ผลของขนาดและความเข้มข้นของซิงก์ออกไซด์ต่อการตอบสนองโดยการเปลี่ยนสีของวัสดุเชิง
ประกอบระดับนาโนเมตรพอลิไดแอซิทิลีน/ซิงก์ออกไซด์ต่ออุณหภูมิและพีเอช

นางสาวศานตมน เพ็งอุบล

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาเทคโนโลยีเซรามิก ภาควิชาวัสดุศาสตร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2557

EFFECTS OF SIZE AND CONCENTRATION OF ZINC OXIDE

ON COLORIMETRIC RESPONSE OF

POLYDIACETYLENE/ZINC OXIDE NANOCOMPOSITES

TO TEMPERATURE AND pH

Miss Sarntamon Pengoubol

A Thesis Submitted in Partial Fulfillment of the Requirements

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Thesis Title	EFFECTS OF SIZE AND CONCENTRATION OF ZINC OXIDE ON COLORIMETRIC RESPONSE OF POLYDIACETYLENE/ZINC OXIDE NANOCOMPOSITES TO TEMPERATURE AND pH
By	Miss Sarntamon Pengoubol
Field of Study	Ceramic Technology
Thesis Advisor	Assistant ProfessorNisanart Traiphol

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

‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒Dean of the Faculty of Science

(ProfessorSupot Hannongbua)

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(Assistant ProfessorNisanart Traiphol)

‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒Examiner

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‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒Examiner

(Dr.Stephan T.dubas)

‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒‒External Examiner

(Dr.Sirapat Pratontep)

ศานตมน เพ็งอุบล : ผลของขนาดและความเข้มข้นของซิงก์ออกไซด์ต่อการตอบสนองโดยการ
เปลี่ยนสีของวัสดุเชิงประกอบระดับนาโนเมตรพอลิไดแอซิทิลีน/ซิงก์ออกไซด์ต่ออุณหภูมิและ
พีเอช (EFFECTS OF SIZE AND CONCENTRATION OF ZINC OXIDE ON
COLORIMETRIC RESPONSE OF POLYDIACETYLENE/ZINC OXIDE
NANOCOMPOSITES TO TEMPERATURE AND pH) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: นิศา
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งานวิจัยนี้ศึกษาผลของความเข้มข้นและขนาดของซิงก์ออกไซด์ต่อสมบัติของวัสดุเชิงประกอบ
ระดับนาโนเมตรพอลิไดแอเซทิลีน/ซิงก์ออกไซค์ สำหรับประยุกต์ใช้ในเทคโนโลยีการตรวจวัด ใน
การศึกษาผลของความเข้มข้นของซิงค์ออกไซด์จะใช้อนุภาคที่มีขนาด 65 นาโนเมตร โดยปรับเปลี่ยน
ความเข้มข้นเป็นร้อยละ 5 10 15 20 30 และ 50 โดยน้ำหนักของไดแอซิทิลีนมอนอเมอร์ สำหรับ
การศึกษาผลของขนาดอนุภาคซิงก์ออกไซด์จะใช้อนุภาคที่มีขนาด 65 174 224 นาโนเมตร รวมทั้ง
อนุภาคที่ผ่านการเผาผนึกซึ่งมีขนาดในช่วง 4-7 ไมโครเมตร มอนอเมอร์ที่ใช้ในการศึกษา คือ 10,12-เพน
ตะโคซะไดอายน์โนอิกแอซิด (พีซีดีเอ)และ 5,7-เฮกซะเดกคะไดอายน์โนอิกแอซิด (เอชดีดีเอ) จาก
การศึกษาพบว่า วัสดุเชิงประกอบพอลิไดแอซิทิลีน/ซิงก์ออกไซด์ที่เตรียมโดยใช้ซิงก์ออกไซด์ร้อยละ 5 ไม่
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ซึ่งคาดว่าเกิดจากปริมาณมอนอเมอร์บนพื้นผิวของซิงก์ออกไซด์มีน้อยลงและอยู่ห่างกันมากขึ้นจึงไม่
สามารถเกิดการพอลิเมอไรซ์ได้ วัสดุเชิงประกอบพอลิ(พีซีดีเอ)/ซิงก์ออกไซด์ทั้งหมดเปลี่ยนสีจากน้ำเงิน
เป็นแดงที่อุณหภูมิ ~75 องศาเซลเซียส และแสดงพฤติกรรมการเปลี่ยนสีแบบผันกลับได้เมื่อลดอุณหภูมิ
ลง วัสดุเชิงประกอบพอลิ(เอชดีดีเอ)/ซิงก์ออกไซด์เปลี่ยนสีจากน้ำเงินเป็นม่วงที่อุณหภูมิ ~60 องศา
เซลเซียส และแสดงการเปลี่ยนสีแบบผันกลับได้บางส่วน เมื่อทำการเตรียมวัสดุเชิงประกอบด้วยอนุภาค
ซิงก์ออกไซด์ที่มีขนาดต่างกัน พบว่าอุณหภูมิที่เกิดการเปลี่ยนสีของวัสดุเชิงประกอบไม่มีการเปลี่ยนแปลง
อย่างไรก็ตาม พฤติกรรมการเปลี่ยนสีแบบผันกลับได้บางส่วนเกิดได้ชัดเจนมากขึ้นเมื่ออนุภาคซิงก์
ออกไซด์มีขนาดใหญ่ขึ้น ซึ่งคาดว่าเป็นผลมาจากพื้นที่ผิวที่ลดลง โดยอนุภาคขนาด 174 และ 224 นาโน
เมตร ที่ผ่านการเผาผนึก อาจมีพื้นที่ผิวไม่เพียงพอสำหรับการเกาะของไดแอซิทิลีนมอนอเมอร์ทั้งหมด
ทำให้มีมอนอเมอร์เหลือในระบบและเกิดเป็นเวสิเคิลบริสุทธิ์ ดังนั้นวัสดุเชิงประกอบจึงแสดงพฤติกรรม
การเปลี่ยนสีแบบผันกลับได้บางส่วน สำหรับการตอบสนองต่อความเป็นกรด-เบส พบว่าพอลิ(เอชดีดีเอ)/
ซิงก์ออกไซด์มีความไวในการตอบสนองมากกว่าพอลิ(พีซีดีเอ)/ซิงก์ออกไซด์ นอกจากนี้ วัสดุเชิงประกอบ
ที่เตรียมด้วยอนุภาคที่ไม่ผ่านการเผาผนึกจะมีการตอบสนองโดยการเปลี่ยนสีต่อความเป็นกรด-เบส
มากกว่าวัสดุที่เตรียมด้วยอนุภาคที่ผ่านการเผาผนึก

ภาควิชา วัสดุศาสตร์	ลายมือชื่อนิสิต	_____
สาขาวิชา เทคโนโลยีเซรามิก	ลายมือชื่อ อ.ที่ปรึกษาหลัก	_____
ปีการศึกษา 2557		

5572125523 : MAJOR CERAMIC TECHNOLOGY

KEYWORDS: POLYDIACETYLENE / COLOR TRANSITION / OPTICAL SENSOR

SARNTAMON PENGOUBOL: EFFECTS OF SIZE AND CONCENTRATION OF ZINC OXIDE ON COLORIMETRIC RESPONSE OF POLYDIACETYLENE/ZINC OXIDE NANOCOMPOSITES TO TEMPERATURE AND pH. ADVISOR: ASST. PROF.NISANART TRAIPHOL, 139 pp.

This research studies effects of ZnO concentration and particle size on properties of PDA/ZnO nanocomposite for sensing technology. To investigate the effect of ZnO concentration, ZnO with particle size of 65 nm is used and the concentrations are varied from 5, 10, 15, 20, 30 and 50wt% based on DA monomer. For studying the effect of particle size, as-received ZnO with sizes of 65, 174 and 224 nm are used along with their calcined particles with size in the range of 4-7µm. Monomers used in this research are 10,12-pentacosadiaynoic acid (PCDA) and 5,7-hexadecadiynoic acid (HDDA). PDA/ZnO nanocomposites prepared with 5 wt% ZnO are unstable. At 10-15 wt% ZnO, the suspensions are deep blue, showing high amount of polymerized materials. At higher ZnO concentration, less polymerized materials occur. This could be due to fewer amounts of monomers on ZnO surface with separate distance too long to be polymerized. All poly(PCDA)/ZnO nanocomposite changes from blue to red at ~75oC and exhibits completely reversible behavior upon cooling. Poly(HDDA)/ZnO nanocomposite changes from blue to purple ~60oC and exhibits partially reversible thermochromism. Color transition temperatures are similar for PDA/ZnO nanocomposites prepared with various ZnO sizes. However, the partially reversible thermochromism is more obvious when ZnO size increases. This could result from decreasing in surface area when size increases. For calcined 174 and 224 nm-ZnO, the particles could have insufficient surface area for all DA monomers to arrange on. Some DA monomers could remain in the system and form pure vesicles. Therefore, the nanocomposites exhibit partially reversible thermochromic behavior. For pH response, it is found that poly(HDDA)/ZnO is more sensitive than poly(PCDA)/ZnO nanocomposites. In addition, the nanocomposites prepared with as-received ZnO exhibit higher degree of colorimetric response to pH than the ones prepared with calcined particles.

Department:	Materials Science	Student's Signature _____
Field of Study:	Ceramic Technology	Advisor's Signature _____
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จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

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Chapter I

INTRODUCTION

1.1. Background and motivations

Nowadays, the development of nanotechnology has extensively progressed to increase comfort and safety for consumer. One area of interest in nanotechnology sensing materials based on colorimetric responses. These materials exhibit color transition upon changes in the environment, which can be observed by the naked eyes. One of the materials for this application is polydiacetylene (PDA), which is conjugated polymer with interesting chromic properties. PDA vesicles can be easily prepared by dispersing diacetylene(DA) monomers in water and polymerized under UV irradiation without chemical initiators or catalyst. PDA vesicles exhibit color transition from blue to red when subjected to various external stimuli such as temperature, pH, solvent, biomolecules, and others.

Diacetylenen monomer is an amphiphilic molecule that consists of polar head and long alkyl tail, which can assemble into a stable bilayer structure in aqueous medium. UV irradiation leads to polymerization, producing PDA with deep blue color. Recently, many researchers have developed chromic properties of PDA vesicles for using in wide range of application. The successful method is the modification of chemical structure such as side chain or head group of the polymer to increase attractive interaction within the assemblies. Nevertheless, this method is very complicate and requires expensive chemicals or catalysts. Afterwards, researchers studied the preparation of PDA in nanocomposite form, by adding metal oxide, which improve their properties. The metal oxides used in previous such as silica (SiO_2), titanium oxide (TiO_2), zinc oxide (ZnO), aluminium oxide (Al_2O_3), calcium oxide (CaO), and magnesium oxide (MgO). Metal oxide particles act as templates for PDA to adsorp on the surface.This method improves rearrangement of DA monomer with advantages of simplicity and low cost.

PDA/ZnO nanocomposite has been successfully prepared and extensively studied by our research group. This nanocomposite interestingly exhibits different colorimetric behavior comparing to PDA vesicles. This is due to the strong attractive interaction between $Zn-OH_2^+$ at the surface of ZnO and carboxylate head groups of PDA, which can restrict side chain dynamics upon subjected to stimuli. The color transition of the nanocomposites takes place at higher temperature compared to pure PDA and can be reversible when cooling to room temperature. In part of pH, PDA/ZnO nanocomposite is sensitive to acid. The color transition of nanocomposites response to acid. Moreover, the strong ionic interaction between carboxylate heads to PDA and ZnO surface drastically alter the color-transition behavior at high pH region.

In this research, we study effect of size and concentration of ZnO nanoparticels on colorimetric behavior of PDA/ZnO nanocomposites The variation in concentration of ZnO nanoparticles is expected to alter layer thickness of PDA adsorped on ZnO surface. ZnO nanoparticles with various sizes are expected to influence the stress of the PDA backbone. By varying these parameters, Colorimetric response of the PDA/ZnO nanocomposite could be controlled.

1.2. Objectives

     1.   To study the effects of ZnO concentration on colorimetric responses of PDA/ZnO nanocomposites to temperature and pH.

     2.   To study the effects of ZnO size on colorimetric responses of PDA/ZnO nanocomposites to temperature and pH.

1.3. Expected outcome

     Colorimetric responses of PDA/ZnO nanocomposites can be controlled and utilized in sensing appllications.

CHAPTER II

THEORIES AND LITERATURE REVIEWS

2.1. Conjugated polymers

Conjugated polymer is organic macromolecules which consist at least of one backbone chain of alternating double- and single-bonds. This material is of interest for applying in sensor technology because of its interesting optical and electrical properties. The p_z-orbitals of the carbon atoms, which forms the π -orbitals of the alternating double-and single-bonds are connected. The π -orbitals of the double-bonds overlap over the single bonds. Therefore, the π -electrons can easily move from one bond to the other. When conjugated polymer is subjected to external stimuli, chain conformation changes and π –orbitals are rearranged. Conjugation length, i.e. the length that electrons can delocalize in polymer chain, is shortened. Electrons require higher energy to cross from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Therefore, these materials exhibit color transition, which can be applied to sensor technology. One of the simple conjugated polymers is polyacetylene, which consists only of a single chain of alternating single- and double-bonds show in Fig. 2.1[1]

Fig. 2. 1The simple structure of a conjugated polymer which consist only of a single chain of alternating single- and double-bonds[1]

2.2.   Polydiacetylene (PDA)

Diacetylene (DA) monomer (Fig 2.2) is an amphiphilic molecule that consists of carboxylic head group and long alkyl tail. This monomer can arrange into bilayer structure in aqueous medium at suitable condition and can be polymerized under UV irradiation by 1,4-addition reaction to form polymer backbone[2] (Fig 2.3). When polydiacetylene is subjected to external stimuli such as temperature, pH, solvent or other chemicals[3] (Fig2.4), this color changes from blue to red or purple .Therefore, the color transition of polydiacetylene can be easily detected by the naked eyes. From this interesting property, polydiacetylene is applied as a sensor for detecting temperature, pH, biological, molecules and chemicals.

Fig. 2. 2. Diacetylene monomer

Fig. 2. 3. Preparation of polydiacetylene[2]

Fig. 2. 4. Color transition of polydiacetylene upon (a) increasing temperature and (b) addition of solvents[3]

The differences of polydiacetylene from other conjugated polymer[4] are

       1.   Polydiacetylene can be easily prepared in water to form liposome or vesicles, which can be fabricated in matrix for sensing devices. Normally, synthesis of conjugated polymer that can dissolves in water. It has complicated and long time for synthesis because the functional group of side chain has polar so polydiacetylene has interesting because it can prepared in water.

       2.   Polydiacetylene can be polymerized under UV irradiation without the need of chemical initiators or catalysts.

       3.   Polydiacetylene exhibit color transition behavior. This can be easily detected by naked eyes. It changes color from blue (λ_{max} 640 nm) to red ($\lambda_{max} \sim$ 540 nm) when subjected to external stimuli such as temperature, pH, organic solvents, stress and interaction between ligand–receptor. (Fig 2.5a).

       4.   Polydiacetylene exhibit fluorescence property. When polydiacetylene is subjected to external stimuli, its red phase exhibits fluorescence (Fig 2.5b). This can be used to detect temperature in microchannel to instead of using the thermocouple.

Fig. 2. 5. Color transition of polydiacetylene subject to (a) color transition and (b) fluorescence [3]

Polydiacetylene can be prepared from polymerization of diacetylene monomer under UV irradiation. Different types of monomer can form different bilayer structures. Structure of polydiacetylene monomer, hydration and color of suspensions after polymerization are shown in table 2.1

The significant property of polydiacetylene vesicles is color property and colorimetric transition of the material. Excitation energy of electron that results in color transition of polydiacetylene vesicles depends on many factors such as cohesive condition of monomer and form external stimulation (heat, mechanical stress, acid-base or solvents) All of these factors affect colorimetric transition of the material. Usually, when polydiacetylene is disturbed by stimulators, the color changes from blue to red. The highest light absorption in blue form is in the range of 620- 640 nm and red form is between 490- 540 nm. The extent of blue-red color transition can be easily determined by calculating percentage of colorimetric response (%CR) using the following fomular [5].

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

$$PB = A_{blue}/(A_{blue} + A_{red}) \times 100\%$$

where: PB is the value obtained from the vesicle solution after appearance of the color change

PB_0 is the blue/red ratio of the control sample

A_{blue} is the absorbance measured from blue component

A_{red} is the absorbance measured from red component

Table 1 Strcuture of polydiacetylene , hydrationand color of suspension after polymerization. Y = hydration and N = no hydration [3]

Diacetylene Lipid Structure	Hydra-tion	Polymer Formation
	Y	Blue
	Y	Blue
	Y	Purple
	Y	Orange
	Y	Purple
	Y	Purple
	Y	Red
	Y	N
	Y	Black
	Y	Red
	N	N
	Y	N
	Y	N
	Y	N

2.3. Mechanism of color transition

Polydiacetylene vesicles have a unique property of changing their color when response to environmental variations such as temperature alteration, acid-base and adding molecules or solvents into the system. This property is desired for sensing applications, which can analyze or observe the transition by naked eyes

2.3.1. Colorimetric response to temperature

The effect of heat that causes colorimetric transition of polydiacetylene vesicle is an interesting topic and widely studied. Most colorimetric transitions of PDA caused by temperatures are occurring in one direction; from blue to red and irreversible.

Generally, interaction of polydiacetylene group occurs at the head group of chains, i.e. the hydrogen bond establishment, which connect between head group and another one. This interaction is the main factor because the arrangement of methylene chain in polydiacetylene structure. In this area, the bended structure may occur during polymerization process under UV irradiation. The transition or bending of structure will lead to mechanical stress accumulation within the chain. In case of irreversible colorimetric transition, heat causes the hydrogen bond connected the head groups becomes weaker. This helps to relief mechanical stress in methylene chain, resulting in bending of π orbital at the main chain. Further increasing of temperature causes more relief of mechanical stress until the hydrogen bond is broken. The deformed structure could not reverse to its former structure even though the temperature decreases. The rupture of hydrogen bond and structure transition lead to the incline in conjugate phase due to hardly movement of electrons in structure. This affects the state of the electron and absorbance in a way that valence band is lower, which imply the wider gap between the HOMO-LUMO In this situation, electrons have to absorb the higher energy level in order to jump over the gap. That means the absorbance at the shorter wavelengths is occurred and the color turns into red[6].

D.J. Ahn and et al[7] presented the mechanism of color transition when increasing temperature of PDAs as shown in Fig 2.6. They explained that in blue phase, interactions of head group (aromatic interactions, hydrogen bonding, etc.) controlled the molecular orientation and caused strain in the side chain of PDAs. The increasing of temperature breaks head group interactions, which releases mechanical strain and causes distortion of the conjugated backbone PDA change to red color. Since the head group interactions were destroyed, the original molecular structure cannot be resumed when cooling to room temperature. Thus, the color transition is irreversible.

Fig. 2. 6.A mechanism of chromic responses to temperature[7]

2.3.2. Colorimetric response to acid-base

Acid-base variation is another stimulator that causes color transition of polydiacetylene. Adding more base to polydiacetylene system affects to the interaction between neighboring head groups of polydiacetylene. Rising of OH^- in the system traps proton of carboxylic acid head group and changes to carboxylate. This causes repulsion between the negative carboxylate ion (COO^-), resulting in movement or bending of the main the backbone chain. The organized pi-orbitals in the main are distributed, causing difficulty in dislocation of electrons in the structure. Therefore, energy gap between the Highest Occupied Molecular Orbital (HOMO) and

the Lowest Unoccupied Molecular Orbital (LUMO) is widen, causing electrons to absorb higher energy. Then, polydiacetylene exhibits to red color to naked eyes.

Kew and Hall[8] studied the colorimetric response to acid-base of carboxy diminished polydiacetylene vesicles. Diacetylene monomer was 10,12-tricosadiynoic acid (TRCDA). This PDA exhibited irreversible blue-red transition when pH increased. However, pH < 4 has no effects on the color of TRCDA vesicles. They explained that the colorimetric response of the PDA to NaOH is resulted from two steps show in Fig. 2.7. First, the proton was detached from carboxylic head groups upon addition of OH⁻ ions. Second, sodium cations interacted with carboxylate groups resulting in color transition from blue to red.

