_6H_5$ to study the effect of alkyl chain length on polymerization. Results demonstrated in Figure 1.6 showed that monomers were packed by hydrogen bonding between the urethane groups, but the arrangement of the diacetylene moieties depended on the alkyl chain length. They found that the DA-4UPh and DA-6UPh crystals polymerized upon γ-irradiation, while no polymerization occured in the DA-5UPh crystal. Thus the reactivity of the DA-mUPh crystals upon γ-irradiation was different depending whether the alkyl chain length (m) is odd or even. The difference can be explained by the distance between the neighboring carbon atoms of the diacetylene groups.

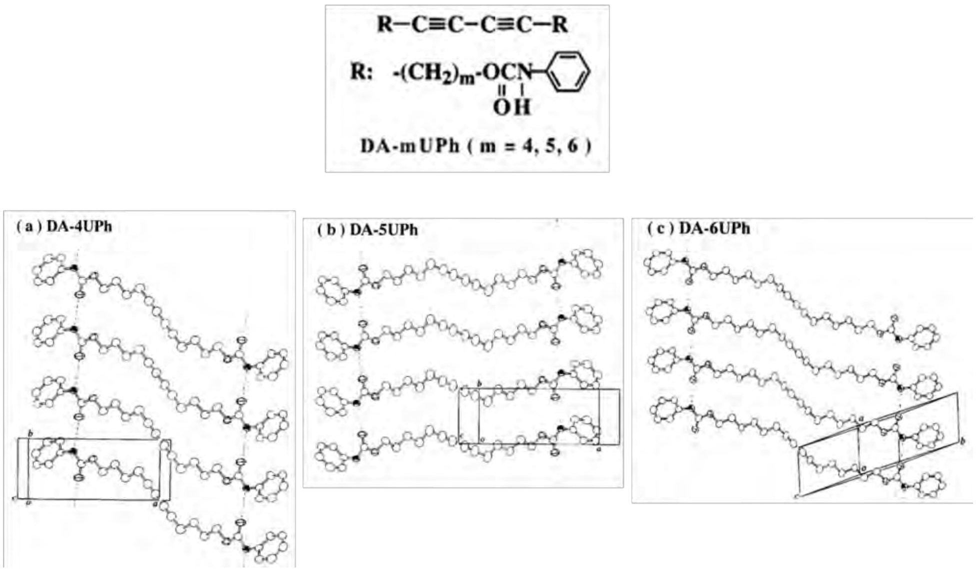


Figure 1.6 Crystal structure of (a) DA-4UPh, (b) DA-5UPh and (c) DA-6UPh

In 2003, Ahn and co-worker [7] prepared diacetylene derivatives containing an unsubstituted anilide group (2) and carboxy-substituted (ortho-, meta-, and para-) anilide groups (3) - (5) to probe the formation of hydrogen bonding which resulted in 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 1.7).

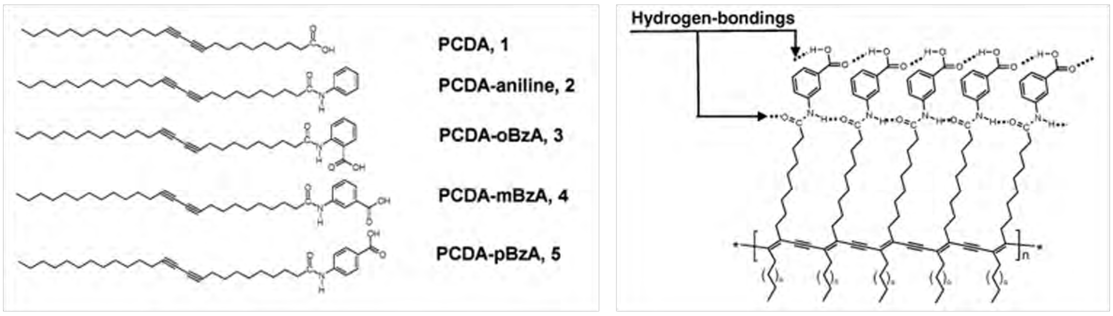


Figure 1.7 Structure of investigated monomers and schematic of enhanced hydrogen-bonding at terminal carboxyl and amide-carbonyl groups

In 2004, Aoki and co-worker [13] synthesized a series of photopolymerizable organogelators that possess simple amide structures, different alkylene chain lengths, and either optically active or racemic 3,7-dimethyl-1-octylamine units. The alkylene chain length of these compounds exhibited a prominent odd/even effect with respect to the photopolymerization in the gel state and was accompanied by a stereostructural effect on the gelation ability (Figure 1.8).

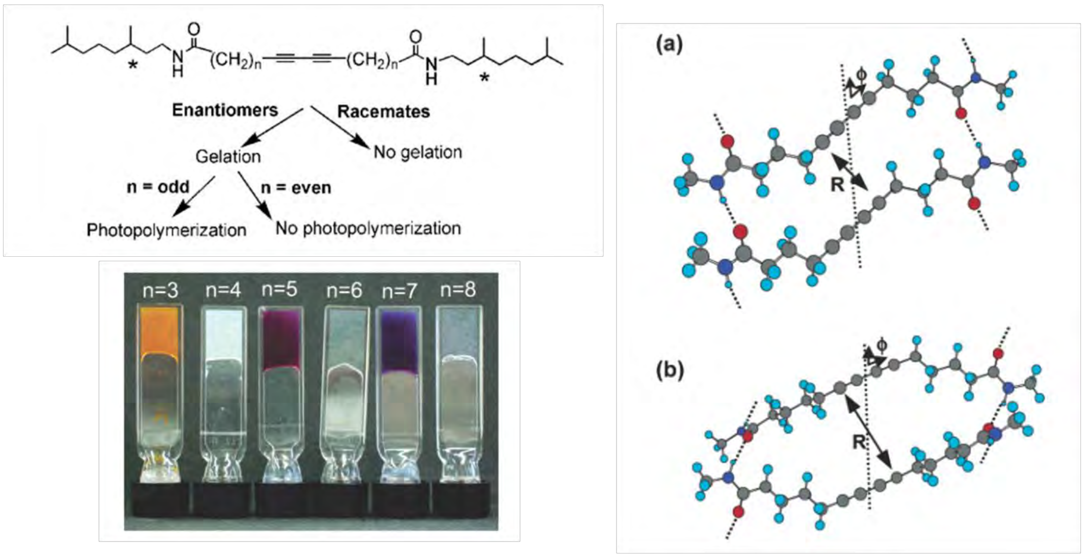


Figure 1.8 A photographic image of the photoirradiated cyclohexane gels of compounds and schematic representation of the results obtained from the calculations of the theoretical structures: (a) n=3 and (b) n=4

In 2005, Kim and co-worker [3] worked on continuing to fine tune DA structure which affected thermochromism of polydiacetylenes. They synthesized DA monomer as shown in Figure 1.5 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 (Figure 1.9). 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. The results demonstrated that well developed hydrogen-bonding and aromatic interactions between headgroups are essential for complete recovery of the length of the conjugated π-electron chain following thermal stimulus. The results of this comprehensive investigation allow for the first time the rational design of reversible colorimetric sensors based on polydiacetylene supramolecules.

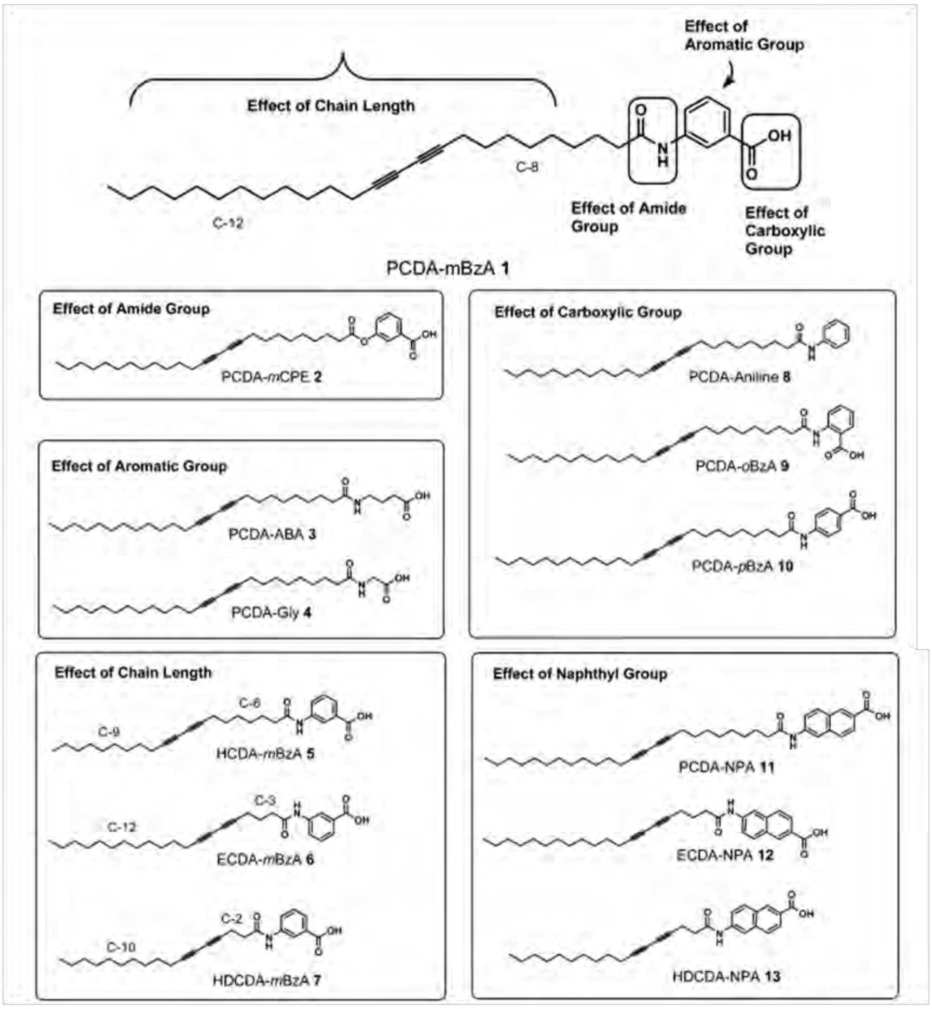


Figure 1.9 Structures of diacetylene lipids investigated for thermochromism

In 2006, Pang and co-worker [37] studied the topopolymerization of sodium 10,12-pentacosadiynoate (PCDA-Na) microcrystals. The results demonstrated the lattice dimensional change of the metastable PDA crystals prepared by topochemical polymerization of PCDA-Na microcrystals. Releasing the internal strain by thermal agitation increased the effective conjugation length, producing an irreversible red-to-blue color change. The electrostatic interactions also resulted in a stable PDA crystals that showed a reversible blue-to-red thermochromatism (Figure 1.10).

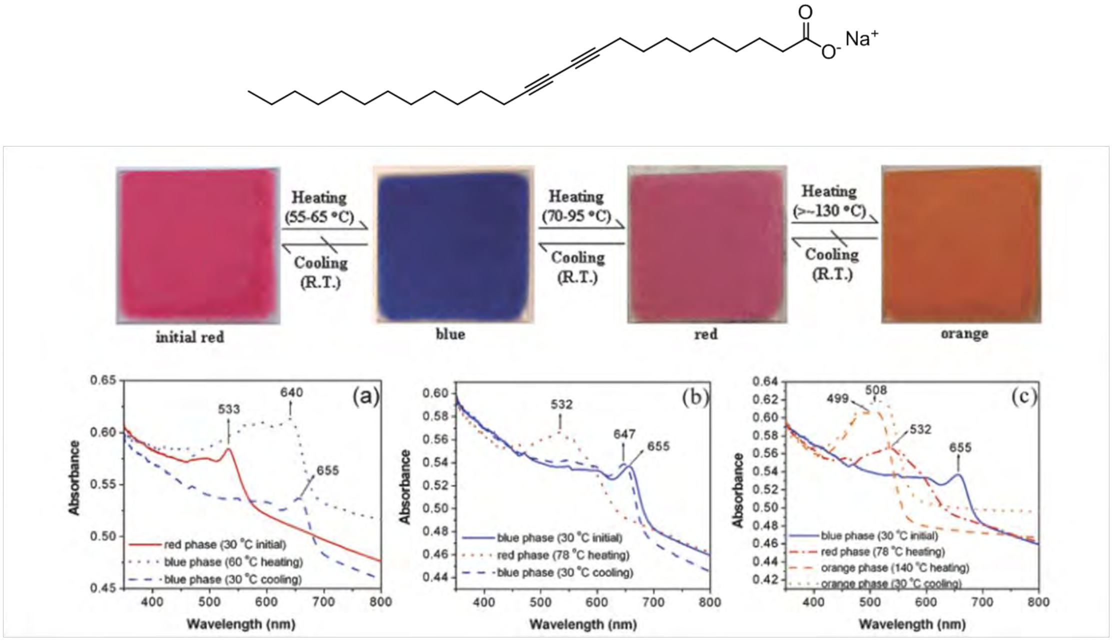


Figure 1.10 Photographs (top) of PDA-Na color transitions at different temperatures and the corresponding visible absorption spectrum (bottom) for the color transitions: irreversible red to blue (a), reversible blue to red (b), and irreversible red to orange (c)

In 2007, Lee and co-worker [5] studied the colorimetric reversibility of polydiacetylene supramolecules. Diacetylene monomers used in the study are shown in Figure 1.11. Irreversible color change of a PCDA 1-derived PDA solution was demonstrated by monitoring of the chromic transition during the heating and cooling process. PDAs derived from PCDA-*m*BzA 2 showed complete thermally promoted colorimetric reversibility. In contrast, a solution of polymer vesicles prepared from PCDA-*m*CPE 3, an ester analog of PCDA-*m*BzA 2, did not display thermally stimulated colorimetric reversibility, indicating the significant role played by internal hydrogen-bondable amide groups in governing the reversibility of the color change.
Another important factor in controlling the reversibility of thermochromism is aromatic interactions between the headgroups. The colorimetric irreversibility observed with PDAs made from PCDA-ABA (4) demonstrated this feature. The *para*-substituted diacetylene lipid PCDA-*p*BzA (5) generated stable, blue-colored polymer vesicles in aqueous solution that displays complete colorimetric reversibility. This observation indicated that the position of the carboxylic group did not affect the reversible thermochromism. Alkyl chain length was found to have a negligible effect on the colorimetric reversibility of the resulting polymerized vesicles, as demonstrated by the complete reversibility observed for solutions containing

polymeric vesicles made from HCDA-*m*BzA 6. The amine and hydroxy-terminated diacetylenic lipids PCDA-EDEA (7) and PCDA-EA (8), respectively, produced colorimetrically irreversible PDAs. Finally, the naphthyl group containing PDAs derived from PCDA-NPA 9 showed reversible thermochromism.

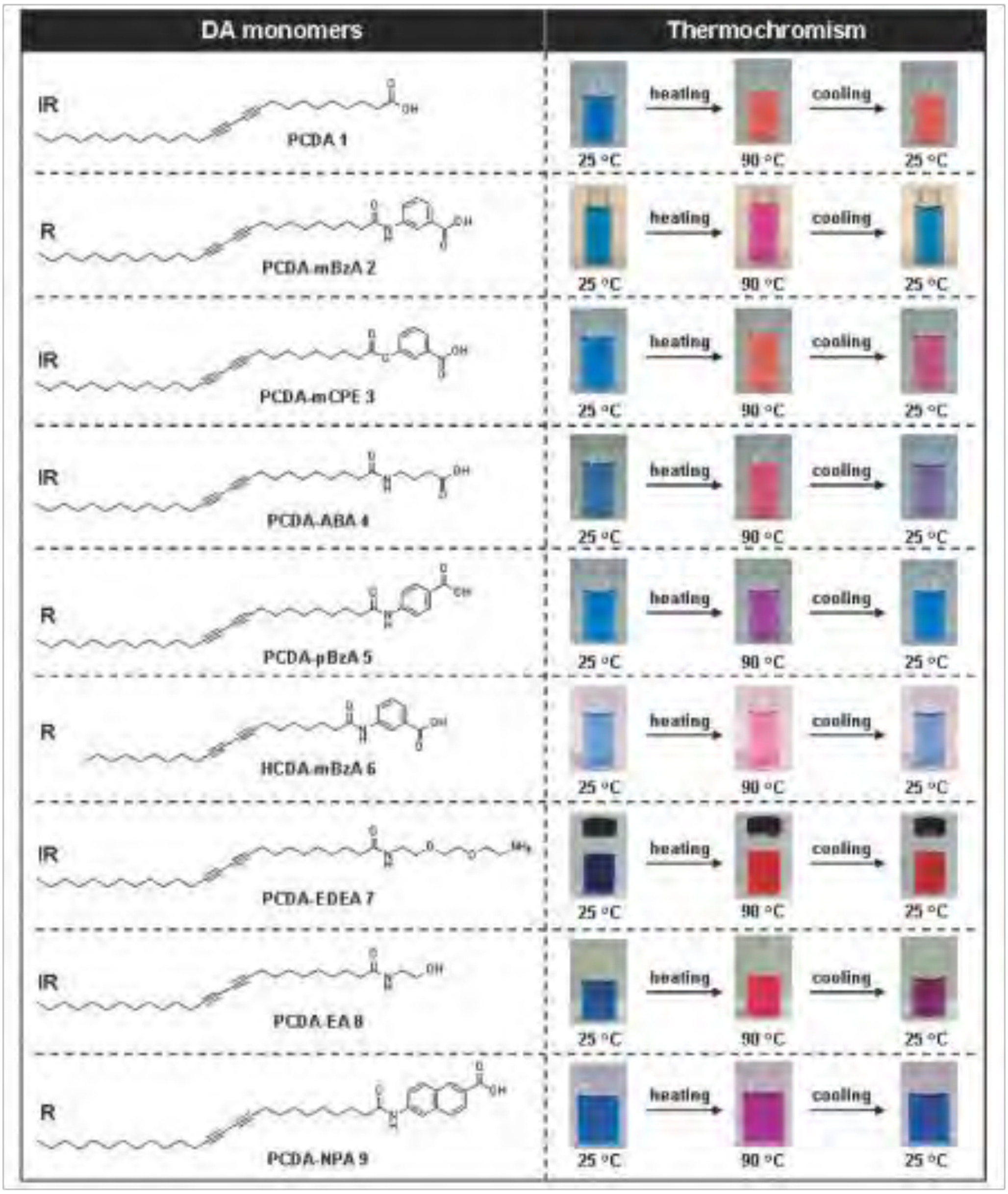


Figure 1.11 Diacetylene monomers and photographs of PDA solutions that display irreversible (IR) or reversible (R) thermochromism

In 2007, Fujita and co-worker [38] surveyed the stable conformation of 24 mers of G_3 and G_4 by molecular modeling calculation (MMFF94) as seen in Figure 1.12 and studied the effects of methylene side chain number on the color of polymers. They prepared polymer gel in hexane which exhibited blue color when the number of methylene side chain was even while exhibited red color when the number of methylene side chain was odd. They proposed that the differences were caused by different bending angle of polymer chain whereby the “odd monomer” had more bending than the “even monomer”. Higher degree of polymer chain bending produced less backbone conjugation which decreased degree of polymerization.

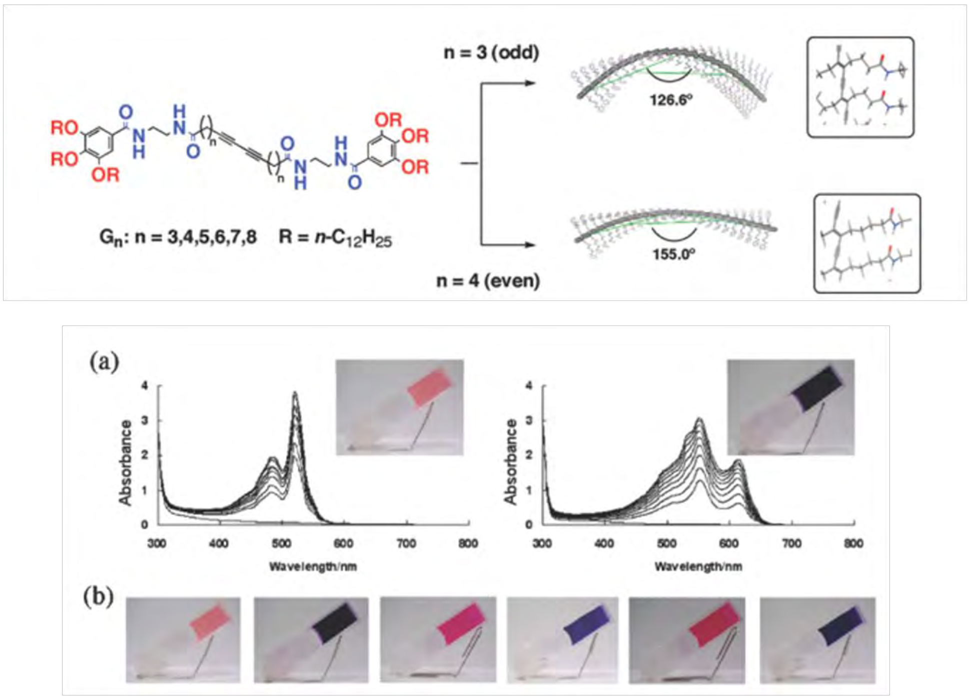


Figure 1.12 Chemical structure of G_n and the optimized conformation of 24 mers of (upper) polyG_3 and (lower) polyG_4 and (a) Time-dependence (0-180 min) of UV-vis spectruml change on photoirradiation to the hexane gels (2.5 g dm^{-3}) prepared from G_3 (left) and G_4 (right), and photographs of the 3-hour-photoirradiated gels (insets); (b) photographs of hexane gels of G_3-G_8 (2.5 g dm^{-3}) after photoirradiation for 3 h

In 2008, Ye and co-worker [8] studied morphology, structure and chromatic properties of azobenzene-substituted polydiacetylene (Figure 1.13). An azobenzene mesogen-substituted polydiacetylene, which self-assembled into stacks of bilayered two-dimensional structures, showed a reversible chromatic transition with a wide thermochromic transition temperature range. The critical transition temperature was 105 °C for completely reversible thermochromic transition and 150 °C for partially reversible thermochromic transition, respectively. These results demonstrated that the strong intermolecular interaction (π–π stacking) between side chains and the maintenance of lamellar crystal structures at high temperature were essential requirements for the complete reversibility of thermochromism of PDA films.

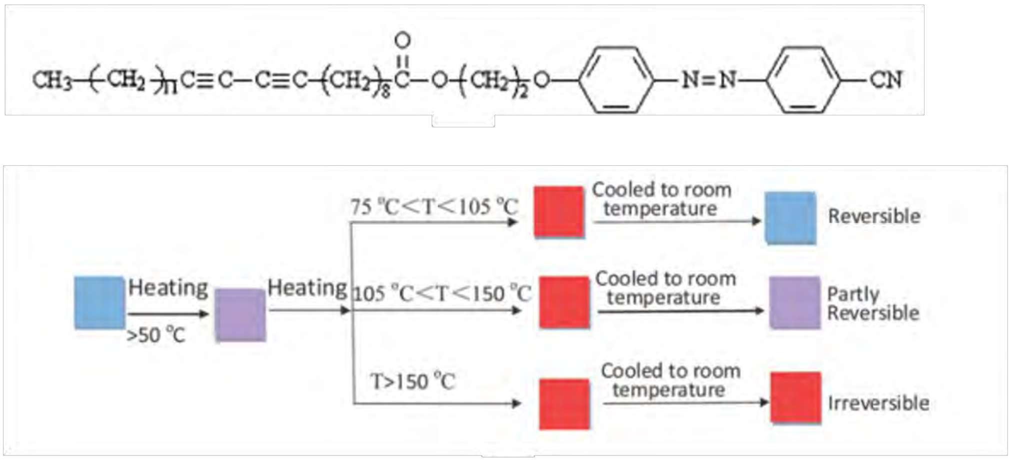


Figure 1.13 Investigated structure and schematic diagram of the thermochromic phase transition for PDA films

In 2008, Gu and co-worker [6] prepared a mixture of irreversible polydiacetylene (PCDA) and PVP (polyvinylpyrolidine). Colorimetrically reversible thromochrmism was achieved in temperature range of 20 - 85 °C. The authors proposed a “brick and motar” structure in which PVP/PCDA nanoaggregates was generated due to intramolecular hydrogen bonding between carboxylic of PCDA with pyrolidine (Figure 1.14). These arrangements caused the color reversibility of the blending product during the thermal cycle. The cooperative interaction between PVP and PDA through tethering carboxylic acid head groups in the side chains of PDA to PVP layers via hydrogen bonding was believed to be responsible for reversible conformational transitions between the “red” and “blue” states.

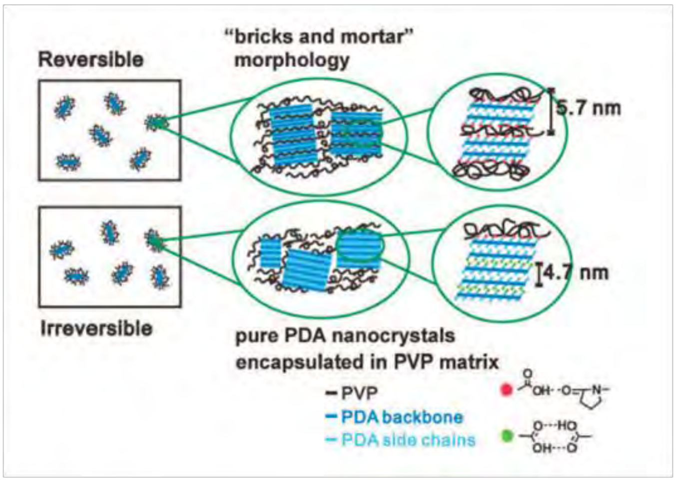


Figure 1.14 Schematic illustration of the “Bricks and Mortar” morphology and pure PDA nanocrystals

In 2010, Wacharasindhu and co-worker [2] reported on a strategy for tunning thermochromic properties of polydiacetylene through amido hydrogen bonding to create a universal temperature sensing materials (Figure 1.15). The results indicated that color transition temperature and thermochromic reversibility of polydiacetylenes can be tuned by the variation of the number of internal amide functional groups in the monomers and the structures of the linkers between the amide groups. Both color transition temperature and reversibility of polydiacteylenes were found to be mainly associated with the number and orientation of the hydrogen bond forming groups.

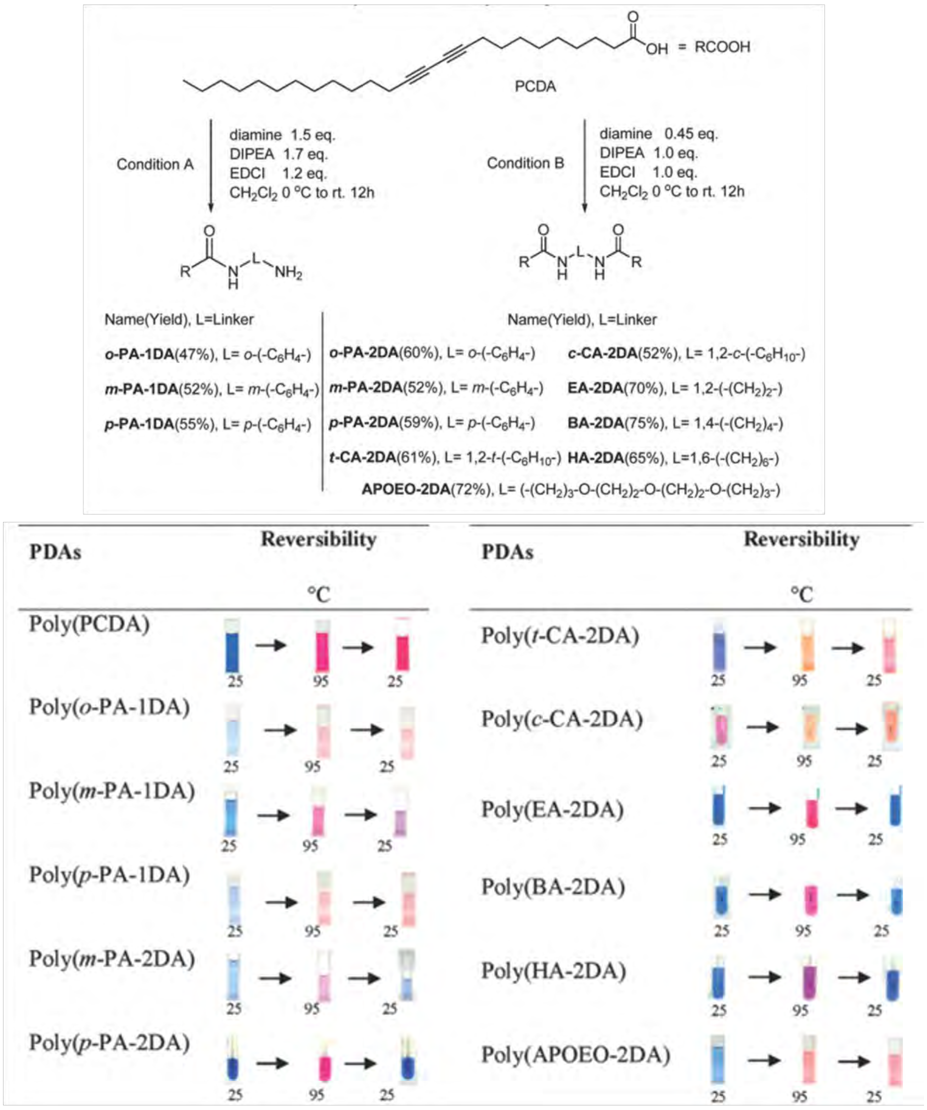


Figure 1.15 Thermochromic reversibility of the PDA sols illustrated by color photographs

In 2010, Phollookin and co-worker [39] tried to tune the thermochromic reversibility of polydiacetylenes (Figure 1.16). They found that tuning of color transition temperature of thermochromically reversible diyndiamide series of polydiacetylenes (PDAs) can be achieved by systematic variation of the length of methylene spacer (m) between the diyne and the diamide headgroup as well as the number of methylene units (n) in the hydrophobic tail. While the decrease of n value enhances the thermal sensitivity resulting in lower color transition temperature, the effect of m value is not as straight forward. Therefore m = 2 and 4 (even number), the diamide side-chains of the PDAs form extraordinary strong hydrogen bonding accommodated by the well positioned ene-yne backbone in opposite to m = 3 (odd number). Thus m played the odd-even effect on thermal stability.