Fig. 2. 7. Transmission electron microscopy of dehydrated 0.50 mM TRCDA blue-phase vesicles before (i) and after (ii) basification to form the red-phase by the addition of 1 molar equivalent of 0.1 N NaOH. Scheme for the proposed structural transition that accompanies the blue-red color transition[8]

The morphology of PDA upon increasing pH was studied using TEM as shown in Fig.2.7. At the normal condition (before basification(i)), mainly well-defined assemblies of blue-phase PDA were presented. For red-phase after PDA basification (ii), the polymer aggregration was observed. The morphology of the particles in red phase was not globular but faceted. These morphology transitions in red phase were explained irreversible colorimetric transition when increasing pH.

2.4. Improving chromic properties of PDAs

The chromic properties of PDAs depend on the molecular structure of polymer. Generally, the response of PDA by color transition due to environmental variations occurs in irreversible process. When polydiacetylene vesicles is stimulated and the color changes from blue to red, it cannot reverse to their original color after the stimulator is removed. To alter the color transition behavior of the PDA, there are many researches on developing the PDA with reversible color transition behavior.

The strength of interaction within head group of diacetylene is the vital key element controlling colorimetric transition behavior. Hence, most researches focus on the development in structure and molecular configuration for the strongest interaction within head group. The modification of functional group within head group of PCDA by chemical approach is widely used for synthesizing new conjugated polymers of diaccetylene. For example, the substitution of carboxyl group in diacetylene with phenylacetamide[9],monoamide or diamide group[10]. However, these substitutions require toxic and expensive chemical and also complicated chemical approaches.

2.4.1. Chemical Modification process

Many research groups developed properties of PDAs by increasing interactions of side chains or head groups using chemicals modification[4, 7, 9-11]. Most of these works usually focused on the colorimetric transition response of PDAs to

temperature. J-M Kim and et al[4] presented polydiacetylene prepared from PCDA-mBzA1, bearing terminal m-carboxyphenylamido groups. This material a exhibited completely reversible color transition behavior. They studied the effects of (1) carboxylic group, (2) alkyl chain length, (3) amide hydrogen bonding, and (4) aromatic interactions on reversibility thermochromism. The structure of diacetylene monomers are show in Fig. 2.8. The thermochromic behaviors of polydiacetylene derivative liposome solution are shown in Fig. 2.9. The thermochromic behavior of these PDA supramolecules was reversible due to strong, intergrated double hydrogen-bonding networks and aromatic interaction in head groups of the supramolecular assemblies (vesicles and films), Therefore, the PDA supermoleculars can be recovering to their initial molecular structures and average π-electron conjugation length after cooling.

Fig. 2. 8. Structures of DA monomers investigated for thermochromism[4]

Fig. 2. 9. Absorbance spectra of PDA derivatives liposome solution upon heating and cooling process[4]

X. Chen and et al[9] systhesized a new conjugated polymer based on polydiacetylene by changing the head group of polydiacetylene to phenyl acetamide group as show in Fig. 2.10. This PDA solution exhibited color transition from blue to red when temperature increased to 70°C. Fig.2.11a and b show the absorption spectra of the PDA measured between heating and cooling, respectively. The absorbance at 625 nm significantly dropped and the peak at 535 nm increased when the temperature increased to 70°C. After PDA solution was cooling to 30°C, the peak at 625 nm was recovered and the solution exhibited purple phase as show in Fig. 2.12

Fig. 2. 10. Synthesis of monomer[9]

Fig. 2. 11. Absorption spectra of PDA solution (a) heating (b) cooling[9]

They explained the reversible thermochromic property of this PDA to be resulted from strong head group interaction. The introduction of phenylacetamide head into PDA derivative can increase intermolecular interaction (including **π**- **π** stacking from pheyl groups and hydrogen bonding from amide groups) between side chains. This enhanced thermal stability and resulted in the reversible thermochromic properties.

Fig. 2. 12. Photograph of different color stage at 30oC and 70oC[9]

2.4.2. Addition of nanoparticles

Colorimetric mechanism of polydiacetylene vesicle happens when stimulated from outside. The side chain changes, for example, breaking bond between head group. Changing direction or agglomeration of the side chain causes the stress and change structure of the main chain. Electron state and absorbance also change, leading to color change from blue to red. The behavior of color changing depends on the degree of rearrangement of polydiacetylene structure. By adding nanoparticles into the system, the change of side chain, and, thus, backbone of polydiacetylene subjected to stimuli is altered. This causes colorimetric behavior to be different from pure polydiacetylene vesicle. In addition, properties of materials can be improved and adjusted by addition of nanoparticles.

Nanoparticles of metal and metal oxide are the main components for the preparation of PDA/metal or metal oxide nanocomposite suspensions. Addition of metals and metal oxide is not only altered molecular configuration of polydiacetylene but also improved the properties of the nanocomposite as desired. Examples of metal and metal oxide nanoparticles ues for preparation of the nanocomposite are as followed Zinc oxide (ZnO)[12],and Titanium dioxide (TiO$_2$)[13] can absorb UV light. In addition, Nanoparticles of iron oxide, i.e. magnetite (Fe$_3$O$_4$) have magnetic property. In addition, nanoparticles of silica (SiO$_2$)[14] and silver (Ag) have been use as template for PDA assembliesPDA/metal PDA/metal oxide nanocomposites have been reported to different color transition behaviors.

In 2006, Yan-lei Su[15] studied the preparation of polydiacetylene nanocomposite and silica to use as a sensor in for surfactants. Silica nanoparticles with average size of 46 nm were synthesized by hydrolysis method using TEOS in ethanol. The DA monomer used in this work is 10,12-pentacosadiynoic acid (PCDA). PCDA was dissolved in ethanol and silica nanoparticle solution then stirring at 20°C for 4 h. lastly, the solution was irradiated by UV light. In this work PCDA aggregates in solution without silica nanoparticles could not be polymerized. With silica nanoparticles, PCDA absorbed on silica surface. Silica nanoparticles acted as template, which helped to arrange disorder molecules of PCDA to become more organized as shown in fig 2.13. After the nanocomposite suspension was irradiated with UV light, the color of suspension change to deep blue phase. When SDS was added into the polydiacetylene/silica nanocomposite solution. The nanocomposite has little chromatic response cause the repulsive coulombic interaction between the negatively charged headgroups of anionic surfactant SDS and the polymerized PCDA hinders the approach of SDS to the polydiacetylene.

Fig. 2. 13. Schematic illustration of the adsorption of PCDA aggregates on the surface of SiO$_2$ nanoparticles, and the formation of ordered PCDA arrangement on the surface of SiO$_2$ nanoparticles.[15]

The chromatic transition of nanocomposites from blue to red exhibited when increaseing temperature to 70°C (Fig. 2.14a). Futhermore, the chromic transition of nanocomposite occurrd upon adding surfactants (Fig 2.14b) The addition of CTAB or Triton X-100 resulting in color transition of PDA/SiO$_2$ nanocomposite from blue to red phase.

Fig. 2. 14. UV-visible absorption spectra of PDA/SiO$_2$ nanocomposites subjected to (a) increasing temperature and (b) adding of surfactants[15]

In 2009, Takahiro Yokoyama et al[16] developed the hybridize nanocrystal composed of polydiacetylene nanocrystal and silver(Ag) nanoparticle by co-precipitation method. In this work, silver nanoparticles prepared by reaction of $AgNO_3$ and trisodium citrate at boiling and DA monomer was 10,12-heptacosadiynoic acid (14,8-ADA). TEM images of Ag/polydiacetylene hybridized nanocrystals were show in Fig. 2.15. It revealed that Ag core were coated with poly(14,8-ADA) shell of ~5 nm in thickness.

Fig. 2. 15. TEM images of core/shell hybridized nanocrystals composed of Ag nanoparticles core and poly(14,8-ADA) shell. The scale bar corresponds to 50 nm[16].

Absorbance spectra of core/shell hybridized nanocrystals aqueous before and after UV irradiation were shown in Fig 2.16. The broad large peak at 460 nm attributed to localized surface plasmon resonance from Ag nanoparticles. After UV irradiation, absorption peak appeared at 540 nm as a shoulder. The inset in Fig. 2.16a show spectrum at around 500-600 nm after UV irradiation. The excitonic absorption peak attributed to red phase of poly(14,8-ADA) shell. This is due to distribution of the π-conjugated backbone of poly(14,8-ADA) anchoring effect and curvature effect of Ag nanoparticles core. Fig.2.16b showed absorption peak in the range from 580 to 650 nm for blue phase. The absorption peak of red phase was blue-shifted to around 500 to 550 nm.

Fig. 2. 16. (a) UV-vis spectra of the hybridized nanocrystals aqueous dispersion

before (dotted line) and after (solid line) UV irradiation. The inset

indicates the differential spectrum before and after UV irradiation.

(b) UV-vis spectra of poly(14,8-ADA) nanocrystals aqueous dispersion in

the blue phase (dotted line) and the red phase (solid line)[16]

In 2011, X. Chen et al[17] successfully prepared PDA/Fe_3O_4 nanocomposite. The synthesis of the megnetochromatic polydiacetylene by incorporation of Fe3O4 nanoparticals was shown in Fig. 2.17a. The Fe_3O_4 nanoparticles consisted of hydroxide groups on their outer surface, which interacted with carboxyl group of diacetylene monomer. DA monomers were coated on Fe_3O_4 surface as shown in Fig. 2.17b. The thin layers of DA monomer on Fe_3O_4 surface were observed by relatively lighter contrast. After evaporation of solvent, the nanocomposite films were polymerized under UV irradiation and exhibited blue color.

Fig. 2. 17. (a) Schematic show the systhesis of the magnetochromatic polydiacetylene by incorporation of Fe_3O_4 nanoparticles. (b) TEM image of Fe_3O_4 composite nanoparticles derived from $CH_3(CH_2)_9CCCC(CH_2)_3COOH$[17]

Optical microscopy and SEM images in Fig. 2.18 illustrated morphology of nanocomposite films. The nanocomposite film was crystalline-like structure (Fig. 2.18a,b). In Fig. 2.18c, the Fe3O4 particles were observed to disperse in PDA matrices. Under AC magnetic field, the derived PDA/ Fe_3O_4 film exhibited color transition from blue to red, which easily observed by naked eyes. Photographs of nanocomposite film in blue and red phase were shown in Fig. 2.18d,

Fig. 2. 18. (a) Optical microscopy image, (b) SEM image and (C) SEM image at higher magnification of the nanocomposite film. (d) Photographs of the PDA/Fe_3O_4 composite film before and after color changes upon exposure to AC[17]

2.5. Polydiacetylene/ZnO nanocomposite

Nanoparticles of Zinc oxide are of interest in our research group for preparation of PDA/metal oxide nanocomposite. In 2011, N. Traiphol et al[18] successfully prepared poly(PCDA)ZnO nanocomposite, which exhibited different thermochromism from pure poly(PCDA). Generally, surface ions of zinc oxide particles in water consisted of a group of Zn-OH, $Zn-OH_2^+$ and $Zn-O^-$. The proportion of these functional group depended on pH of the solvent. Zinc oxide has isoelectric point at pH around to 9. Thus, in acidic condition, surface of zinc oxide particles will mostly consisted of Zn-OH and $Zn-OH_2^+$. When mixing ZnO suspension with DA monomer solution of weak acidic pH, diacetylene (DA) monomer can self-arrange on zinc oxide surface. The $Zn-OH$ and $Zn-OH_2^+$ ions of zinc oxide particle will interacted with carboxylic and carboxylate functional head groups of diacetylene monomer. The acting force caused the molecules of diacetylene to dislocate or rearrange with difficulty when subjected to external stimuli. This, in turn, affect the color transition behavior of the poly(PCDA)/ZnO nanocomposite. Interaction between PDA and ZnO in the nanocomposite is shown in Fig 2.19.

Fig. 2. 19. Illuatration of hydrogen bonding and ionic interaction between –COOH and –COO of PCDA and Zn-OH and $Zn-OH_2^+$ group at surface of ZnO nanoparticles [18]

The poly(PCDA)/ZnO nanocomposite exhibited an interesting thermochromic response. The color of nanocomposite change to purple phase at 85°C compare to red phase at 74°C for pure poly(PCDA) (Fig. 2.20). After cooling to room temperature color of the nanocomposite can change back to the original blue. Moreover, the reversibility of its color can be repeated more than 10 heating-cooling, (Fig. 2.21),

Fig. 2. 20. Absorption spectra of (a) pure ply(PCDA) vesicle (b) poly(PCDA)/ZnO nanocomposite in aqueous suspension when increasing temperature[18]

Because of the zinc oxide particle to in the system, strong interaction between zinc oxide surface and carboxylate head group caused the polymer chain to become more organized. Heating caused a small movement of the side chains. Transformation of the backbone that occured at high temperature can reverse back to the former planar after reducing to room temperature. From the testing of colorimetric transition with temperature in nanocomposite films, 2 steps color transition occurred. At 100°C, the reversible color transition occured following up by the reversible color transition from purple to red at 145°C. Fig. 2.21 illustrate reversible color transition of polydiacetylene/zinc oxide nanocomposite.

Fig. 2. 21. The irreversible colorimetric (%CR) (●) pure poly(PCDA) and (■)
poly(PCDA)/ZnO17% nanocomposite as a function of annealing
temperature[18]

A. Chanakul et al[19] studied the effect of typed of diacetylene monomer to thermochromism of polydiacetylene/zinc oxide nanocomposite. The DA monomers used in this work were 5,7-hexadecadiynoic acid (HDDA), 10,12- pentacosadiynoic acid (PCDA) and 10,12-tricosadiynoic acid (TCDA) with vary alkyl chain length as shown in Fig. 2.22. It was found that the color transition of the nanocomposite can be controlled by using various DA monomers.

Fig. 2. 22. Ionic interaction between –COO- group of PDAs and ZnO-OH$_2^+$ group[19]

The shortening of DA monomer, HDDA, decreased the color transition temperature of the nanocomposite because of the decrease in dispersion interaction with in the assemblies. The decrease in alkyl chain length supported backbone rigidity, which in turn influences the interfacial interactions and color transition behaviors. The heterogeneity of interfacial interaction were detected in system of poly(HDDA)/ZnO nanocomposite with relatively short alkyl chain length. The color transition of nanocomposite is less pronounced, and the color stability is lower compared with the other nanocomposites as show in Fig. 2.23. When the temperature is increased above 60°C, the color of poly(PCDA) and poly(TCDA) change from blue to red. After cooling to 30°C, the poly(PDA) exhibit irreversible processed. In poly(HDDA) system in which the alkyl chain is much shorter, the initial blue color is unstable at room temperature. In the system of PDA/ZnO nanocomposite, it is rather different. All nanocomposites change color at higher temperature. Poly(PCDA)/ZnO poly(TCDA)/ZnO and poly(HDDA)/ZnO nanocomposite change color at 80°C, 70°C, and 60°C, respectively. At 90°C the nanocomposites exhibit in purple phase and all nanocomposites can be reversed to blue phase when cooling to 30°C

Fig. 2. 23. Color photographs of (a) pure poly(PCDA) (b) poly(PCDA)/ZnO
(c) poly(TCDA) (d) poly(TCDA)/ZnO (e) poly(HDDA)/ZnO nanocomposite
upon increase temperature from 30°C to 90°C and cooling to room
temperature[19]

A. Chanakul et al[20] studied effects of pH to polydiacetylene/zinc oxide nanocomposite prepared with different diacetylene monomers, 5,7-hexadecadiynoic acid (HDDA), 10,12- pentacosadiynoic acid (PCDA) and 10,12-tricosadiynoic acid (TCDA). Results were shown in Fig.2.24.

The color-transition behaviors of pure poly(PCDA) and poly(TCDA) vesicles were normally investigated in high pH region. In low pH region, the addition of H+ ions hardly affected the color of vesicles. In basic condition, poly(TCDA) exhibited irreversible blue to red color transition when increasing pH above 8. The color transition completed at pH ~ 10. The pure poly(PCDA) exhibited in similar color transition. However, the color transition took place at higher pH compared to that of the poly(TCDA).

In contrast, the poly(PCDA)/ZnO nanocomposite was sensitive to acid. The suspension changed to reddish purple at pH 1. This result showed that the incorporation of ZnO nanoparticles promoted the colorimetric response of poly(PCDA)to acid. Moreover, the strong ionic interaction between carboxylate heads groups of poly(PCDA) and ZnO surface drastically altered the color transition behaviors at high pH. However, it required much higher concentration of OH^- to induce the color transition compared to the system of pure poly(PCDA) vesicle. The color transition of poly(TCDA)/ZnO nanocomposite occured at much lower concentration of H^+ ions compared with system of poly(PCDA)/ZnO nanocomposite. For the response to basic condition, the increase in pH caused similar color transition behavior in the system of poly(TCDA)/ZnO compared to poly(PCDA)/ZnO nanocomposite.

The investigation of poly(HDDA)/ZnO nanocomposite provided rather interesting result. The color transition of poly(HDDA)/ZnO nanocomposite was lower than that of poly(PCDA)/ZnO and poly(TCDA)/ZnO system. In addition, poly(HDDA)/ZnO nanocomposite was also sensitive to the basic condition. This study showed that the PDA-based material with dual colorimetric response to both acidic and basic pH can be produced by preparing PDA/ZnO nanocomposite.

Fig. 2. 24. Photographs of aqueous suspentions of (a) pure poly(TCDA), (b) poly(PCDA)/ZnO, (c) poly(TCDA)/ZnO, and (d) poly(HDDA)/ZnO nanocomposite in different pH[20]

A. Patlolla and et al[21] prepared the poly(PCDA)/ZnO nanocomposite with four different particle sizes. Size of the ZnO used were ranged from 2.1 to 1100 nm. The prepared poly(PCDA)/ZnO nanocomposites exhibited blue phase. The nanocomposites showed reversible thermochromism when using ZnO crystallite size range from 300 nm and below. They explained the head group of ZnO interaction discussed above is impeded when the crystallite size of ZnO is above 300 nm. Both blue and red phase spectra of poly(PCDA)/ZnO nanocomposite are the same as poly(PCDA). In blue phase, peak was shown at ~ 640 nm with vibronic peak at 590 nm. In red, phase due to decreasing of conjugation length, peak was shown at 540 nm and vibronic peak at ~ 490 nm (Fig. 2.25).

Fig. 2. 25. UV-visible spectra at 25 °C of poly(PCDA)/ZnO nanocomposites with three
different crystallite sizes of ZnO: (a) poly(PCDA)/ ZnO (1000 nm) in irreversible
red (gray) and blue (black) phases, (b) poly(PCDA)/annealed ZnO (11000 nm)
in irreversible red (gray) and blue (black) phases, and (c) poly(PCDA)/
nanocrystalline ZnO (300 nm) showing the spectrum in the reversible red
phase which rapidly converts back to blue (gray) and the spectrum in the
blue phase (black)[21]

2.6. Zinc Oxide

Zinc oxide (ZnO)[22] is an inorganic compound with molar mass of 81.408
g/mol. It is amphoteric oxide, which can act both acid and base. ZnO is nearly
insoluble in water and alcohol. Its structure can be separated into 3 types below;

1. Hexagonal wurtzite –the most stable structure at ambient conditions

2. Cubic Zincblend- Created by planting ZnO on the substrate with a
cubic crystal structure.

3. Cubic rocksalt- can be found at high pressure (approximately 10
GikaPascal) only

Fig. 2. 26. Stick-and-ball representation ofZnOcrystal structures:

(a) hexagonal wurtzite , (b) cubic zinc blende, and(c) cubic rocksalt [22].

Zinc Oxide is a semiconductor material, with band gap of 3.37 eV, good transparency, high electron mobility, strong room-temperature luminescence, and also good piezoelectric. Therefore, zinc oxide is the most attractive material in emerging applications such as solar cells, sensors, piezoelectric devices, thin film transistor and light-emitting diodes. Moreover, it can also apply in new innovation such as transparent electrodes in liquid crystal display and energy saving windows.

Not only good semiconductor properties it also possesses high light refractive index, high heat capacity, high thermal conductivity, low expansion temperature, high melting point, high chemical stability, good bacteria restriction (a use in anti-bacteria medicine), and good UV protection (able to prevent both UV-A and UV-Ba, use in sun block products). Moreover, Zinc Oxide (ZnO) powder is used as an additive to other materials and products such as glasses, plastics, cement, rubber, lubricant, glue, food, battery and etc. The application of zinc oxide (ZnO) also emerges in biological field such as the application of zinc oxide powders in biosensor.

2.7. Principles and techniques of analysis

In this study, we have used various techniques to analyze characteristics of polydiacetylene/ZnO nanocomposite suspension such as (1) UV-Vis spectroscopy in absorpbance mode for studying colorimetric behavior of nanocomposite when subjected to external stimuli. (2) Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) for studying microstructure and morphology. (3) Laser light scattering for analyzing size distribution of nanoparticles. (4) Infrared (IR) spectroscopy for studying functional groups of the nanocomposite. The principles of various analytical used in this study are as follwed.

2.7.1 UV-Vis spectroscopy

Ultra violet and visible spectroscopy [22-26] is a technique that used to measure light quantity and light intensity between Ultraviolet (180 - 400nm) and visible light (400-800nm), which is absorbed or passes through a substance. Wavelength of the absorbed light is proportioned to type and concentration of a sample under interestigation. Most organic compounds can absorb light in UV or visible region. This is the reason why this technique is routinely used in analytical chemistry for quantitative determination of different analytes. By passing the light (UV-Vis region) to analyte, the electrons in a molecule absorb some part of passing light and move from ground state to exciting state. The absorbed light is equal to the transition energy of the electron in molecule. The remaining light is then reflected, scattered or transmitted through analyte. According to Beer-Lambert's law, the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. Hence, UV-Vis spectroscopy can be used to determine the concentration and type of the absorber in a solution.

Lambert's law stated that "absorbed light is directly proportional to cross section thickness of medium that light pass through" as shown in Fig. 2.27

$$I_t = I_0 \times 10^{-kt}$$

Fig. 2. 27.Beer-Lambert's light absorption law[26]

Beer's law stated that "absorbed light is directly proportion to the concentration of substance in liquid". The calculation of Beer's law is the same as Lambert's law as shown in the formula below

$$I_t = I_0 \times 10^{-kc}$$

Combining two laws (Beer-Lambert's law) gives new equation which is

$$I_t = I_0 \times 10^{-\varepsilon cl}$$

The transmittance (T) is expressed in the equation below

$$T = I_t/I_0 \text{ or } \%T = I_t/I_0 \times 100$$

The Absorbance (A) is calculated based on the equation below

$$A = \text{Log } I_0/I_t$$

$$A = -\text{Log}T = 2-\text{Log}\%T \text{ or } A = \varepsilon cl$$

Where ε= absorption coefficient with units L mol^{-1} cm^{-1}

c = concentration of compound in solution, expressed in mol L'1

l = path length of sample – the path length of the cuvette in

which the sample is contained, expressed in centimetres.

When light absorption occured in sample, electrons in molecule are stimulated from ground state to excited state in which the energy difference is equal to wavelength energy or photons which are absorbed by electron. The transition of electron caused by UV – Vis can be occurred in 2 forms.

1.   n$\rightarrow$ ℼ* is the alteration of electrons which does not create bonding or lone pair electrons in oxide sulfide nitride and halogen compounds from ground state to ℼ* - orbital with higher energy

2.   ℼ$\rightarrow$ ℼ* is the alteration of ℼ-electron from ℼ-orbital in ground state to ℼ*-orbital. These can be found in molecule that has group functions with ability to absorb UV-vis, mostly have unsaturated bonding (double bond or triple bond). For example, C=O, C=C, -N=N- and –NO_2. The energy level of electron transition is shown in Fig. 2.28.

Fig. 2. 28. Energy levels of electron transition[27]

Once electrons in molecule receive appropriate energy, they absorb the light for the transition; the wavelength which absorption occurs is presented in absorption spectrum. The solvent in which absorbing species is dissolved also has an effect on the spectrum of the species. If the absorption spectrum shifts to longer wavelength, this phenomenon called "red shift". In contrast, the absorption spectrum which shifts to shorter wavelength is called "blue shift". Other terms relate to absorption of sample are "hyperchromic" and "hypochromic". The hypochromic effect describes the increase of absorption of sample. Inversely, the decrease of absorption is expressed as hypochromic effect as shown in fig. 2.29.

Fig. 2. 29. The translocation of absorption spectrum[26]

2.7.2. Electron Microscopy[28-30]

Electron Microscopy is a type of microscope that uses an electron beam instead of normal light to illuminate a specimen and produce a magnified image. Since wavelength of an electron beam are 100,000 shorter than light wavelength, electron microscopy can achieve higher magnification and details compared to light microscope. Electron microscopy can distinguish details of small particle in ranges of 10 A0 to 0.1 nm up to 0.2 μm. Hence, the electron microscope can achieve the magnification up to about 500,000x. Electron microscope can be separated into 2

main types which are Scanning electron Microscope and Transmission electron microscope.

Scanning electron microscope (SEM) is a microscope with the highest magnification capacity up to 10 nm. The SEM produces images by probing the specimen with a focused electron beam that is scanned across a rectangular area of the specimen. When the electron beam interacts with the specimen, it loses energy by a variety of mechanisms. The lost energy is converted into alternative forms such as heat, emission of low-energy secondary electrons and high-energy backscattered electrons. These emissions provide signals carrying information about of the specimen surface, such as its topography and composition. The image displayed by an SEM is in 3D format. Hence, it is suitable to use in morphology and surface study of samples.

Transmission electron microscope (TEM) uses high voltage electron beam to create an image. The electron beam is produced by an electron gun, commonly fitted with a tungsten filament cathode as the electron source. The electron beam is accelerated by an anode with respect to the cathode, focused by electrostatic and electromagnetic lenses, and transmitted through the specimen that is in part transparent to electrons and in part scatters them out of the beam. When it emerges from the specimen, the electron beam carries information about the structure of the specimen that is magnified by the objective lens system of the microscope. The spatial variation in the image may be viewed by projecting the magnified electron image onto a fluorescent viewing screen. The image displayed by a TEM is in 2D format. The objects that have high atomic number, display in black. The objects that have fewer atomic numbers, display in white color. The ability of SEM and TEM is shown in Table 2.2

Table 2 The ability of SEM compare with TEM

Device ability	SEM	TEM
Magnification	10 - 100,000x	1,000 - 500,000x
Detail identification	6 – 10 nm	0.14 – 0.2 nm
Appearance of image	Signal	Direct shadow
Image format	3D	2D
Usage	Surface	Inside structure

2.7.3. Laser light scattering [31, 32]

Laser light scattering is a technique that uses to characterize particle size and particle size distribution. When light travels to particles that suspend in the solution, some of the light pass through the sample, creating the refraction angles, and some are scattered. Scattering of the light depends on the size and number of the particles. The small particles scatter light larger angle than the angles more than bigger particles. The scattering light pattern is then sent to detector and processed to the distribution of particle size as shown in fig. 2.30.

Fig. 2. 30. Light scattering principles [31]

Size and size distribution of particles can be calculated by comparing scattering pattern to light theory. The small particles that smaller than laser wavelength will obey Rayleigh theory. The particle that is bigger than laser wavelength will obey Fraunhofer approximation, which stats that the intensity of the light which scattered is related to the amount of each size of particles while the angle of scattered light beam is inversely proportional to particles size. However, there are the limitations in Fraunhofer approximation which are; the particles size must greater than light wavelength, particles must be opaque, every particle size must scatter the light in equal efficiency and refraction index of particles and medium must be different. Because of many limitations of Fraunhofer approximation, Mie's theory is used at the present so that it can measure every type of particles including particles that is smaller than 50 μm.

Fig. 2. 31. Mie theory scattering[32]

The Rayleigh and Mie are not different mechanisms, Rayleigh scattering occurs when the particle is electrically small and phase shift across the particle is small. The particle is much smaller than the wavelength. Rayleigh scattering scatters energy with a radiation pattern like a dipole. If the particle is of the order of the size of the wavelength, Mie scattering occurs. With Mie scattering, there is more forward scattering and a forward radiation lobe[33].

The intensity of the scattered radiation for Raleigh scattering is

$$ I = I_0 \frac{(1 + cos^2\theta)}{2R^2} \left(\frac{2\pi}{\lambda}\right)^4 \left(\frac{n^2 - 1}{n^2 + 2}\right)^2 \left(\frac{D}{2}\right)^6 $$

Where   n is the refractive indeed of the material,

D is the diameter,

λ is the wavelength,

θ is the scattering angle. Note that the forward scatter equals the backscatters and at θ = 90o scattering is half of the forward/back scatter.

2.7.4. Infrared Spectroscopy [34-36]

Infrared spectroscopy is the spectroscopy that uses to identify chemical formula or quantify the amount of solution by using infrared ray. Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristics of their structures. These absorptions cause the transfiguration of bonding in molecule, i.e. vibration, rotation etc., in different frequency, which is a specific value that can characterize bonding and functional group in the sample solution. The range of infrared in electromagnetic spectrum that condition information on organic compound lied in 4000 – 660 cm-1. (cm-1 is the number of waves per second). The basic of molecular vibration can be separated into 2 forms;

1. Stretching vibration. There are 2 types of stretching vibration, which are symmetric stretching and asymmetric stretching.

2. Bending vibration occurs between isotopes with different bond angles, which make atomic position changes from former ligand. There are 4 types of angle alteration between 2 bonds;

2.1 Scissoring: the tremor bent in the same plane but in opposite directions

2.2 Rocking: the tremor bent in the same plane and the same direction

2.3 Wagging: the tremor bent in one plane with the direction of motion as well. Vibration is usually due to the non-linear molecules.

2.4 Twisting, the tremor off the plane, but alternating the direction of motion.

Fig. 2. 32. Stretching and bending vibration mode [34]

Many types of bond stretch in different frequencies so IR spectrum indicates the type of bonding, of the existing that exists molecules. In table 2.3 show stretching frequencies of bonding in general organics.

Table 3 The stretching frequencies of bonding in general organics.[34]

Bond	Type of Compound	Wavenumber(cm^{-1})
C-H	Alkanes	2960 - 2850 (s) stretch
		1470–1350(v)scissoring and bending
	CH$_3$ Umbrel Deformation	1380(m-w)Doublet–isopropyl,t-butyl
C-H	Alkenes	3080 – 3020(m) stretch
		1000 – 675(s) bend
C-H	Aromatic Rings	3100 – 3000(m)stretch
	Phenyl Ring Substitution Bands	870 – 675(s) stretch
	Phenyl Ring SubstitutionOvertones	2000 – 1600(w) fingerprintregion
C-H	Alkynes	3333 – 3267(s) stretch
		700 – 610(b) bend
C=C	Alkenes	1680 – 1640(m,w) stretch
C≡C	Alkynes	2260 – 2100(w,sh) stretch
C=C	Aromatic Rings	1600, 1500(w) stretch
C-O	Alcohol,Ether,Carboxylic acid,Ester	1260- 1000(s) stretch
C=O	Aldehydes,Ketones,Carboxylicacid, Ester	1760 – 1670(s) stretch
O-H	Monomeric–Alcohols,Phenols	3640 – 3160(s,br) stretch
	Hydrogen–bonded–Alcohols,	3600 – 3200(b) stretch
	Carboxylic acids	3000 – 2500(b) stretch
N-H	Amines	3500 – 3300(m) stretch
		1650 – 1580(m) stretch
C-N	Amines	1340 – 1020(m) stretch
C≡N	Nitriles	2260 – 2220(v) stretch
NO$_2$	Nitro Compounds	1660–1500(s)asymmetricalstretch
		1390–1260(s) asymmetricalstretch

v- variable, m – medium, s – strong, br – broad,w - weak

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1. Materials

3.1.1. ZnO nanoparticles

ZnO nanoparticles used in this study were purchased from Nano Materials Technology (Thailand). Size of ZnO nanoparticles were labeled by the company as < 20 nm, < 200 nm and < 1μm. Morphology and primary size of ZnO nanoparticles were studied by Scanning Electron Microscope, SEM (JEOL LSM 6400). Samples were prepared by dropping ZnO suspension onto a glass slide and coating with gold.Particles size distribution of ZnO nanoparticles were also studied by laser light scattering technique (Mastersizer 2000, Malvern Instruments). Samples were prepared by dispersing ZnO nanoparticles in deionized water using ultrasonic probe.

3.1.2. Diacetylene monomers

Diacetylene or DA monomers used in this study were 5,7-hexadecadiynoic acid (HDDA) and 10,12- pentacosadiynoic acid (PCDA), commercially available from fluka.

In this study, we choose 5,7-hexadecadiynoic acid (HDDA) and 10,12-pentacosadiynoic acid (PCDA) for diacetylene monomer to prepared polydiacetylenen (Fig 3.1.). In PCDA, molecule structure of side chain has two triple bonds in position 10 and 12. In HDDA, molecule structure of side chain has two triple bonds too, but in position 5 and 7. The tail of structure is alkyl tail that have hydrophobic property or do not like water. The head of structure is carboxcyl group (-COOH), which has polar on head group of structure so it has hydrophilic property. It can be easily prepared by dispersing in water by using ultrasonics and appropriate to use in molecule sensor beacause mostly molecule was detected in biology such as

protein carbohydrate and neucliic acid etc can dissolve in only water so water solubility or water compatibility was important for design conjugated polymer sensors.

Fig. 3. 1. Structure of 5,7-hexadecadiynoic acid (HDDA) and 10,12- pentacosadiynoic acid (PCDA).

3.2. Preparation of PDA/ZnO nanocomposites

In this study, PDA/ZnO nanocomposites were prepared from two types of diacetylene monomer.To study the effects of ZnO concentration, we used the as-received ZnO of 65.31 nm and varied concentrations to be 5, 10, 15, 20, 30 and 50 wt% based on the monomers. Weights of DA monomer and ZnO in this study are shown in Table 3.1. For effects of ZnO size, as-received ZnO nanoparticles of size 65.31, 174.56 and 224.54 nm were used along with the calcined batches of those nanoparticles at 1000°C. In this case, concentration of ZnO nanoparticles was fixed at 10wt%. Nanocomposites were prepared as followed

Table 4 Weigh of diacetylene monomer and ZnO nanoparticles used in preparation
of PDA/ZnO nanocomposites

ZnO (wt%)	HDDA (g)	ZnO (g)	PCDA (g)	ZnO (g)
5	0.0070	0.0004	0.0076	0.0004
10	0.0070	0.0007	0.0076	0.0009
15	0.0070	0.0010	0.0076	0.0013
20	0.0070	0.0014	0.0076	0.0019
30	0.0070	0.0021	0.0076	0.0033
50	0.0070	0.0070	0.0076	0.0076

1. Diacetylene monomers were purified by dissolving in chloroform. Polymerized materials were removed by filtered the suspensions with 0.45 μm pore size nylon membrane and heated to completely evaporate chloroform.

2. ZnO nanoparticles were dispersed in deionized water by probe sonication (Ultrasonic liquid processors, Vibra-CellTM VC 505) for 10 minutes.

3. ZnO suspensions were added into the purified diacetylene monomers. Then, the mixed suspensions were sonicated by ultrasonic bath at around 80°C for 1 h to co-disperse the ZnO nanoparticle and diacetylene monomer into aqueous medium.

4. The suspensions were kept at~4°C for 24 h.

5. Finally, the suspensions were irradiated by ordinary UV light ($\lambda \sim 254$ nm, 10 W) for 1 min for 5,7-hexadecadiynoic acid (HDDA) and 5 min for 10,12-pentacosadiynoic acid (PCDA) . Schematic of preparation of PDA/ZnO nanocomposites is illustrated in Fig.3.2.

Fig. 3. 2. Prepration of PDA/ZnO nanocomposite

3.3. Characterizations of polydiacetylene/ZnO nanocomposites

3.3.1. Morphology

Morphology of nanocomposite was studied by Transmission Electron Microscope, TEM (JEM – 2100). Samples were prepared by drop casting the suspensions onto copper grid. By measured sample of concentration 5wt% and 30wt% for poly(PCDA)/ZnO and 5wt%, 15wt% and 30wt% for poly(HDDA)/ZnO nanocomposite. For study morphology and primary size of the nanocomposite.

3.3.2. Absorption spectra

Light absorption properties of nanocomposites were studies by UV-Vis Spectrometer (Specord S 100 B, Analytik Jena) by diluting nanocomposite suspension with deionize water. The suspension was filled in quartz cuvette and measured the absorbance in the wavelength (λ) of 300 – 800 nm. Deionize water used as a blank reference.

3.3.3. Functional group

Functional groups of nanocomposite were investigated by FT-IR (Perkin Elmer Spectrum GX spectromerter) in transmittance mode to study interfacial interaction between ZnO nanoparticles and PDA head groups. The samples were prepared by mixing dried PDA/ZnO nanocomposites with KBr and pressed into pellets. The measurement was carried in the range of wavenumber from 1300-3000 cm-1.

3.4. Colorimetric response of PDA/ZnO nanocomposites

3.4.1. Thermochromic behavior

Thermochromic behaviors of PDA/ZnO nanocomposites were investigated by heating from 30°C to 90°C. Photograps of nanocomposite at various temperatures were taken. Then, the color stablility of PDA/ZnO nanocomposite was investigated by heating to 90°C then cooling to 30°C for cycles. Photographs and absorbance spectra (UV-Vis spectrometer (Analytik Jena Specord S100)) were recorded for 10 heating-coolimg cycle. %CR at each cycle was calculated using equation from chapter 2.2.

3.4.2 pH response

Colorimetric response to pH of PDA/ZnO nanocomposites were investigated by using UV-Vis spectrometer (Analytik Jena Specord S100). The pH of the suspensions was adjusted by adding NaOH or HCl solution into the aqueous suspensions to adjust pH in the range of 0.95 – 13.05. Photograps and absorbance spectra were recorded. The colorimetric response (%CR) was calculated by equation

in chapter 2.2. to quantify the magnitude of blue-red transition of the PDA vesicles and the nanocomposites. For the poly(PCDA)/ZnO the color changed from blue to purple with absorbance at 580 nm. Therefore, the calculation of PB value used A_{580} (purple) instead of A_{540}. For poly(HDDA)/ZnO nanocomposite, absorption peaks of blue and purple phases were detected at 660 nm and 600 nm, respectively. Therefore, we used the absorbance at 660 nm (A_{660}(blue)) and 600 nm (A_{600}(purple)) for the calculation of CR values.

3.5. Experimental diagram

```
┌─────────────────────────────────────┐
│ 10,12-pentacosadiynoic acid (PCDA)   │        ┌──────────────────────────────┐
│                                      │        │ ZnO    nanoparticles+DI  water: │
= │     5,7-hexadecadiynoic acid         │        │ ZnO  concentrations of 5,10, 15, │
│                                      │        │ 20, 30 wt%                       │
└─────────────────────────────────────┘        └──────────────────────────────┘
```

- Dissolved in chloroform
- Filtered 0.45 μm
- Evaporated chloroform at ~50 $^{\circ}$C

Ultrasonicated for 5 min

| Purified DA monomers | ZnO suspension |

Mixed suspension of DA
monomers and ZnO suspensions

- Ultrasonicated at 80 °C for 60 min
- Refrigerated overnight (4°C)
- UV irradiated (λ ~ 254 nm, 10 W)

PDA/ZnO nanocomposite suspensions

- Absorbance spectra
  (UV-VIS Spectrophotometer)

- Microstructure (TEM)

- Functional group (FT-IR)

Colorimetric response to pH and
temperature(UV-vis spectrophotometer)

Part II Effects of ZnO size

ZnO nanoparticles 10 wt% + DI water:
- as-received (size 65.31 nm, 174.56 nm, 224.54 nm)

calcined of size 65.31 nm, 174.56 nm, 224.54 nm at 1000°C

= 10,12-pentacosadiynoic acid (PCDA)

5,7-hexadecadiynoic acid

- Dissolved in chloroform
- Filtered 0.45 μm
- Evaporated chloroform at ~50 $^\circ$C

Ultrasonicated for 5 min

Purified DA monomers

ZnO suspension

Mixed suspension of DA monomers and ZnO suspensions

- Ultrasonicated at 80 °C for 60 min
- Refrigerated overnight (4°C)
- UV irradiated (λ ~ 254 nm, 10 W)

PDA/ZnO nanocomposite suspensions

- Absorbance spectra
  (UV-VIS Spectrophotometer)
- Microstructure (TEM)
- Functional group (FT-IR)

Colorimetric response to pH and temperature(UV-vis spectrophotometer)

CHAPTER lV

RESULTS AND DISCUSSION

In this work, two types of DA monomers, 10,12-pentacosadiynoic acid (PCDA)and 5,7-hexadecadiynoic acid (HDDA) (see Fig. 4.1a) were used for preparing the PDA/ZnO nanocomposites. Fig. 4.1b shows the ionic interaction between $Zn-OH_2^+$ group on the surface of ZnO nanoparticle and –COO group of these two PDAs head group. Variations of alkyl chain length affects chain rigidity including inter- and intrachain interactions resulting in changing of their color transition behaviors[19].