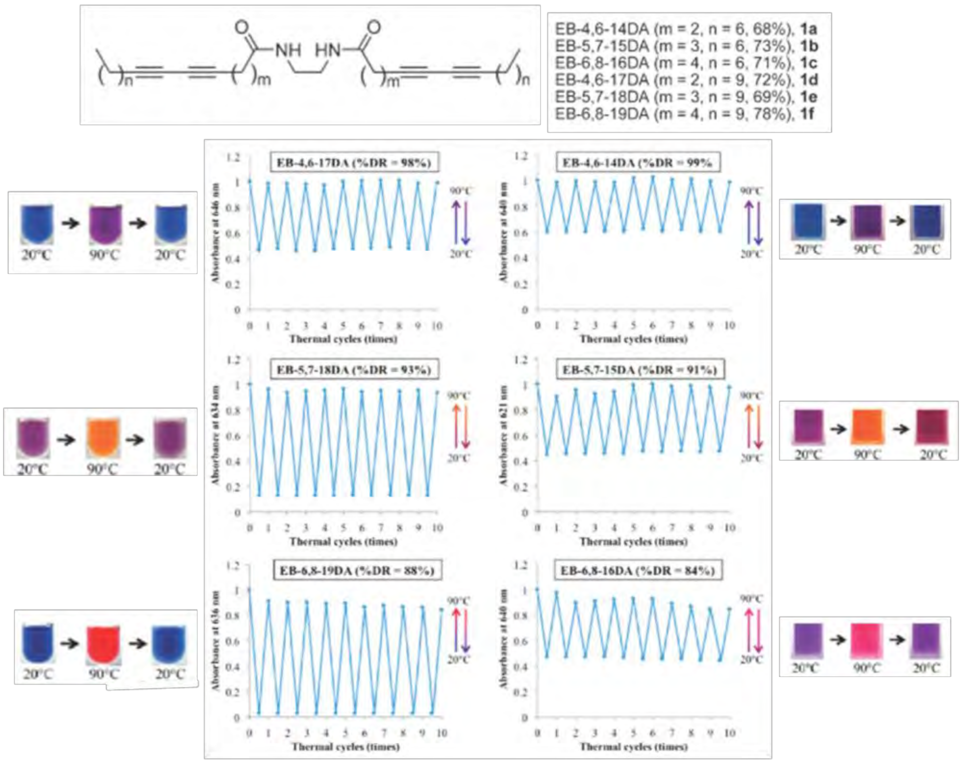


Figure 1.16 Normalized absorbance at the initial λ $_{max}$ (Δλ) of the PDA sols at 20 and 90 °C in the heating/cooling cycles and the degree of reversibility (% DR) of PDAs along with photograph recording

In 2011, Chen and co-worker [40] synthesized a new conjugated polymer based on diacetylene. PDA solution showed a reversible color change from purple-to-red as the temperature is varied between 30 °C and 70 °C, and repeated heating-cooling cycles can lead to the switches between red and purple colors (Figure 1.17). Furthermore, reversible thermochromic behavior was demonstrated in the PVA film embedded PDA molecules.

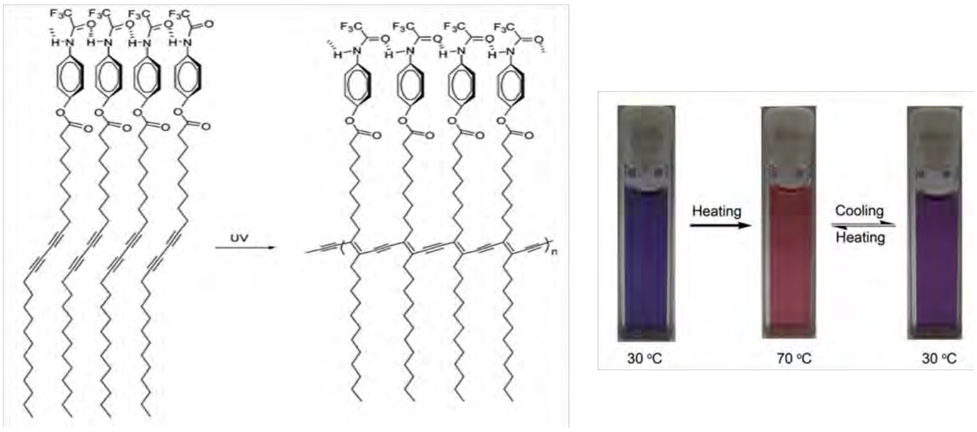
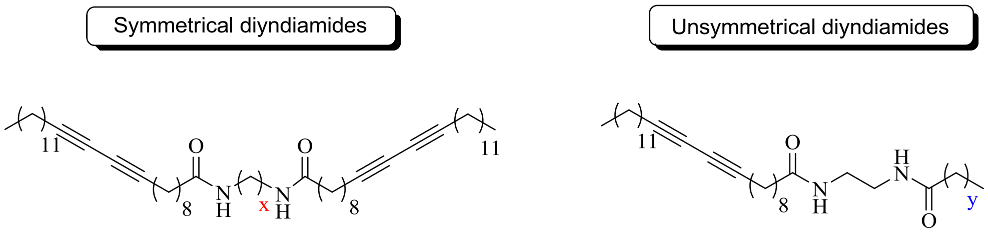


Figure 1.17 The self-assemble and polymerization of monomer and Photographs of different color stages at 30 °C and 70 °C

From the above reviews, hydrogen bonding between polymer side chains is a crucial factor in controlling thermochromic reversibility of polydiacetylene. Previous works have found that amide hydrogen bonding, aromatic interactions and carboxylic groups of diacetylene lipid affected the reversible thermochromism. However, alkyl chain length was found to have a negligible effect on the colorimetric reversibility.

1.4 Objectives and scope of the thesis

The objective of this work is to study the effect of methylenes in either linker or hydrophobic tail on thermochromic reversibility. To achieve the objective, two series of diacetylenic monomers were synthesized. The first series (symmetrical diyndiamide) was designed to study the effect of methylene in the linker. The number of methylene linkers between diamide groups was varied from 2, 3, 4, 5, and 6. In the mean time, the second series (unsymmetrical diyndiamide) was created to learn the effect of hydrophobic tail in which varied number of methylenes in tail part was varied from 0, 1, 4, 8, 12, and 16 carbons.



P_x : x = 2, 3, 4, 5, 6

S_y : y = 0, 1, 4, 8, 12, 16

Scheme 1.1 Structure of investigated monomers in this work

The synthesized compounds are then studied for their properties;

1. Hydration ability and polymerizability was investigated through photographic recorder before and after expose to UV light.
2. Morphology was monitored by dynamic light scattering (DLS) and atomic force microscopy (AFM) technique.
3. Thermochromic properties was observed via UV-vis spectroscopy along with the calculation of colorimetric response (%CR) and degree of reversibility (%DR).

CHAPTER II

EXPERIMENTAL

2.1 Materials

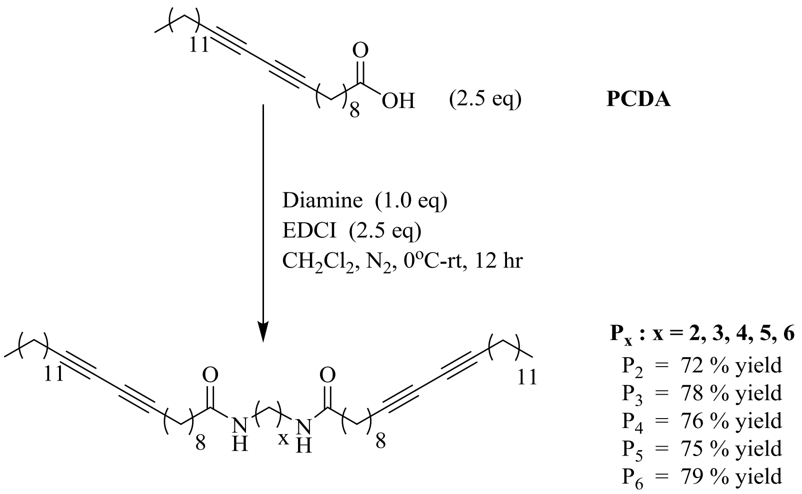
10,12-Pentacosadiynoic acid (PCDA), myristoyl chloride, cadaverine (1,5-Diaminopentane), 1,4-diaminobutane and stearoyl chloride were purchased from Fluka (Switzerland). Acetic anhydride, hexanoic anhydride, decanoic anhydride, propionic anhydride, hexamethylenediamine, 1,3-diaminopropane, 1,2-ethylenediamine and *N*-(3-Dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrochloride (EDCI), N-hydroxysuccinimide (NHS), were purchased from Aldrich (USA). Triethylamine (TEA) (AR grade), ethyl acetate, propane-1-ol, dichloromethane and chloroform were perchased from TSL Chemicals (Thailand). For extraction and chromatography, solvents were commercial grade and they were distilled before use. Column chromatography was performed using Merck silica gel 60 (70-230 mesh). 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 a potassium permanganate solution followed by drying with hot gun to approximately 350 °C.

2.2 Analytical instruments

UV/Vis spectrum were recorded on Varian Cary 100 Bio UV-Visible spectrophotometer (Varian, USA). ^{1}H spectrum and ^{13}C NMR were recorded on Varian Mercury 400 MHz NMR spectrometer (Varian, USA) using the residual solvent proton resonance of $CDCl_3$ at 7.26 ppm as the reference. AFM images were taken on a SPA 400 atomic forced microscope (Seiko, Japan). The dynamic light scattering particle size measurements were performed on a Zetasizer Nano ZS (Malvern instruments, England). UV-irradiation was performed by UV light source (TUV 15W/G15 T18 lamp; Philips, Holland). Sonication was carried out in ultrasonicating bath (Transinic S40H, Elama, Germany).

2.3 Synthesis of diacetylene monomers

2.3.1 Preparation of symmetrical diyndiamide monomers (P_2-P_6)



Scheme 2.1 Synthesis of symmetrical diyndiamide monomers (P_2 - P_6)

General procedure for synthesis of symmetrical diyndiamide: *N*-(3-Dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDCI) (101.6 g, 0.53 mmol) in dichloromethane (3 ml) was added dropwise into a solution of 10,12-pentacosadiynoic acid (PCDA) (0.200 g, 0.53mmol) in dichloromethane (3 mL). The mixture was stirred for 1 hour at 0 °C and warmed up to room temperature. Then add dropwise 1,2-ethylenediamine (14.2 μL, 0.21 mmol) into the mixture and kept stirred 12 hours at room temperature. After that solvent were evaporated and purified by recrystallization in methanol to afford ***N,N′*-ethylenebispentacosa-10,12-diyndiamide (P_2)** as white solid (0.117 g, 72% yield): mp = 125-127 °C; ^{1}H NMR (400MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 6H; -$\underline{CH}_3$), 1.38-1.25 (m, 64H; -$\underline{CH}_2$-), 2.17 (t, *J* = 7.6 Hz, 4H; C=O$\underline{CH}_2$), 2.24 (t, *J* = 7.0 Hz, 8H; C≡CC$\underline{H}_2$), 3.88 (t, *J* = 2.4 Hz, 4H; NH-$\underline{CH}_2$), 6.16 (brs, 2H; $\underline{NH}$C=O).

***N,N′*-propylenebispentacosa-10,12-diyndiamide (P_3):** Synthesized according to above general procedure from 1,3-diaminopropane (17.6 μL, 0.21 mmol), EDCI (101.6 g, 0.53 mmol) and PCDA (0.200 g, 0.53mmol). Purified by recrystallization in methanol to afford P_3 as white solid (0.129 g, 78 %yield): mp = 115-117 °C; ^{1}H NMR (400MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.6 Hz, 6H; -$\underline{CH}_3$), 1.52-1.25 (m, 64H; -CH_2-), 2.25-2.17 (m, 14H; C=OC$\underline{H}_2$, C≡C$\underline{CH}_2$), 3.30-3.25 (q, 4H; -

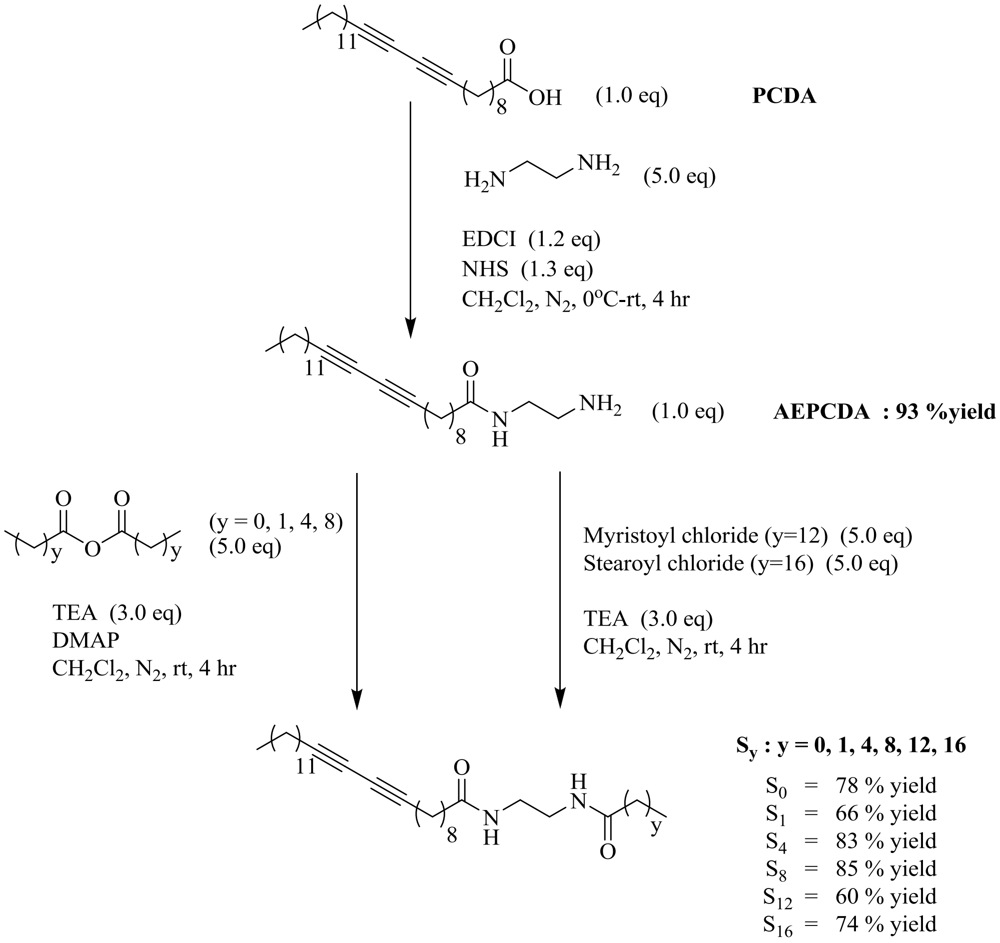
C$\underline{H}_2$-NH$_2$), 6.18 (t, *J* = 5.8 Hz, 2H; NH=CO). HMRS calcd for $C_{53}H_{90}N_2O_2Na$ $[M+Na]^+$: 809.70 ; Found 809.8360.

***N,N'*-butylenebispentacosa-10,12-diyndiamide (P_4):** Synthesized according to above general procedure from 1,4-Diaminobutane (21.0 μL, 0.21 mmol), EDCI (101.6 g, 0.53 mmol) and PCDA (0.200 g, 0.53mmol). Purified by recrystallization in methanol to afford P_4 as white solid (0.128 g, 76 % yield): mp = 135-136 °C; ^{1}H NMR (400MHz, CDCl$_3$): δ = 0.88 (t, *J* = 7.0 Hz, 6H; -$\underline{CH_3}$), 1.54-1.26 (m, 68H; -$\underline{CH_2}$-), 2.17 (t, *J* = 7.6 Hz, 4H; C=O$\underline{CH_2}$), 2.24 (t, *J* = 7.0 Hz, 8H; C≡CC$\underline{H_2}$), 3.28 (t, *J* = 5.6 Hz, 4H; NH-$\underline{CH_2}$), 5.77 (brs, 2H; $\underline{NH}$C=O).

***N,N'*-pentylenebispentacosa-10,12-diyndiamide (P_5):** Synthesized according to above general procedure from cadaverine (1,5-diaminopentane) (24.7 μL, 0.21 mmol), EDCI (101.6 g, 0.53 mmol) and PCDA (0.200 g, 0.53mmol). Purified by recrystallization in methanol to afford P_5 as white solid (0.128 g, 75% yield): mp = 121-123 °C; ^{1}H NMR (400MHz, CDCl$_3$): δ = 0.88 (t, *J* = 6.6 Hz, 6H; -$\underline{CH_3}$), 1.54-1.25 (m, 70H; -$\underline{CH_2}$-), 2.16 (t, *J* = 7.4 Hz, 4H; C=O$\underline{CH_2}$), 2.24 (t, *J* = 7.0 Hz, 8H; C≡CC$\underline{H_2}$), 3.27-3.22 (q, 4H; NH-$\underline{CH_2}$), 5.61 (t, *J* = 5.0 Hz, 2H; $\underline{NH}$C=O). HMRS calcd for $C_{55}H_{95}N_2O_2$ $[M+H]^+$: 815.73 ; Found 815.1518.

***N,N'*-hexamethylenebispentacosa-10,12-diyndiamide (P_6):** Synthesized according to above general procedure from Hexamethylenediamine (24.4 mg, 0.21 mmol), EDCI (101.6 g, 0.53 mmol) and PCDA (0.200 g, 0.53mmol). Purified by recrystallization in methanol to afford P_6 as white solid (0.138 g, 79% yield): mp = 135-137 °C; ^{1}H NMR (400MHz, CDCl$_3$): δ = 0.88 (t, *J* = 6.8 Hz, 6H; -$\underline{CH_3}$), 1.52-1.26 (m, 72H; -$\underline{CH_2}$-), 2.16 (t, *J* = 7.6 Hz, 4H; C=O$\underline{CH_2}$), 2.24 (t, *J* = 7.0 Hz, 8H; C≡CC$\underline{H_2}$), 3.27-3.22 (q, 4H; NH-$\underline{CH_2}$), 5.57 (t, *J* = 4.6 Hz, 2H; $\underline{NH}$C=O).

2.3.2 Preparation of unsymmetrical diyndiamide monomers (S_0-S_{16})



Scheme 2.2 Synthesis of unsymmetrical diyndiamide monomers (S_0 - S_{16})

***N*-(2-aminoethyl)pentacosa-10,12-diyndiamide (AEPCDA)**: *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDCI) (132.3 g, 0.69 mmol) and *N*-hydroxysuccinimide (NHS) (73.7 g, 0.64 mmol) in dichloromethane (3 mL) was added dropwise into a solution of 10,12-pentacosadiynoic acid (PCDA) (0.200 g, 0.53mmol) in dichloromethane (3 mL). The mixture was stirred for 12 hours at 0 °C and warmed up to room temperature. After that the reaction mixture was poured into dichloromethane (20 mL) and extracted with distilled water (4×10 mL). The organic extract was then dried over anhydrous Na_2SO_4, the solvent was removed by rotary evaporator to yiled white solid. Subsequently, the solution of the crude product (0.264 g, 0.56 mmol) in dichloromethane (5 mL) was added dropwise into a solution of ethylenediamine (0.19 mL, 2.80 mmol) in dichloromethane (1 mL). The mixture was stirred for 4 hours at room temperature then the reaction mixture was poured into dichloromethane (20 mL) and was extracted with saturated sodium carbonate solution (20 mL) followed by distilled water (4×10 mL). The organic extract was then dried over anhydrous Na_2SO_4 and purified by column chromatography with ethyl acetate:methanol (70:30 v/v) as an eluent to afford AEPCDA as white solid (0.388g, 93 % yield): mp = 111-114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.88 (t, *J* = 6.7 Hz, 3H; $-C\underline{H}_3$),1.42 (m, 32H, $-C\underline{H}_2-$), 2.18 (t, *J* = 7.6 Hz, 2H; $C{=}OC\underline{H}_2$), 2.23 (t, *J* = 6.8 Hz, 4H; $C{\equiv}CC\underline{H}_2$), 2.84 (t, *J* = 5.7 Hz, 2H; $NH-C\underline{H}_2-$), 3.31 (q, *J* = 5.7 Hz, 2H; $-C\underline{H}_2-NH_2$), 5.95 (brs, $C{=}ON\underline{H}$, 1H).

General procedure for synthesis of unsymmetrical diyndiamide monomers. Stirred solution of AEPCDA (0.100 g, 0.24 mmol), TEA (100.4 μL, 0.72 mmol), DMAP (2-3 crystals) and acetic anhydride (113.4 μL, 1.20 mmol) in dichloromethane (5 mL) for 4 hours. Then extracted the reaction mixture with dichloromethane (20 mL) and followed by distilled water (4×10 mL). The organic extract was dried over anhydrous Na_2SO_4 and purified by column chromatography with ethyl acetate:methanol (95:5 v/v) as an eluent to afford ***N*-(2-acetamidoethyl)pentacosa-10,12-diyndiamide (S_0)**: as white solid (0.081g, 74 %yield): mp = 115-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.88 (t, *J* = 6.4 Hz, 3H; $-C\underline{H}_3$), 1.60-1.24 (m, 32H; $-C\underline{H}_2-$), 1.98 (s, 3H; $C{=}OC\underline{H}_3$), 2.17 (t, *J* = 7.6 Hz, 2H; $C{=}OC\underline{H}_2$), 2.24 (t, *J* = 7.0 Hz, 4H; $C{\equiv}CC\underline{H}_2$), 3.38 (s, 4H; $NH-C\underline{H}_2$), 6.17 (brs, 1H; $C{=}ON\underline{H}$), 6.28 (brs, 1H; $C{=}ON\underline{H}$). HMRS calcd for $C_{29}H_{51}N_2O_2$ $[M+H]^+$: 459.39 ; Found 459.3944, $C_{29}H_{50}N_2O_2Na$ $[M+Na]^+$: 481.39 ; Found 481.3789.

***N*-(2-propionamidoethyl)pentacosa-10,12-diyndiamide (S_1):** Synthesized according to above general procedure from propionic anhydride (254.1 μL, 1.20 mmol), AEPCDA (0.100 g, 0.24 mmol), TEA (100.4 μL, 0.72 mmol) and DMAP (2-3 crystals) in dichloromethane (5 mL) for 4 hours, purified by column chromatography with ethyl acetate (100% v/v) as an eluent to afford S_1 as white solid (0.074g, 66 %yield): mp = 116-117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.88 (t, *J* = 6.8 Hz, 6H; $-C\underline{H}_3$), 1.52-1.25 (m, 32H; $-C\underline{H}_2-$), 2.22-2.15 (m, 4H; $C{=}OC\underline{H}_2$), 2.24 (t, *J* = 5.8 Hz, 4H; $C{\equiv}CC\underline{H}_2$), 3.40 (t, *J* = 2.2 Hz, 4H; $NH-C\underline{H}_2$), 6.19-6.14 (d, 2H; $C{=}ON\underline{H}$). HMRS calcd for $C_{30}H_{52}N_2O_2Na$ $[M+Na]^+$: 495.40 ; Found 495.3923.

***N*-(2-hexanamidoethyl)pentacosa-10,12-diyndiamide (S_4):** Synthesized according to above general procedure from hexanoic anhydride (277.1 μL, 1.20 mmol), AEPCDA (0.100 g, 0.24 mmol), TEA (100.4 μL, 0.72 mmol) and DMAP (2-3 crystals) in dichloromethane (5 mL) for 4 hours, purified by column chromatography with ethyl acetate (100% v/v) as an eluent to afford S_4 as white solid (0.098g, 80 %yield): mp = 118-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.89 (t, *J* = 5.8 Hz, 6H; -C$\underline{H}_3$), 1.63-1.24 (m, 38H; -C$\underline{H}_2$-), 2.16 (t, *J* = 7.4 Hz, 4H; C=OC$\underline{H}_2$), 2.23 (t, *J* = 7.0 Hz, 4H; C≡CC$\underline{H}_2$), 3.38 (s, 4H; NH-C$\underline{H}_2$), 6.28 (brs, 2H; C=ON$\underline{H}$). HMRS calcd for $C_{33}H_{58}N_2O_2Na$ $[M+Na]^+$: 537.45 ; Found 537.4399.

***N*-(2-decanamidoethyl)pentacosa-10,12-diyndiamide (S$_8$):** Synthesized according to above general procedure from decanoic anhydride (442.2 μL, 1.20 mmol), AEPCDA (0.100 g, 0.24 mmol), TEA (100.4 μL, 0.72 mmol) and DMAP (2-3 crystals) in dichloromethane (5 mL) for 4 hours, purified by column chromatography with ethyl acetate (100% v/v) as an eluent to afford S_8 as white solid (0.079g, 58 %yield): mp = 122-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.87 (t, *J* = 6.6 Hz, 6H; -C$\underline{H}_3$), 1.63-1.25 (m, 46H; -C$\underline{H}_2$-), 2.16 (t, *J* = 7.6 Hz, 4H; C=OC$\underline{H}_2$), 2.23 (t, *J* = 7.0 Hz, 4H; C≡CC$\underline{H}_2$), 3.38 (s, 4H; NH-C$\underline{H}_2$), 6.38 (brs, 2H; C=ON$\underline{H}$). HMRS calcd for $C_{37}H_{66}N_2O_2Na$ $[M+Na]^+$: 593.51 ; Found 593.4970.

***N*-(2-myristamidoethyl)pentacosa-10,12-diyndiamide (S$_{12}$):** Synthesized according to above general procedure from myristoyl chloride (488.1 μL, 1.20 mmol), AEPCDA (0.100 g, 0.24 mmol), TEA (100.4 μL, 0.72 mmol) and DMAP (2-3 crystals) in dichloromethane (5 mL) for 4 hours, purified by column chromatography with ethyl acetate (100% v/v) as an eluent to afford S_4 (mp = 124-125) as white solid (0.064g, 60 %yield): mp = 124-125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.88 (t, *J* = 7.4 Hz, 6H; -C$\underline{H}_3$), 1.50-1.25 (m, 54H; -C$\underline{H}_2$-), 2.16 (t, *J* = 7.6 Hz, 4H; C=OC$\underline{H}_2$), 2.23 (t, *J* = 6.8 Hz, 4H; C≡CC$\underline{H}_2$), 3.38 (s, 4H; NH-C$\underline{H}_2$), 6.18 (brs, 2H; C=ON$\underline{H}$). HMRS calcd for $C_{41}H_{74}N_2O_2Na$ $[M+Na]^+$: 649.58 ; Found 649.5646.

***N*-(2-stearamidoethyl)pentacosa-10,12-diyndiamide (S$_{16}$):** Synthesized according to above general procedure from stearoyl chloride (403.9 μL, 1.20 mmol), AEPCDA (0.100 g, 0.24 mmol) and TEA (100.4 μL, 0.72 mmol) in dichloromethane (5 mL) for 4 hours, purified by recrystallization with methanol to afford S_{16} as white solid (0.121g, 74 %yield): mp = 124-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.88 (t, *J* = 6.6 Hz, 6H; -C$\underline{H}_3$), 1.61-1.24 (m, 62H; -C$\underline{H}_2$-), 2.17 (t, *J* = 7.8 Hz, 4H; C=OC$\underline{H}_2$), 2.23 (t, *J* = 6.8 Hz, 4H; C≡CC$\underline{H}_2$), 3.38 (s, 4H; NH-C$\underline{H}_2$), 6.19 (brs, 2H; C=ON$\underline{H}$).

2.4 Preparation of polydiacetylene vesicles

Monomers were dissolved in chloroform (0.5 mL) in a test tube and the solvent was removed by nitrogen gas. A volume of Milli-Q water was added to provide the lipid concentration of 1.0 mM. The suspensions were heated to 80-85 ºC and sonicated in an ultrasonicating bath for 40 minutes to 2 hours forming a semitransparent or transparent vesicle solution and filtered through a filter paper (No.1) to give a clear solution. Then solution was kept overnight at 4 ºC. The vesicle solution was irradiated with UV light (254 nm) for 5 minutes at 0 °C to give a blue-colored vesicle solution.

2.5 Characterization of vesicles

2.5.1 UV-Vis spectroscopy

The visible absorbtion spectrum of vesicles solution was taken in a quartz cuvette with 1 cm optical path length on a temperature controlled UV-Vis spectrometer. The spectrum were collected from 800 to 400 nm with the zero absorbance set at 800 nm. The λ_{max} of the blue and the red phase of each sample were determined at 25 and 85 °C.

2.5.2 Dynamic light scattering (DLS)

The mean size of vesicles and the size distribution were determined by nanosizer (Malvern Instrument). Each sample was repeated measurement for 3 times in order to acquire an average data.

2.5.3 Atomic forced microscopy (AFM)

The AFM image were obtained by Multimode SPA400 (Seiko, Japan) in semicontact mode (dynamic mode) using a SI-DF20 cantilever. The image of vesicles was measured on an air-dried sample of polydiacetylene vesicles prepared from a drop of solution on freshly cleaned mica.

2.6 Thermochromism study of polydiacetylene vesicles

2.6.1 Study of color transition temperature (CTT)

The color transition temperature of polydiacetylene sols were monitored by temperature controlled UV-Vis spectrophotometer. The samples were pipetted 3.0 mL to immerse in a quartz cuvette with 1 cm optical path length. The spectrum was collected from 800 to 400 nm with the zero absorbance set at 800 nm. The temperature was heated from 25 to 85 °C. The data were collected after the temperature reach to each setting temperature and waited for 5 minutes.

2.6.2 Colorimetric response (%CR)

The color transition of the polymerized sols at variable temperature was observed by naked eye and photographed by a digital camera. Moreover, the electronic absorption spectrums of the sols were recorded by a temperature variable UV-visible spectrophotometer. Quantitative values for the color transition were determined as percent colorimetric response (%CR) calculated from the following equation.

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

FB is the fraction of blue calculated from $A_{blue}/(A_{blue}+A_{red})$ where A_{blue} and A_{red} are the absorbance at the λ_{max} of the blue and the red forms, respectively, of the polydiacetylenes. FB_0 is the fraction of blue at the original polydiacetylenes before heating. The % DR value, allowed us to classify the reversibility class of PDAs i.e., fully reversible PDA (%DR > 90%), partially reversible PDA (10% < %DR < 90%), and irreversible PDA (%DR < 10%) [2].

2.7 Thermochromic reversibility study of polydiacetylene vesicles

The reversibility of polydiacetylene sols were studied by temperature controlled UV-Vis spectrophotometer. The samples were pipetted 3.0 mL to immerse in a quartz cuvette with 1 cm optical path length. The temperature was set at 25 and 85 °C for 10 cycles. The spectrum was collected from 800 to 400 nm. The λ_{max} of the blue and the red phase of each sample were determined at 25 and 85 °C of every cycle.