Fig. 4. 1. (a) Monomer structures used in this work (b) ionic interaction between ZnO-OH_2^+ group on the surface of ZnO nanoparticle and –COO group of these two PDAs head group[19]

4.1. Effects of ZnO concentration

4.1.1. Morphologies of PDA/ZnO nanocomposites with various ZnO concentrations

Morphologies of PDA/ZnO nanocomposites are illustrated in Fig. 4.2. TEM images show that both poly(PCDA)/ZnO nanocomposites prepared with (a) 5wt% and (b) 30wt% ZnO exhibit spherical shapes. The results are similar to the previous work in our group as shown in Fig 4.2, which also reveals that poly(PCDA) coats on surface of ZnO nanoparticles as layer-by-layer. For poly(PCDA)/ZnO nanocomposites prepared with 17 wt% ZnO. There is no changes in primary size of poly(PCDA)/ZnO nanocomposite with increasing ZnO nanoparticles. However, the size distribution of the nanocomposite is narrower at lower ZnO concentration. For poly(HDDA)/ZnO nanocomposite system (Fig. 4.3c-e), the nanocomposite exhibits irregular shape. Primary size of poly(HDDA)ZnO nanocomposite clearly decreases when the concentration of ZnO is increased to 10 and 30wt%. It should be noted that the white dot in Fig. 4.3.(a) and (e) is defects of copper grid.

Fig. 4. 2. TEM image of poly(PCDA)/ZnO nanocomposite at 17wt% concentration of ZnO nanoparticle.

Fig. 4. 3. TEM image of (a)poly(PCDA)/ZnO 5wt% (b)poly(PCDA) 30wt% (c)
poly(HDDA)/ZnO 5wt% (d) poly(HDDA)/ZnO 10wt%
(e) poly(HDDA)/ZnO 30wt%

For poly(HDDA)system, it has been reported that the nanocomposite size can
be up to about 600 nm with average size of 200 nm. While in system of
poly(HDDA)/ZnO nanocomposite, their average size decreases to 150 nm. Thus, the
presence of ZnO nanoparticles influences the self-assembling behavior of the DA
monomer[1].The result in this study shows that at 5wt% ZnO, the poly(HDDA)/ZnO
nanocomposite possibly forms both pure poly(HDDA) and nanocomposites, leading
to large size. Increasing ZnO concentrations to 10wt% and 30wt%, nanocomposite
could be completely formed on the surface, leading to smaller size as shown in Fig.
4.3 (c-e). All TEM images show that PDAs coat on ZnO surface.

4.1.2. Optical properties of PDA/ZnO nanocomposites with various ZnO concentrations

Absorption spectra of blue phase of poly(PCDA)/ZnO and poly(HDDA)/ZnO nanocomposites prepared by using 5-50 wt% ZnO are illustrated in Fig.4.4. (a) and (b), respectively. Absorption spectra of aqeous suspensions of pure PDA assemblies in blue phase are also included for comparison purpose. The spectrum of pure poly(PCDA) exhibits a typical peak at 637 nm with broad shoulder at 586 nm. The red shift of spectrum is much larger in poly(HDDA) system, where λ_{max} is detected at 673 nm with board shoulder around 600 nm. For the system of poly(PCDA)/ZnO nanocomposites (Fig.4.4a), all spectra exhibit a typical peak at 640 nm with broad shoulder at 590 nm. A weak, low-energy band at about 675 nm is also observed, indicating the existence of PDA chains with relatively long conjugation length. In the system of poly(HDDA)/ZnO nanocomposites with 10-50 wt% ZnO (Fig. 4.4b) absorbance spectra exhibit a peak at 660 nm with broad shoulder at 600 nm. However, at 5wt% ZnO, the λ_{max} is detected at ~ 680 nm similar to the spectrum of pure poly(HDDA). This indicates the increase in conjugation length of PDA backbone when their alkyl chain length is shorted and brings to the increase in PDA chain rigidity, which in turn promotes the molecular packing. At increasing ZnO concentrations from 20wt% to 50wt%, both nanocomposite systems exhibit a new peak at 370 nm, corresponding to UV absorption by ZnO.

Fig. 4. 4. Absorption spectra of PDA/ZnO nanocomposites in blue phase (a)

poly(PCDA)/ZnO nanocomposites (b) poly(HDDA)/ZnO nanocomposite

The relative concentrations of poly(PCDA)/ZnO and poly(HDDA)/ZNO nanocomposites are calculated using the absorbance at λ_{max}, which are at 640 nm and 660 nm for poly(PCDA)/ZnO and poly(HDDA)/ZnO nanocomposites, respectively. The results in Fig. 4.5a and b can be used to imply the quantity of polymerized materials after irradiating with UV. In poly(PCDA)/ZnO, 5wt% ZnO nanocomposite are not stable. Its color fluctuates from batch to batch. Thus, the spectra are not used to calculate the relative nanocomposite concentration. The nanocomposite prepared by using 10wt% ZnO provides the highest concentration of polymerized nanocomposite. The aqueous suspension exhibits in the darkest deep blue color. With increasing the concentration of ZnO to 20-30wt%, the relative concentration of the nanocomposite significantly decreases. At ZnO concentration of 50wt%, the relative concentration of the polymerized nanocomposite is the lowest. The aqueous suspension shows the lightest blue color, cloudy and easily precipitates.

Result of the poly(HDDA)/ZnO nanocomposite is illustrated in Fig.4.5b. At 5wt% ZnO, the aqueous suspension exhibits purple phase due to the existence of poly(HDDA), which is unstable at room temperature. Thus, relative concentration of the 5wt% ZnO nanocomposite is not calculated to compare with the others. At 10-30wt% ZnO, the relative concentration of the poly(HDDA)/ZnO nanocomposite are similar. The lowest concentration is found for the nanocomposites with 50wt% ZnO, in which the suspension is blue and cloudy.

Since peak shifting is not clearly observed for the nanocomposites prepared with various ZnO concentrations (Fig. 4.3), arrangement of PDAs on ZnO surface are similar. However, ZnO concentration affects the amount of polymerized materials, which in turn, affects the final concentration of the nanocomposites. At 10-15 wt% ZnO, the aqueous suspensions are deep blue, showing high amount of polymerized materials. On the other hand, at 30-50 wt%, the suspensions with pale blue are observed, indicating less polymerized materials. This could be due to fewer amounts of monomers on ZnO surface with separate distance too long to be polymerized. In addition, high ZnO amounts could block UV during polymerization by UV irradiation.

Thus, there is insufficient UV for polymerization in the system with high ZnO amounts.
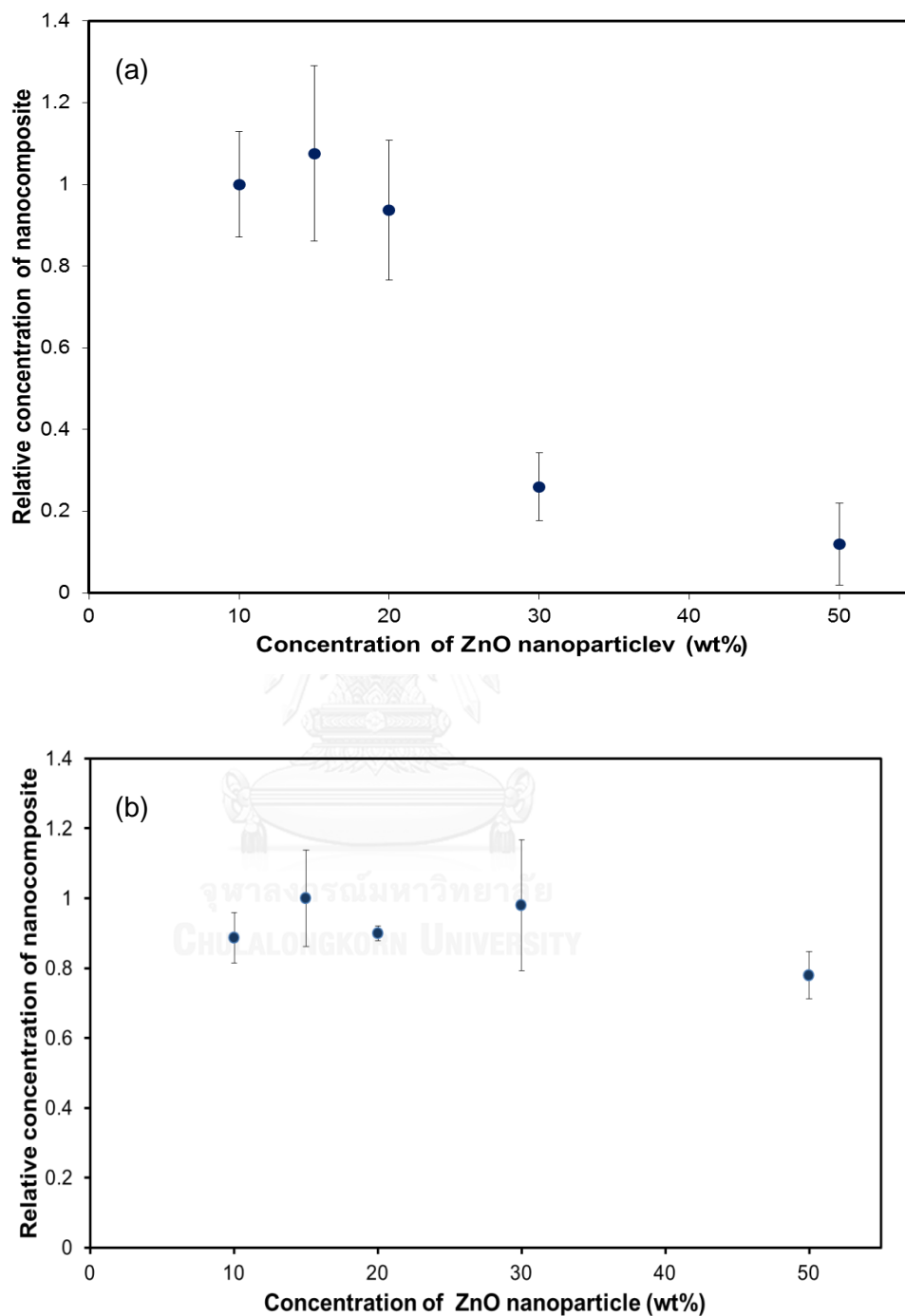

Fig. 4. 5. Relative concentration of (a) poly(PCDA)/ZnO nanocomposites and
(b) poly(HDDA)/ZnO nanocomposite prepared by using 5 to 50wt% ZnO

4.1.3. Functional groups of PDA/ZnO nanocomposites with various ZnO concentrations

The interactions between surface of ZnO nanoparticles and PDA head group are investigated by utilizing infrared (IR) spectroscopy. Fig. 4.6. compares the IR spectra of the pure PDAs and the PDA/ZnO nanocomposites prepared by using various concentrations of ZnO nanoparticles. For both pure PDAs and nanocomposites, the peak at 2848, 2918 and 2954 cm^{-1} correspond to V_s(CH2), V_{as}(CH$_2$) and V_{as}(CH$_3$), respectively. The pure PDAs exhibit a broad peak near 1690 cm-1 indicating hydrogen-bonded carbonyl stretching of –COOH head group. Peaks range from 1470 to 1420 cm^{-1} are assigned to methylene scissoring, δ (CH$_2$), of the alkyl side chain.

In the system of poly(PCDA)/ZnO nanocomposites (Fig. 4.6a), the new peak appears at 1535 and 1396 cm^{-1}, corresponding to antisymmetric, V_{as}(COO), and symmetric, V_s(COO), stretching vibrations, respectively, of carboxylate anion[20]. These results are in agreement with our previous study, which support the existence of ionic interaction between the Zn-OH$_2^+$ group at the surface of ZnO nanoparticles and the carboxylate head group of PDAs. A weak peak at 1720 cm^{-1} indicated vibration of –COOH groups that do not form hydrogen bonds with their neighboring groups is observed, especially in the nanocomposites prepared by using 20wt% and 50wt% ZnO. This could result from fewer amounts of monomers on ZnO surface with large separate distance.

In system of poly(HDDA)/ZnO nanocomposite prepared by using ZnO concentration of 10wt% and 20wt% ZnO (Fig. 4.6b) show interesting pattern. The absorption bands corresponding to V_{as}(COOH), V_s(COOH) and the stretching vibrations of carboxylate anion split into multiple peaks. The peaks at 1587, 1544 and 1523 cm-1 indicate V_{as}(COO) while V_s(COO) vibration shows peaks at 1423, 1400 and 1373 cm-1. It was reported that the location of V_s(COO) and V_{as}(COO) of PDA carboxylate head group depended on type of specific interaction with cation. Therefore, interactions with various strength between Zn-OH$_2^+$ group at ZnO surface and poly(HDDA) head group are observed, indicating by differences in vibrational

spring constant. This could result from rigid conjugated backbone and short alkyl side chain of the poly(HDDA) that is forced to curve around the substrate.

Fig. 4.6b shows that spectrum of the poly(HDDA)/ZnO with 5wt% ZnO exhibits peaks at 1690 and 1712cm^{-1}, which is similar to spectrum of the pure poly(HDDA). These peaks are attributed to hydrogen-bond carbonyl stretching of COOH group. This indicates the existence of the pure poly(HDDA) in the poly(HDDA)/ZnO nanocomposite system prepared with 5 wt% ZnO. With increasing ZnO to 10wt% and 20wt%, peaks at 1690 and 1720 cm^{-1} clearly decrease, indicating formation of more nanocomposite in the system.
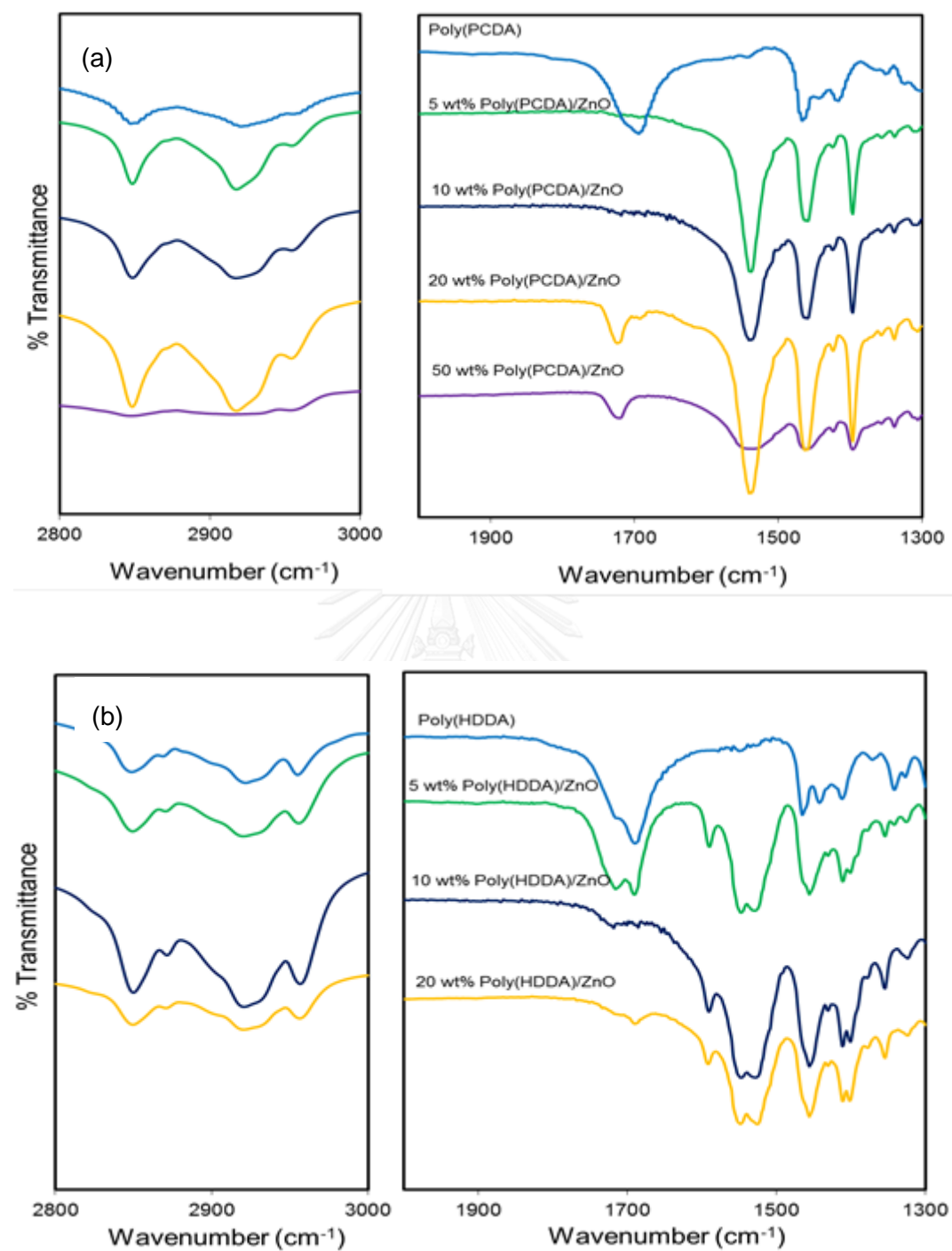
จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

Fig. 4. 6. FT-IR spectra of (a) poly(PCDA)/ZnO and (b) poly(HDDA)/ZnO nanocomposites prepared by using various concentrations of ZnO. Samples are in blue phase and embedded in KBr pellets. .

4.1.4. Thermochromism of PDA/ZnO nanocomposites with various ZnO concentrations

It is known that PDAs exihibit color transition when subjected to thermal stimulus by incease temperature. The dynamics of PDA segments including conjugated backbone and alkyl tail are promoted. The rearrengement of molecular segments occurs when the inter-intrachain interaction within PDA assemblies are sufficiently weaken, leading to changing of the electronic state of conjugated backbone. The HOMO-LUMO energy gap of the perturbed PDAs is widen, resulting in the color transition from blue to purple, red or orange. The color transition of PDAs depends on the extent of local perturbation. Previous studies showed that decreasing of alkyl chain length in system of PDAs with carboxylic head group leads to the decrease of color-transition temperature[19]. In this study, we attmpt to control color transition temperature of PDA/ZnO nanocomposites. Effects of DA monomers and concentration of ZnO are focused in this part.

PDA/ZnO nanocomposites change color from blue to red or purple when subjected to increasing temperature. Color transition temperature and the color at 90°C of the nanocomposites are affected by ZnO concentration and alkyl chain length of the DA monomer[15]. Fig. 4.7. illustrates thermochromic response of the poly(PCDA)/ZnO in the temperature range of 30-90°C. Poly(PCDA)/ZnO prepared with 5 wt% ZnO exhibits blue color, indicating that the nanocomposites are completely formed. At 10-15 wt% ZnO, the poly(PCDA)/ZnO change color at 70°C. With increasing ZnO concentration (20-50 wt%), the color transition temperature increases to 80°C. At 90°C, the nanocomposites with 5-15 wt% ZnO turn red, while the ones with 20-50 wt% ZnO are purple. Upon cooling to 30°C, all poly(PCDA)/ZnO change back to their original blue color. For the nanocomposites prepared with 30 and 50wt% ZnO, precipitation occur during the experiment.

The increase in color transition temperature with increasing ZnO concentration could be explained based on PDA layer thickness. At low ZnO concentration, PDA molecules coat on ZnO surface as a multilayer structure. The molecular interaction is weaker for the layer further from ZnO surface. Therefore, the

outermost layer could distort and change color at relatively low temperature. At higher ZnO concentration, PDA layer on the ZnO surface are thinner. Interactions between ZnO and PDA are stronger. Thus, the nanocomposites change color at higher temperature.

Thermochromism of the poly(HDDA)/ZnO are show in Fig. 4.8. Results exhibit similar trend to those of the poly(PCDA)/ZnO. Poly(HDDA)/ZnO at 5wt% ZnO exhibit in purple phase while higher of ZnO concentration nanocomposite exhibit in blue phase. This is because, at 5 wt%, there are both pure poly(HDDA) and poly(HDDA)/ZnO nanocomposites, which exhibit purple and blue, respectively. Therefore, the final color of the poly(HDDA)/ZnO nanocomposites prepared with 5wt% ZnO are purple.

The color transition occurs when increases temperature to 60°C. At 90°C, all poly(HDDA)/ZnO exhibit purple color with more red phase in the ones with lower ZnO concentrations. Reversible thermochromism is also observed upon cooling to 30°C. Same explanations based on PDA layer thickness are also applied.