2.7.1 Degree of reversibility (%DR)

To classify the reversible property of PDAs, the blue phase absorption in the cycles experiment were translated into degree of reversibility (%DR) representing percent recovery of the maximum absorption of the blue phase with respect to the first cycle according to the following equation.

$$\%DR = 100 \times \Delta A_{ave}/\Delta A_0$$

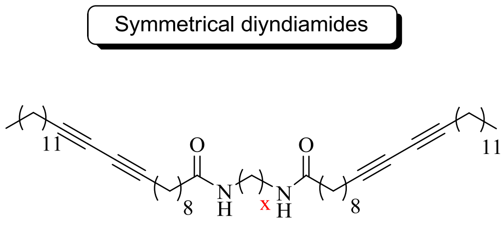
ΔA is the difference of absorbance of blue phase between 25 °C and 85 °C in each cycle. ΔA_{ave} is the ΔA averaged from the 2^{nd} to 10^{th} cycles and ΔA_0 is ΔA of the first cycle [2].

CHAPTER III

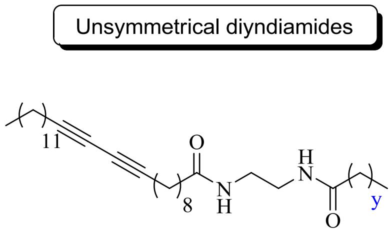
RESULTS AND DISCUSSION

3.1 Synthesis of diacetylene lipid monomers

In this work, the effects of the number of methylene units within the linker and hydrophobic of the diyndiamide diacetylene monomer tail on the thermochromic reversibility of their PDAs are studied from two series of monomers. The first series (symmetrical diyndiamide) are designed to study the effect of methylene within the linker by varying the number of methylene units between the two amide groups. The second diacetylene series (unsymmetrical diyndiamide) are designed for the investigation of the effect of the number of the methylene units within the tail part.



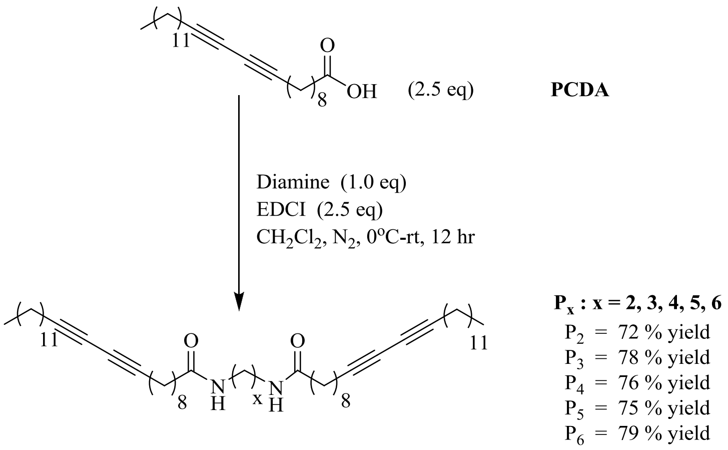
$P_x : x = 2, 3, 4, 5, 6$



$S_y : y = 0, 1, 4, 8, 12, 16$

3.1.1 Synthesis of symmetrical diyndiamide monomer ($P_2 – P_6$)

To synthesize symmetrical diyndiamide, 2.5 equivalents of 10,12-pentacosadiynoic acid (PCDA) was reacted with 1.0 equivalent diamine such as 1,2-ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane and hexametylenediamine as a nucleophile in the presence of *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDCI) as an amide coupling agent to provide diamidodiacetylenes derivatives (P_2 – P_6) as shown in Scheme 3.1. The desired products were isolated as a white solid by recrystallization in MeOH in good yields (72-79 %).



P_x : x = 2, 3, 4, 5, 6
P_2 = 72 % yield
P_3 = 78 % yield
P_4 = 76 % yield
P_5 = 75 % yield
P_6 = 79 % yield

Scheme 3.1 Synthesis of symmetrical diyndiamide monomers (P_2 - P_6)

The ^{1}H NMR spectrum of the prepared symmetrical diyndiamide monomers in $CDCl_3$ are shown in Figure 3.1. All the signals can be assigned according to their structures. The spectrum of starting material PCDA showed the signals of the methylene protons next to the carboxylic carbonyl group (proton t) at 2.3 ppm and the methylene protons next to triple bond (proton l,m) at 2.1 ppm. Upon the conversion of carboxylic group to the amido groups of P_2 - P_6, the new diamide groups showed the signals of amido N-H protons (proton u) at of 5.6 - 6.0 ppm while the methylene protons connected to the amide groups (proton v) appeared at chemical shift (δ) 3.2 - 3.3 ppm. The patterns of those signals in the spectrum of P_2 - P_6 are similar to each other but they are only slightly different attributed to the number of methylene linkers (w and x). Moreover, methylene protons next to the carbonyl groups of P_2 - P_6 (proton t) signals had shifted down field in the comparison with PCDA confirming the functional group conversion of carboxylic acid to amide groups.

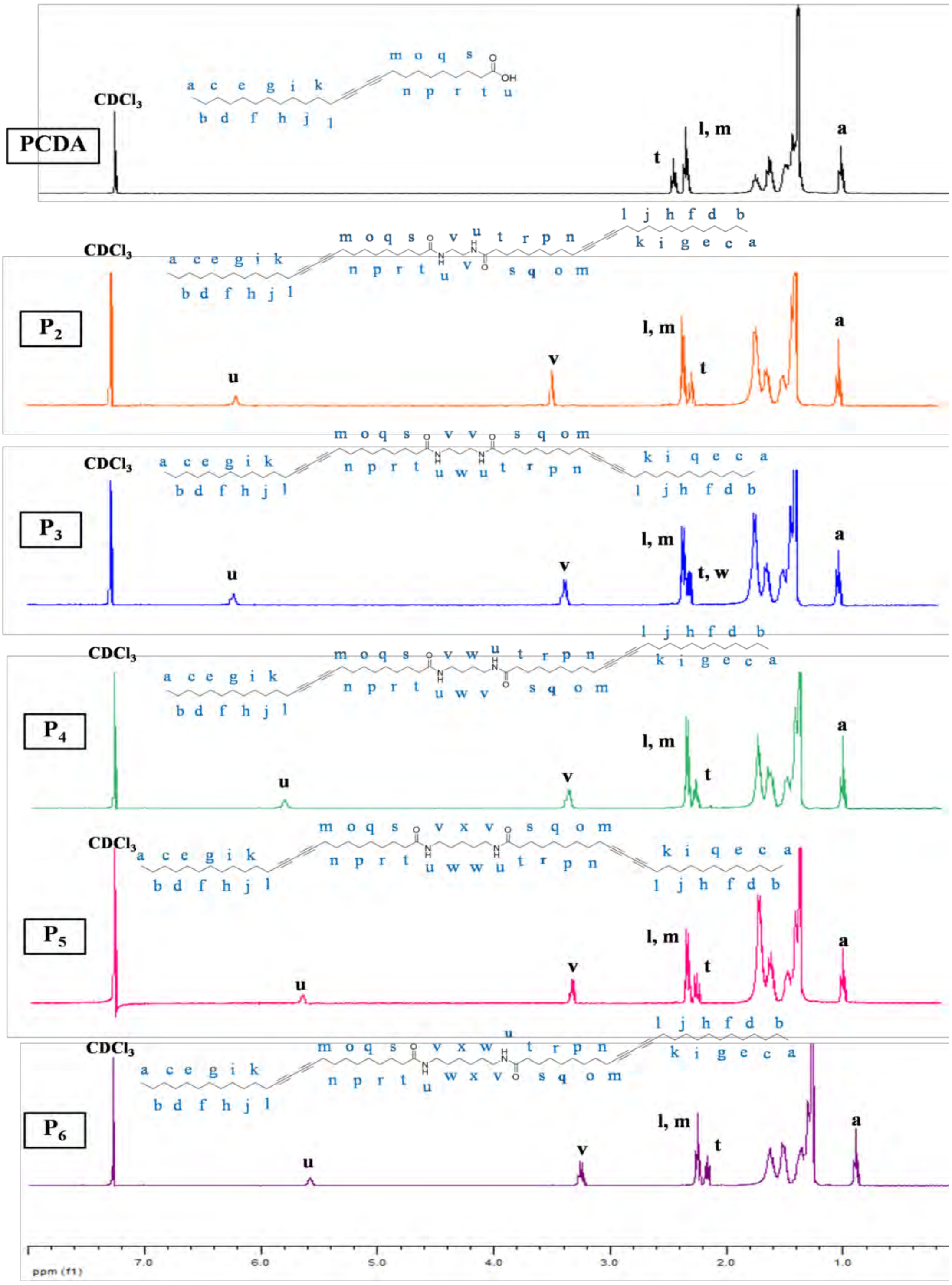
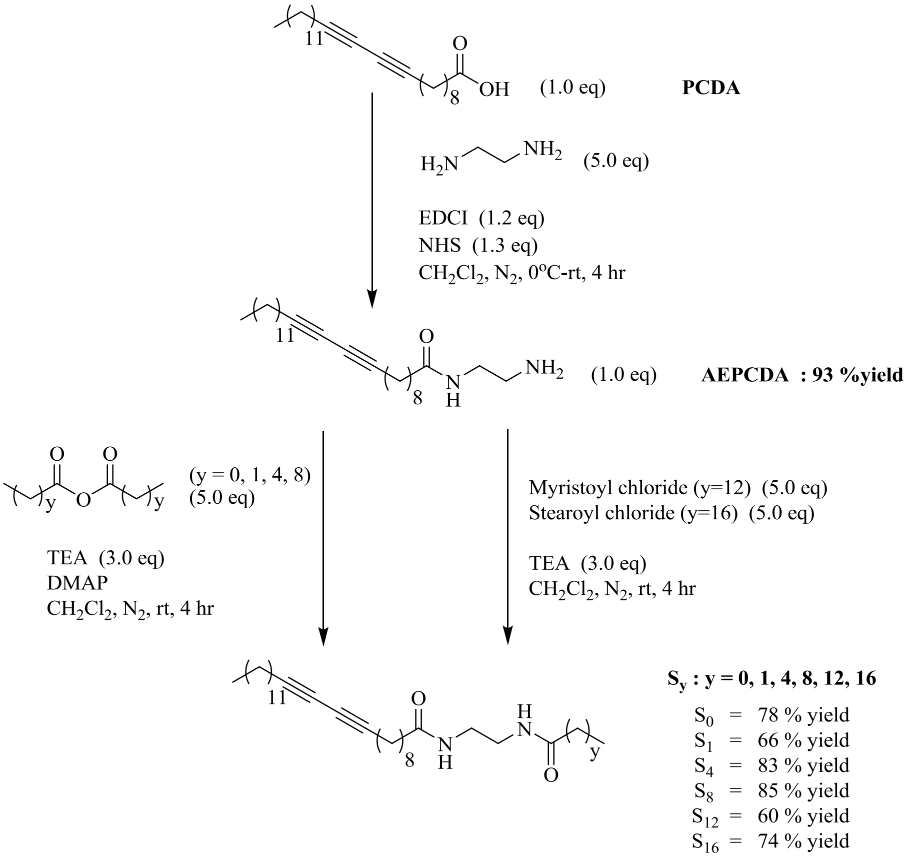


Figure 3.1 ^{1}H NMR spectrum of symmetrical diyndiamide monomers (P_2 - P_6)

3.1.2 Synthesis of unsymmetrical diyndiamide monomer (S_0 - S_{16})

The first step to synthesize unsymmetrical diyndiamide series is the preparation of *N*-(2-aminoethyl)pentacosa-10,12-diyndiamide (AEPCDA) (scheme 3.2). To begin with, PCDA was reacted with 5.0 equivalents of 1,2-ethylenediamine in the presence of EDCI and N-hydroxysuccinimide (NHS) to convert the carboxylic group to amide group. Then AEPCDA was isolated as a white solid after column purification in 93% yield. Next, AEPCDA were acylation with the appropriate anhydride i.e. acetic anhydride, propionic anhydride, hexanoic anhydride and decanoic anhydride under basic condition to generate the desired monomers S_0, S_1, S_4 and S_8 in good to fair yields (66-85%) after column chromatography. On the other hands, reaction between AEPCDA with myristoyl chloride and stearoyl chloride in the presence of triethylamine as a base generated the desired S_{12} and S_{16} in 60 and 74% yields respectively (scheme 3.2).



Scheme 3.2 Synthesis of unsymmetrical diyndiamide monomers (S_0 - S_{16})

The ^{1}H NMR spectrum of prepared unsymmetrical diyndiamide monomers in $CDCl_3$ are shown in Figure 3.2. All the signals can be assigned according to their structures. The signals in the spectrum of the products are obviously distinctive to AEPCDA. For example, The chemical shift at around 3.4 of unsymmetrical diyndiamide were assigned as signal of methylene protons next to N-H (proton v,w). Also, The two broad signals (proton u, x) at around δ 6.2-6.4 ppm belong to the two amido N-H while the signal around 2.8 ppm of AEPCDA (proton w) disappeared. Those evident had confirmed the successful acylation of AEPCDA. In addition, the protons in the aliphatic chain of prepared compounds gave the signal in the range between 1.5 - 2.5 ppm and their integration increased in according to number methylene of at the tail part of monomers.

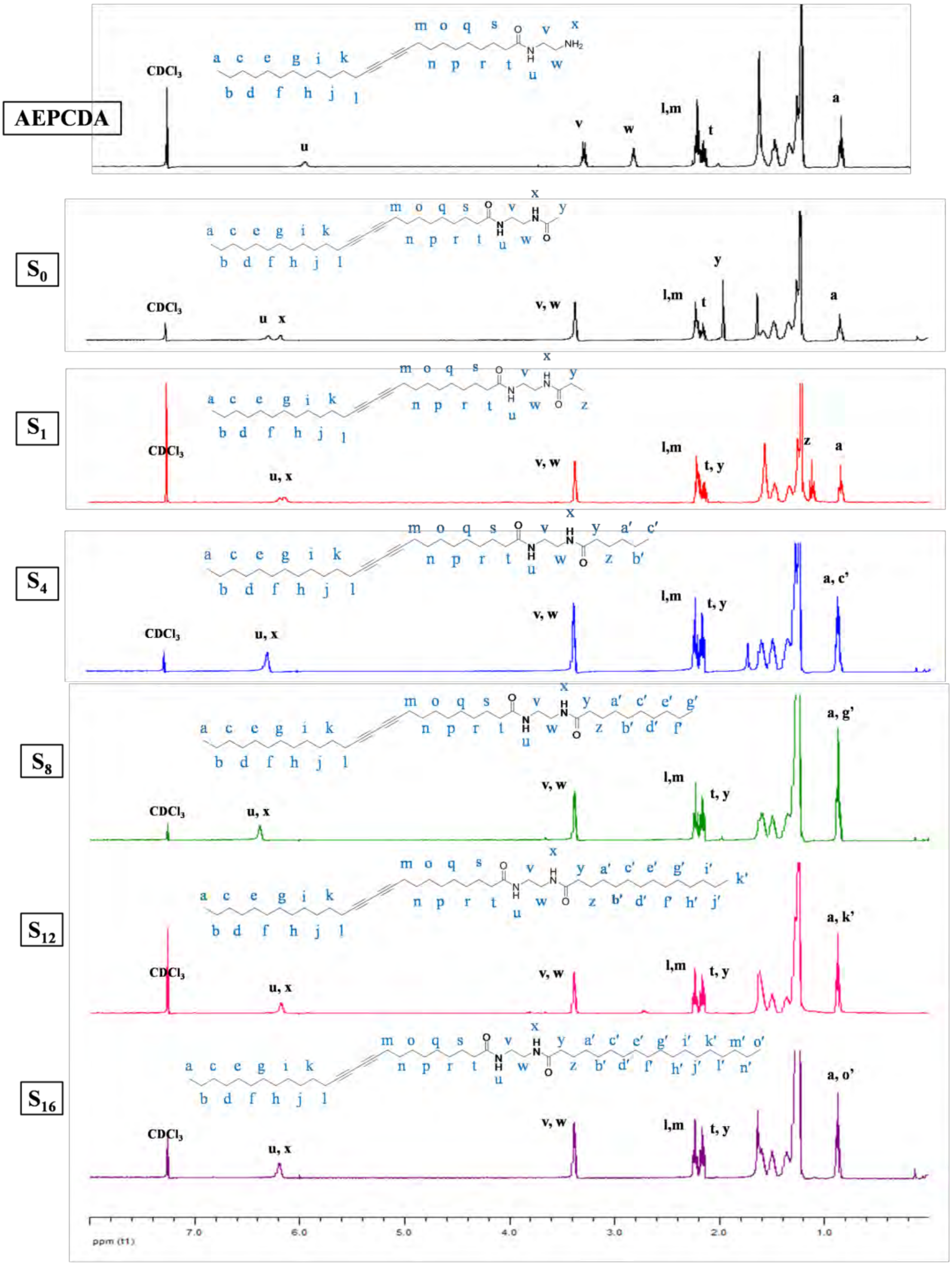


Figure 3.2 ^{1}H NMR spectrum of unsymmetrical diyndiamide monomers (S_0 - S_{16})

3.2 Preparation of polydiacetylene sols and characterization

3.2.1 Polymerizaion of diacetylene monomers

To study the thermochromism of desired PDAs, all prepared diacetylene monomers were converted to polydiacetylenes sol. To prepare polydiacetylene sols, all synthesized monomers were dissolved in chloroform (0.5 mL) and dispersed in water which described in Chapter 2. Then the solution was irradiated with UV light (254 nm) for 5 minutes at 0 °C to give a blue-color solution. These results indicated the formation of ene-yne conjugated polydiacetylenes. The ability to be hydrated and the color of polymerized diacetylenes were presented in Figure 3.3. Upon sonication at 80-85 °C for 40 minutes, poly(P_2), Poly(P_4), Poly(P_6), poly(S_0), poly(S_1) and poly(S_4) transformed into pale blue sols while poly(P_3), poly(S_8), poly(S_{12}) and poly(S_{16}) showed poor hydration due to high melting points. To solve this problem, those monomers were subjected to heating and sonicating process until a clear solution appeared, prior the polymerization. Fascinatingly, the blue sol of poly(P_3), poly(P_4), poly(P_6) and poly(S_0) displayed unusual long maximum absorption band (λ_{max}) near 700 nm along with the typical phonon side band around 590 nm. Notably, the sol of these PDA exhibited the most intense blue color comparing to the others. However, the origin of this low energy absorption remains mysterious to the author. On the other hand, poly(P_2), poly(S_1), poly(S_4), poly(S_8), poly(S_{12}) and poly(S_{16}) have the maximum absorption band at around 640 nm and near 590 nm indicating the π-π^* electronic transition with double bond vibronic coupling. Except that poly(P_5) transformed into pale purple color after photopolymerization and have the maximum absorption band at 620 nm. It is probably owing to its poor packing and weak hydrogen bond between two amido groups. The author will explain more details in the next section.

Our symmetrical diyndiamide series showed interesting trend in relationship between number of methylenes linker and hydratability. The PDA having even methylenes linker such as poly(P_2), poly(P_4) and poly(P_6) showed good hydratability while PDA with odd methylenes linker i.e. poly(P_3) and poly(P_5) displayed poor hydratability due to their capability to form self-assembly resulted in generation of poor hydrogen bond between two amido groups. For unsymmetrical diyndiamide series, increasing methylene numbers led to poor hydration because of an increase in monomer melting point.

Symmetrical diyndiamide	Linker (x)	Hydratability	Color before polymerized	Color after polymerized	λ_{max} (nm)
P_2	2	Good			640, 590
P_3	3	Fair			698, 633, 586
P_4	4	Good			685, 637, 585
P_5	5	Fair			620
P_6	6	Good			685, 639, 586
Unsymmetrical diyndiamide	**Linker (y)**	**Hydratability**	**Color before polymerized**	**Color after polymerized**	**λ_{max} (nm)**
S_0	0	Good			692, 634
S_1	1	Good			635, 586
S_4	4	Good			638, 589
S_8	8	Fair			638, 589
S_{12}	12	Fair			633, 583
S_{16}	16	Fair			632, 581

*Good = translucent sol obtained and fair = semitranslucent sol obtained

Figure 3.3 Hydration property of diacetylene monomers upon sonication in MilliQ water, color appearance, and the maximum absorption wavelength (λ_{max}) of the polydiacetylene sols after UV irradiation

3.2.2 Morphology of polydiacetylene sols

The sizes and shapes of the lipid assembled particles of PDA sols derived from unsymmetrical diyndiamide (S_0, S_1, S_4, S_8, S_{12} andS_{16}) were determined by dynamic light scattering (DLS) technique and atomic force microscopy (AFM). The DLS size distribution revealed that average hydrodynamic diameter of the particles was in the range of 181 - 345 nm (Figure 3.4). The sols from poly(S_0) showed the large average size around 345 nm while the average size of poly(S_4), poly(S_8) and poly(S_{16}) were found in the similar range between 181-196 nm . According to the DLS data, the sizes were in the following order: poly(S_{16}) < poly(S_8) < poly(S_4) < poly(S_0) which is related to the number of methyl group (y) in the monomers. Our results indicated a reverse correlation between the number of methylene unit (y) and average particle size of PDA sols. An increasing in methylene units (y) led to a size reduction of PDA sols.

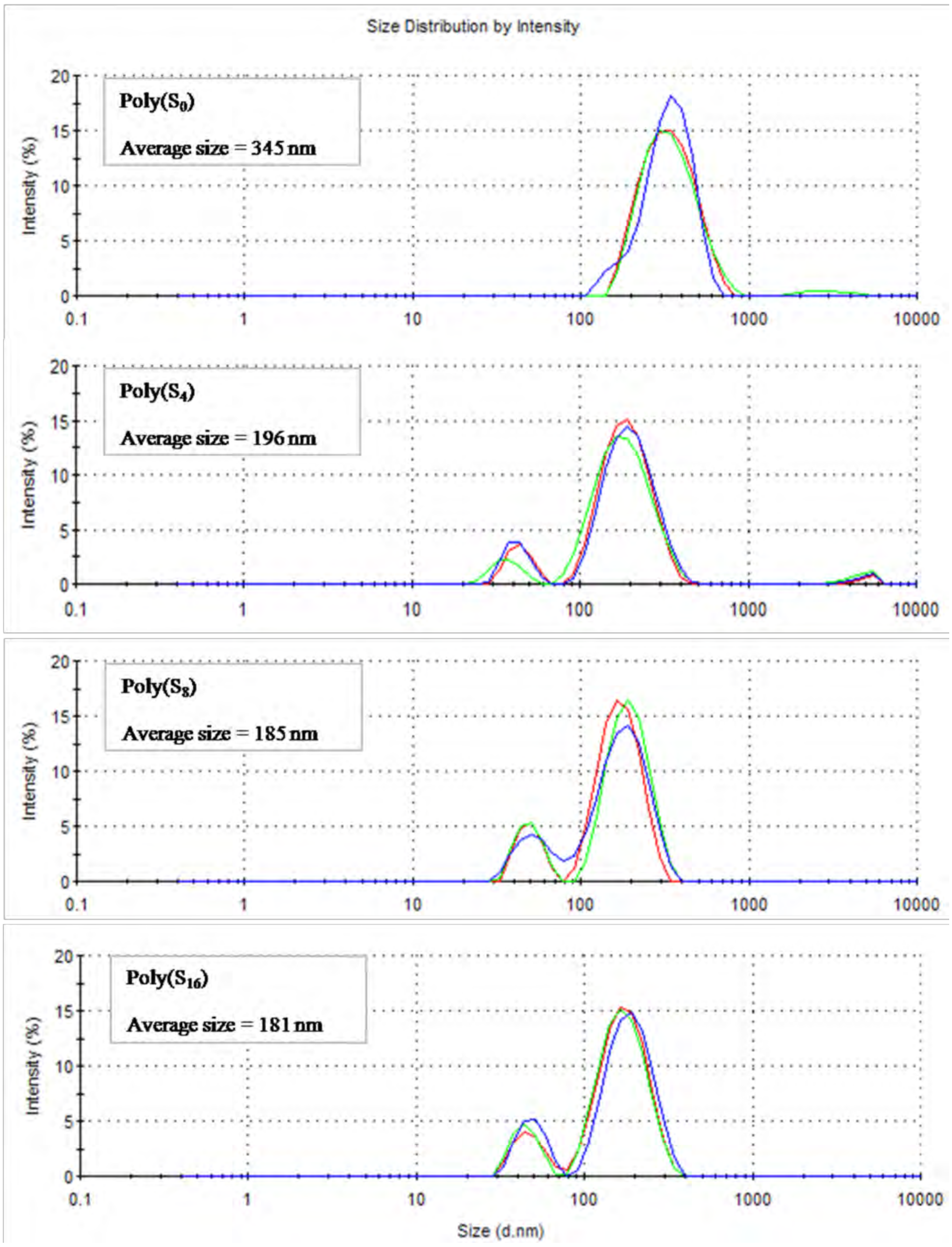
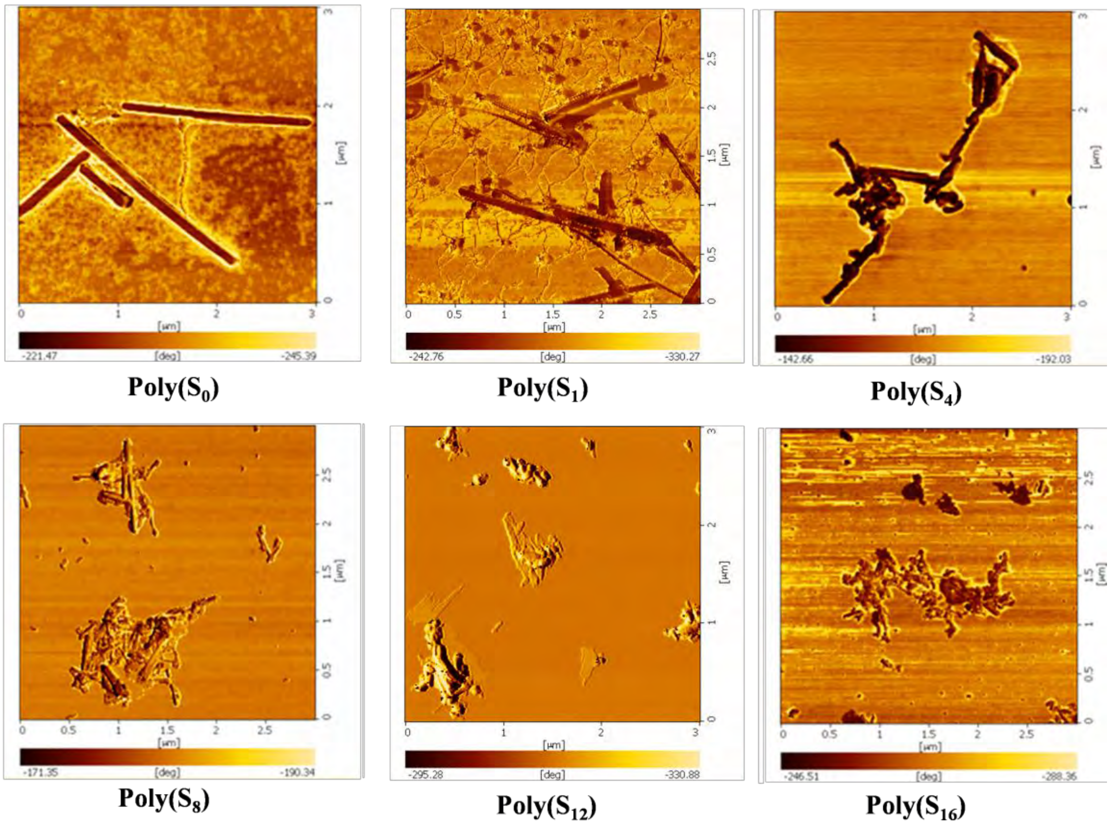


Figure 3.4 Particle size distribution of poly(S_0), poly(S_4), poly(S_8) and poly(S_{16}) sols from dynamic light scattering technique (DLS)

In addition, the self-assembled aggregates of the prepared PDAs derived from unsymmetrical diyndiamide (S_0, S_1, S_4, S_8, S_{12} and S_{16}) were studied with AFM as shown in Figure 3.5. The PDAs sols derived from poly(S_0) formed long rods with a diameter around 0.1 μm and length above 1.5 μm. On the other hand, poly(S_1) and poly(S_4) illustrated the mixtures of mainly rod-like structure with the length around 0.5 - 1 µm. In case of the poly(S_8), poly(S_{12}) and poly(S_{16}), the smaller mixed rod and spherical-like particle with high degree of aggregation were observed. These results are in good agreement with the DLS results indicating that the longer of hydrophobic alkyl chain in the polymer side chain, the smaller the particle size formed.



Poly(S_0) **Poly(S_1)** **Poly(S_4)**

Poly(S_8) **Poly(S_{12})** **Poly(S_{16})**

Figure 3.5 Atomic Force Microscopy (AFM) images of poly(S_0), poly(S_1), poly(S_4), poly(S_8), poly(S_{12}) and poly(S_{16}) sols

Next, the author applied structural guideline for predicting an aggregate morphology in Figure 3.6 to analyze the self-assemble structure of synthesized unsymmetrical diyndiamide (S_0, S_1, S_4, S_8, S_{12} and S_{16}). A lipid can be described by several variables. The surface area of the headgroup when the lipids are packed so as to maximize the attractive forces and minimize the repulsive forces is defined as the optimal headgroup area, a_0. The hydrocarbon tail is described by two terms: the volume, v, is assumed to be fluid and incompressible, and the critical chain length, l_c, is the maximum effective length the chains can assume. Using these variables, Israelachvili proposed an optimal surface area per polar headgroup, which depends on the packing parameter, $P = v/(a_0 \times l_c)$ (Figure 3.6) [41-42]. If $P < 1/3$, the amphiphile has a tendency to form spherical micelles; if $1/3 < P < 1/2$, cylindrical micelles will be favored; if $1/2 < P < 1$, bilayers with a spontaneous curvature (vesicles) are produced; if $P = 1$, planar bilayers will be favored; and if $P > 1$, micellar aggregates with a reverse curvature will be formed.