It can be observed that color transition of the poly(HDDA)/ZnO is less obvious comparing to the poly(PCDA)/ZnO. This effect of alkyl chain length has been reported in the previous work [20]. In the poly(HDDA)/ZnO, there are various types of interfacial interactions. These interactions of different strength cause a gradual change in color of the nanocomposites. In addition, short alkyl chain of poly(HDDA) increases backbone rigidity, causing difficulties in color transition.

Fig. 4. 7. The color transition of poly(PCDA)/ZnO nanocomposites upon increasing
temperature from 30℃ to 90℃ and then cooling to 30℃

Fig. 4. 8. The color transition of poly(HDDA)/ZnO nanocomposites upon increasing temperature from 30°C to 90°C and then cooling to 30°C

4.1.5. Thermal stability of PDA/ZnO nanocomposites with various ZnO concentrations

The absorption spectra of poly(PCDA)/ZnO nanocomposites are illustrated in Fig. 4.9. λ_{max} is at 640 nm and vibronic peak is at 590 nm, exhibiting deep blue color at 30°C. When increasing the temperature to 90°C, λ_{max} shifts to 540 nm while broad shoulder peak at 670 disappears. The nanocomposites exhibit purple in color. After cooling the aqueous suspensions to 30°C, the nanocomposites reverse to the initial phase, indicating high thermal stability of poly(PCDA)/ZnO nanocomposites.

Thermal stability of the poly(PCDA)/ZnO is investigated. The aqueous suspensions are subjected to multiple heating/cooling for 10 cycles, switching

between 30 and 90°C. The purple color of poly(PCDA)/ZnO nanocomposites at 90°C reverses to original blue color after cooling to 30°C. In system of poly(PCDA)/ZnO, the color reversibility can be repeated for more than 10 heating/cooling cycle as shown in the plot of CR value (see Fig. 4.10.), indicating high thermal stability.

Absorbance spectra of poly(HDDA)/ZnO subjected to heating-cooling cycles are shown in Fig. 4.11. At 5wt% ZnO, the aqueous suspension at room temperature is purple with peaks at 680 and 540 nm. With increasing of temperature to 90°C, blue shift to about 540 nm occurs and the peak continuously grows with increasing cycle. After cooling to 30°C, peak are observed at 660 nm. With 10-50 wt% ZnO, the aqueous suspensions show peak at 660 nm and vibronic peak at 600 nm. Increasing temperature to 90°C, the peak at 610 nm and the vibronic peak at 540 nm are observed. The nanocomposites exhibit purple phase. After cooling to 30°C, the spectra show peaks at 660 nm and 540 nm. The nanocomposites exhibit blue phase. Thermal stability of the poly(HDDA)/ZnO is illustrated in Fig. 4.12.

The poly(HDDA)/ZnO nanocompositeswith 5 wt% ZnO changes back to its original color in the first two heating-cooling cycles. The reversible process is incomplete in the next two cycles. After that, the nanocomposites exhibit irreversible thermochromic behavior. At 20-50wt% ZnO, the nanocomposites exhibit an incomplete reversible process in the first cycle. Later on, the nanocomposites exhibit irreversible thermochromic behavior.

Fig. 4. 9. Absorption spectra during heating-cooling cycle of poly(PCDA)/ZnO nanocomposites at (a) 5wt% (b) 10wt%(c) 15wt% (d) 20wt% (e) 30wt% (f) 50wt% ZnO

Fig. 4. 10. Changes of %CR during 10 heating/cooling cycles switching between 25 $^{\circ}$C and 90oC of poly(PCDA)/ZnO nanocomposites at (a) 5wt% (b) 10wt%(c) 15wt% (d) 20wt% (e) 30wt% (f) 50wt% ZnO
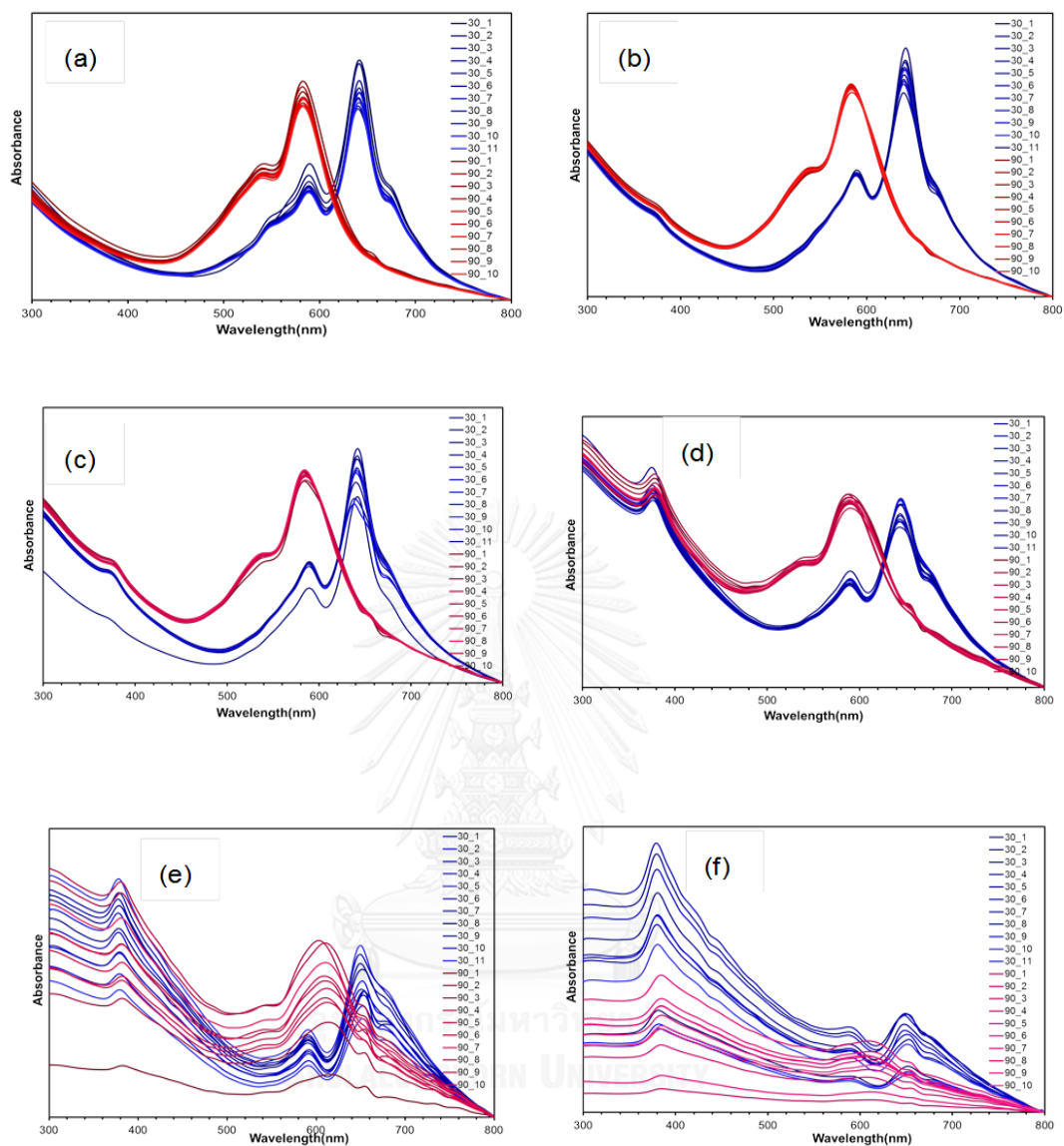
Fig. 4. 11. Absorption spectra during heating-cooling cycle of poly(HDDA)/ZnO nanocomposites at (a) 5wt% (b) 10wt%(c) 15wt% (d) 20wt% (e) 30wt% (f) 50wt% ZnO
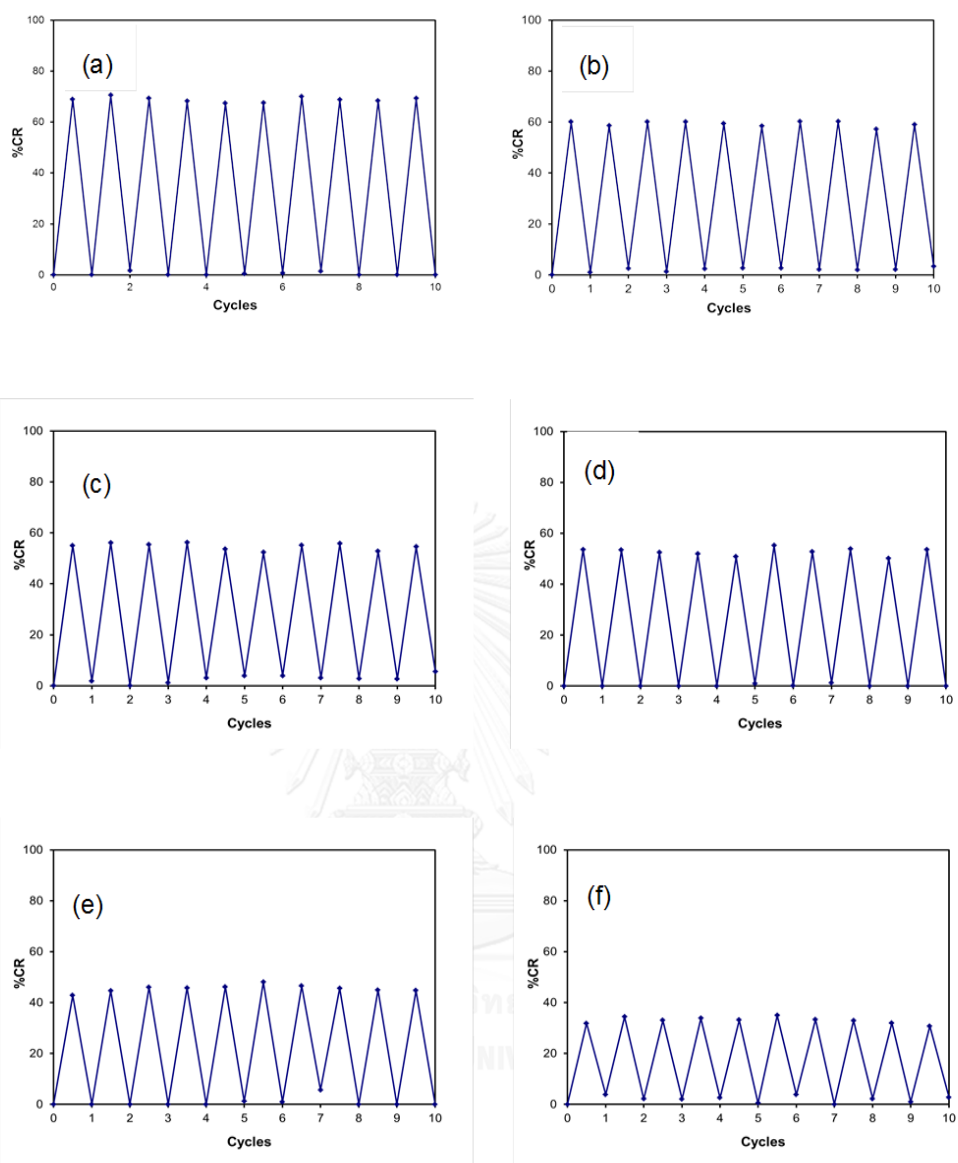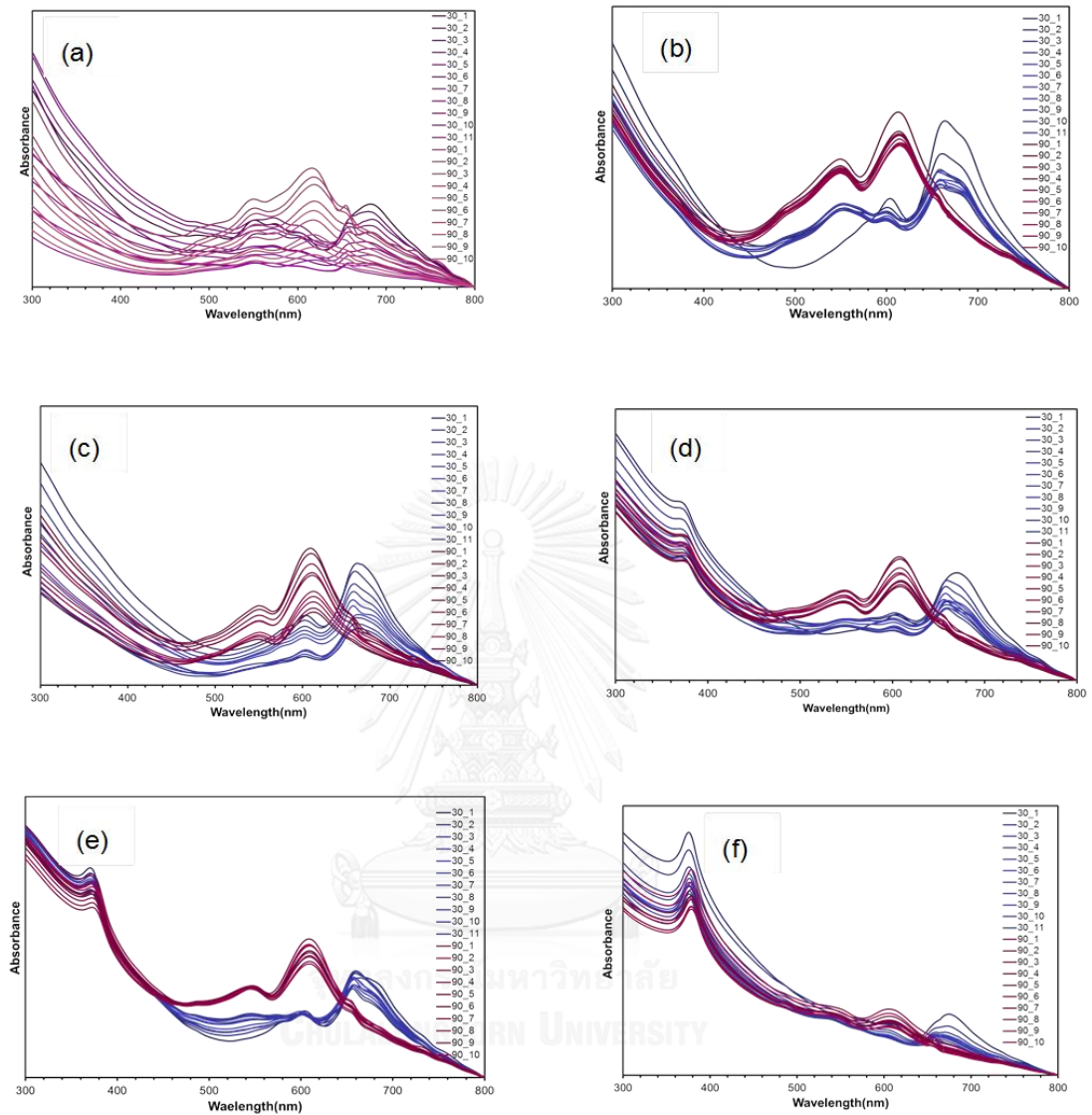
Fig. 4. 12. Changes of %CR during 10 heating/cooling cycles switching between 30°C and 90°C of poly(HDDA)/ZnO nanocomposites at (a) 5wt% (b) 10wt%(c) 15wt% (d) 20wt% (e) 30wt% (f) 50wt% ZnO

Photograph showing color stability of the poly(PCDA)/ZnO and poly(HDDA)/ZnO nanocomposites during heating-cooling cycles are in Fig. 4.13. The poly(PCDA)/ZnO nanocomposites exhibit high color stability (Fig. 4.13a). Their thermochromic transition is fully reversible for 10 heating-cooling cycles. The strong interfacial interactions in this system limit the segmental reorientation upon increasing temperature, so the original chain conformation can be returned upon cooling to room temperature[19]. At 5-10 wt% ZnO, the suspensions exhibit partially reversible when subjected to heating/cooling cycles. This is due to combination of pure poly(HDDA) and poly(HDDA)/ZnO nanocomposite in the system. At 15 wt% ZnO, the nanocomposite exhibits completely reversible. For 20 wt% ZnO, the reversibility is almost complete with a trace of peak at 540 nm. At 20-50wt% ZnO, the nanocomposites exhibit partially reversible in %CR plots. However, this is likely due to precipitation of the suspensions that causes errors in calculations.

The results of poly(HDDA)/ZnO are shown in Fig. 4.13b. A complete reversible thermochromic behavior can be obtained at ZnO concentrations of 15 wt%. This also results from variation in PDA layer thickness of nanocomposites prepared with different ZnO concentrations.

Fig. 4. 13. Color stability of the aqueous suspensions of (a) poly(PCDA)/ZnO and (b) poly(HDDA)/ZnO nanocomposites subjected to heating-cooling between 30℃ to 90℃ for 10 cycles.

4.1.6. Color response to pH of PDA/ZnO nanocomposites with various ZnO concentrations

Absorption spectra of poly(PCDA)/ZnO nanocomposites measured upon the decrease of pH are illustrated in Fig. 4.14. It can be observed that the addition of H+ ion affect the color of the nanocomposite suspensions. In system of poly(PCDA)/ZnO nanocomposites, the new peak at 550 nm is detected when pH decreased. The peak continuously grows upon further adding H+ ions. At 5-20wt% ZnO, the nanocomposites change color from blue to purple when pH decreased to lower than 3. At 30-50wt% ZnO, the nanocomposites change color from blue to purple at around pH ~ 1. Decreasing of pH also causes dissolution of ZnO. Therefore, the peak at 370nm, corresponding to UV absorbance of ZnO, disappears when pH is lower than 5. From the plot of %CR shown in Fig. 4.16a, it can be observed that the degree of color transition upon decreasing pH is lower for the nanocomposites with higher ZnO concentration. At 5-15wt%ZnO, the nanocomposite change color at around pH ~ 6 while 20-30wt% change color at lower pH. At 50wt%, the nanocomposite do not change color

Fig. 4. 14. Absorption spectra upon decreasing pH of poly(PCDA)/ZnO

nanocomposites prepared with various ZnO concentrations (a) 5wt%

(b) 10wt%(c) 15wt% (d) 20wt% (e) 30wt% (f) 50wt% ZnO

Absorption spectra upon increasing pH of poly(PCDA)/ZnO nanocomposite suspensions are shown in Fig. 4.15. It can be observed that the absorption patterns of all nanocomposites are not different from the original when adjusting pH from 7 to 12. At pH ~ 13, the minor peak at ~ 547 nm is observed in 50wt% ZnO nanocomposite, corresponding to red phase. The aqueous suspension exhibits purple color. The plot of %CR shown in Fig. 4.16b indicates that the nanocomposites does not change color at pH lower than 12. Increasing pH to 13, a slight color change is observed only for the 50wt% ZnO nanocomposite.
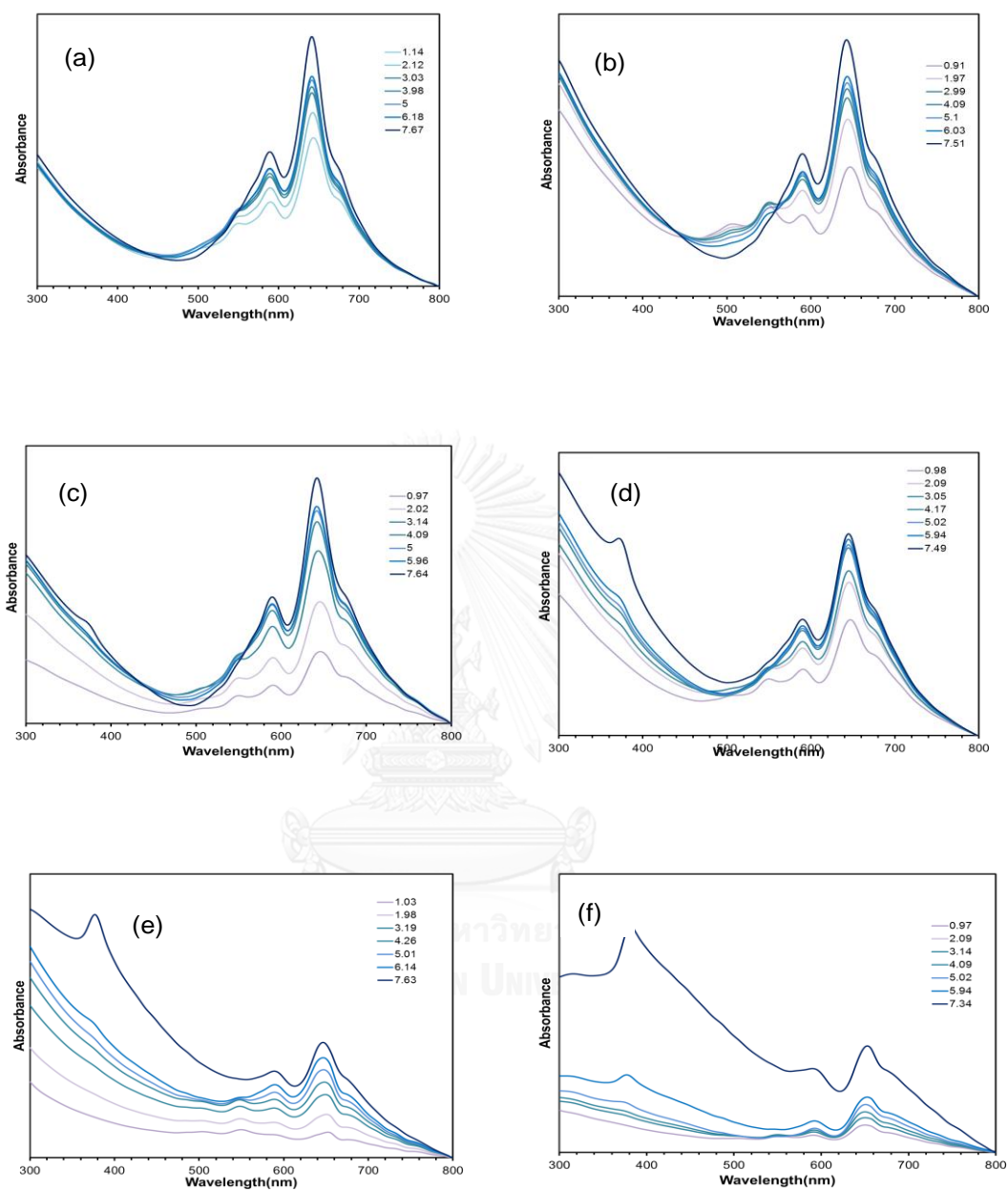
Fig. 4. 15. Absorption spectra upon increasing pH of poly(PCDA)/ZnO nanocomposites prepared with various ZnO concentrations (a) 5wt% (b) 10wt%(c) 15wt% (d) 20wt% (e) 30wt% (f) 50wt% ZnO

Fig. 4. 16. Colorimetric response to (a) acid and (b) base of poly(PCDA)/ZnO nanocomposites prepared with various ZnO concentrations

The color photograph upon variation of pH of poly(PCDA)/ZnO nanocomposites are illustrated in Fig. 4.17. The nanocomposites with 5-20wt% ZnO are purple when decreasing pH to 2, while the nanocomposites with 30-50wt% ZnO exhibit purple when decreasing pH to 5. In basic condition, poly(PCDA)/ZnO, at 5-30wt% ZnO, the nanocomposites does not change color. At 50wt%, the nanocomposite change color from blue to purple at pH around ~13.

Fig. 4. 17. Color photograph upon variation of pH of poly(PCDA)/ZnO nanocomposites prepared with various of ZnO concentrations

Absorption spectra upon decreasing pH of poly(HDDA)/ZnO nanocomposites are illustrated in Fig.4.18. The color transition when adding H^+ ion is clearly observed in all nanocomposites. The new peak at 540 nm is detected when decreasing pH to around 5 and peak continuously grow upon further adding H^+ ions. At 5wt% ZnO, the nanocomposite starts with purple phase and exhibits color transition from purple to red at pH 4. The complete blue-red transition is observed at pH ~ 3. At 10-50wt% ZnO, the nanocomposites exhibit color transition from blue to purple at pH ~5. The complete blue-red transition is observed at pH ~ 3. The plot of %CR in Fig. 4.20a shows the color transition at pH ~ 5 in all nanocomposites. Similar to the system of poly (PCDA)/ZnO nanocomposites, the magnitude of color change is higher for the poly(HDDA)/ZnO nanocomposites with lower ZnO concentrations. For example, at pH 1, the %CR value of the poly(HDDA)/ZnO at 10wt% ZnO is around 65% while the 50wt% ZnO nanocomposite shows %CR of only 35%.
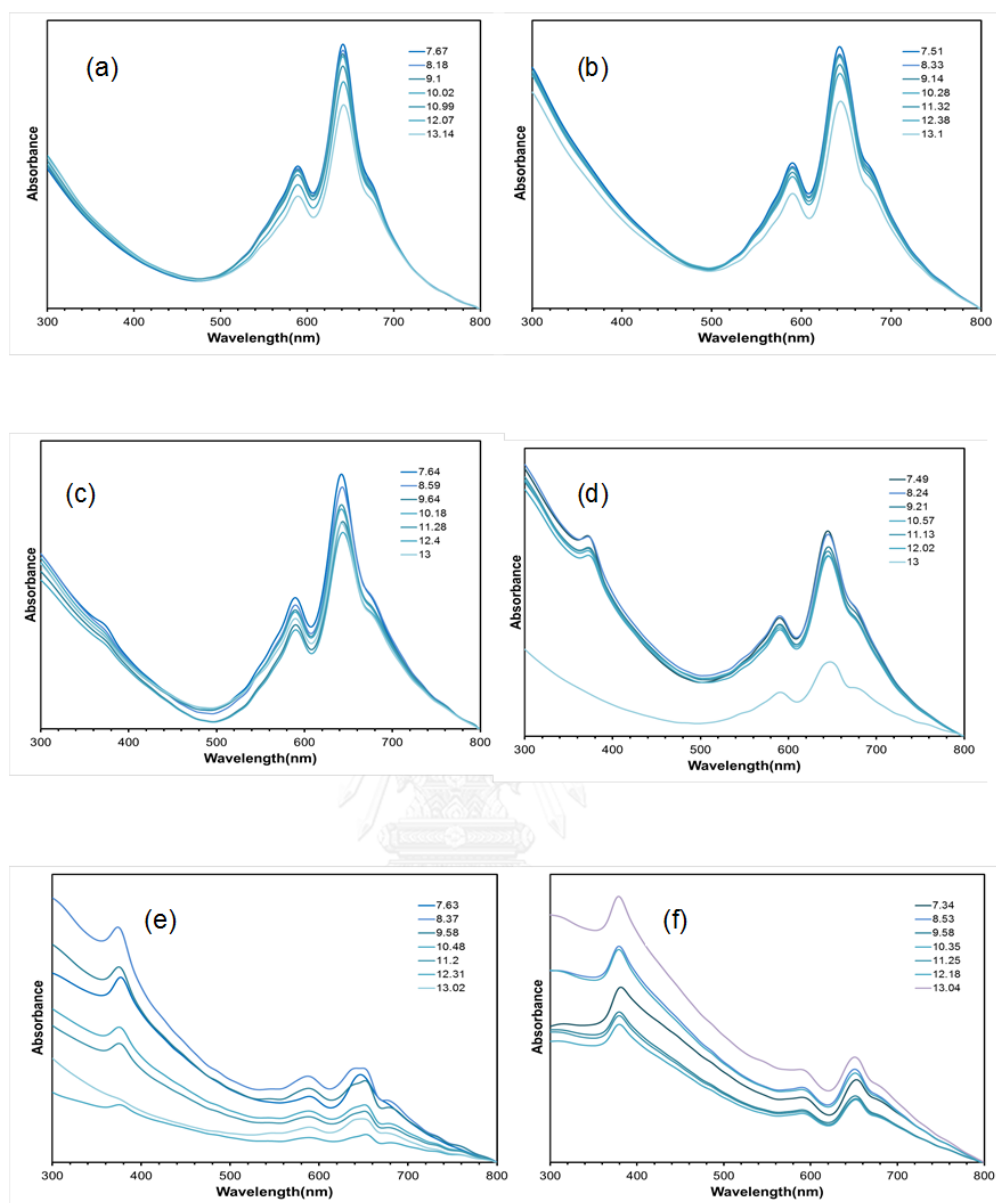
Fig. 4. 18. Absorption spectra upon decreasing pH of poly(HDDA)/ZnO

nanocomposites prepared with various ZnO concentrations (a) 5wt% (b)
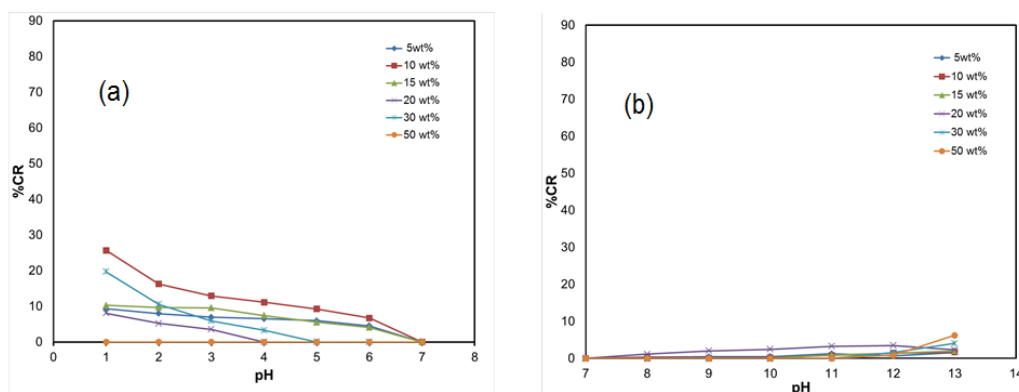
10wt%(c) 15wt% (d) 20wt% (e) 30wt% (f) 50wt% ZnO

The absorption spectra upon increasing pH of poly(HDDA)/ZnO nanocomposites are shown in Fig.4.19. The color transition when adding OH⁻ ions is clearly observed in all nanocomposites. A small peak around 550 nm is detected at pH ~11 and the peak continuously grows when increasing pH. Poly(HDDA)/ZnO nanocomposite at 5wt% ZnO starts with purple phase and does not exhibit color transition when increasing pH to ~12. Slight color change is observed at pH ~13 from decreasing of the absorbance spectra of nanocomposite. For the nanocomposites with higher ZnO concentrations, the complete blue-red transition occurs at pH more than 13 with a small peak at 650 nm. The plot of %CR shown in Fig. 4.20b indicates that color transition of nanocomposites takes place at pH ~11. The magnitude of color change decreases when the concentration of ZnO is higher
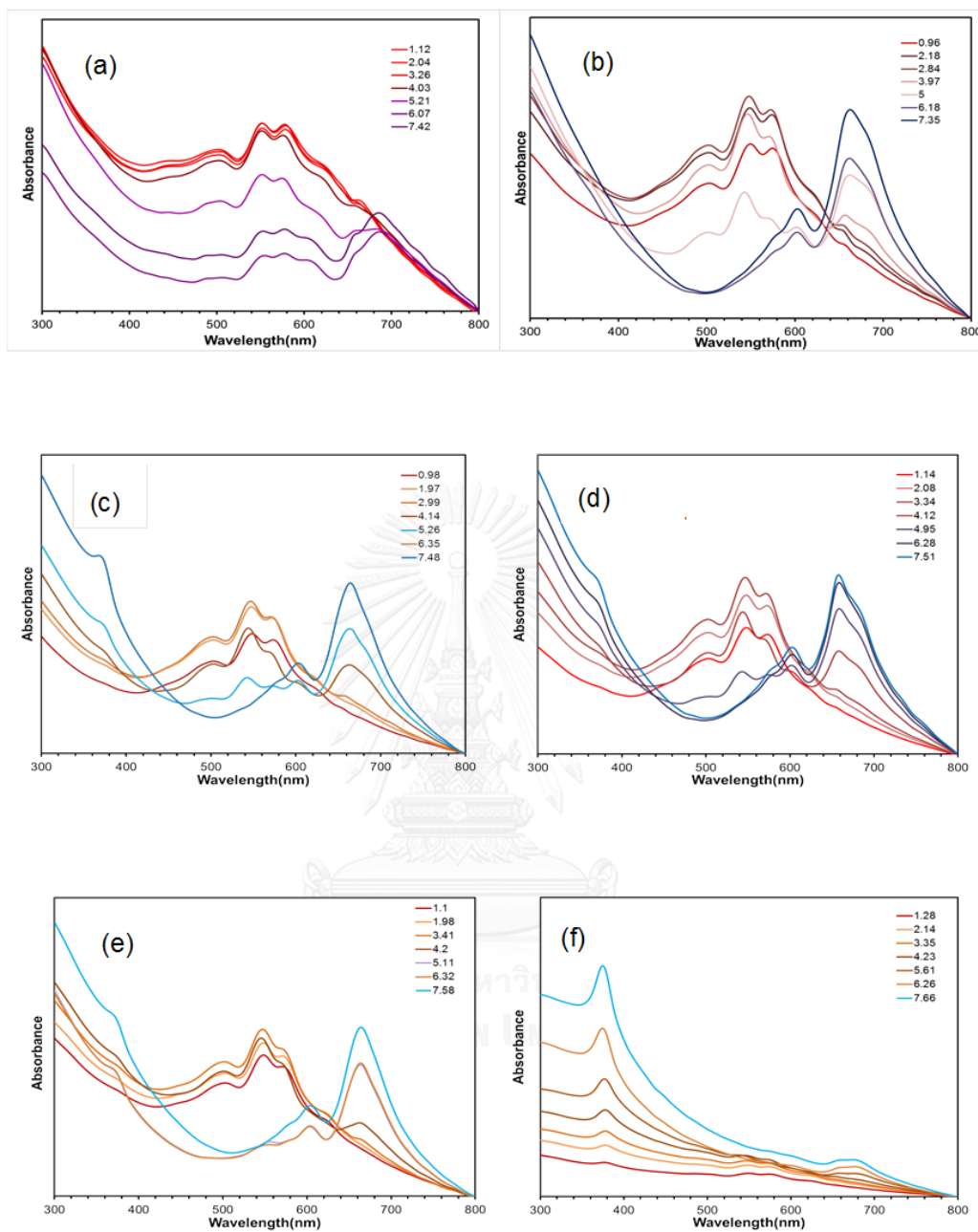
Fig. 4. 19. Absorption spectra upon increasing pH of poly(HDDA)/ZnO

nanocomposites prepared with various ZnO concentrations (a) 5wt%

(b) 10wt%(c) 15wt% (d) 20wt% (e) 30wt% (f) 50wt% ZnO

Fig. 4. 20. Colorimetric response to (a) acid and (b) base of poly(HDDA)/ZnO nanocomposites prepared with various ZnO concentrations

The color photograph upon variation of pH of poly(HDDA)/ZnO nanocomposites are illustrated in Fig. 4.21. It can be clearly observed that the color transition of samples takes place in both acid and basic conditions. At 5wt% ZnO, the nanocomposite starts with purple phase. The nanocomposite exhibits color transition at pH 5 and 13. At 10-50wt% ZnO, the nanocomposites exhibit color change at pH 5 and 11.

Fig. 4. 21. Color photograph upon variation of pH of poly(HDDA)/ZnO

nanocomposites prepared with various of ZnO concentrations

Colorimetric response to pH of PDA/ZnO nanocomposites has been previously reported. In low pH region, the ZnO nanoparticles decompose, leading to breaking of the interactions between carboxylate head groups and positive ions at ZnO surface. The repulsive ionic interaction between free carboxylate head groups causes segmental rearrangement, resulting in the color transition. For high pH region, OH⁻ ions abstract acidic protons of the carboxylic head groups, resulting in negatively charge carboxylate groups, which repels each others. In system of poly(HDDA)/ZnO nanocomposite, the dispersive of PDA layer is weak cause of its short constituent alkyl segmants. Thus, the replusive force can be induce the segmental rearrangement of some poly(HDDA) chains, effective to partial color transition. For poly(PCDA)/ZnO nanocomposite, the alkyl segment are longer. Further addition of OH- ions (pH 13), the dissolution of ZnO nanoparticles occurs, resulting in color transition of the system[20]. Fig. 4. 22 illustrates the proposed mechanism for color transition of PDA/ZnO nanocomposite under acidic and basic conditions.

Fig. 4. 22. The proposed mechanism for color transition of poly(HDDA)/ZnO nanocomposite at various of pH [21]

To support the proposed mechanism, IR spectra of blue-phase poly(HDDA)/ZnO and red-phase poly(HDDA)/ZnO obtained at pH = 3.1 and pH = 12.61 are reported in the article [20]. IR spectrum of the blue phase shows peaks at 2848, 2918, and 2954 cm-1 corresponding to V_s(CH2), V_{as}(CH2), and V_{as}(CH3), respectively. The V_{as}(COO) peaks are detected at 1590, 1548, and 1530 cm-1 while the peaks at 1412, 1403, and 1380 cm-1 are assigned to V_s(COO) vibration. This observation indicates that the strength of interfacial interactions between poly(HDDA) carboxylate heads and ZnO nanoparticles is not homogeneous. For red phase, peaks are shown at the same position indicated that the alkyl side chains keep their conformation resulting to color transition. However, the band representing asymmetric V_{as}(COO) of carboxylate head decreases significantly in the acidic region (pH ~ 3.1) while a new band at 1690 cm-1 grows simultaneously. The appearance of this new peak indicates the presence of hydrogen-bonded –COOH head group in the system. Therefore, the decrease in pH transforms the carboxylate head of poly(HDDA) into the carboxylic one, which in turn destroys the ionic interfacial interaction with ZnO nanoparticles. The decrease in interfacial interaction allows segmental rearrangement, resulting in the color transition. Fig. 4.23 illustrates FT-IR spectra of blue-phase poly(HDDA)/ZnO and red-phase poly(HDDA)/ZnO nanocomposites obtained at pH = 3.1 and pH = 12.61.

Fig. 4. 23. FT-IR spectra of blue-phase poly(HDDA)/ZnO and red-phase

poly(HDDA)/ZnO nanocomposites obtained at pH = 3.1 and

pH = 12.61[20].

4.2. Effects of ZnO size on properties of PDA/ZnO nanocomposites

4.2.1. Morphologies of ZnO nanoparticles

The average size of as-received ZnO nanoparticles in Fig. 4.24a, b and c were determined and reported as 65.31nm, 174.56 nm and 224.42 nm, respectively. The SEM images show that ZnO nanoparticles with average size of 65.31nm exhibit spherical shape while ZnO nanoparticles with average size of 174.56nm and 224.42 nm exhibit rectangular shape. These three ZnO nanoparticles are calcined at 1000°C 2h and morphologies of particles derived from ZnO of sizes 65.31 nm, 174.56nm and 224.42 nm are shown in Fig. 4.24 d, e and f, respectively for . It can be observed that particles are fused together with surface morphology totally different from the as-received ones. Average sizes of calcined particles are in the range of 4-7 μm. Thus, by calcining, the surface area of particles could be reduced by orders of magnitude.

Fig. 4. 24. SEM image of size of ZnO nanoparticles (a) 65.31 nm (b) 174.56 (c) 224.42 nm(d) calcined 65.31 nm (e) calcined 174.56 nm and (f) calcined 224.42 nm

4.2.2. Optical properties of PDA/ZnO nancomposites prepared with ZnO of various sizes

Absorption spectra of as-prepared poly(PCDA)/ZnO and poly(HDDA)/ZnO nanocomposites prepared by using as-received ZnO with different sizes and calcined ZnO for 10wt% are illustrated in Fig. 4. 25a. In the system of poly(PCDA)/ZnO nanocomposites (a), all spectra exhibit a typical peak at 640 nm with broad shoulder at 590 nm. A weak low-energy band at about 675 nm is also observed, indicating the existence of PDA chains with relatively long conjugation length. In the system of poly(HDDA)/ZnO nanocomposite (b), the red shift can be observed. The λ_{max} is detected at 663 nm with broad shoulder around 600 nm. The nanocomposites prepared from all as-received ZnO nanoparticles and calcined 65 nm-ZnO exhibit blue phase after polymerization. Poly(HDDA)/ZnO nanocomposite tends to present some red phase when using calcined 175 nm- and 224 nm-ZnO size. The absorbance spectra show peak at 540 and 660 nm, indicating coexisting of red and blue phases.