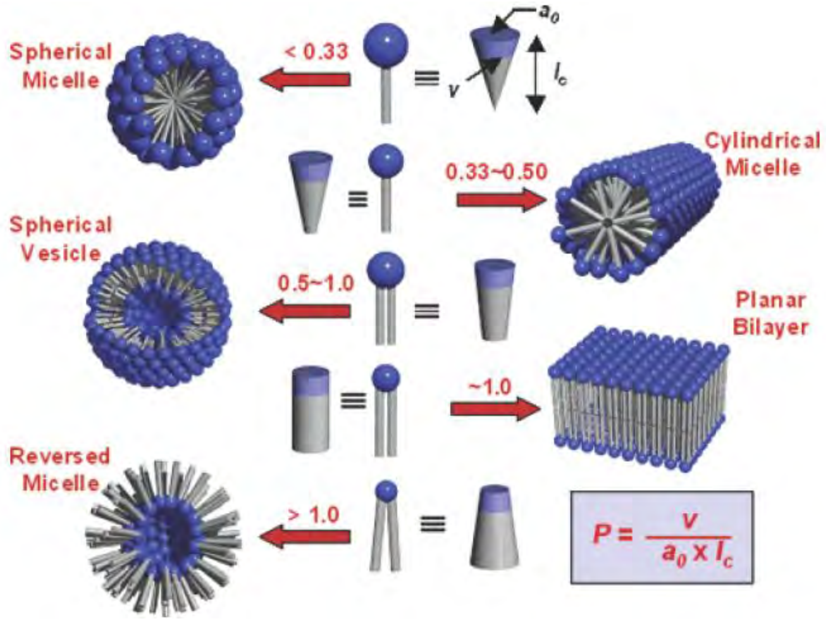


Figure 3.6 Various self-assembled morphologies depending on the critical packing parameter (P) of each lipid

Applying the above guideline, the self-assembly of poly S_0 and poly S_{16} are explained based on molecular packing of their lipid monomers as depicted in Figure 3.7. We hypothesized that for S_0 monomer, the shortest methylene chain in the tail part contributed to repulsion among alkyl side chain resulted in poor packing while $S_{16,}$ having the longest methylene chain, divided hydrophobic interaction between alkyl side chain. From the packing parameter equation: $P = v/(a_0 \times l_c)$, the author hypothesized that increasing methylene number would increase volume of hydrophobic chain (v) while the other variables remain unchanged (a and l) in both monomers. So the packing parameter of monomer that contained the longer methylene chain would be greater than the shorter one. AFM showed that poly(S_0) have a rod like structure. We believed that S_0 would form a cylindrical micelle due to its short methylene side chain. The packing parameter might be in the range of 0.33-0.50 based on Figure 3.6. For S_{16}, the hydrophobic effect causes aggregation and holds the bilayer together [43] thus packing parameter might be in the range of 0.50-1.00 which is preferable to form a spherical vesicle.

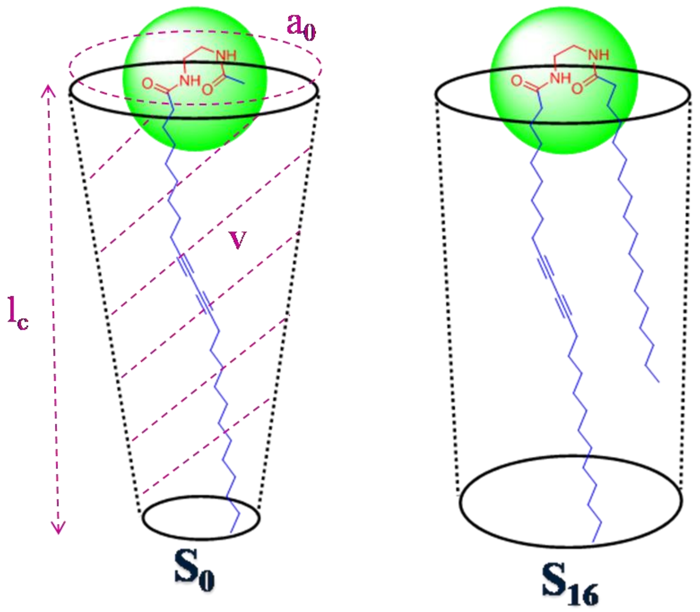


Figure 3.7 Schematic illustration of self-assembled prediction based on the critical packing parameter (P) of S_0 and S_{16}

3.3 Thermochromic properties of polydiacetylene sols

Thermochomic study of all PDA was executed by heating PDA sols stepwise from 25 °C to 85 °C and monitored by UV absorption spectrometer along with photograph recorder. Figure 3.8 revealed the relationship between temperature, electronic absorption spectrum and color appearance of PDA derived from symmetrical diyndiamides and symmetrical diyndiamides, respectively. In general, upon increasing temperature, absorption and the phonon side band of all prepared PDAs decreased and shifted toward a shorter wavelength. Moreover, the blue to red color transition occurred simultaneously with an increase in temperature. However, the color transition was diverse among them. For symmetrical diyndiamide series, poly(P_2), poly(P_4) and poly(P_6) displayed the higher color temperature transition (CTT) (75 - 85 °C) in comparison with poly(P_3) and poly(P_5). Notably, the color of PDAs derived from P_4 and P_6 remained blue-purple at 85 °C indicating the very high color transition. Nevertheless, the PDA containing the odd methylenes linker such as poly(P_3) and poly(P_5) changed to red completely at 85 °C together with the absorption band gradually shifted from 690 to 550 nm. Interestingly, when compared the color transition temperature of PDA with even methylenes spacer (x = 2, 4, 6), CTT is increased with increase the number of methylene. However, the PDA with odd methylene spacer (x = 3, 5) displayed a different trend. The CTT of those PDAs decreased while increasing number of methylene. Poly(P_3) displayed blue to red color change around 60 - 70 °C while color transition temperature of poly (P_5) were 35 - 45 °C.

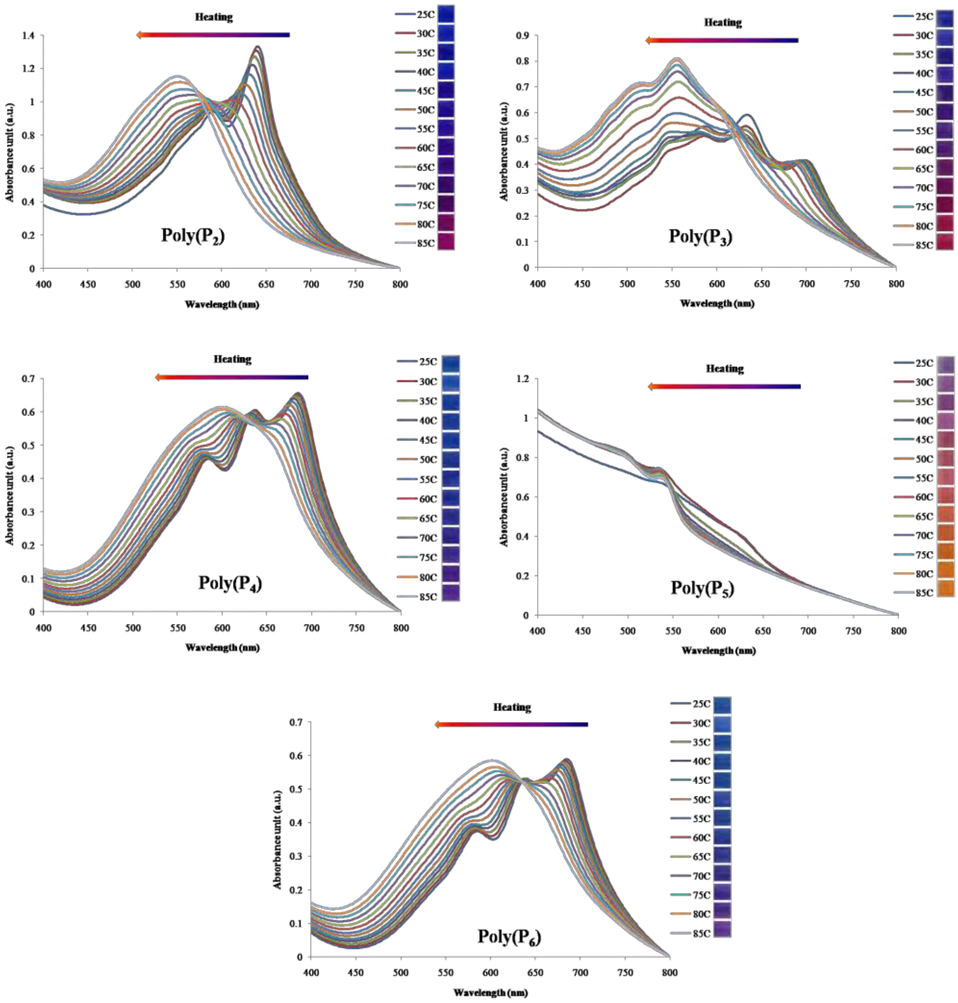


Figure 3.8 Electronic absorption spectrum of 0.5 mM symmetrical diyndiamide (P_2 - P_6) sols upon stepwise heating from 25 to 85 °C along with the color appearance of the sols from photographic record

For unsymmetrical diyndiamide series, the blue sols of PDAs from poly(S_0) turn completely red at 85 °C with the absorption band gradually shifted from 692 to 555 nm (Figure 3.9). Similarly, the absorption band of poly(S_1), poly(S_4), poly(S_8), poly(S_{12}) and poly(S_{16}) displayed the hypsochromic shift from λ_{max} *ca*. 640 to 550 nm accompanied with color change to either red or purple at 85 °C. Interestingly, the color transition temperatures of PDAs derived from unsymmetrical diyndiamides lipid are diverse. The PDA sols derived from poly(S_0), poly(S_1) and poly(S_4) turned red around 50 - 60 °C. Higher color transition were observed in case of PDAs prepared from poly(S_8), poly(S_{12}) and poly(S_{16}) carrying the more number of methylene tail (y = 8, 12 and 16 respectively). The blue sols of poly(S_8) and poly(S_{12}) turned red around 60 - 70 °C while the color of poly(S_{16}) did not appear as red sol even at 85 °C. These results can be explained by the relationship between number of methylenes in the tail part and the response to temperature.

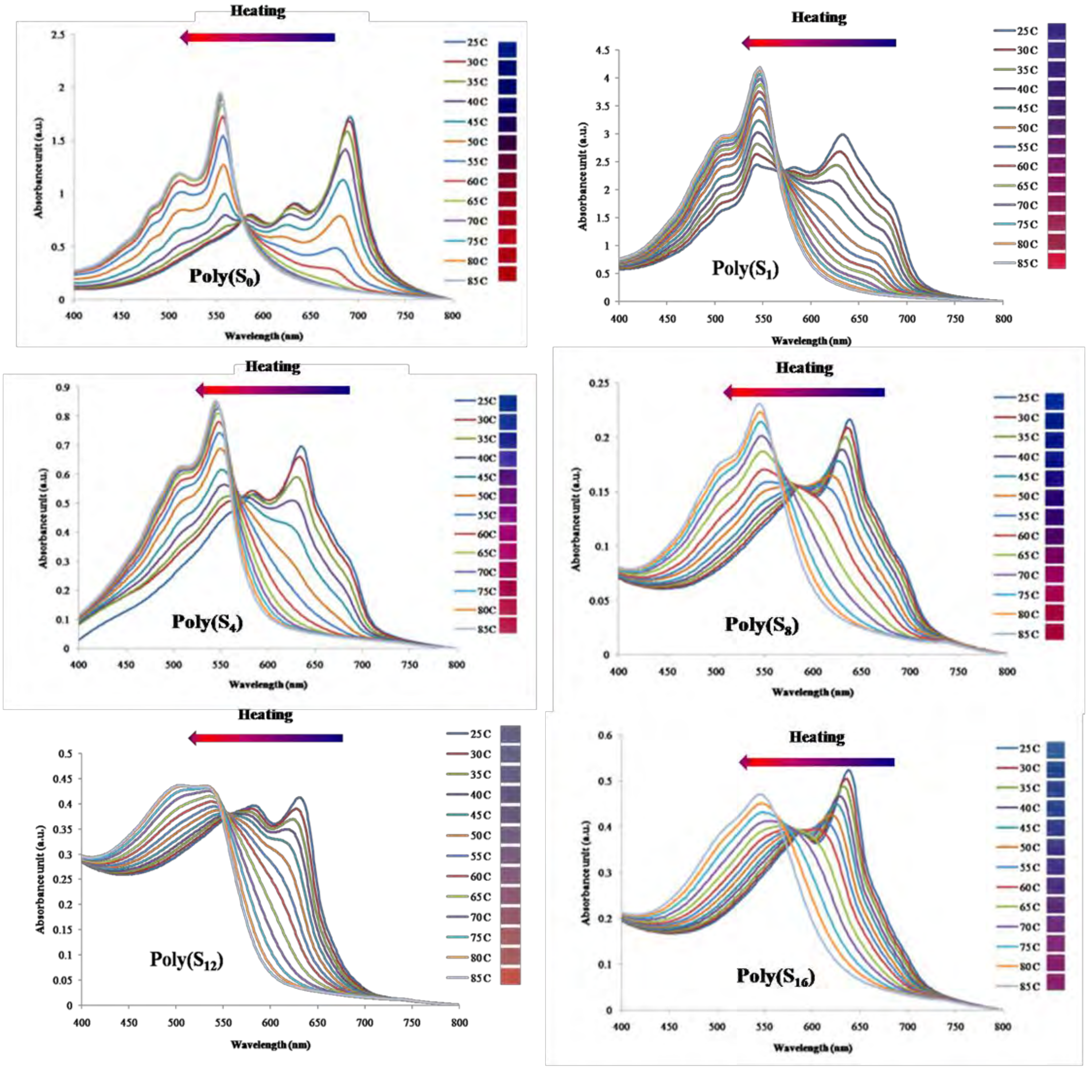


Figure 3.9 Electronic absorption spectrum of 0.5 mM unsymmetrical diyndiamide (S_0 - S_{16}) sols upon stepwise heating from 25 to 85 °C along with the color appearance of the sols from photographic record

3.3.1 Colorimetric response (%CR)

Data from absorbance spectrum along with photographic recording of polydiacetylene (Figure 3.8 and 3.9) are not to sufficient to quantify color transition temperature. Therefore, the absorbances of all prepared PDA sols during the heating process were translated into colorimetric response (%CR) that is defined as percent change in the maximum absorption of the blue phase with the respect to the total absorption at both red and blue phases. The %CR calculated from the following equation:

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

FB is the fraction of blue calculated from $A_{blue}/(A_{blue}+A_{red})$ where A_{blue} and A_{red} are the absorbance at the λ_{max} of the blue and the red forms, respectively, of the PDAs. FB_0 is the fraction of blue of the original PDAs prior to heating. The plot of %CR against the temperature of all PDAs studied yielded sigmoidal curves as a result of color transition upon raising temperature (Figure 3.10). The slope of these sigmoidal curves can be indicated the response of PDA sols on thermochromism that is sharp slope means rapidly response in the short temperature range. The CTT estimated from %CR for the PDA derived from P_2, P_3, P_4, P_5 and P_6 are found in the following order: poly(P_2) < poly(P_3) < poly(P_5) < poly(P_4) = poly(P_6). The % CR plot showed that poly(P_2) reached 30 %CR in the short temperature range (10 °C) while the rest of polylmers reached to 30 %CR in the longer temperature range (~ 20 °C). The results also showed that even spacers have the smaller %CR than odd spacers and %CR tend to decrease when increasing number of methylenes. Surprisingly poly(P_2) showed the higher %CR than poly(P_3) meaning that poly(P_2) underwent blue-red color change at the lower temperature comparing to poly(P_3). However these are not in good agreement with the naked eye observation from photographic recording (Figure 3.8) which poly(P_3) changed color in the lower temperature range than poly(P_2). Poly(P_4) and poly(P_6) illustrated the lowest %CR. This is caused by the efficient packing of their diacetylene backbones that requires higher level of energy to disturb. On the other hand, odd spacers have higher %CR as they possess weaker hydrogen bonding between amide groups, allowing perturbation at lower temperature. Again this incidence could be attributed to the odd-even effect whereby even methylene spacer tend to be more closely packed than odd spacer. The blue-to-red color transition could be correlated with the release of backbone strain that led to the disturbance of the ene-yne planarity. The release of backbone strain in response to thermal stimulation requires more energy if PDA backbones are closely packed.

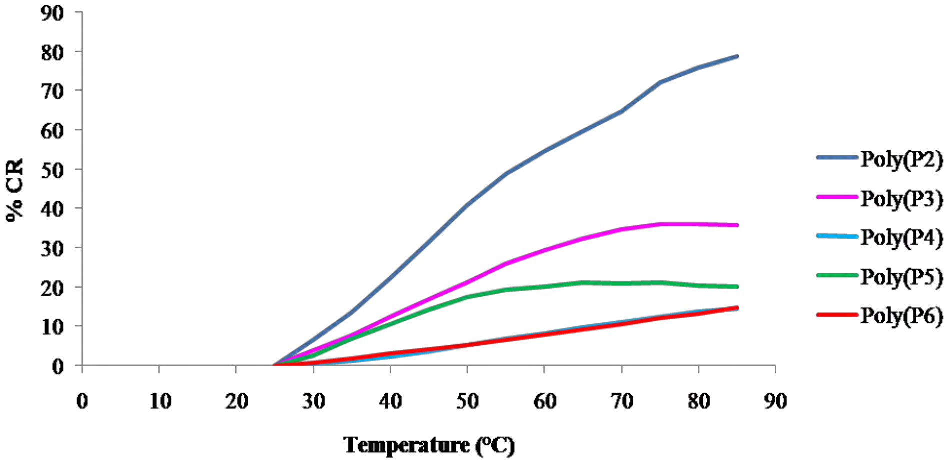


Figure 3.10 The colorimetric responses (%CR) of symmetrical diyndiamide sols during heating processes

In addition, the colorimetric response of PDA sols prepared from S_0, S_1, S_4, S_8, S_{12} and S_{16} were calculated as above mentioned and depicted in Figure 3.11. The order of color transition temperature (CTT) assessed from % CR is found in the following order: poly(S_1) < poly(S_4) < poly(S_0) < poly(S_{12}) < poly(S_8) < poly(S_{16}). This order of CTT is in good agreement with those observed from photographic recording. Moreover, valuable information was gained from the %CR plot. Relatively sharp sigmoid curve were obtained from poly(S_0), poly(S_1) and poly(S_4), meaning that the blue to red color change occurred within a narrow temperature range. The increase of %CR from 20 to 50 was observed within temperature range of 10 °C. However, gradual changes of % CR were observed in case of PDA derived from poly(S_8), poly(S_{12}) and poly(S_{16}). It required temperature raise around 20-25 °C in order to increase %CR from 20 to 50. Once more, hydrophobic interaction between the side chains might be responsible for this occurrence. The blue-to-red color transition was associated with the movement of the side chains that resulted in the release of backbone strain and led to the disturbance of the ene-yne planarity. PDA with the shortest methylene chain length (S_0) have a strong repulsion among alkyl side chain which disturb the hydrogen bonding so the side chain movement is easier than PDA with the longest methylene chain length (S_{16}) that have a strong hydrophobic interaction among each alkyl chain. It is not sure whether hydrogen bonding of PDA having the longest alkyl chain would be stronger or not but the author think that the hydrophobic interaction between alkyl side chain should increase the stability of PDA to thermal stimuli. Side chain movement in response to thermal stimulation requires more energy if the hydrophobic interaction between the side chains and the hydrogen bonding between the head groups are strong. Structurally, all the diacetylene lipids in this series contains two amide groups with varying number of methylene groups in the tail part (y), therefore, hydrophobic interaction between the polymer side chains should be the major reason underlying the color transition temperature behavior in our PDA series.

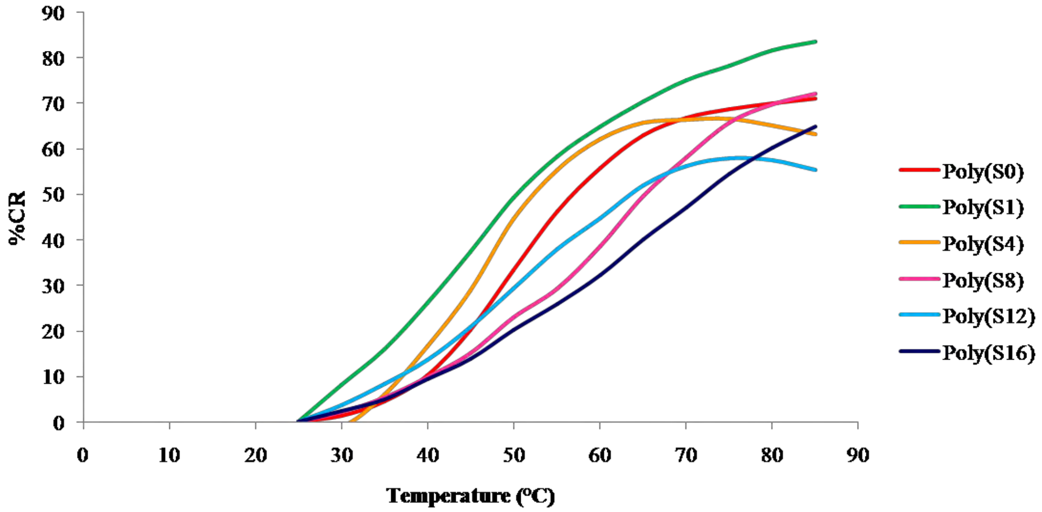


Figure 3.11 The colorimetric responses (%CR) of unsymmetrical diyndiamide sols during heating processes

3.4 Reversibility thermochromism of polydiacetylene sols

Subsequently, we focused on thermochromic reversibility of PDA sols. The objective was to verify the relationship between number of methylene and thermochromic properties and to prove the effect of one and two diynes on thermochromic reversibility. To study thermochromic reversibility, PDA sols were heated up to 85 °C and cooled back to 25 °C while color changes were observed by photographic recorder and UV-Visible spectroscopy (Figure 3.12). At 25 °C, PDA sols prepared from the P_2, P_4 and P_6 displayed the typical blue color corresponding to a visible absorption maximum wavelength at 640 and 700 nm. When the temperature was raised to 85 °C, the absorption maximum of the solution underwent a gradual blue shift to 540 nm along with blue to purple color transition. Upon cooling to 25 °C, the UV-spectrum returned to the original blue and displayed blue color. On the other hand, UV-spectrum of poly(P_3) and poly(P_5) remain unchanged when cooled back to

25 °C and the color did not return to the original blue. The result suggested that close packing in case of PDA having even methylene spacer affected the reversibility due to their strong hydrogen bonding. Therefore two diacetyelene units on the monomer such as those on PDA derived from symmetrical diyndiamides:poly(P_4) and poly(P_6) is required for full thermochromic reversibility.

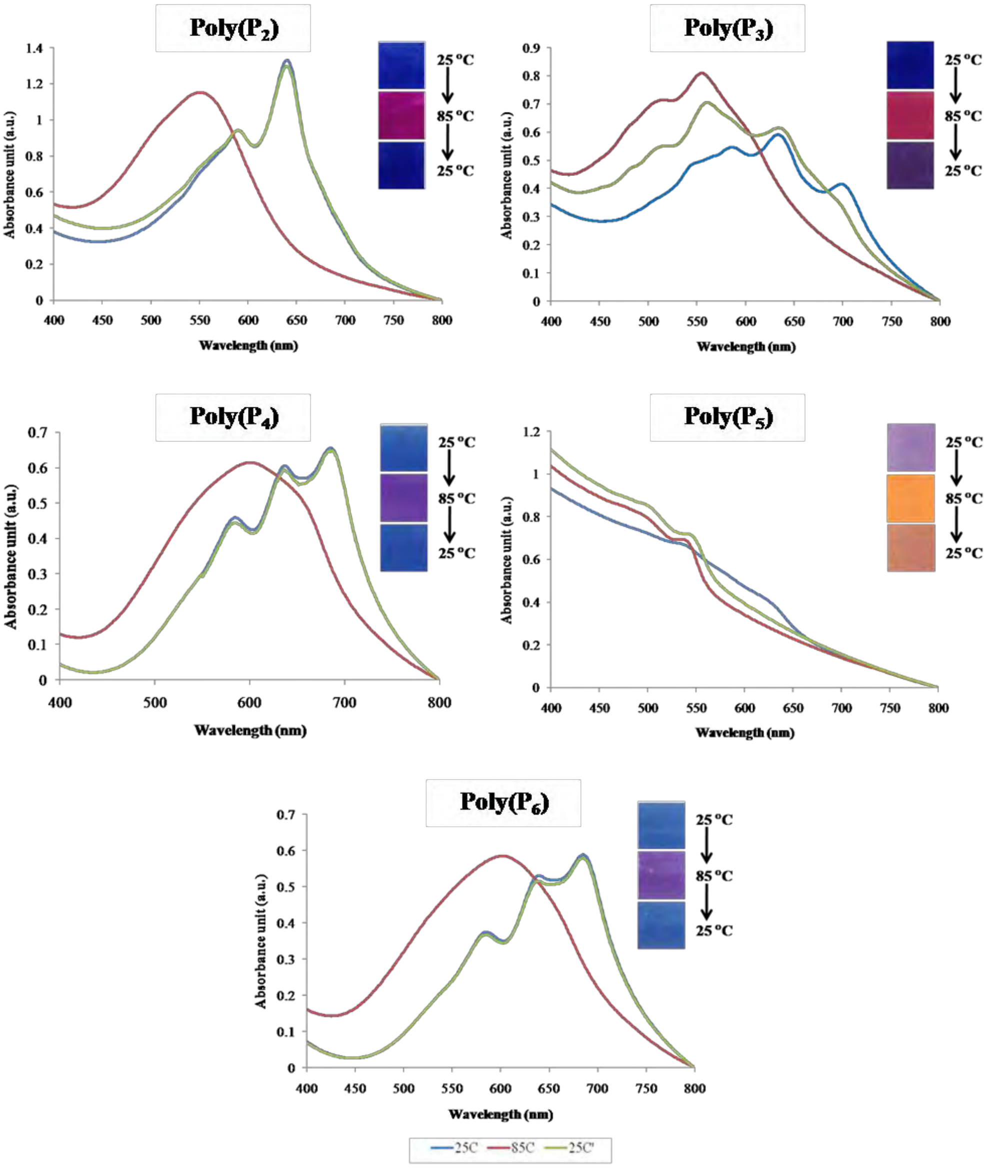


Figure 3.12 Photographs and visible spectroscopic monitoring of the symmetrical diyndiamide sols during thermal cycles

In contrast, the thermochromic reversibility of PDA derived from unsymmetrical diyndiamide showed different calorimetric response. At room temperature, a solution of the PDA vesicle, prepared from the poly(S_0), displayed the typical blue color corresponding to a visible absorption maximum wavelength at 640 nm (Figure 3.13). When the temperature was raised from 25 to 85 °C, the absorption maximum of the solution underwent a gradual blue shift to 540 nm along with blue to orange color transition. Upon cooling to 25 °C, the UV-spectrum however remain unchanged and the color did not return to the original blue but displayed the pink color. These results suggest thermally stimulated colorimetric irreversibility of the poly(S_0). On the other hand, the thermochromic investigation of PDA sols derived from poly(S_4), poly(S_8) and poly(S_{12}) which have a longer methylene unit (y = 4, 8 and 12 respectively), gave contrasting results. The color of poly(S_4), poly(S_8) and poly(S_{12}) solution changed from blue to pink upon heating, and the pink color reversed to purple and blue-purple respectively, when the solution was cooled to 25 °C. Also, UV absorption spectrum revealed that partial recovery of the peak at ca. 632 nm upon cooling the solution back to 25 °C was observed. Even though the color and the UV-spectrum were not restored to the original upon cooling back to 25 °C, some degree of recovery were showed in comparison with the poly(S_0). These phenomena indicated a partially reversible property of these PDAs. Finally, spectroscopic monitoring along with naked eye observation demonstrated that PDA sols prepared from poly(S_{16}) lipid displayed complete colorimetric reversibility upon thermal stimuli. During the heating and cooling process, peak at 640 and 580 nm could be recovered without significant loss of intensity and the blue color shade before heating and after cooling back to 25 °C were perfectly matched. This result suggested that only one diacetylene unit is necessary for full thermal reversibility, given that the other diacetylene unit is substituted with alkyl chain of satisfactory length. In this case, at least 16 methylene units are required for full reversibility of PDA derived from unsymmetrical diyndiamide.

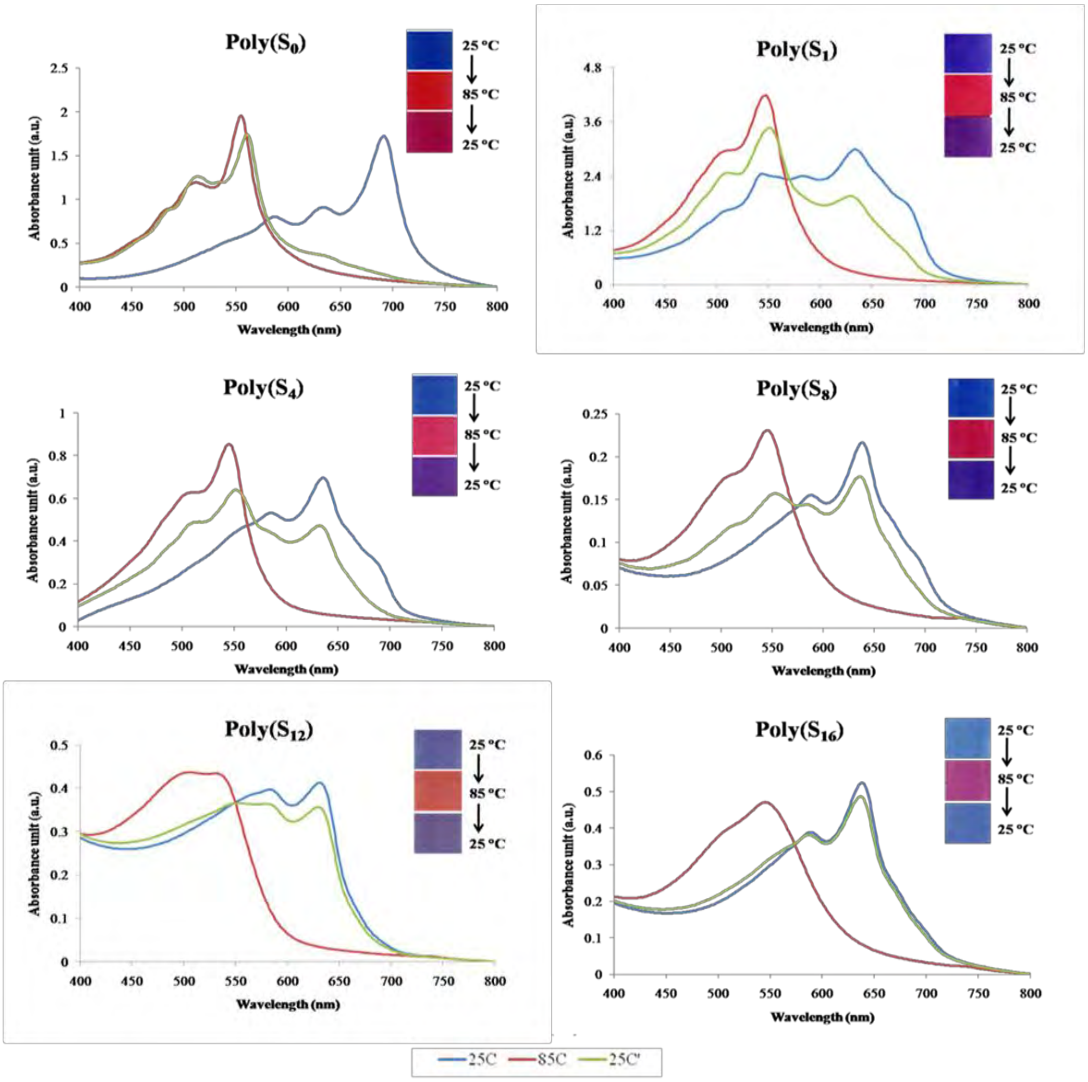


Figure 3.13 Photographs and visible spectroscopic monitoring of the unsymmetrical diyndiamide sols during thermal cycles

3.4.1 Degree of reversibility (%DR)

To study the stability of thermochromic reversibility, we subjected PDA sols to 10 heating-cooling processes from 25°C - 85°C. To calculate the degree of thermochromic reversibility, we monitored absorbance of the PDA sols at their initial λ_{max} at blue phase for ten heating/cooling cycles between 25 - 85° C. The plots of the absorbance against the cycle number were represented in Figure 3.14 and 3.15. After the first heat treatment, the blue absorbance of all PDAs decreased and upon the second heat treatment, the intensity of initial λ_{max} at blue phase recovered differently among the PDAs.

For symmetrical diyndiamide series, poly(P_5) showed few color recovery while poly(P_3) illustrated half color recovery. Poly(P_4) and poly(P_6) on the other hand demonstrated virtually full recovery of the initial absorbance in every cycles. Also blue to red color transition of these PDA occurred even after ten cycles of heating and cooling, without reduction in color intensity.

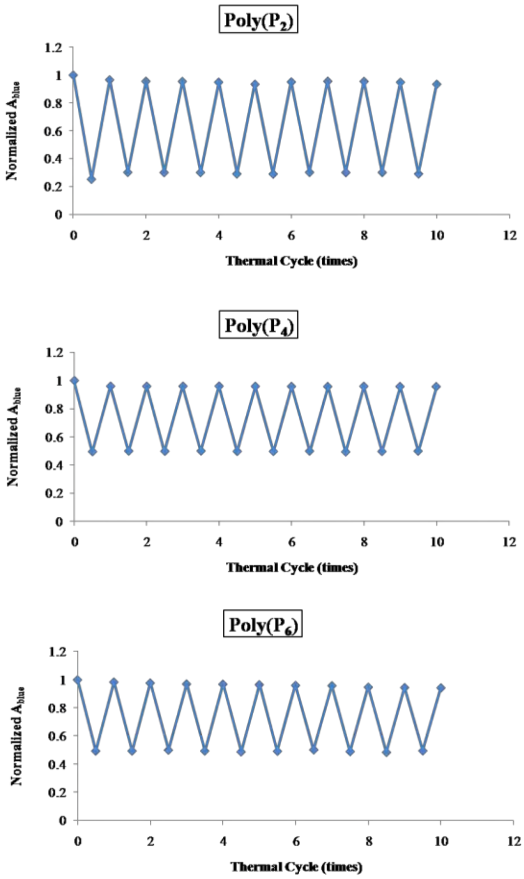


Figure 3.14 Normalized absorbances at the initial λ_{max} of the symmetrical diyndiamide sols at 25 and 85 °C in the heating-cooling cycles

In unsymmetrical diyndiamide series, we observed a few color recovery of poly(S_0) after the second heating-cooling cycle, it appeared as pink color at both 85 and 25 °C. The small recovery observed in these PDAs is governed by either the second difference in the side chain packing or the alteration of the vibronic state population at different temperatures. Poly(S_1) and poly(S_4) showed a half color recovery in opposite to poly(S_8) and poly(S_{12}) which demonstrated almost full color recovery. Remarkably, the poly(S_{16}) depicted the virtually full recovery of the initial absorbance in every cycles.

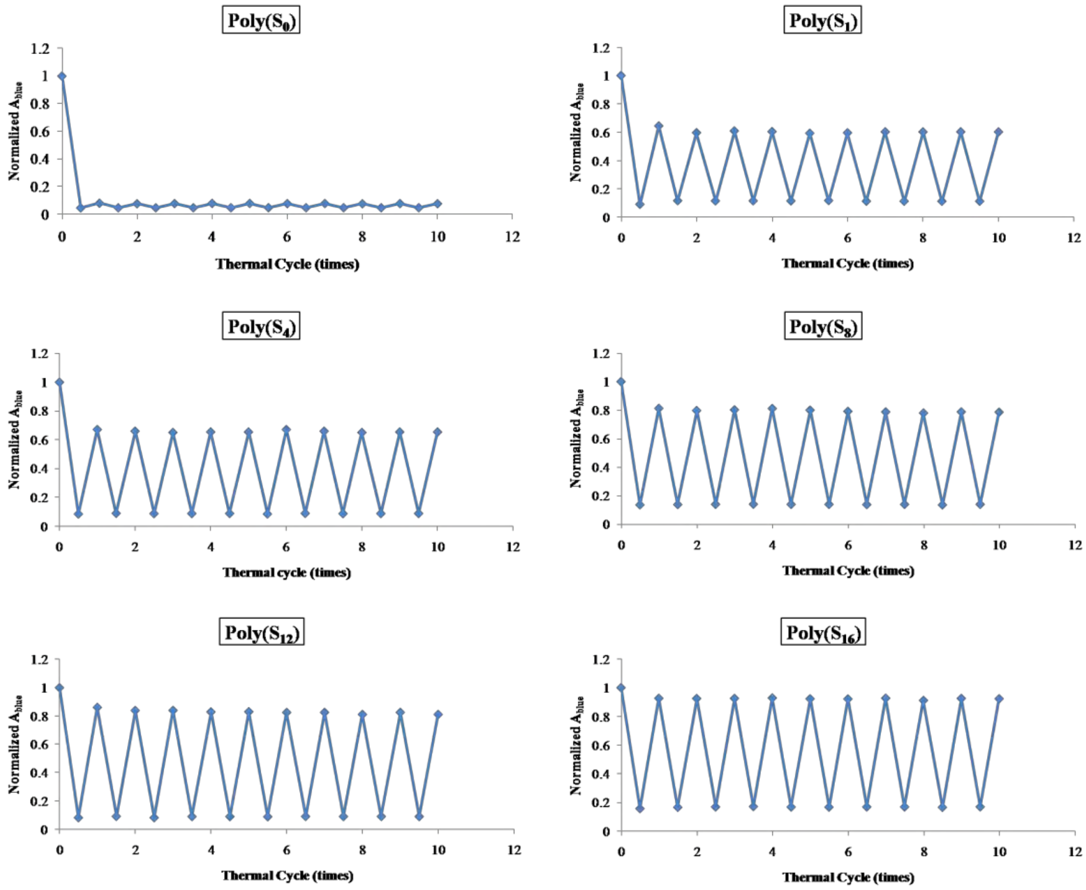


Figure 3.15 Normalized absorbances at the initial λ_{max} of the unsymmetrical diyndiamide sols at 25 and 85 °C in the heating-cooling cycles

To execute a quantitative analysis of thermochromic reversibility, we calculated degree of reversibility (%DR) of PDAs which is the average value of the absorbance change (ΔA_{avg}) from the second to ninth heating is compared against the absorbance change in the first heating (ΔA_1) according to the following equation:

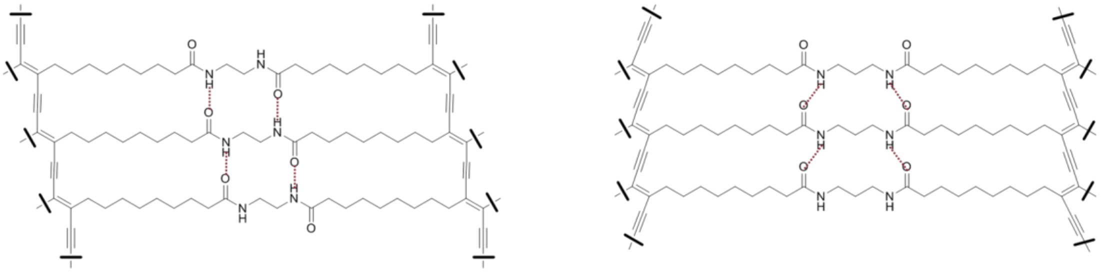
$$\%DR = 100 \times (\Delta A_{avg} / \Delta A_1)$$

where $\Delta A = A_{25}$ °C – A_{85} °C. The % DR value, allowed us to classify the reversibility class of PDAs i.e., fully reversible PDA (%DR > 90%), partially reversible PDA (10% < %DR < 90%), and irreversible PDA (%DR < 10%). [2] The absorbance of PDA during the heating and cooling cycles was evaluated using the above equation and summarized in table 3.1

Table 3.1 Classification of polydiacetylene sols

Symmetrical diynamide	**Linker (x)**	**Degree of reversibility (%DR)**	**Classification of PDA**
Poly(P_2)	2	88	High color reversible
Poly(P_3)	3	65	Low color reversible
Poly(P_4)	4	91	High color reversible
Poly(P_5)	5	20	Low color reversible
Poly(P_6)	6	93	High color reversible
Unsymmetrical diynamide	**Linker (y)**	**Degree of reversibility (%DR)**	**Classification of PDA**
Poly(S_0)	0	3	Low color reversible
Poly(S_1)	1	54	Low color reversible
Poly(S_4)	4	62	Low color reversible
Poly(S_8)	8	77	High color reversible
Poly(S_{12})	12	80	High color reversible
Poly(S_{16})	16	90	High color reversible

From table 3.1, the %DR of PDA derived from symmetrical diyndiamides were found in the following order: poly(P_5) < poly(P_3) < poly(P_2) < poly(P_4) < poly(P_6). PDAs with even number of methylene spacer exhibited high color reversibility with %DR in the range of 88-93% upon heating and cooling process while PDAs having odd number of methylene spacer showed low color reversibility having the %DR between 20-65%. Notably, for the symmetrical diyndiamide series, %DR of even methylene spacers tends to increase with increasing number of methylene. In contrast to PDA containing the odd methylene spacer, %DR tends to decrease when increasing the number of methylene. The intramolecular side chain interaction is perhaps the main contribution governing this trend. The recovery of blue-to-red transition is associated with hydrophobic interaction between the side chains and the hydrogen bonding between the head groups. During the heading process, it not only caused the blue to red color transition but also the side chain movement resulting in the release of backbone strain or the disturbance of the ene-yne planarity. If the hydrophobic interaction between the side chains and the hydrogen bonding are strong enough, PDA will be able to restore the original conformation and backbone strains upon the cooling back to the original temperature. In such case, the color of PDA will change back to its original blue color. For the PDA series prepared from symmetrical diyndiamides, the side chain of all PDA are equal (C25) but different in the methylene linkers. The results indicated that the number of methylene play an important role in color recovery upon heating-cooling process. We hypothesized that PDAs possessing even-numbered methylene linker should have a stronger hydrogen bonding than one having odd-numbered methylenes linker. Figure 3.16 (left) displayed the purposed molecular orientation of poly(P_2), which represented the PDA having the even-numbered methylene linker. Such PDA showed well positioned ene-yne backbone. On the other hands, poly(P_3) prepared from symmetrical diyndiamide carrying odd-numbered methylene number, has a mismatched hydrogen bonding between side chain (Figure 3.16 right). This caused a weak hydrogen bonding leading to irreversible thermochromism of those PDAs.



Poly(P_2) **Poly(P_3)**

Figure 3.16 Hypothetical packing of poly(P_2) and poly(P_3)

For the PDAs derived from the unsymmetrical bisdynamide, the degree of reversibility of PDAs is found in the following order: poly(S_0) < poly(S_1) < poly(S_4) < poly(S_8) < poly(S_{12}) < poly(S_{16}) (Bottom half of table 3.1). The results suggested that thermochromic reversibility of these PDAs is related to the number of methylene unit Results showed that %DR of PDA derived from unsymmetrical diyndiamide increases with an increase in number of methylene group. Presumably, lengthening of methylene side chain induced a good hydrophobic interaction between hydrophobic tails making the packing of polymer side chain more efficient. For example, poly(S_0) which have the shortest methylene chain length (y = 0) exhibited the repulsion among alkyl sides chain,so it caused the weak hydrogen bonding among diamido head groups. On the other hand, poly(S_{16}) which possessed the longest methylene chain length (y = 16), demonstrated the strongest hydrophobic interaction (Figure 3.17)). Hydrophobic interaction allows tighter interaction, leading to the enhancement of hydrogen bonding among diamido headgroups. Our results confirmed the effect of methylene chain length on the thermochromic reversibility. The length of alkyl chain is the key determining factor as caused by the strong hydrophobic interaction among polymer side chain. Moreover, this result suggested that only one diacetylene unit is necessary for full thermal reversibility, given that the other diacetylene unit is substituted with alkyl chain of satisfactory length. In this case, at least 16 methylene units are required for full reversibility of PDA derived from unsymmetrical diyndiamide.

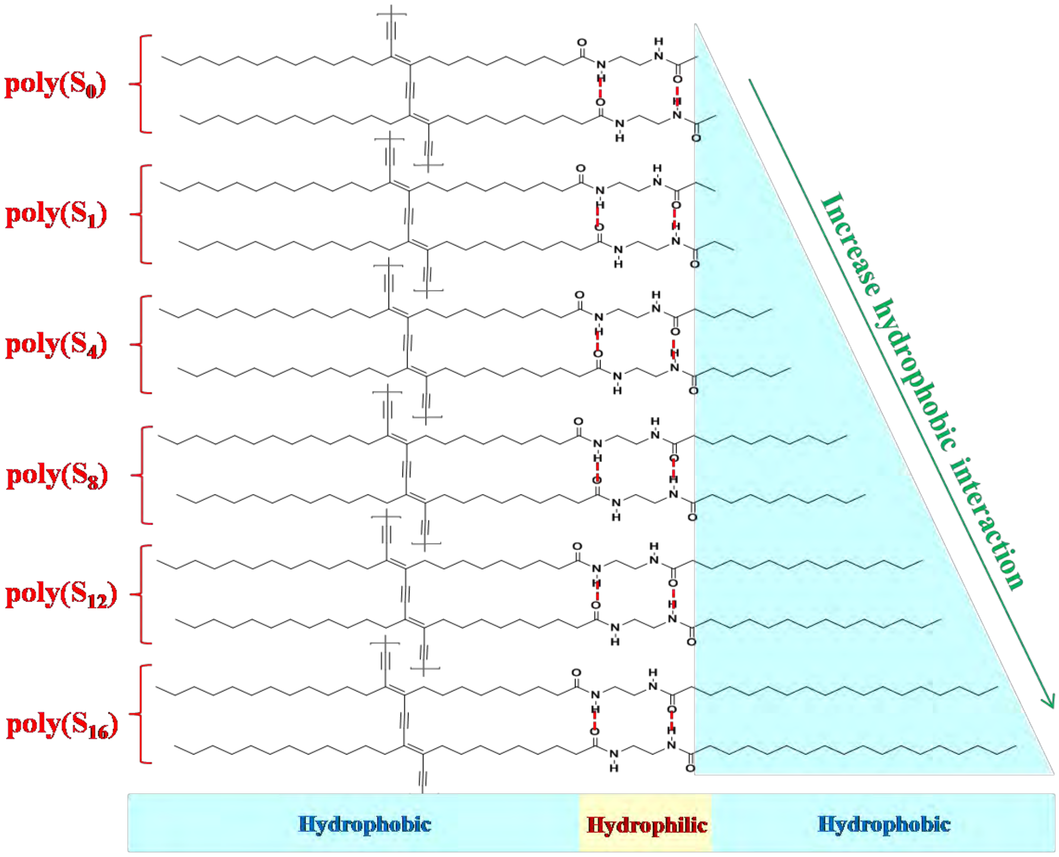


Figure 3.17 Schematic illustration of poly(S_0), poly(S_1), poly(S_4), poly(S_8), poly(S_{12}) and poly(S_{16}) packing

CHAPTER IV

CONCLUSION

4.1 Conclusion

The author successfully synthesized five symmetrical (P_2-P_6) and six unsymmetrical (S_0-S_{16}) diyndiamide monomers in good to fair yields. All of them can be dispersed in Milli-Q water and converted to polydiacetylene sols via photopolymerization. The latter morphology was observed through DLS and AFM technique. Small mixed rod and spherical-like particle with high degree of aggregation were observed. These results are in good agreement with the DLS results indicating that the longer of hydrophobic alkyl chain in the polymer side chain, the smaller the particle size formed. This behavior can be explained by the strength of hydrogen bonding between two amide groups. For S_0 monomer, the shortest methylene chain in the tail part contributed to repulsion among alkyl side chain resulting in poor hydrogen bonding while S_{16}, the longest methylene chain provided hydrophobic interaction between alkyl side chain resulting in an enhancement of hydrogen bonding. Thermochromism of those two series were studied by electronic absorption spectroscopy along with photographic recording. PDAs with even-numbered methylene spacer exhibited full color reversibility with %DR in the range of 88-93% upon heating and cooling process while PDAs having odd-numbered methylene spacer showed partial color reversibility having the %DR between 20-65%. Notably, for the symmetrical diyndiamide series, %DR of even-numbdered methylene spacers tends to increase with increasing the number of methylene. In contrast to PDA containing the odd-numbered methylene spacer, %DR tend to decrease when increasing the number of methylene. In unsymmetrical diyndiamide series, we replaced one diacetylene unit with simple aliphatic alkyl side chain and found that only one diacetylene unit with the satisfactory alkyl chain length is necessary for full thermal reversibility. The result indicated that at least 16 methylene units are required for full reversibility of PDA derived from unsymmetrical diyndiamides. The intramolecular side chain interaction is perhaps the main factor governing this trend. The recovery of blue-to-red transition is associated with hydrophobic interaction between the side chains and the hydrogen bonding between the head groups. If the hydrophobic interaction between the side chains and the hydrogen bonding are strong enough, PDA will be able to restore the original conformation and backbone strains upon the cooling back to the original temperature. The results signify that hydrophobicity enhances side chain packing which improve the thermochromic recovery.

From these result, the author devised a new strategy to control the thermochromic reversibility of PDA. The author also developed a novel strategy to control the shape of PDA assembled in aqueous media by varying methylene chain length. These results provide a guideline for the structural design of PDA to be used as universal temperature indicator.

4.2 Suggestion for future works

Fabrication of synthesized PDAs on to film, filter paper or other supporting material should be explored. Subsequently, thermochromic effects should be investigated and applications based on other chromic processes investigated.

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APPENDICES

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

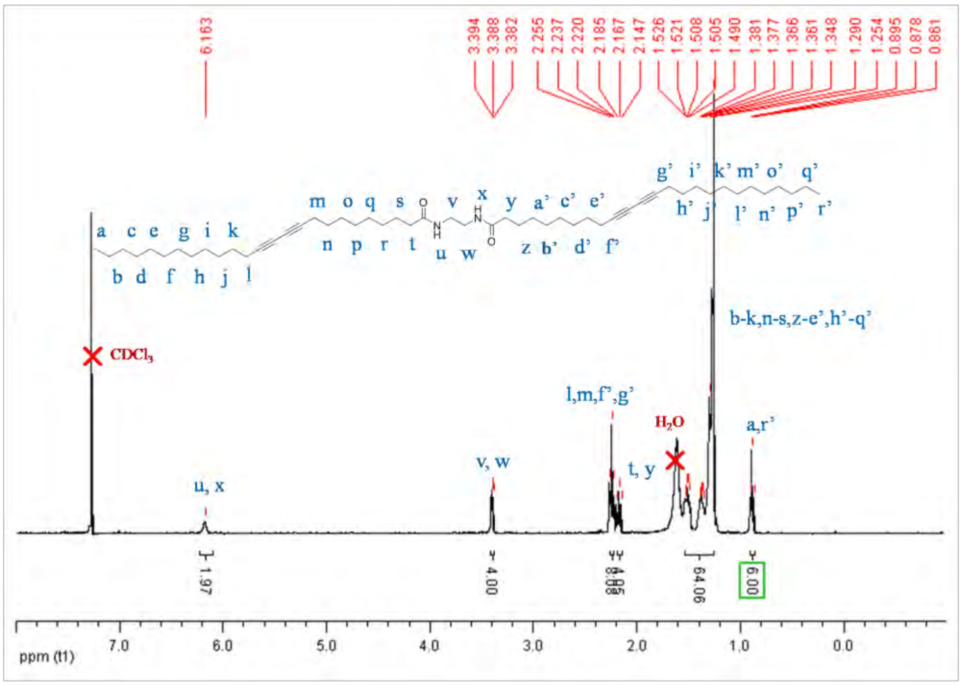


Figure A1: ^{1}H NMR spectrum of *N,N'*-ethylenebispentacosa-10,12-diyndiamide (P_2) in $CDCl_3$

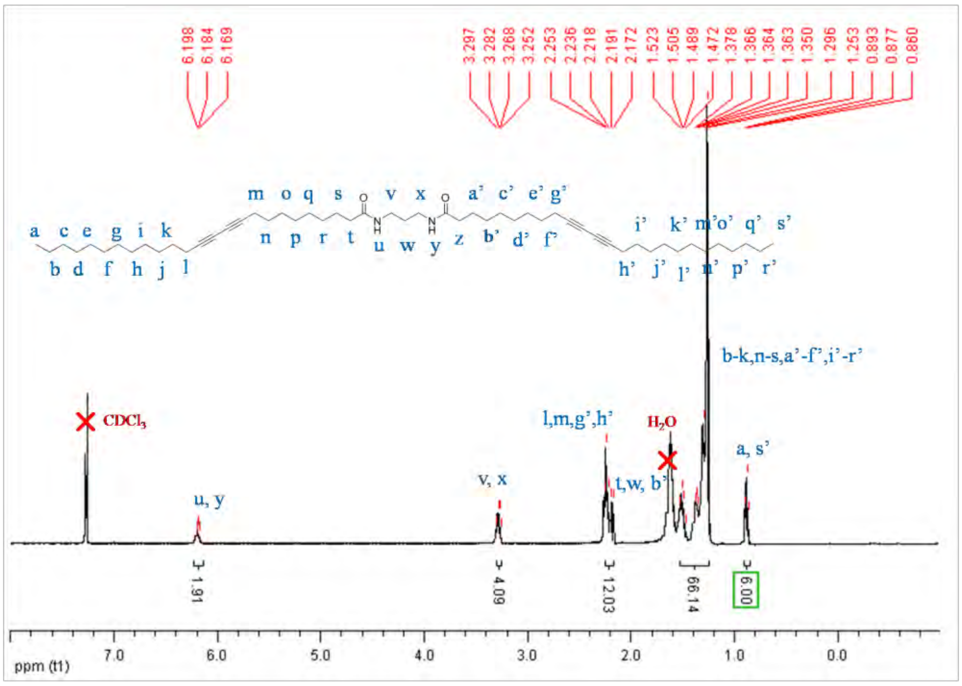


Figure A2: ^{1}H NMR spectrum of *N,N'*-propylenebispentacosa-10,12-diyndiamide (P_3) in $CDCl_3$

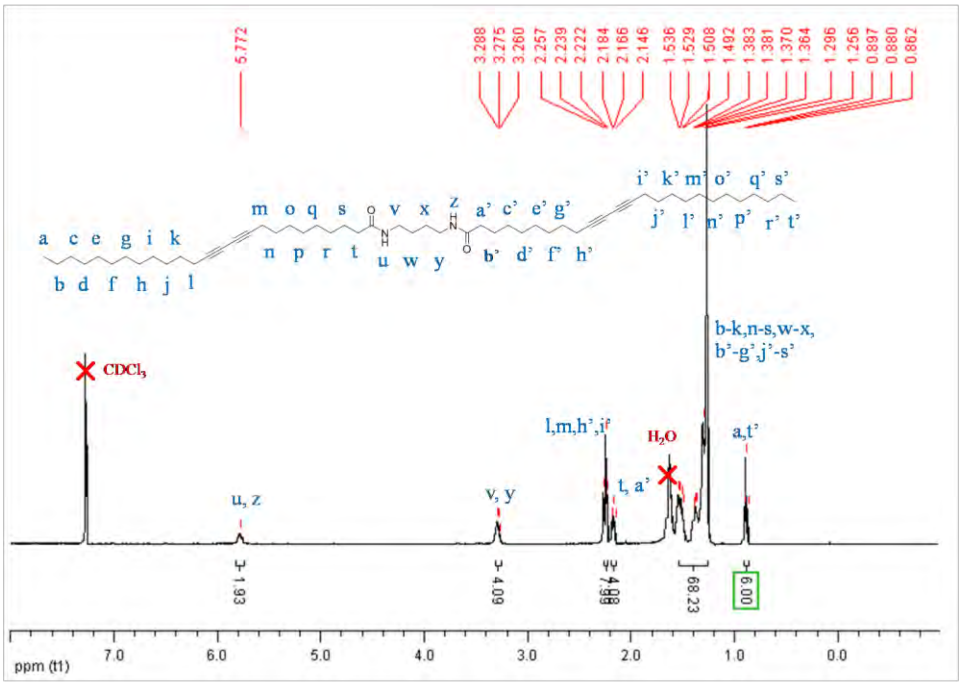


Figure A3: ^{1}H NMR spectrum of *N,N′*-butylenebispentacosa-10,12-diyndiamide (P_4) in $CDCl_3$

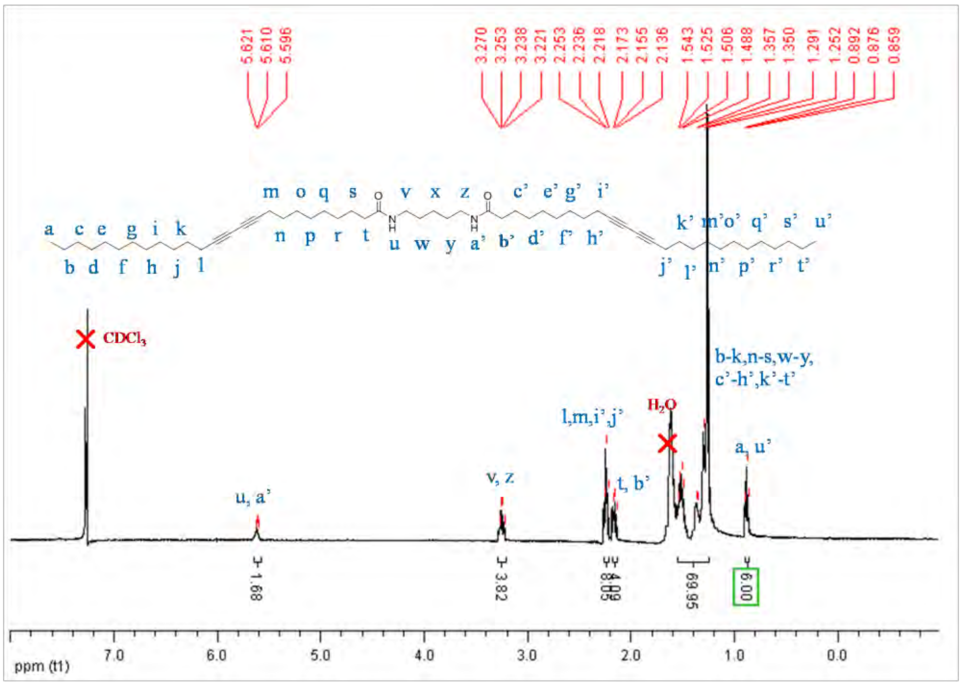


Figure A4: ^{1}H NMR spectrum of *N,N′*-pentylenebispentacosa-10,12-diyndiamide (P_5) in $CDCl_3$

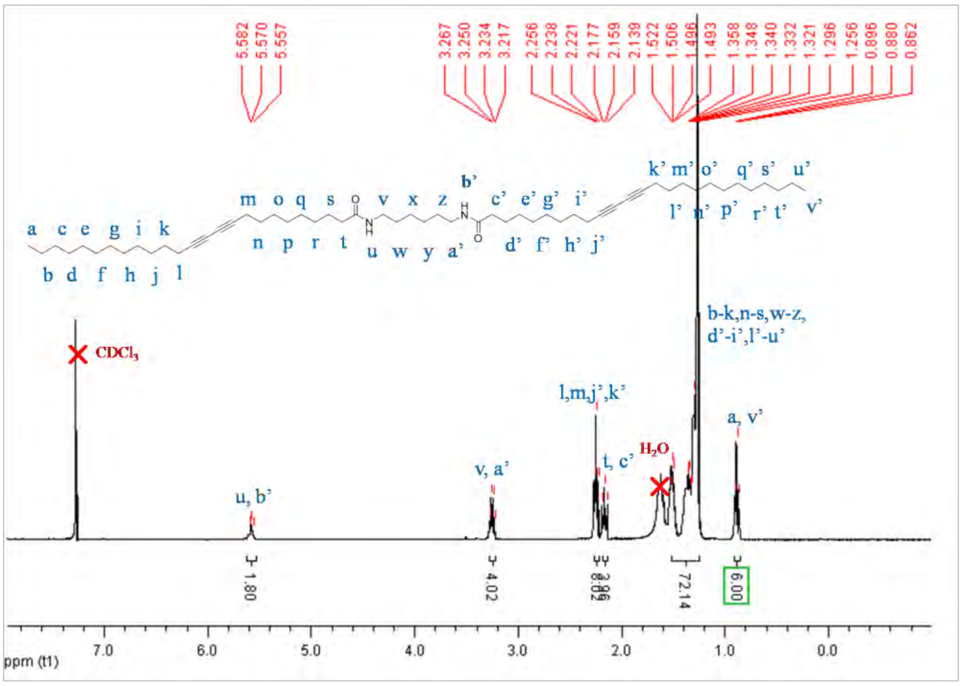


Figure A5: ^{1}H NMR spectrum of *N,N′*-hexamethylenebispentacosa-10,12-diyndiamide (P_6) in $CDCl_3$