Fig. 4. 25. Absorption spectra of as-prepared PDA/ZnO nanocomposites (a)
poly(PCDA)/ZnO and(b) poly(HDDA)/ZnO nanocomposites

4.2.3. Functional groups of PDA/ZnO nancomposites prepared with ZnO of various sizes

The interaction between surface of ZnO nanoparticles and PDA head group are investigated by utilizing infrared (IR) spectroscopy. Fig. 4.26a compares the IR spectra of pure poly(PCDA) and poly(PCDA)/ZnO nanocomposites prepared by using as-received and calcined 65 nm-ZnO. The spectrum of poly(PCDA) shows peak at 2848, 2918 and 2954 cm-1 correspond to $\mathbf{V}_s(CH_2)$, $\mathbf{V}_{as}$ (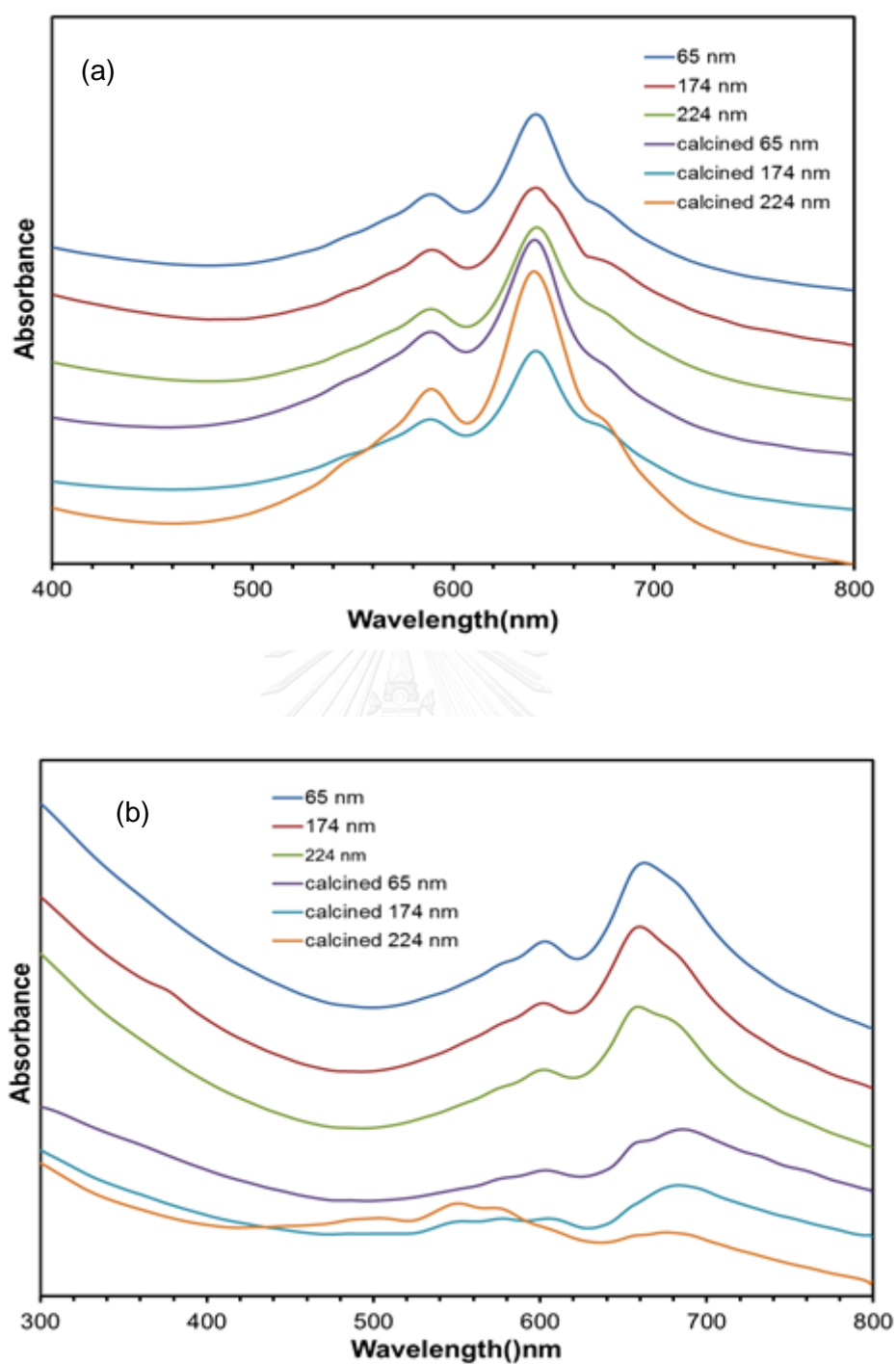CH_2) and $\mathbf{V}_{as}(CH_3)$, respectively. A broad peak near 1690 cm-1 is indicated hydrogen-bonded carbonyl stretching of –COOH head group and peaks range from 1470 to 1420 cm-1 are assigned to methylene scissoring, $\mathbf{\delta}(CH_2)$, of the alkyl side chain[19]. In the system of poly(PCDA)/ZnO nanocomposites peaks appear at 1535 and 1396 cm-1 corresponding to antisymmetric, $\mathbf{V}_{as}(COO)$, and symmetric, $\mathbf{V}_s(COO)$, stretching vibrations, respectively, of carboxylate anion[20]. This supports the occurance of ionic interaction between the $Zn\text{-}OH_2^+$ group at the surface of ZnO nanoparticles and the carboxylate head groups. Weak peaks at $1690 cm^{-1}$ and $1716 cm^{-1}$ are also observed, which indicate vibration of -COOH groups that do not form hydrogen bonds with their neighboring groups. This indicates the presence of pure poly(PCDA) in the system.

In the system of poly(HDDA)/ZnO nanocomposite prepared by using as-received 65 nm ZnO (Fig. 4.26b), the stretching vibrations of carboxylate anion split into multiple peaks. The peaks at 1587, 1544 and $1523 cm^{-1}$ indicate $\mathbf{V}_{as}(COO)$ while the peaks at 1423, 1400 and $1373 cm^{-1}$ represent $\mathbf{V}_s(COO)$. Therefore, the strength of interaction between $Zn\text{-}OH_2^+$ group at ZnO surface and poly(HDDA) head group is not homogeneous. Weak peaks corresponding to hydrogen-bond carbonyl stretching of COOH group are observed, indicating occurrence of pure poly(HDDA) in system. In the case of poly(HDDA)/ZnO nanocomposite prepared using calcined 65 nm-ZnO, the peaks indicates the existence of the stretching vibrations of carboxylate anion are observed. In addition, the peaks at $1683 cm^{-1}$ and $1702 cm^{-1}$ attributed to hydrogen-bond carbonyl stretching of COOH group are strong. This clearly indicates pure poly(HDDA) in the system.
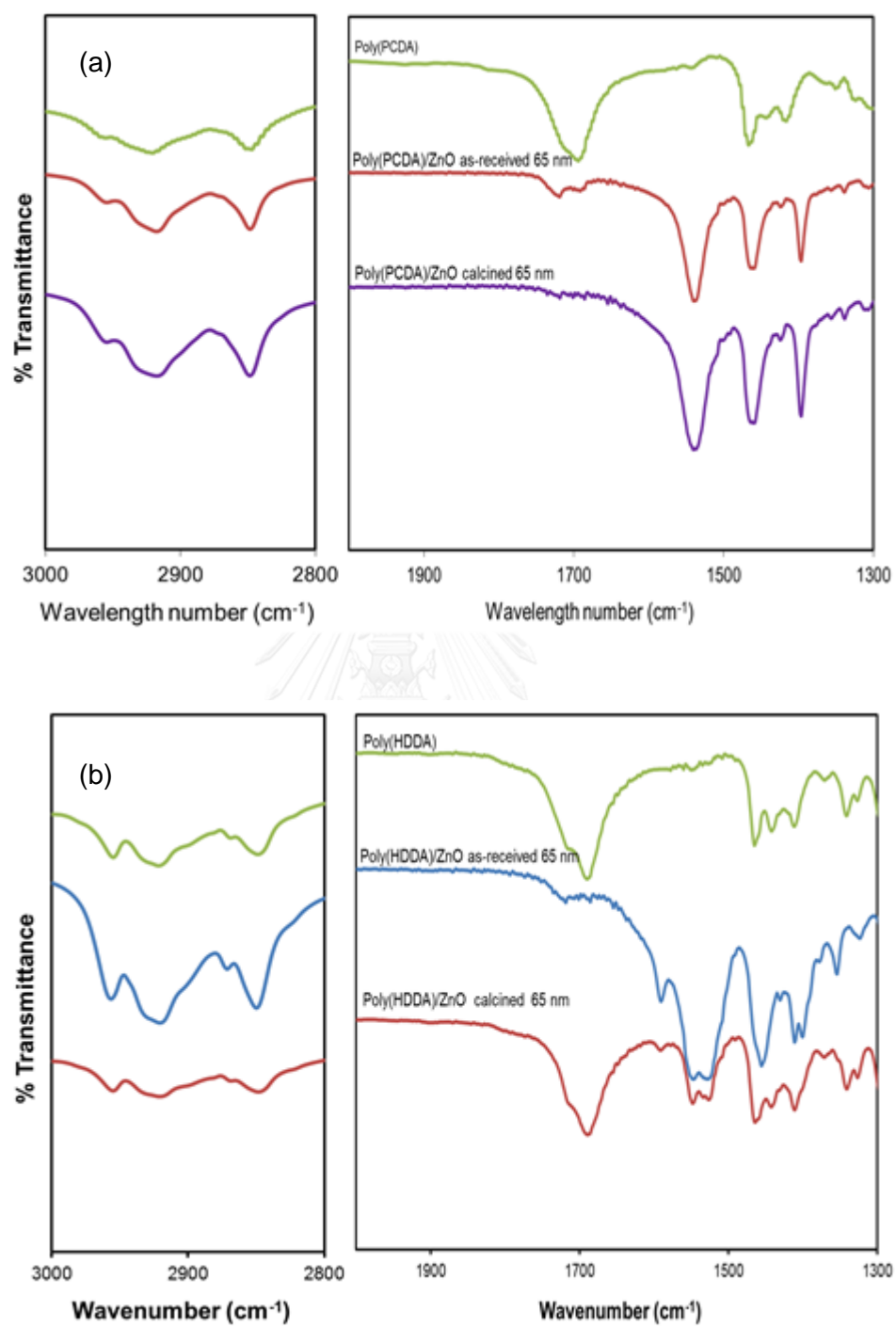
Fig. 4. 26. FT-IR spectra of (a) poly(PCDA)/ZnO and (b) poly(HDDA)/ZnO

nanocomposites prepared by using 65nm and calcined 65 nm

4.2.4. Thermochromism of PDA/ZnO nancomposites prepared with ZnO of various sizes

Thermochromism of the PDA/ZnO nanocomposites prepared by using ZnO of various sizes are investigated upon increasing temperature from 30oC-90oC. The color photographs of the aqueous suspensions of poly(PCDA)/ZnO nanocomposites are shown in Fig. 4.27. All the poly(PCDA)/ZnO nanocomposites exhibit similar color transition temperature around 70-75°C. At 90°C, all poly(PCDA)/ZnO nanocomposites turn red. After cooling to 30oC, the nanocomposite prepared using as-received ZnO of all sizes and calcined 65 nm-ZnO can completely return to the initial blue. For the nanocompoisites prepared with calcined 174 and 224 nm-ZnO, their colors partially reverse after cooling to 30°C. The absorbance spectra at 90°C (Fig.4.29) of the nanocompoisites prepared with as-received ZnO of all sizes and calcined 65 nm-ZnO show peak at 580 nm while spectra of the ones prepared with calcined 174 and 224 nm-ZnO exhibit red phase peak with λ_{max} at 540 nm.

The incomplete reversibility that takes place in the nanocomposites prepared using calcined 174 and 224 nm-ZnO could be explained based on decreasing of surface area of ZnO. By calcining, ZnO particles agglomerate and surface area decreases. The larger of the starting particles leads to the lower surface area of the calcined particles. For calcined 174 and 224 nm-ZnO, the particles could have insufficient surface area for all DA monomers to arrange on. Some DA monomers could remain in the system and form pure vesicles. Therefore, the nanocomposites exhibit partially reversible thermochromic behavior.

Fig. 4. 27. The color transition of poly(PCDA)/ZnO nanocomposites upon increasing temperature from 30℃ to 90℃ and then cooling to 30℃

Thermochromism of the poly(HDDA)/ZnO are show in Fig. 4.28. Results exhibit similar trend to those of the poly(PCDA)/ZnO. All nanocomposites exhibit color transition when increasing temperature to 50°C. At 90°C, all the nanocomposites exhibit purple color. Upon cooling to 30°C, partially reversible behavior is observed. It has been reported that poly(HDDA)/ZnO prepared with the as-received 65 nm-ZnO exhibits partially reversible thermochromism due to the heterogeneity of interfacial interactions within the system[19]. By calcining particles, effects from decreasing in surface area are included as explained in the previous section. Combining both effects, the poly(HDDA)/ZnO exhibits partially reversible thermochromism.
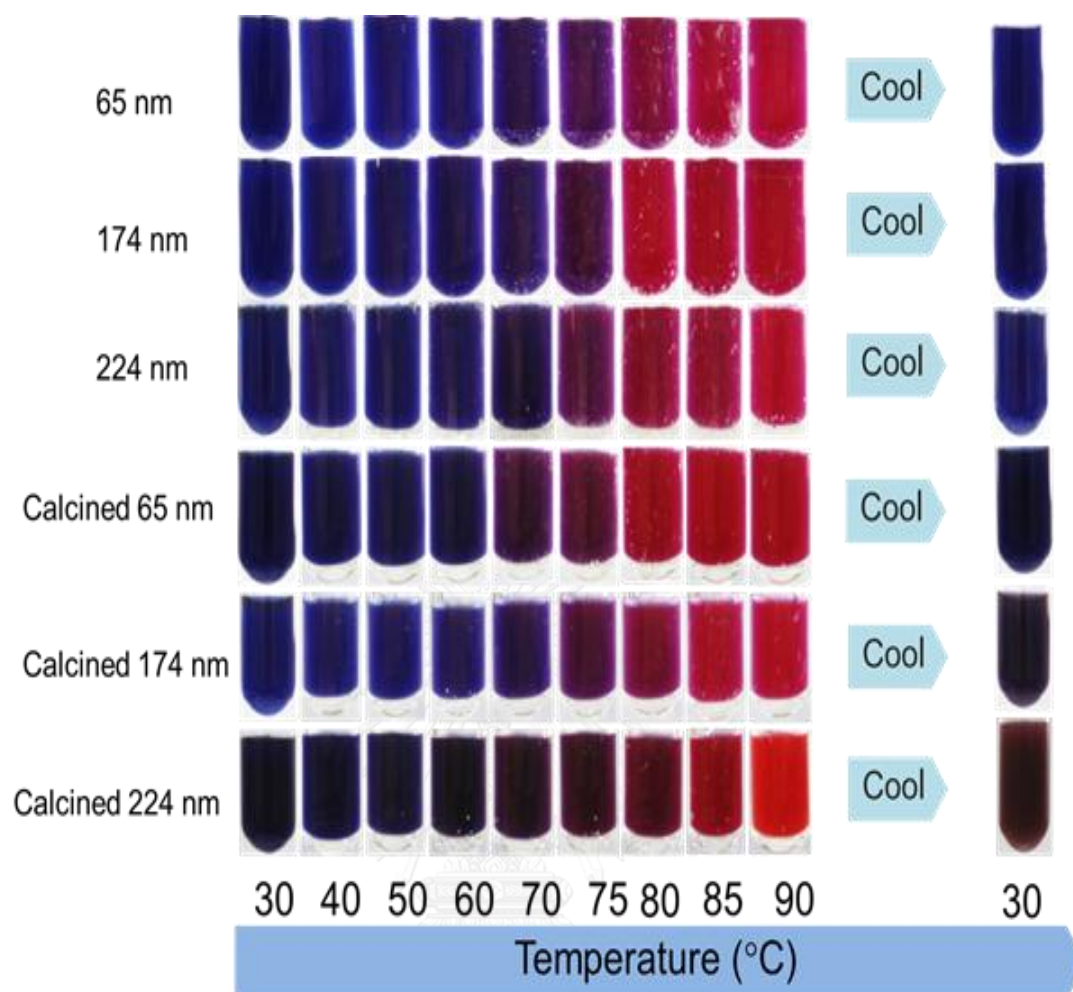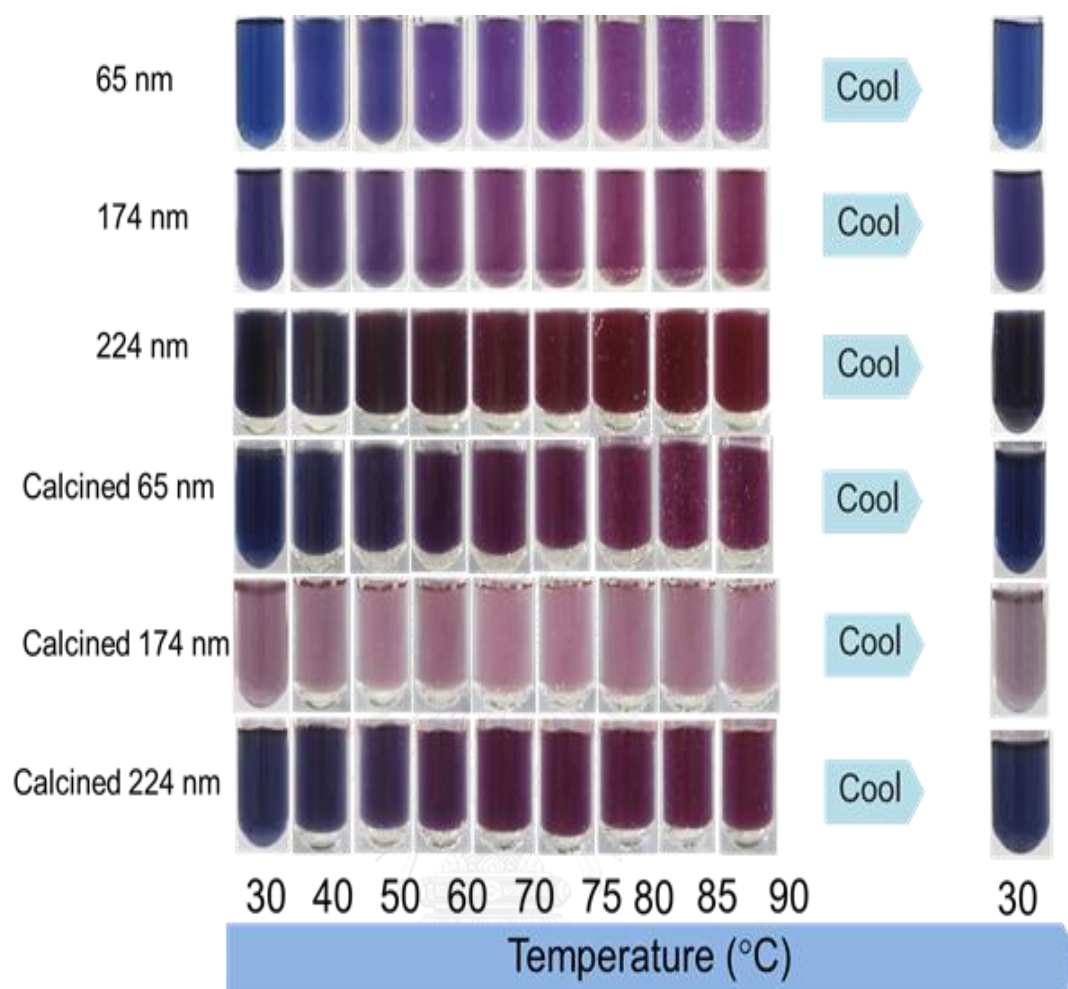
Fig. 4. 28. The color transition of poly(HDDA)/ZnO nanocomposites upon increasing temperature from 30°C to 90°C and then cooling to 30°C

4.2.5. Thermal stability of PDA/ZnO nancomposites prepared with ZnO of various sizes

The absorption spectra of all nanocomposites upon heating and cooling for 10 cycles is illustrated in Fig. 4.29. The poly(PCDA)/ZnO nanocomposites in blue phase show λmax at 640 nm and vibronic peak at 590 nm at 30oC. The poly(PCDA)/ZnO prepared with as-received ZnO of sizes 65-174 nm, spectra at 90°C show peak at 580 nm. After cooling to 30°C, peak at 640 nm recover, indicating completely reversible thermochromism of the nanocomposites. With increasing ZnO size and decreasing surface area by calcining, partially reversible thermochromism can be observed more clearly. After cooling to 30°C from 90°C, peaks at 580 and 540 nm are observed (Fig. 4.29 (c-d)). The growth of peak at 540 nm is detected in nanocomposites prepared from calcined 174 and 224 nm-ZnO. The plot of %CR values at each heating-cooling cycle is shown in Fig. 4.30. The poly(PCDA)/ZnO prepared with as-received ZnO of sizes 65-174 nm exhibit completely reversible thermochromism while the one prepared calcined 174 and 224 nm-ZnO clearly show partially reversibility.