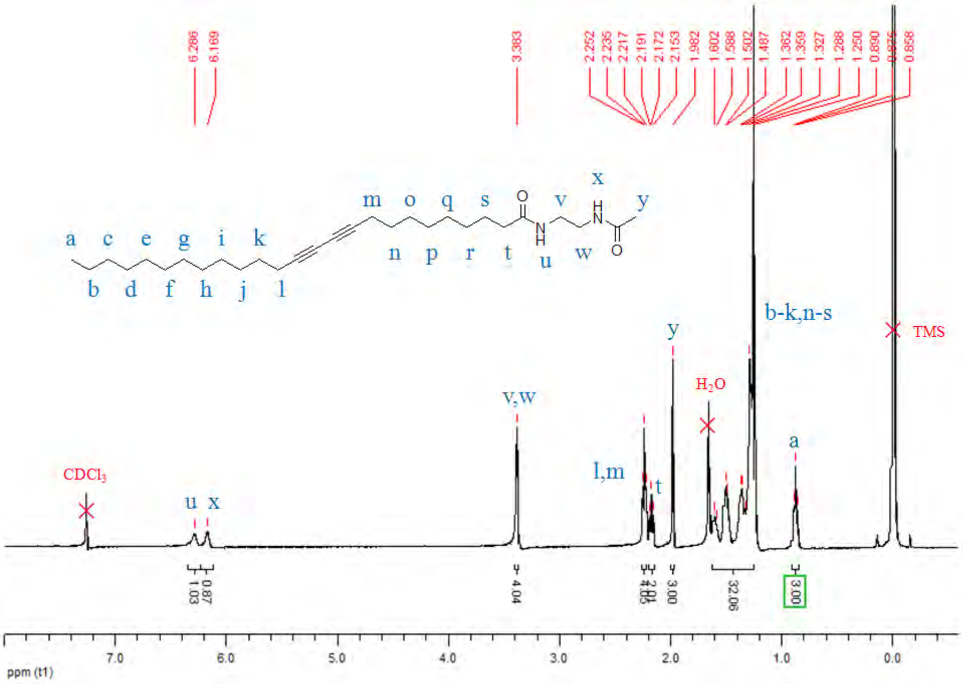


Figure A6: ^{1}H NMR spectrum of *N*-(2-acetamidoethyl)pentacosa-10,12-diyndiamide (S_0) in $CDCl_3$

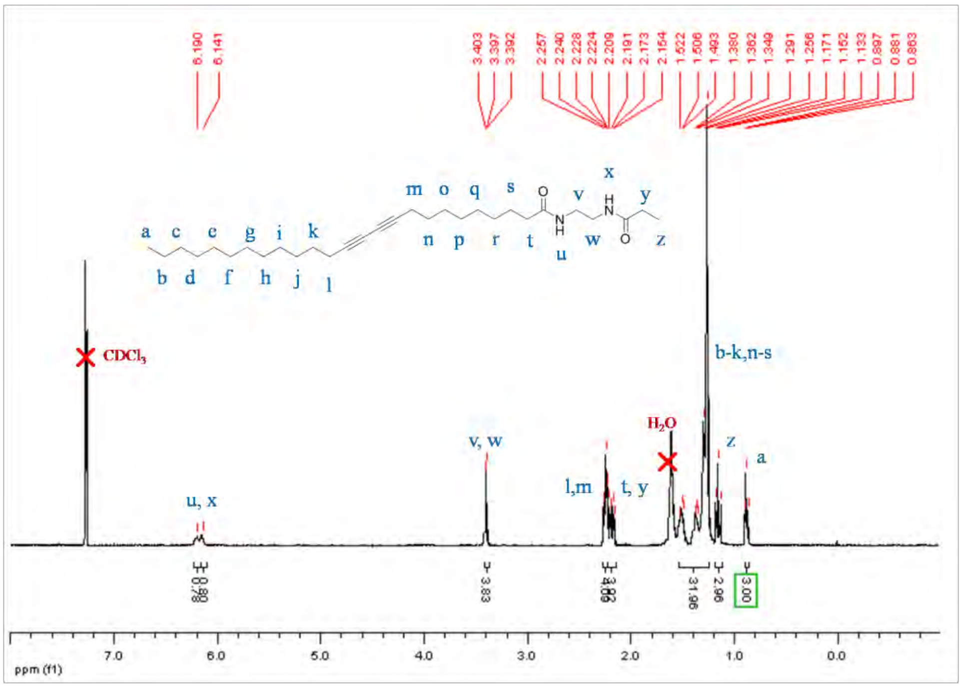


Figure A7: ^{1}H NMR spectrum of *N*-(2-propionamidoethyl)pentacosa-10,12-diyndiamide (S_1) in $CDCl_3$

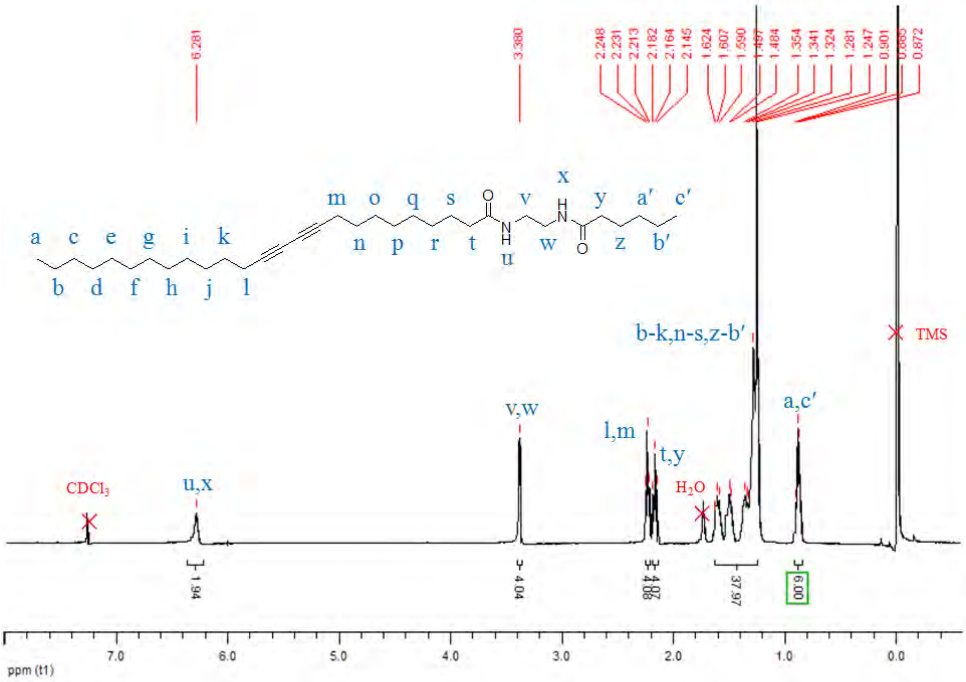


Figure A8: ^{1}H NMR spectrum of *N*-(2-hexanamidoethyl)pentacosa-10,12-diyndiamide (S_4) in $CDCl_3$

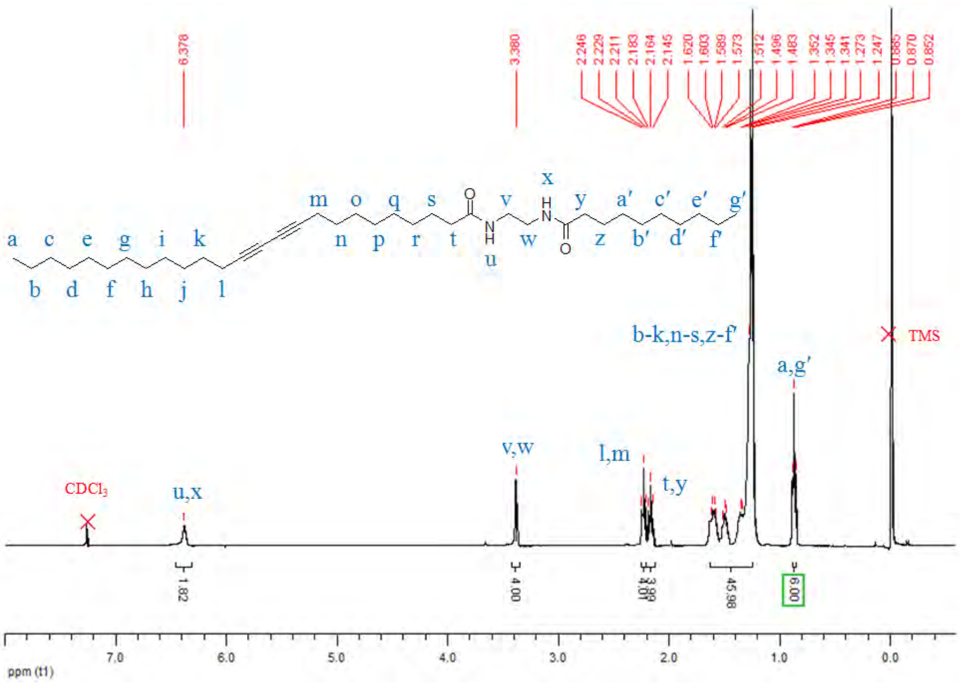


Figure A9: ^{1}H NMR spectrum of *N*-(2-decanamidoethyl)pentacosa-10,12-diyndiamide (S_8) in $CDCl_3$

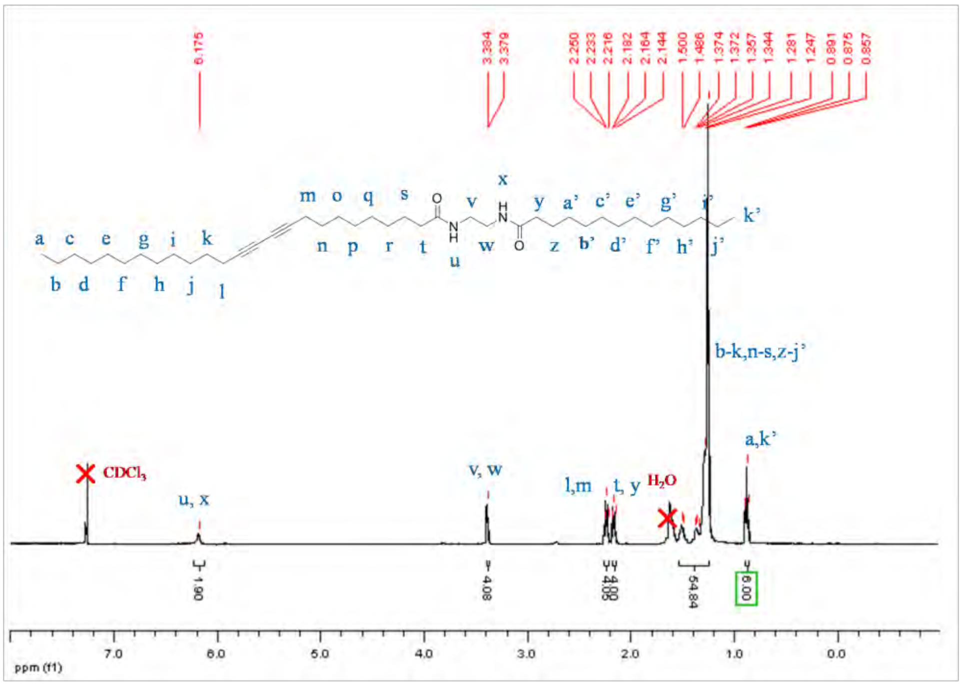


Figure A10: ^{1}H NMR spectrum of *N*-(2-myristamidoethyl)pentacosa-10,12-diyndiamide (S_{12}) in $CDCl_3$

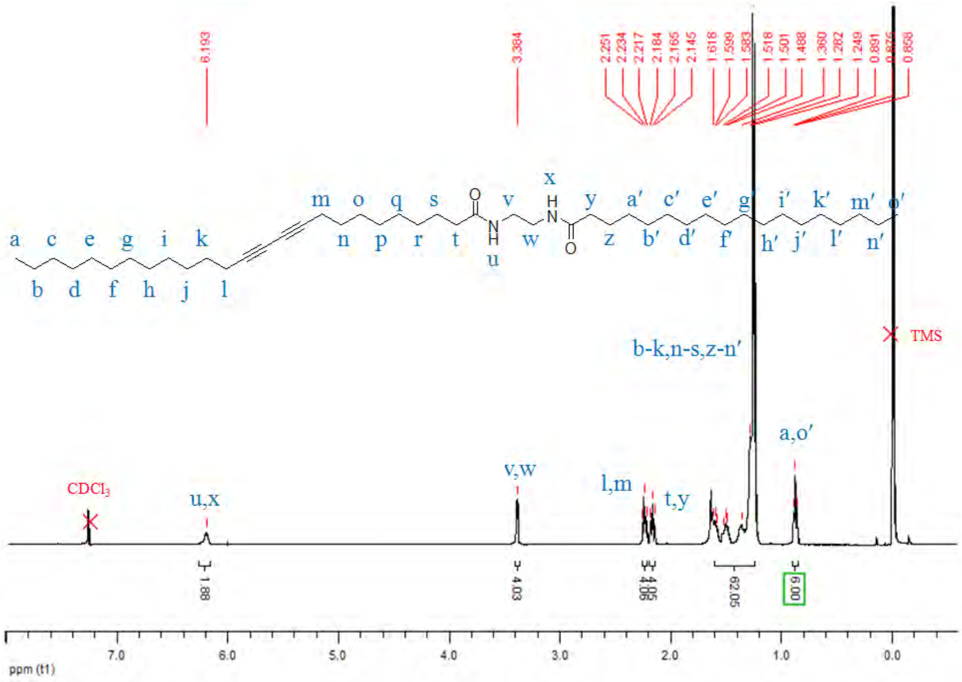


Figure A11: ^{1}H NMR spectrum of *N*-(2-stearamidoethyl)pentacosa-10,12-diyndiamide (S_{16}) in $CDCl_3$

Appendix B: ^{13}C NMR spectrum of synthesized monomers

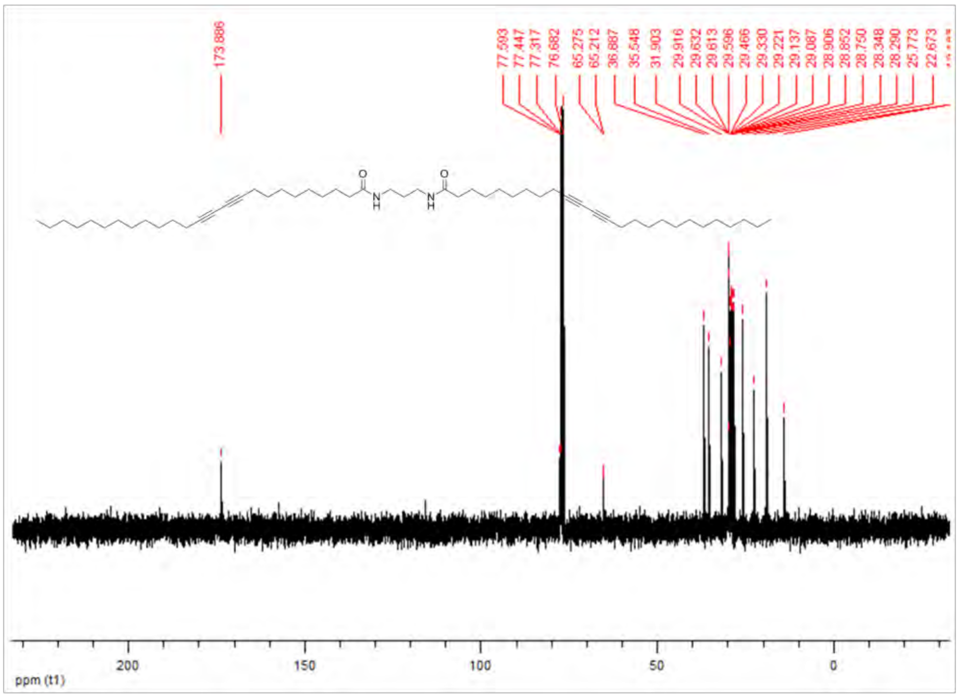


Figure B1: ^{13}C NMR spectrum of *N,N'*-propylenebispentacosa-10,12-diyndiamide (P_3) in $CDCl_3$

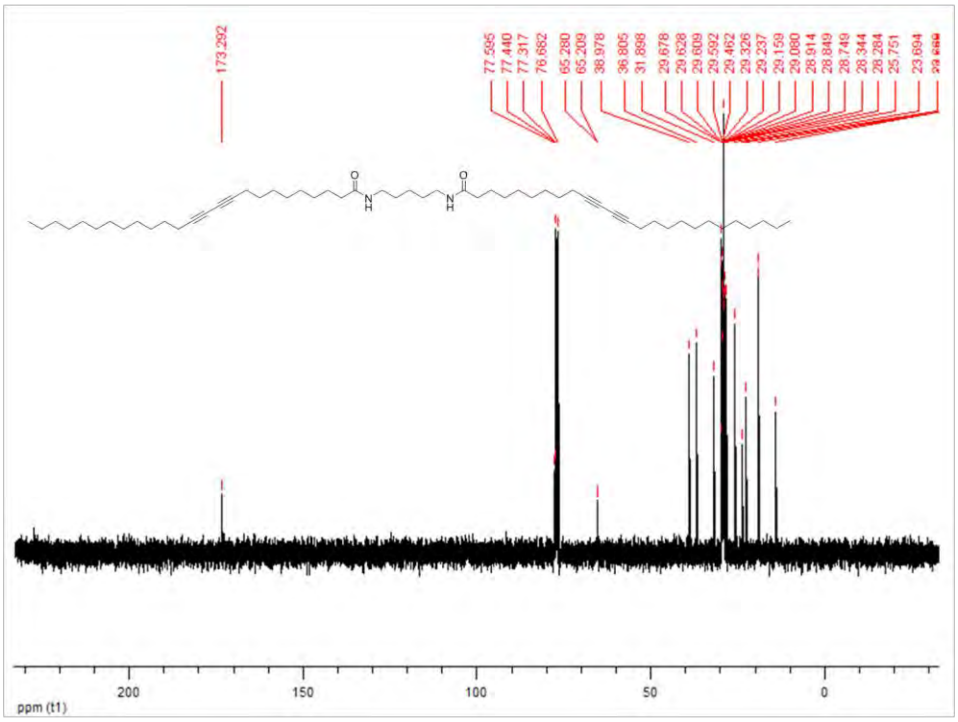


Figure B2: ^{13}C NMR spectrum of *N,N'*- pentylenebispentacosa-10,12-diyndiamide (P_5) in $CDCl_3$

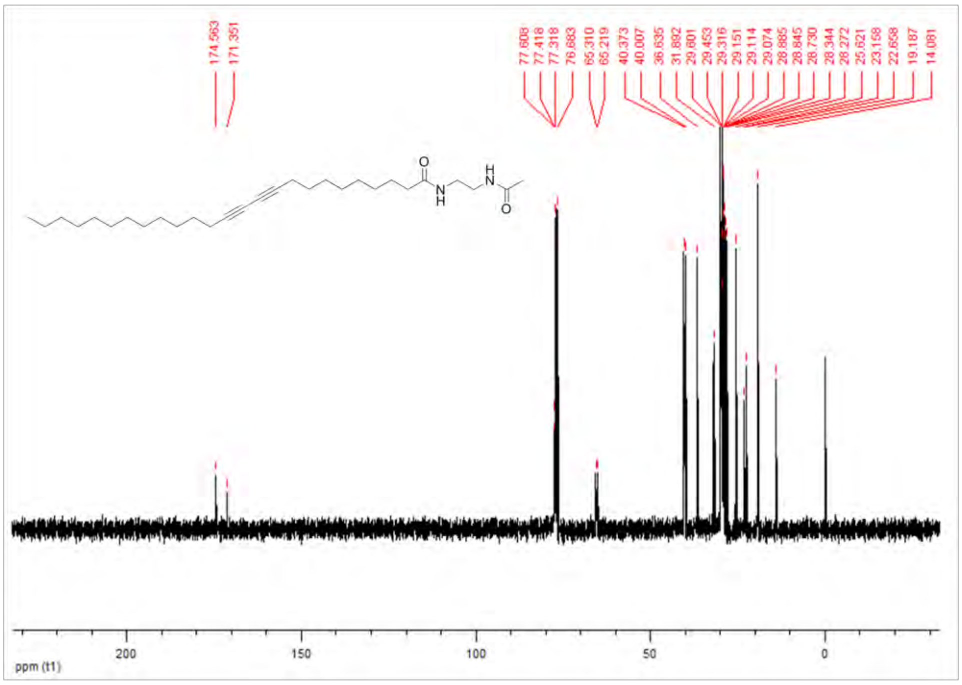


Figure B3: ^{13}C NMR spectrum of *N*-(2-acetamidoethyl)pentacosa-10,12-diyndiamide (S_0) in $CDCl_3$

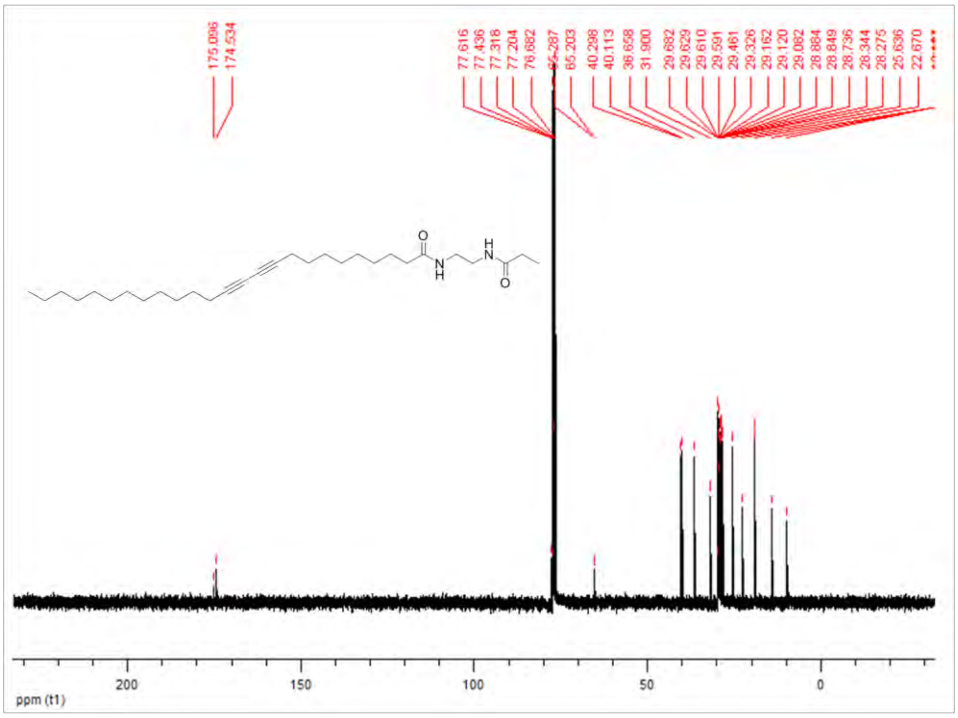


Figure B4: ^{13}C NMR spectrum of *N*-(2-propionamidoethyl)pentacosa-10,12-diyndiamide (S_1) in $CDCl_3$

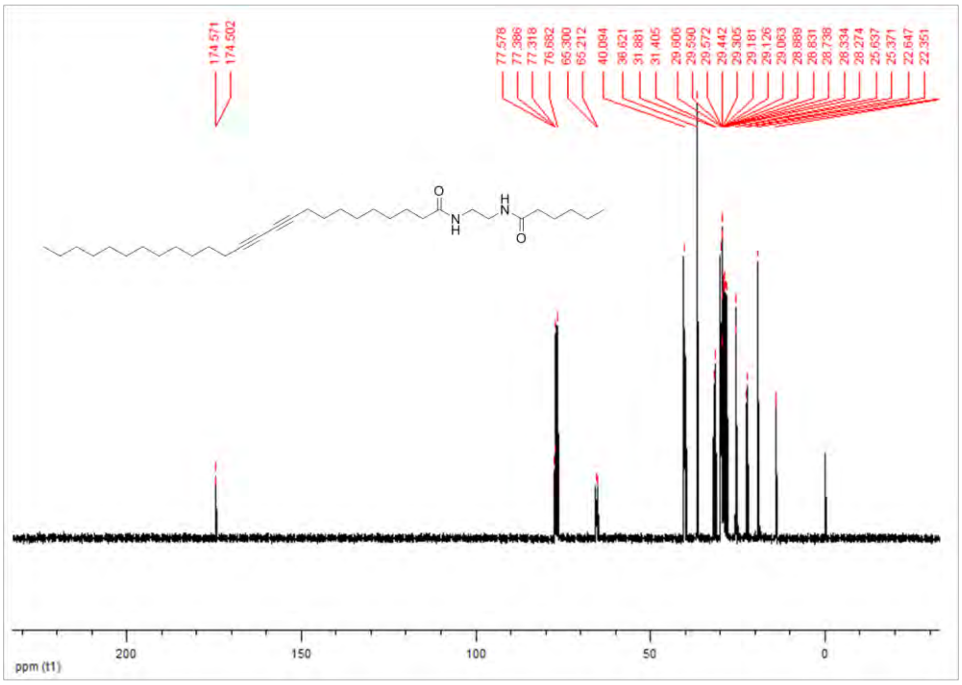


Figure B5: ^{13}C NMR spectrum of *N*-(2-hexanamidoethyl)pentacosa-10,12-diyndiamide (S_4) in $CDCl_3$

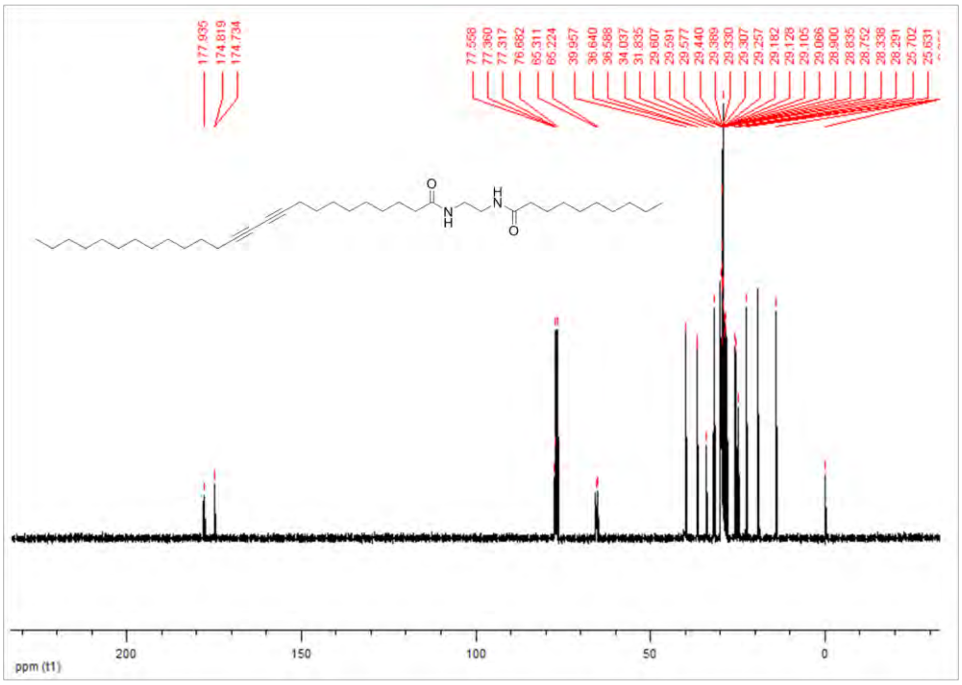


Figure B6: ^{13}C NMR spectrum of *N*-(2-decanamidoethyl)pentacosa-10,12-diyndiamide (S_8) in $CDCl_3$

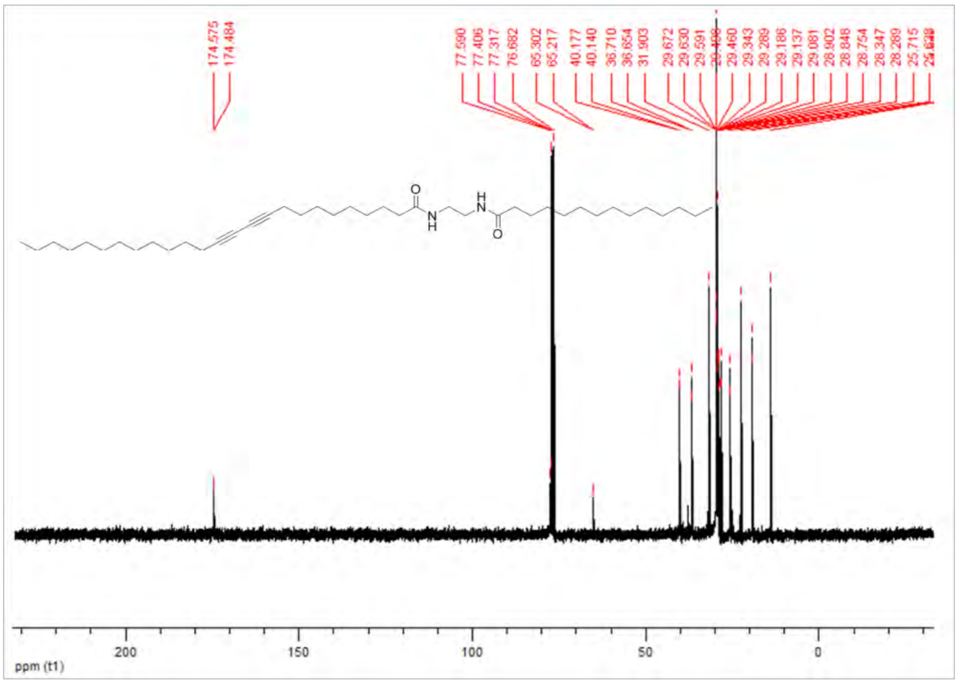


Figure B7: ^{13}C NMR spectrum of *N*-(2-myristamidoethyl)pentacosa-10,12-diyndiamide (S_{12}) in $CDCl_3$

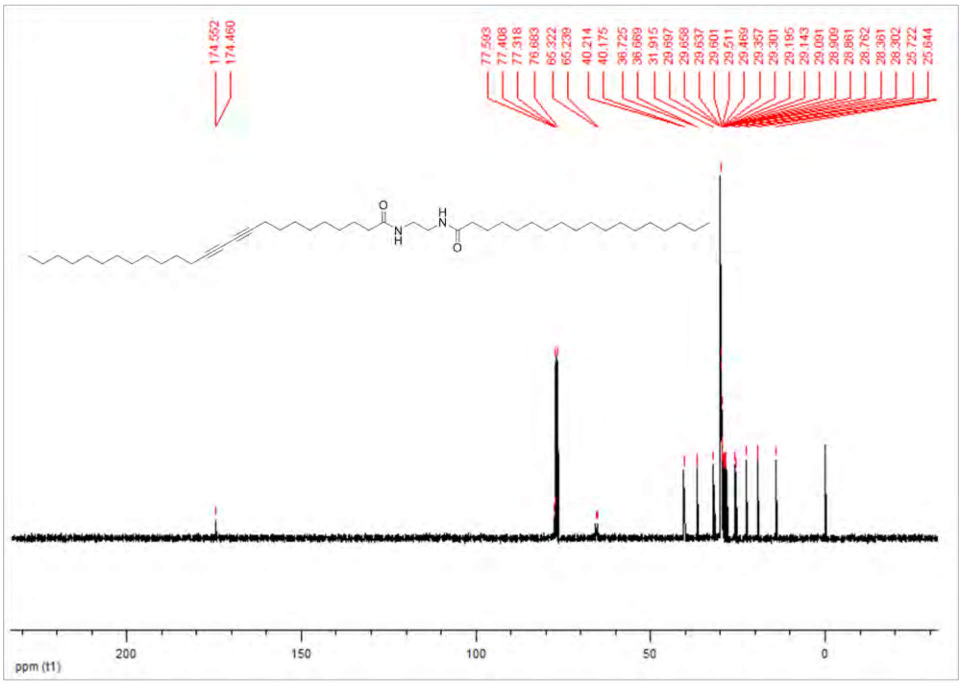
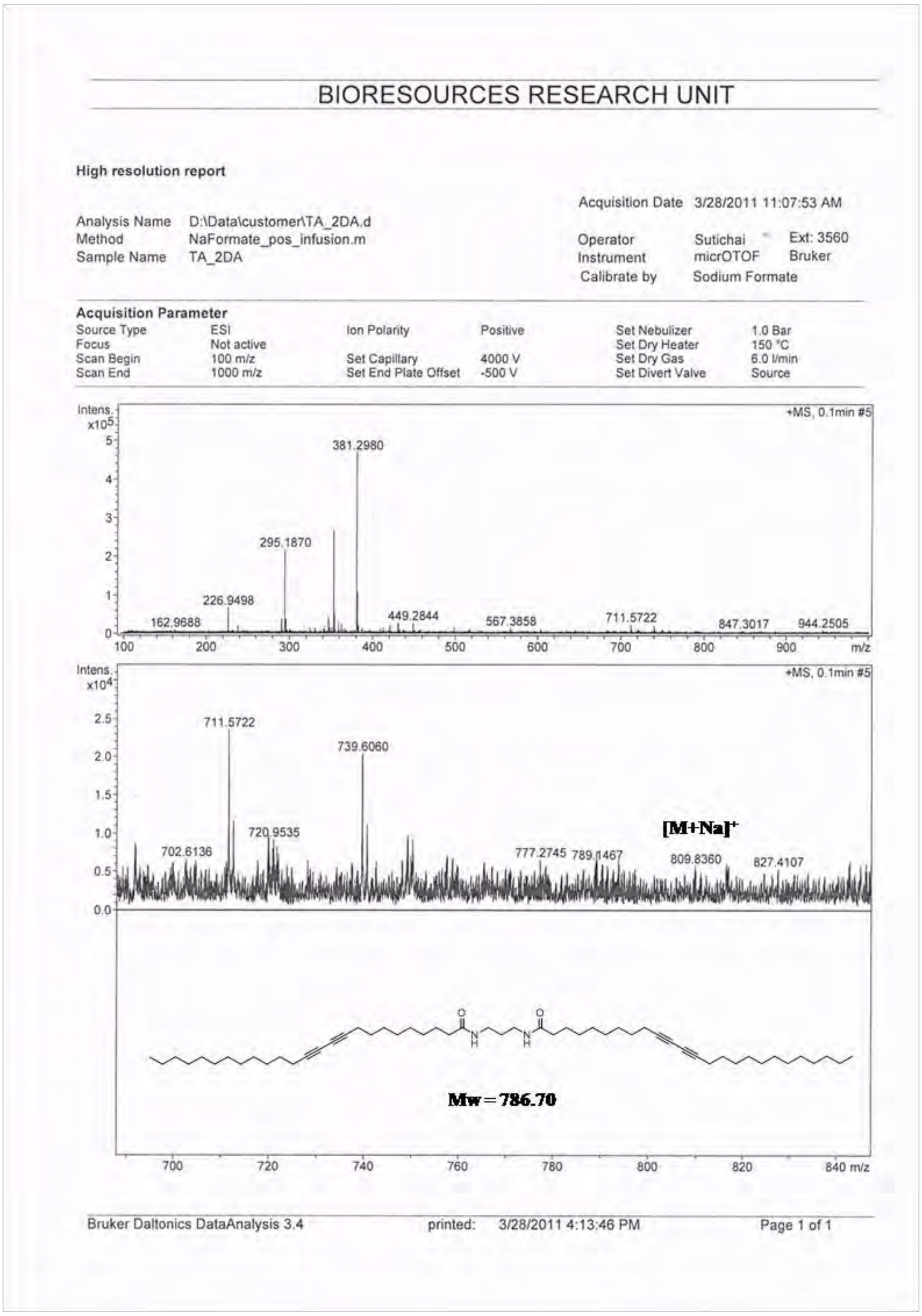


Figure B8: ^{13}C NMR spectrum of *N*-(2-stearamidoethyl)pentacosa-10,12-diyndiamide (S_{16}) in $CDCl_3$

Appendix C: Mass spectrum of synthesized monomers



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High resolution report

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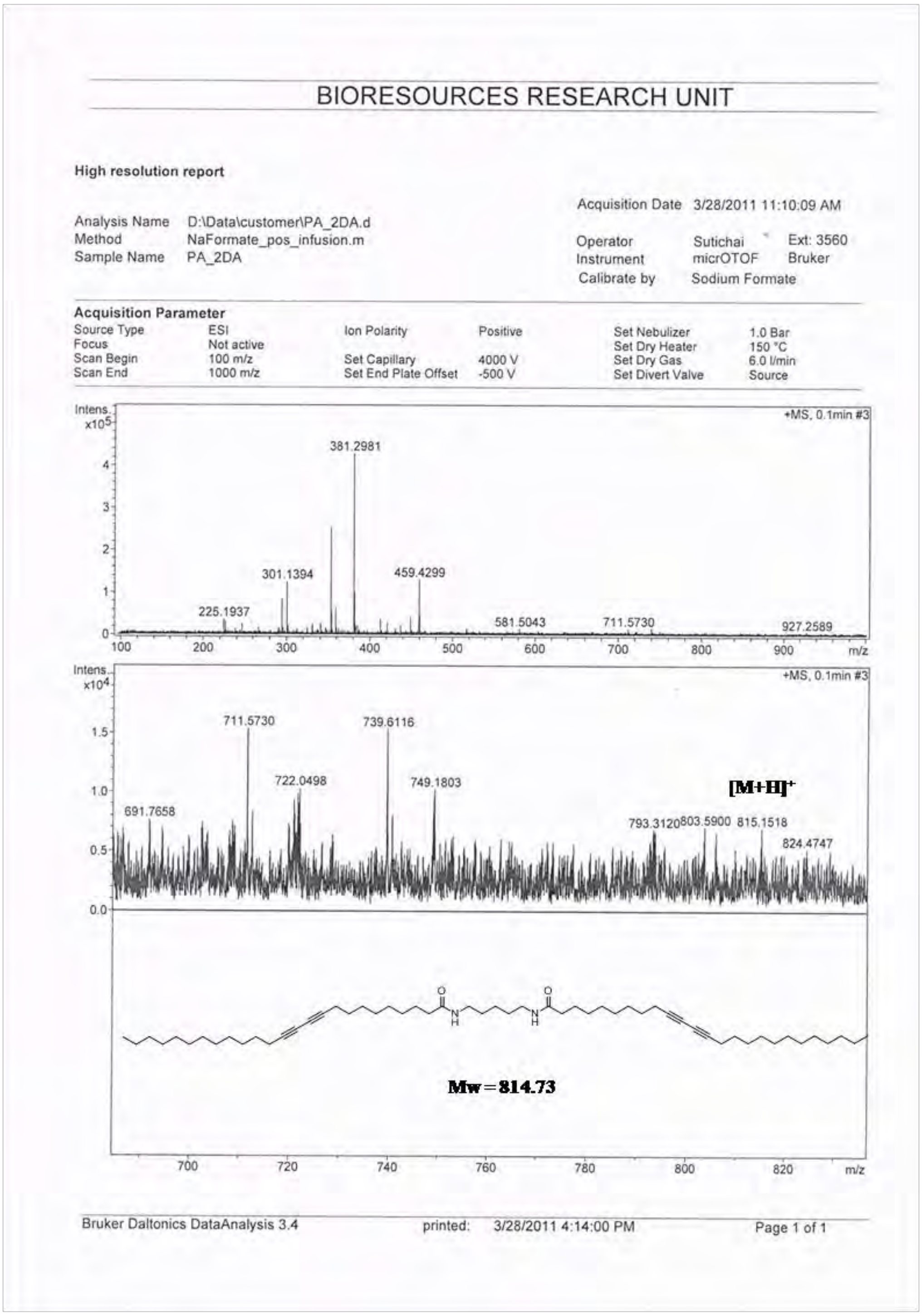
Bruker Daltonics DataAnalysis 3.4 printed: 3/28/2011 4:13:46 PM Page 1 of 1

Figure C1: Mass spectrum of *N,N′*-propylenebispentacosa-10,12-diyndiamide (P_3)



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Bruker Daltonics DataAnalysis 3.4 printed: 3/28/2011 4:14:00 PM Page 1 of 1

Figure C2: Mass spectrum of *N,N′*- pentylenebispentacosa-10,12-diyndiamide (P_5)

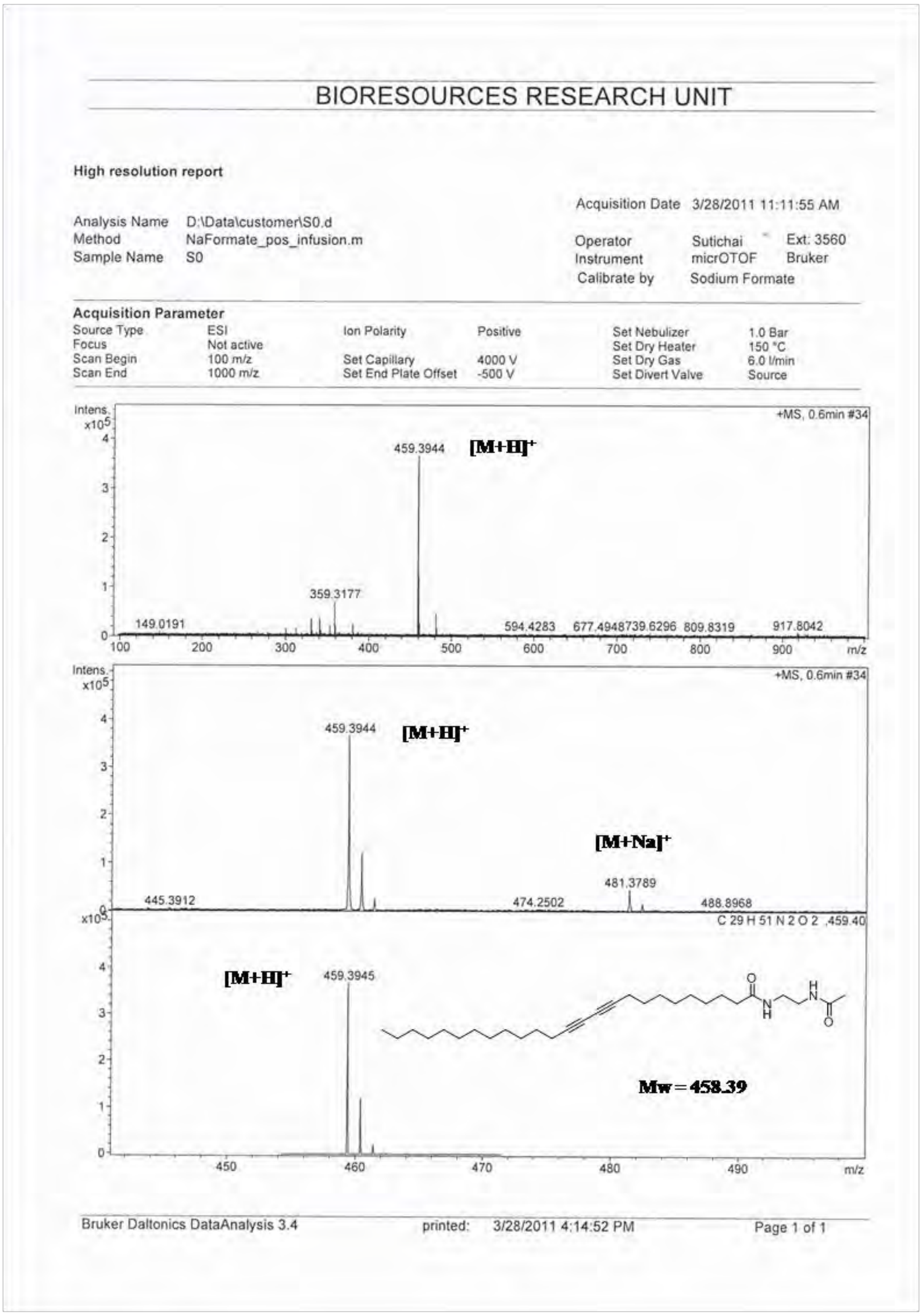

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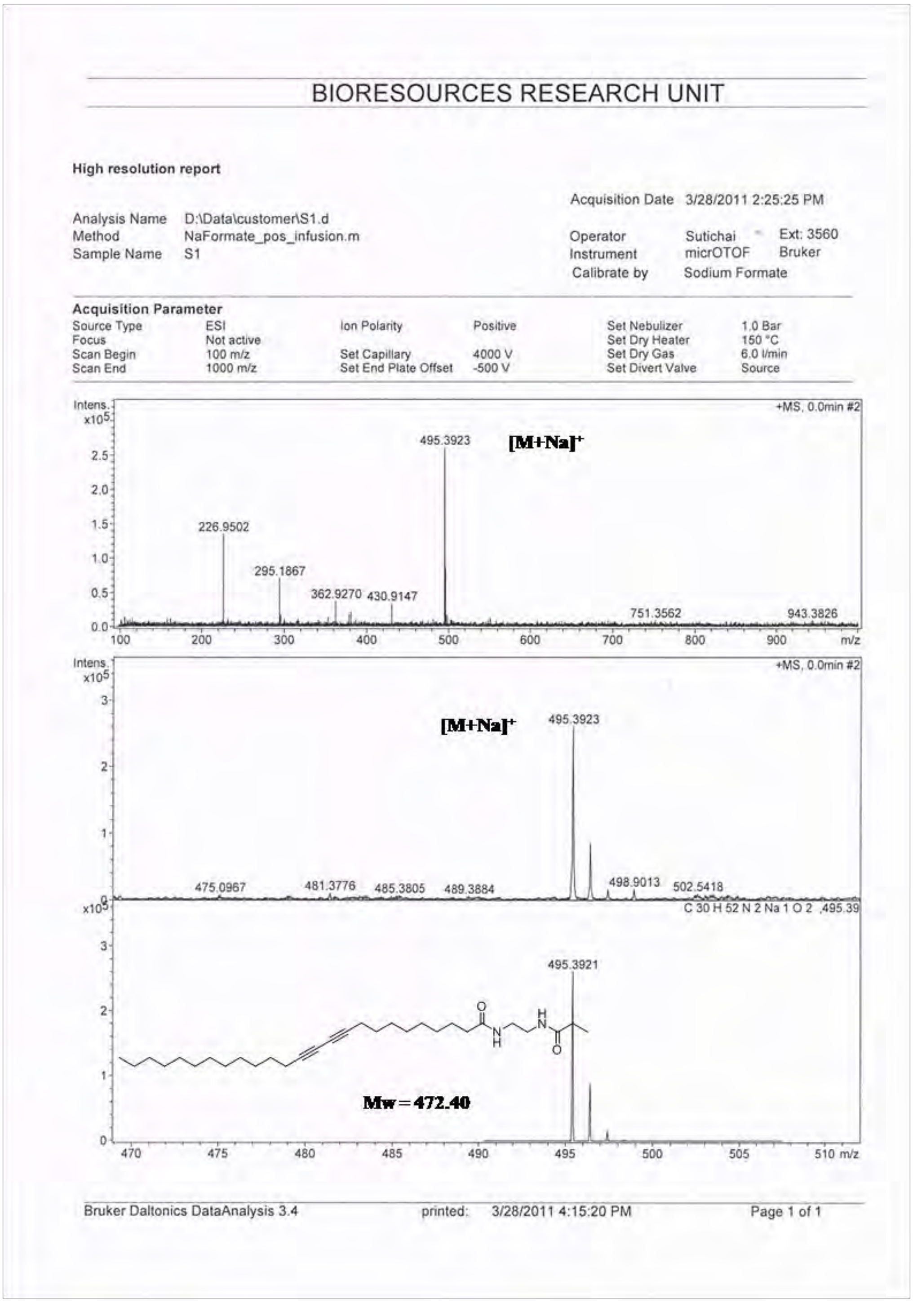
Figure C3: Mass spectrum of *N*-(2-acetamidoethyl)pentacosa-10,12-diyndiamide (S_0)



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Bruker Daltonics DataAnalysis 3.4 printed: 3/28/2011 4:15:20 PM Page 1 of 1

Figure C4: Mass spectrum of *N*-(2-propionamidoethyl)pentacosa-10,12-diyndiamide (S_1)

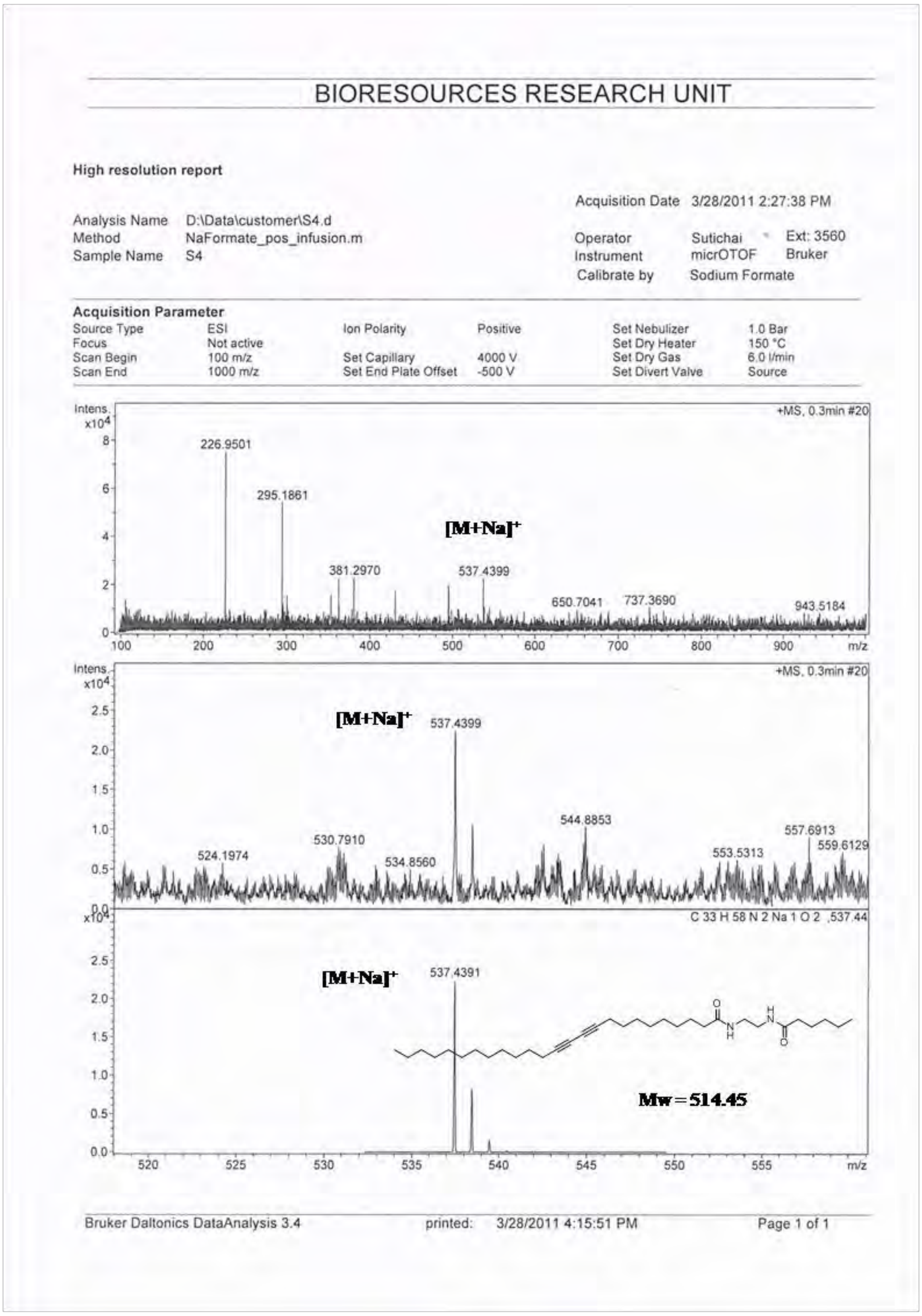

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Figure C5: Mass spectrum of *N*-(2-hexanamidoethyl)pentacosa-10,12-diyndiamide (S_4)

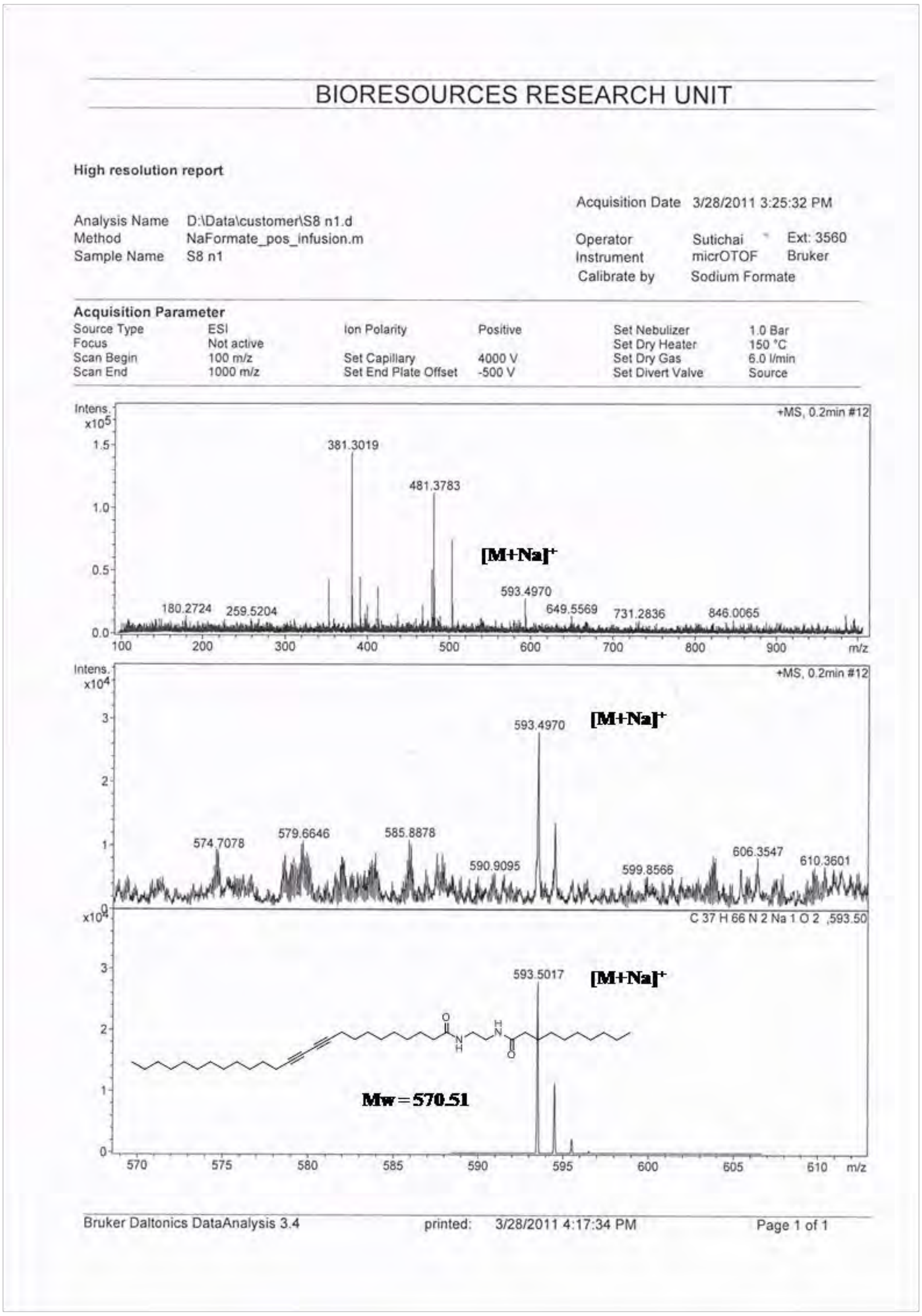

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Figure C6: Mass spectrum of *N*-(2-decanamidoethyl)pentacosa-10,12-diyndiamide (S_8)

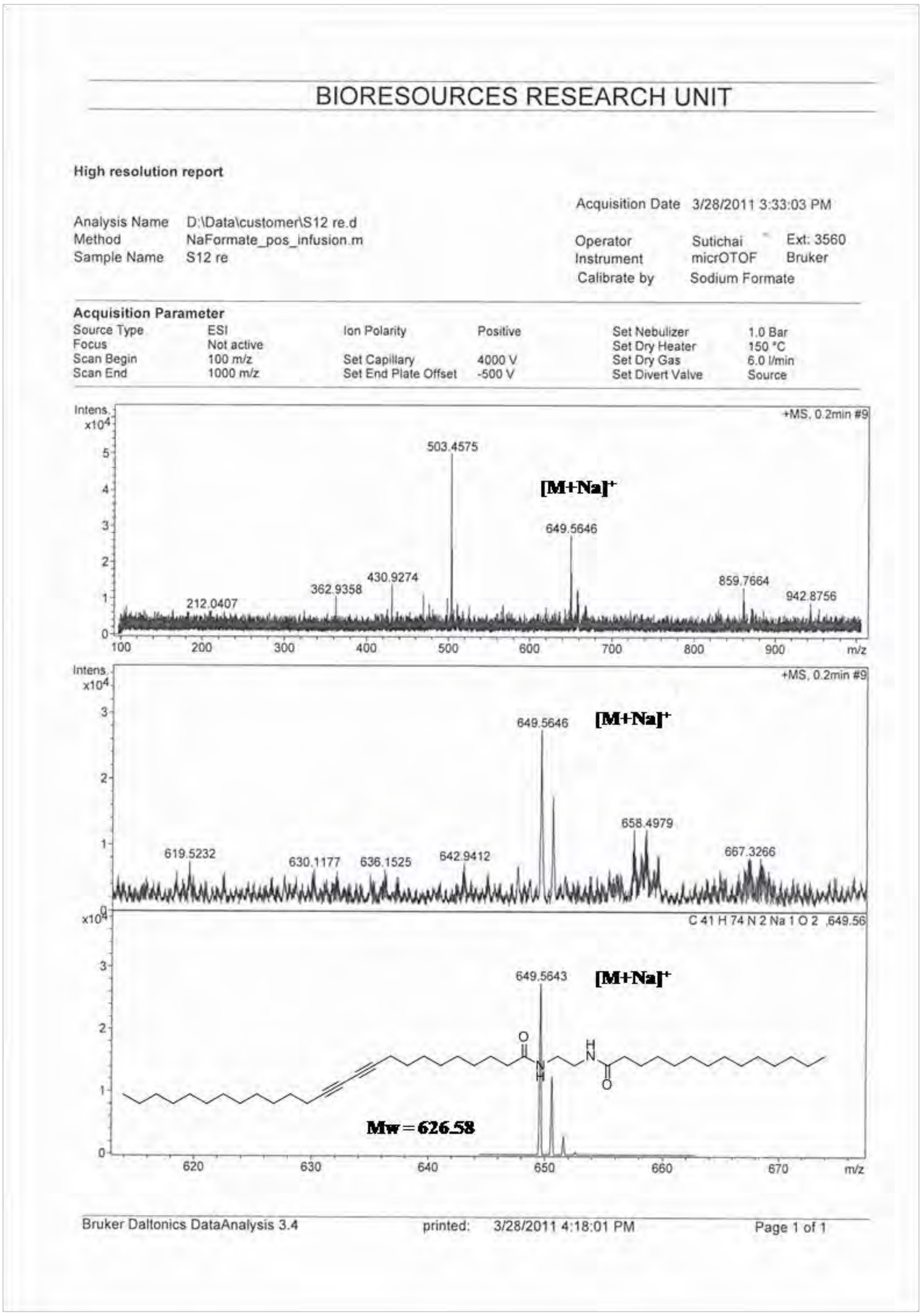

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Figure C7: Mass spectrum of *N*-(2-myristamidoethyl)pentacosa-10,12-diyndiamide (S_{12})

Appendix D: FTIR spectrum of synthesized monomers

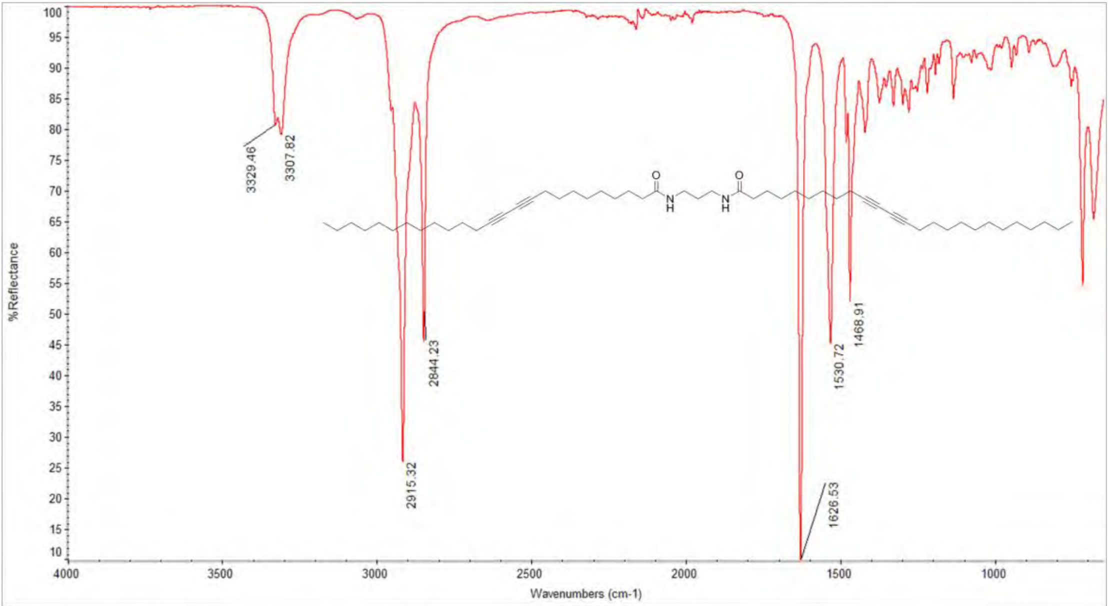

Figure D1: FTIR spectrum of *N,N′*-propylenebispentacosa-10,12-diyndiamide (P_3)

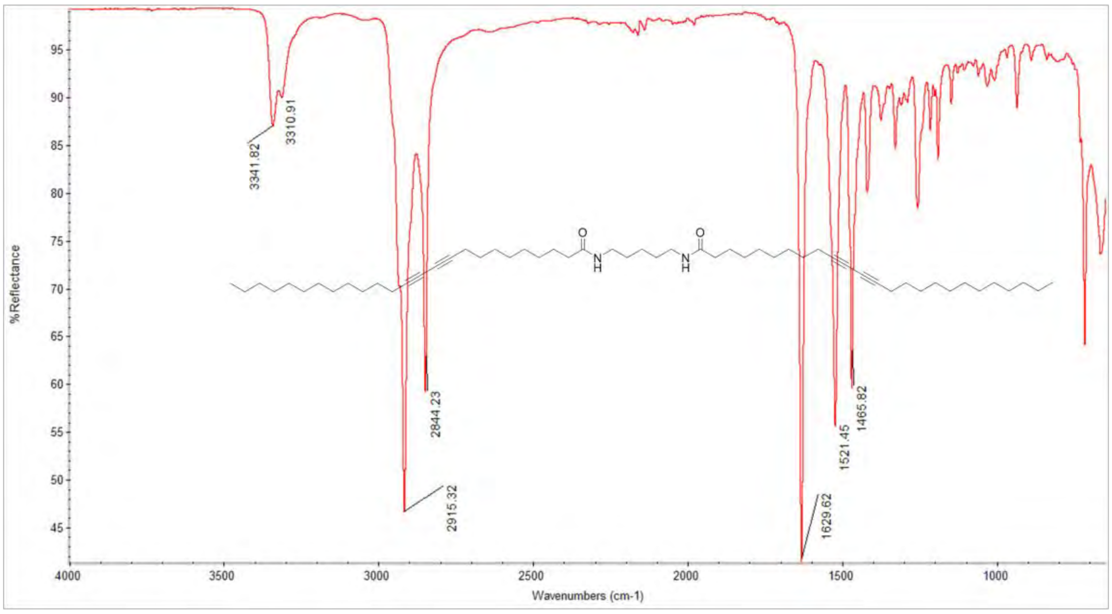

Figure D2: FTIR spectrum of *N,N′*- pentylenebispentacosa-10,12-diyndiamide (P_5)

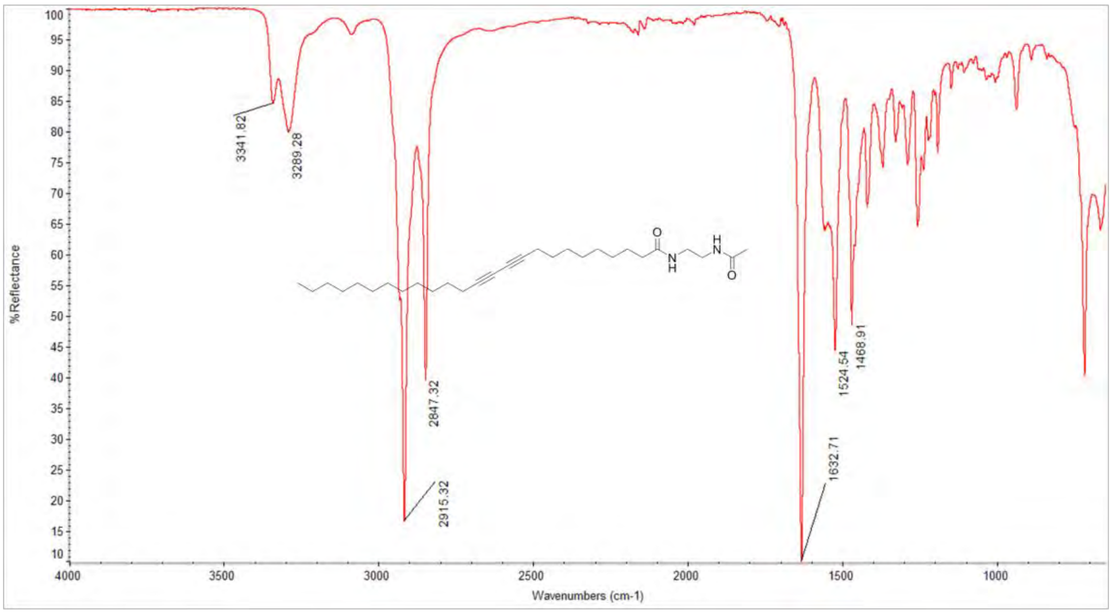

Figure D3: FTIR spectrum of *N*-(2-acetamidoethyl)pentacosa-10,12-diyndiamide (S_0)

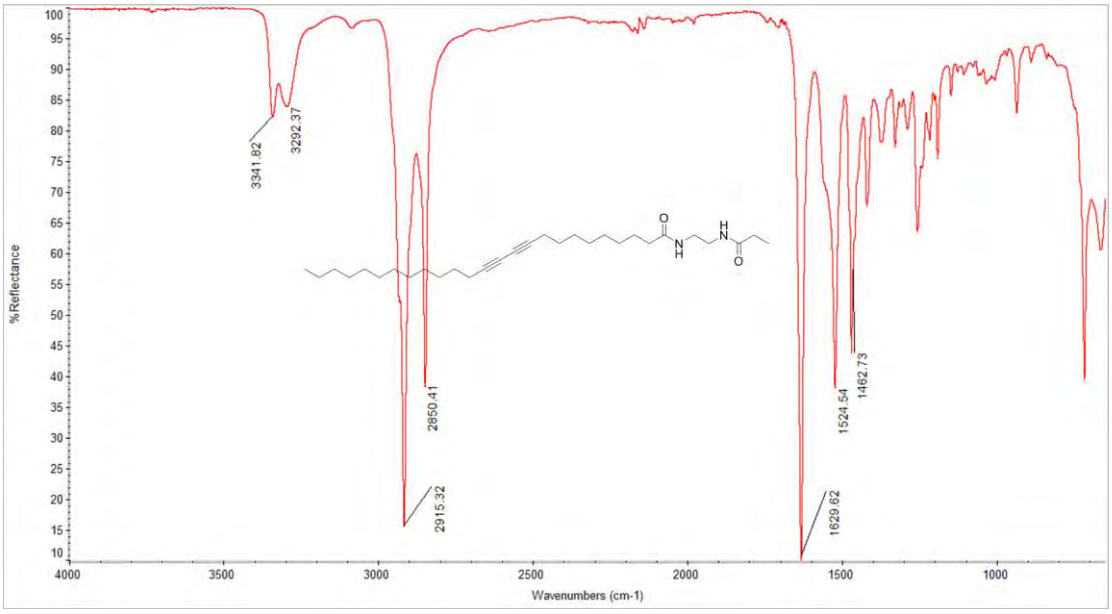

Figure D4: FTIR spectrum of *N*-(2-propionamidoethyl)pentacosa-10,12-diyndiamide (S_1)

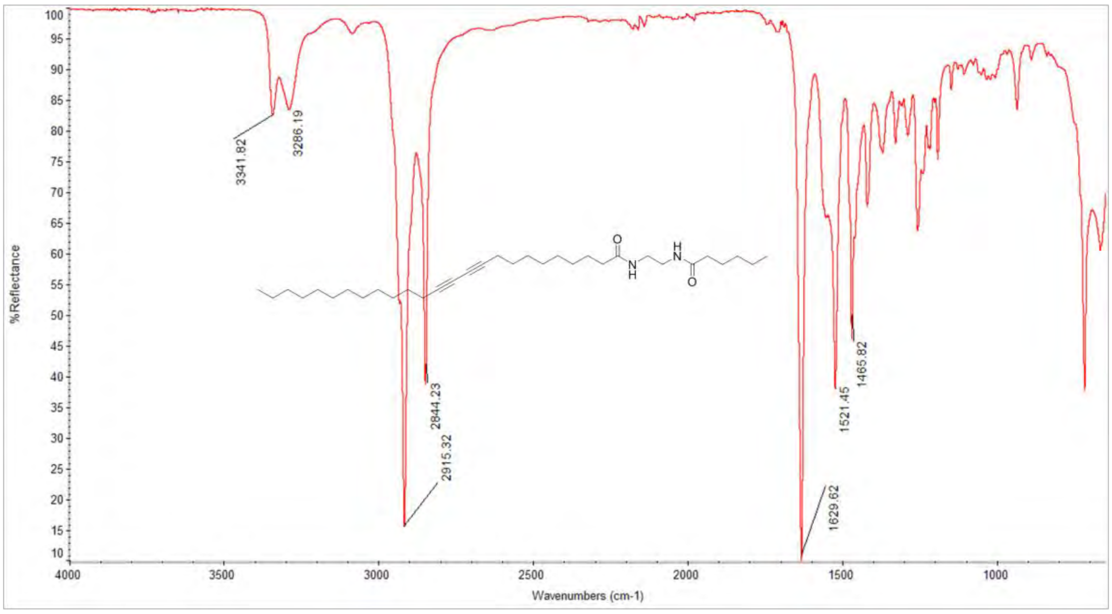

Figure D5: FTIR spectrum of *N*-(2-hexanamidoethyl)pentacosa-10,12-diyndiamide (S_4)

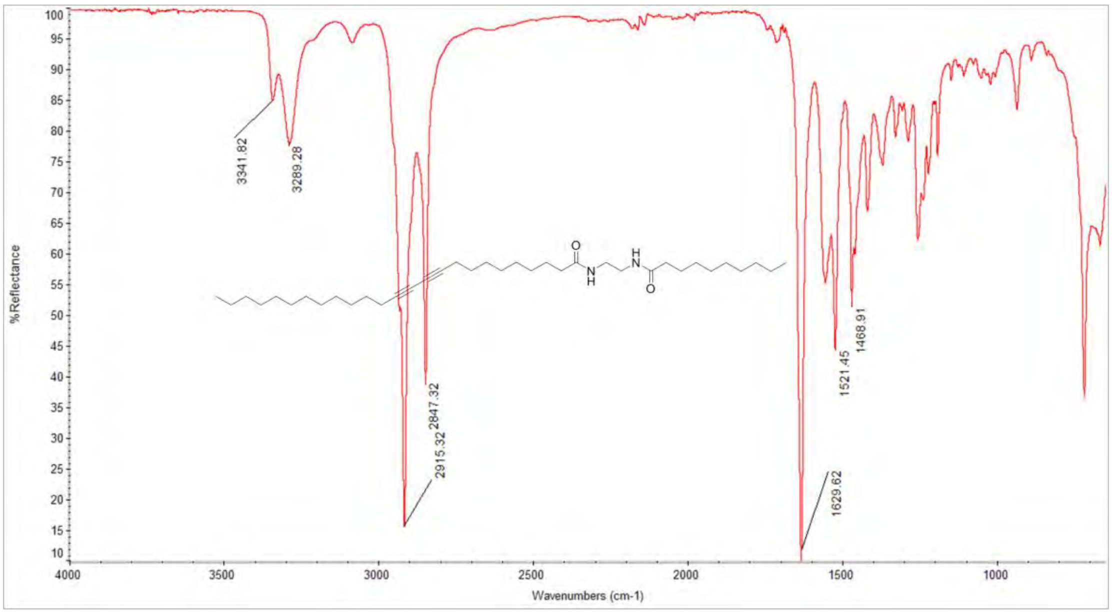

Figure D6: FTIR spectrum of *N*-(2-decanamidoethyl)pentacosa-10,12-diyndiamide (S_8)

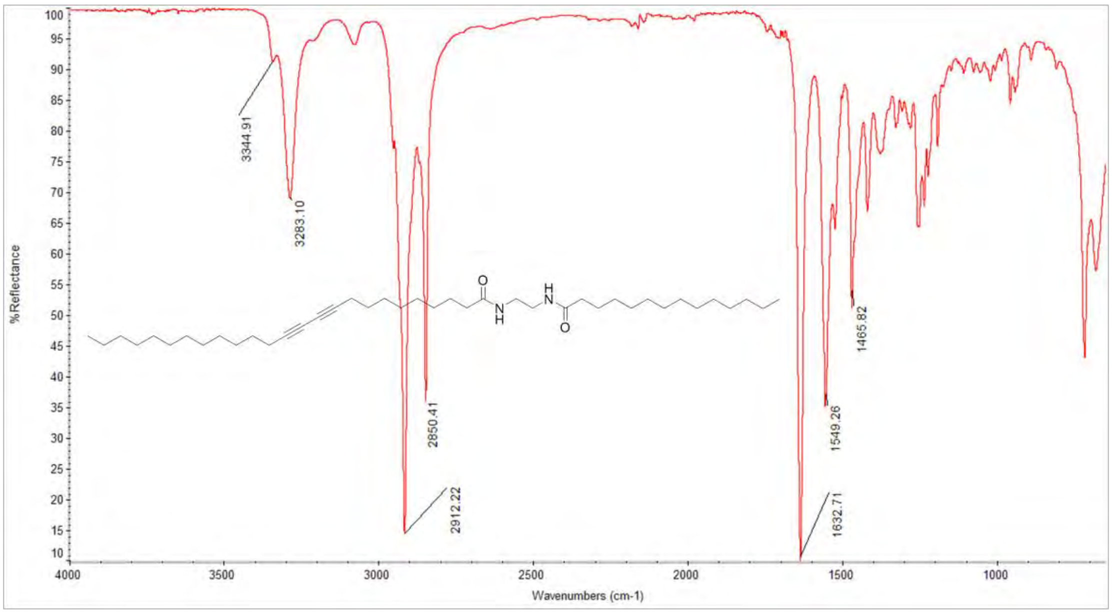

Figure D7: FTIR spectrum of *N*-(2-myristamidoethyl)pentacosa-10,12-diyndiamide (S_{12})

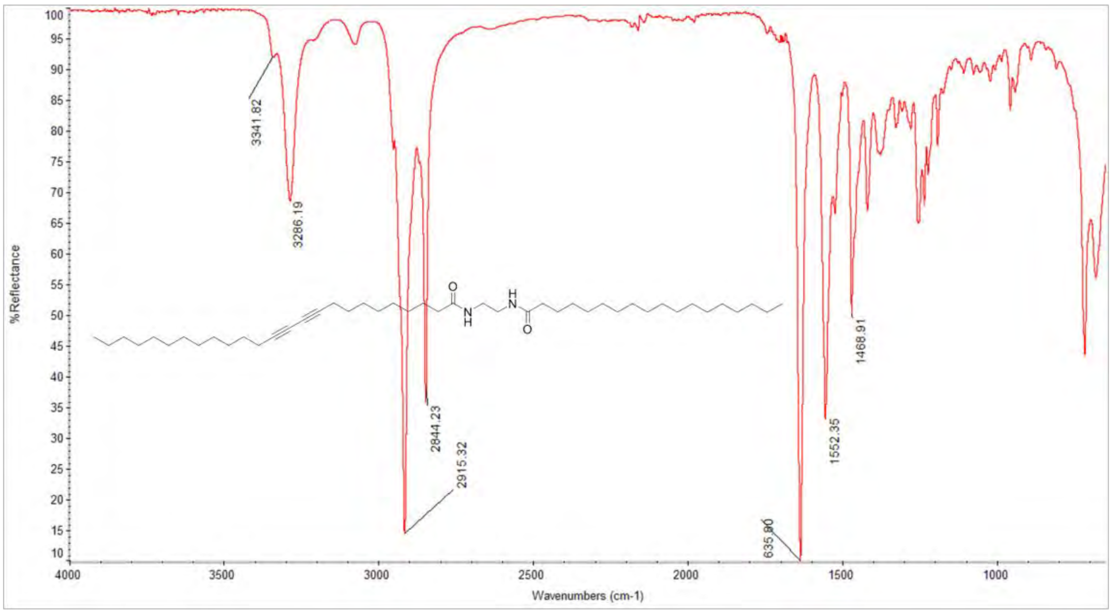

Figure D8: FTIR spectrum of *N*-(2-stearamidoethyl)pentacosa-10,12-diyndiamide (S_{16})

Appendix E: Particle size distribution of polydiacetylene sols from dynamic light scattering technique (DLS)

	Particle size (nm)
1st	344.8
2nd	351.2
3rd	338.6
Mean	344.9

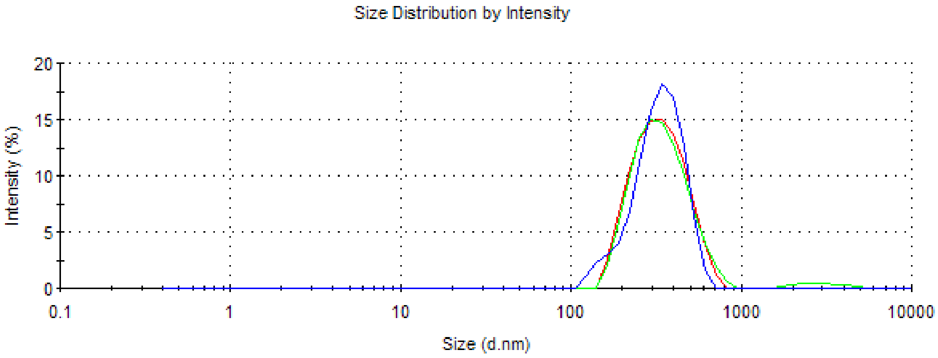

Figure E1: Particle size distribution of poly(S_0) sols

	Particle size (nm)
1st	195.4
2nd	189.3
3rd	204.1
Mean	196.3

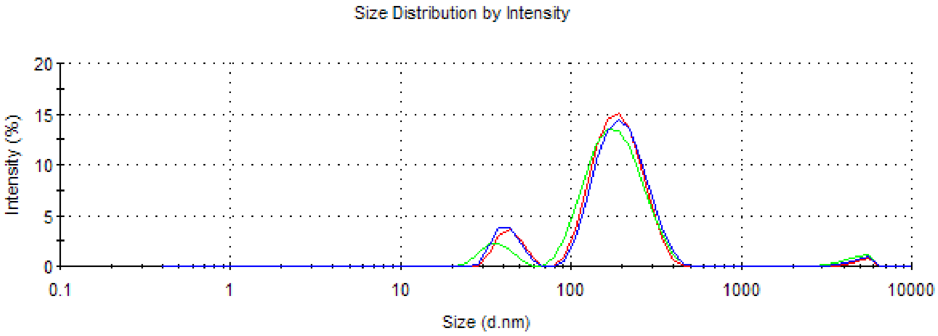

Figure E2: Particle size distribution of poly(S_4) sols

	Particle size (nm)
1st	174.6
2nd	196.4
3rd	184.3
Mean	185.1

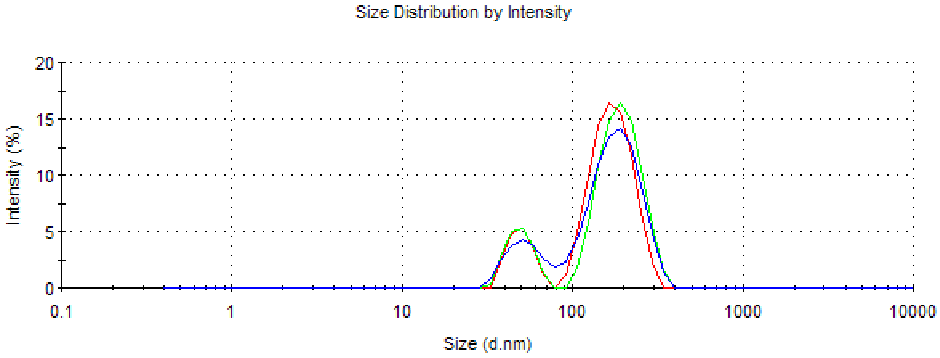

Figure E3: Particle size distribution of poly(S_8) sols

	Particle size (nm)
1st	176.9
2nd	175.0
3rd	191.7
Mean	181.2

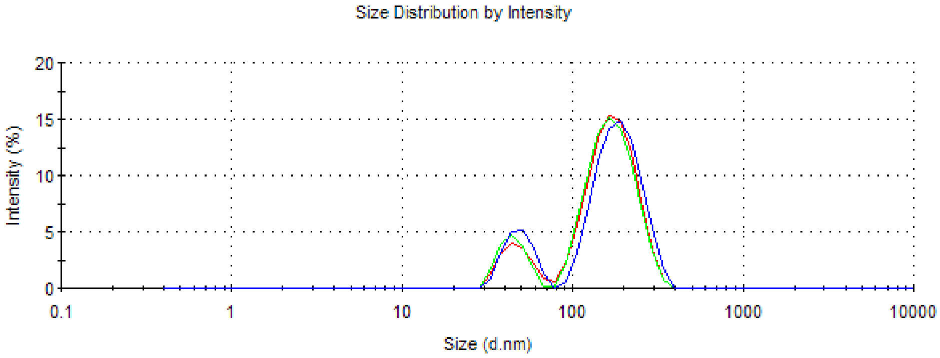

Figure E4: Particle size distribution of poly(S_{16}) sols

Appendix F: Atomic force microscopy (AFM) image of polydiacetylene sols

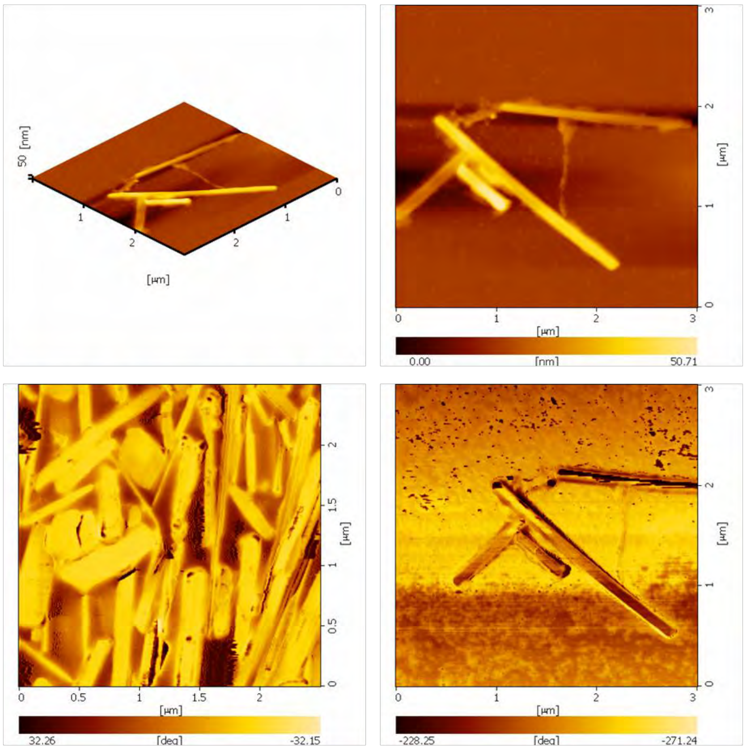

Figure F1: AFM images of dry samples of poly(S_0) sols on mica

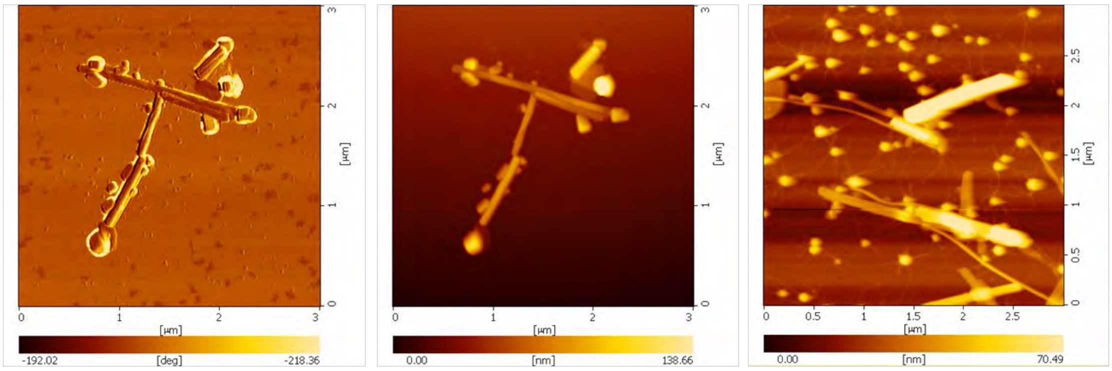

Figure F2: AFM images of dry samples of poly(S_1) sols on mica

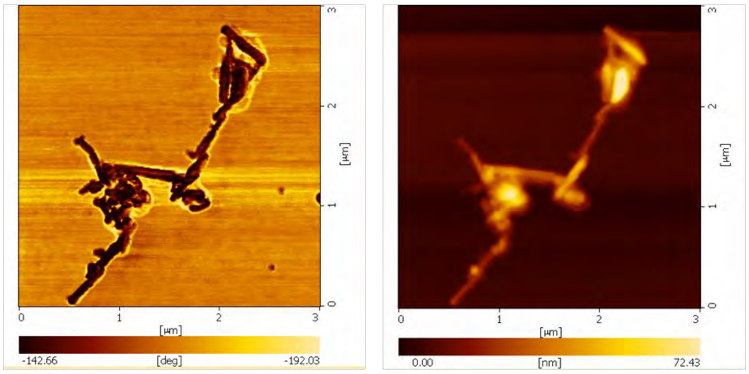

Figure F3: AFM images of dry samples of poly(S_4) sols on mica

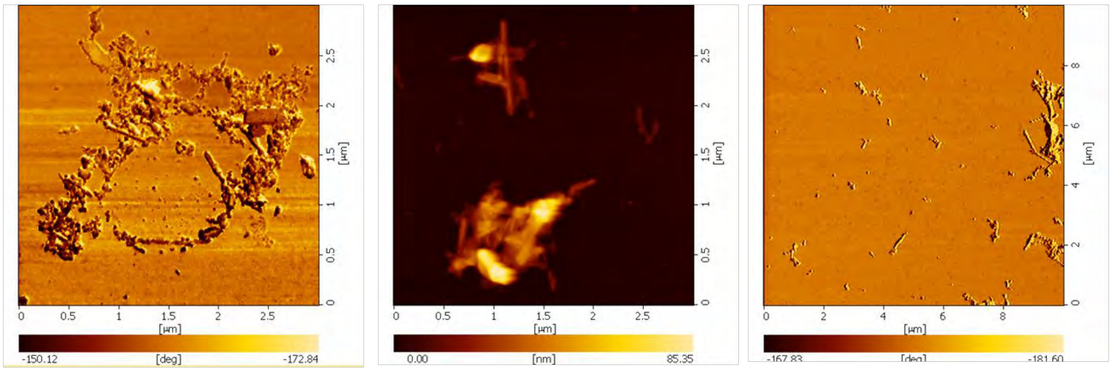

Figure F4: AFM images of dry samples of poly(S_8) sols on mica

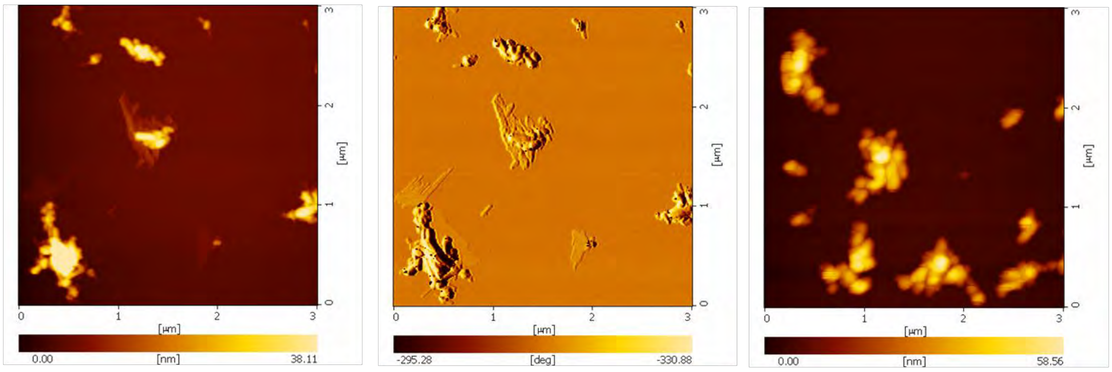

Figure F5: AFM images of dry samples of poly(S_{12}) sols on mica

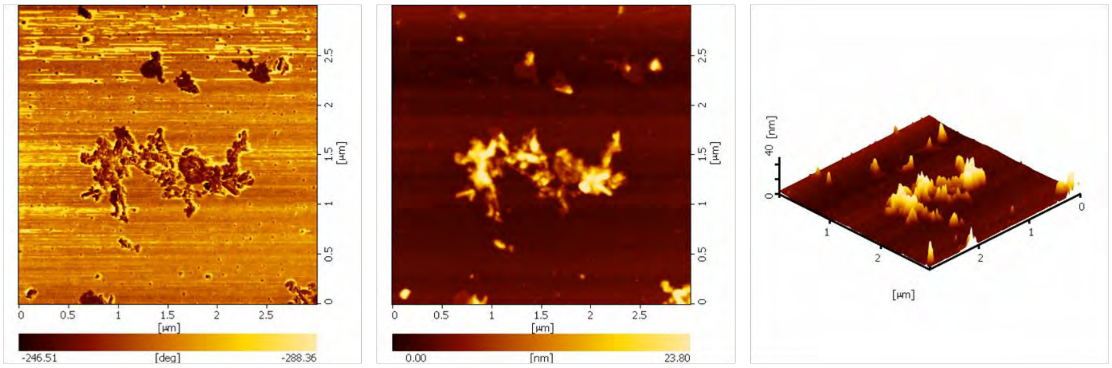

Figure F6: AFM images of dry samples of poly(S_{16}) sols on mica

VITAE

Miss Sasikarn Ampornpun was born on September 14th, 1984 in Phatthalung, Thailand. She received a Bachelor's Degree of Engineering, majoring in Petrochemicals and Polymeric Materials from Faculty of Engineering and Industrial Technology, Silpakorn University in 2007. She has been a graduate student studying Petrochemistry and Polymer Science as her major course from Faculty of Science, Chulalongkorn University. During the master study, she had received a scholarship from the 90th anniversary of Chulalongkorn University Fund. Throughout master study, she had a great opportunity to present her work in poster session in the topic of "Effect of methylene chain length on the thermochromic behaviors of PDAs containing diamido groups" at the 7th International Symposium on Advanced Materials in Asia-Pacific (7th ISAMAP) and the topic of "Effect of odd and even of methylene spacer on thermochromic reversibility of poylydiacetylene derives from symmetrical bisdiynamides lipids" at The 2nd Research Symposium on Petroleum, Petrochemicals, and Advanced Materials and The 17th PPC Symposium on Petroleum, Petrochemicals, and Polymers. And she had a chance to present her work in oral session in the same topic at Pure and Applied Chemistry International Conference (PACCON2011). The finance for joining the conference was supported by National Center of Excellence for Petroleum and Petrochemicals and Advanced Materials (NCE-PPAM), Chulalongkorn University. She graduated in May 2011.

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