In the system of poly(HDDA)/ZnO nanocomposite (Fig 4.31), the suspensions before subjected to heat show peak at 660 nm and vibronic peak at 600 nm. A peak at 550 nm can be observed in poly(HDDA)/ZnO nanocomposites prepared with calcined 174 and 225 nm-ZnO, corresponding to red phase in these systems. Increasing temperature to 90°C, the λ_{max} shifts to about 600 nm with a red phase peak around 540 nm. When cooling to 30°C, the poly(HDDA)/ZnO nanocomposites exhibit similar trend to the poly(PCDA)/ZnO nanocomposites. With increasing size and decreasing surface area, the nanocomposites tend to exhibit less reversibility. However, the effects are more pronounce in the system of poly(PCDA)/ZnO. The plot of CR value is shown in Fig. 4.32. The poly(HDDA)/ZnO is less stable than the poly(PCDA)/ZnO due to shorter alkyl chain length. The poly(HDDA)/ZnO nanocomposites prepared with as-received 65 nm-ZnO is completely reversible only at the first cycle. After that, the nanocomposite is partially reversible. The

nanocomposites prepard using calcined ZnO tend to exhibit lower thermal stability as partially reversible is more pronounce.

Fig. 4. 29. The color transition of poly(PCDA)/ZnO nanocomposites upon increasing
temperature from 30℃ to 90℃ and then cooling to 30℃ for 10 heating-
cooling cycles (a) 65.31 nm (b) 174.56 (c) 224.42 nm(d) calcined 65.31 nm
(e) calcined 174.56 nm and (f) calcined 224.42 nm

Fig. 4. 30. Change of CR during 10 heating/cooling cycles switching between 30 °C and 90°C of poly(PCDA)/ZnO nanocomposites at (a) 65.31 nm (b) 174.56 (c) 224.42 nm(d) calcined 65.31 nm (e) calcined 174.56 nm and (f) calcined 224.42 nm
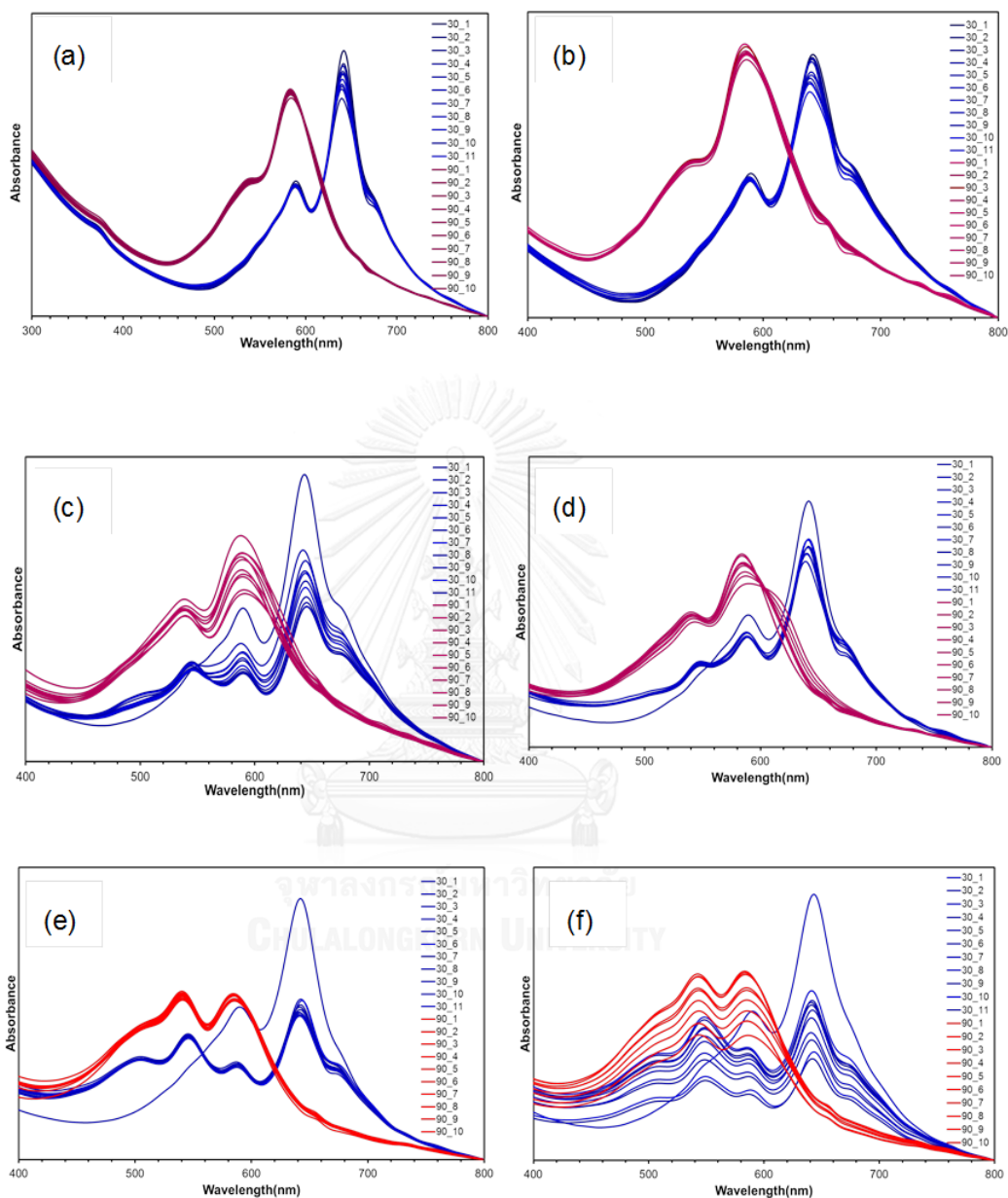
Fig. 4. 31. The color transition of poly(HDDA)/ZnO nanocomposites upon increasing temperature from 30°C to 90°C and then cooling to 30°C for 10 heating-cooling cycles (a) 65.31 nm (b) 174.56 (c) 224.42 nm(d) calcined 65.31 nm (e) calcined 174.56 nm and (f) calcined 224.42 nm
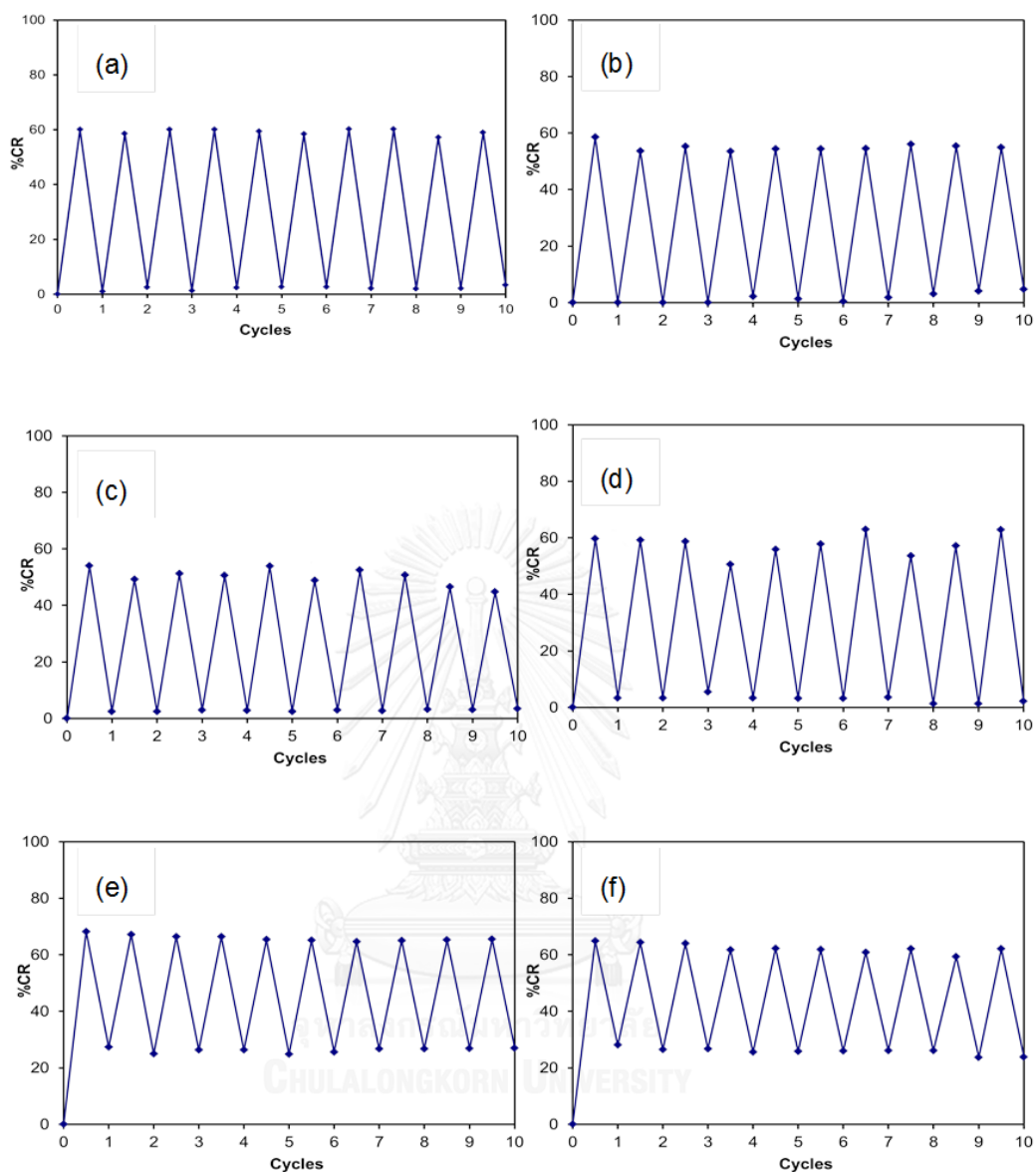
Fig. 4. 32. Change of CR during 10 heating/cooling cycles switching between 25 ^{o}C and 90°C of poly(PCDA)/ZnO nanocomposites at (a) 65.31 nm (b) 174.56 (c) 224.42 nm (d) calcined 65.31 nm (e) calcined 174.56 nm and (f) calcined 224.42 nm
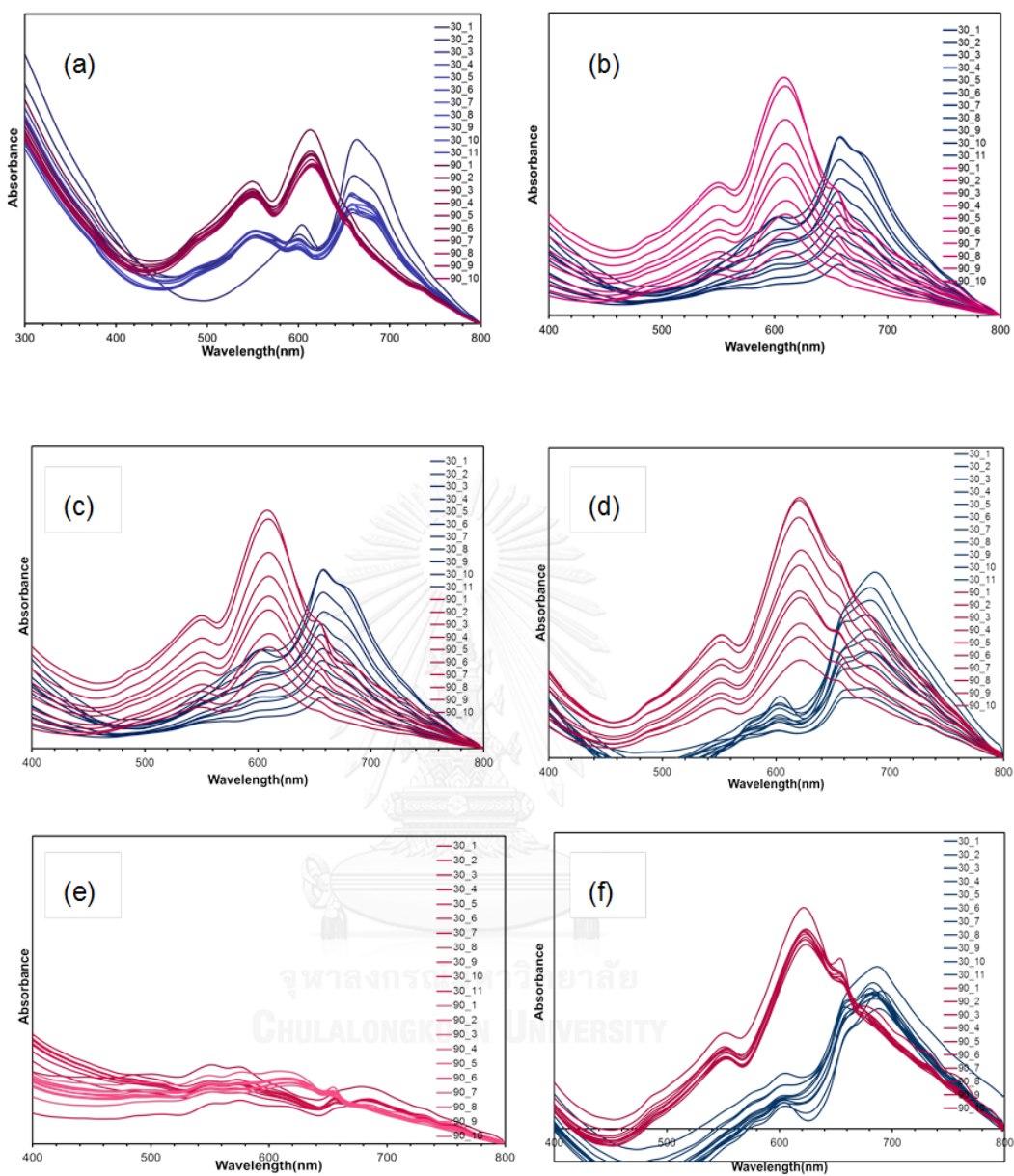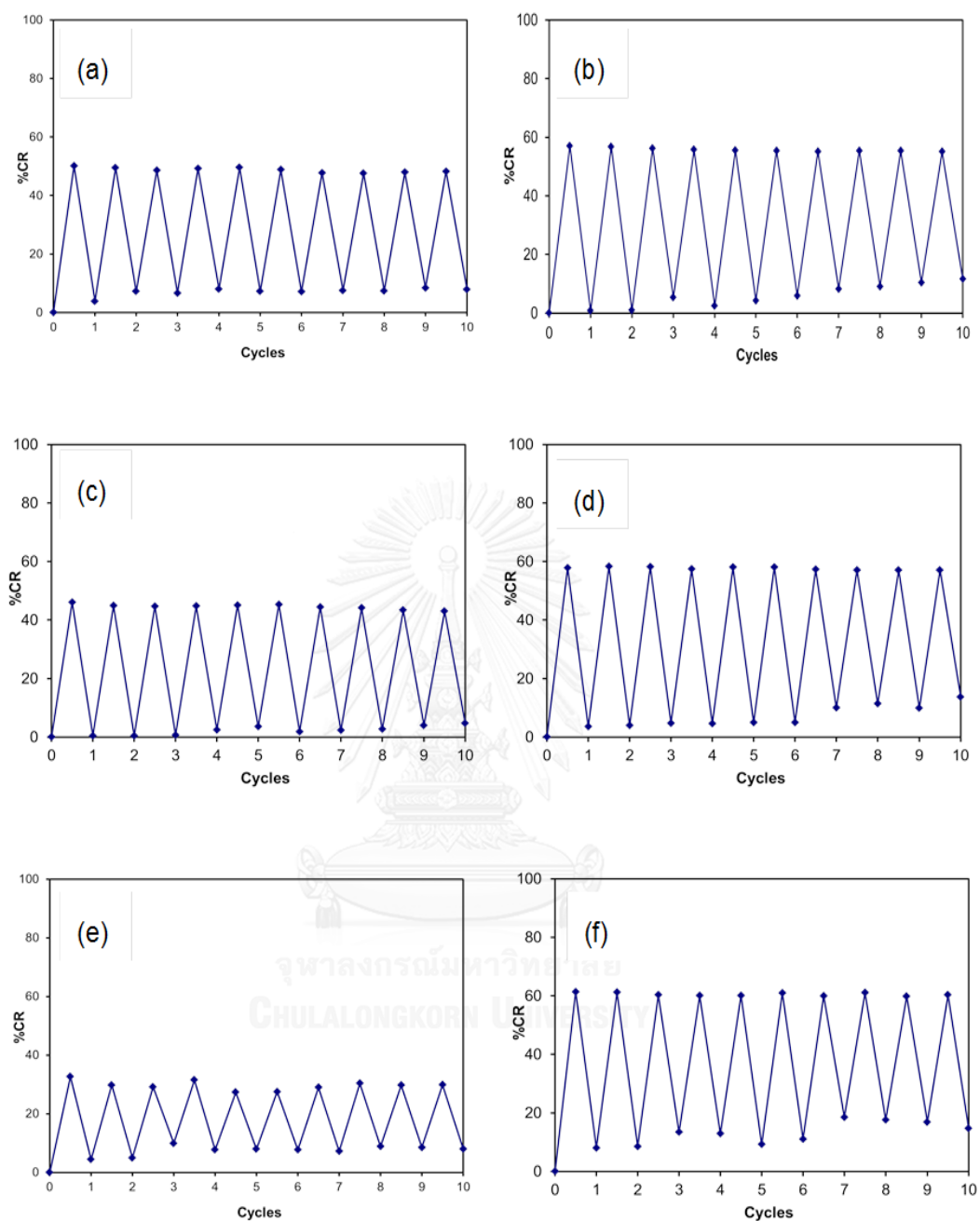
Color photographs of the aqueous suspensions of the nanocomposites subjected to multiple heating/cooling for 10 cycles are show in Fig 4.33. Temperature is switching between 30 and 90°C. The results are in agreement with absorbance spectra in Fig 4.29. and 4.31. In Fig 4.33a the system of poly(PCDA)/ZnO nanocomposite exhibit blue phase at 30°C. When increasing temperature to 90°C, poly(PCDA)/ZnO nanocomposites are in purple phase. After cooling to 30°C, the poly(PCDA)/ZnO nanocomposite prepared with as-received ZnO of all sizes and calcined 65 nm-ZnO can change back to the original blue phase. However, the nanocomposites prepared with calcined 174 and 224 nm-ZnO are partially reversible. Fig 4.33b shows that poly(HDDA)/ZnO nanocomposites at 30°C exhibit blue phase except for the one prepared with calcined 224 nm-ZnO. When increasing temperature to 90°C, the color change from blue to purple and reverse back to blue when cooling to 30°C.

Fig. 4. 33. Color stability of the aqueous suspension of (a) poly(PCDA)/ZnO and (b) poly(HDDA)/ZnO nanocomposites subjected to heating-cooling between 30℃ to 90℃ for 10 cycle.

4.2.6. Colorimetric response to pH of PDA/ZnO nancomposites prepared with ZnO of various sizes

Absorption spectra of poly(PCDA)/ZnO nanocomposites prepared with various ZnO sizes measured upon the decrease of pH are illustrated in Fig. 4.34. It can be observed that the addition of H+ ions affects the color of the nanocomposite suspensions. In the system of poly(PCDA)/ZnO nanocomposite, a new peak at 540 nm is detected when pH is decreased to around ~ 4 and the peak continuously grows upon adding H^{+} ions. However, the strong peak of the blue phase (λ~640 nm) is still remaining although the pH decreased to 0.9. From the plot of %CR shown in Fig. 4.36a, it can be observed that the degree of color transition upon decreasing pH is lower for the nanocomposites prepared using larger size of ZnO. At pH ~1, %CR of the nanocomposite prepared using as-received 65 nm ZnO is 25% while the nanocomposites prepared with larger ZnO exhibit CR up to only 12%.

Fig. 4. 34. Absorption spectra upon de creasing pH of poly(PCDA)/ZnO
nanocomposites prepared with various sizes of ZnO (a) 65.31 nm (b)
174.56 (c) 224.42 nm (d) calcined 65.31 nm (e) calcined 174.56 nm
and (f) calcined 224.42 nm

Absorption spectra upon increasing pH of poly(PCDA)/ZnO nanocomposite suspensions prepared from ZnO of various sizes is shown in Fig. 4.35. It can be observed that the absorption patterns of all nanocomposites at pH from 7-12 are similar. At pH ~13, minor peak at ~ 542 nm is slightly detected, corresponding to the red phase. The plot of %CR shown in Fig. 4.35b indicates that the color transition of all nanocomposites does not take place at pH lower than 11.
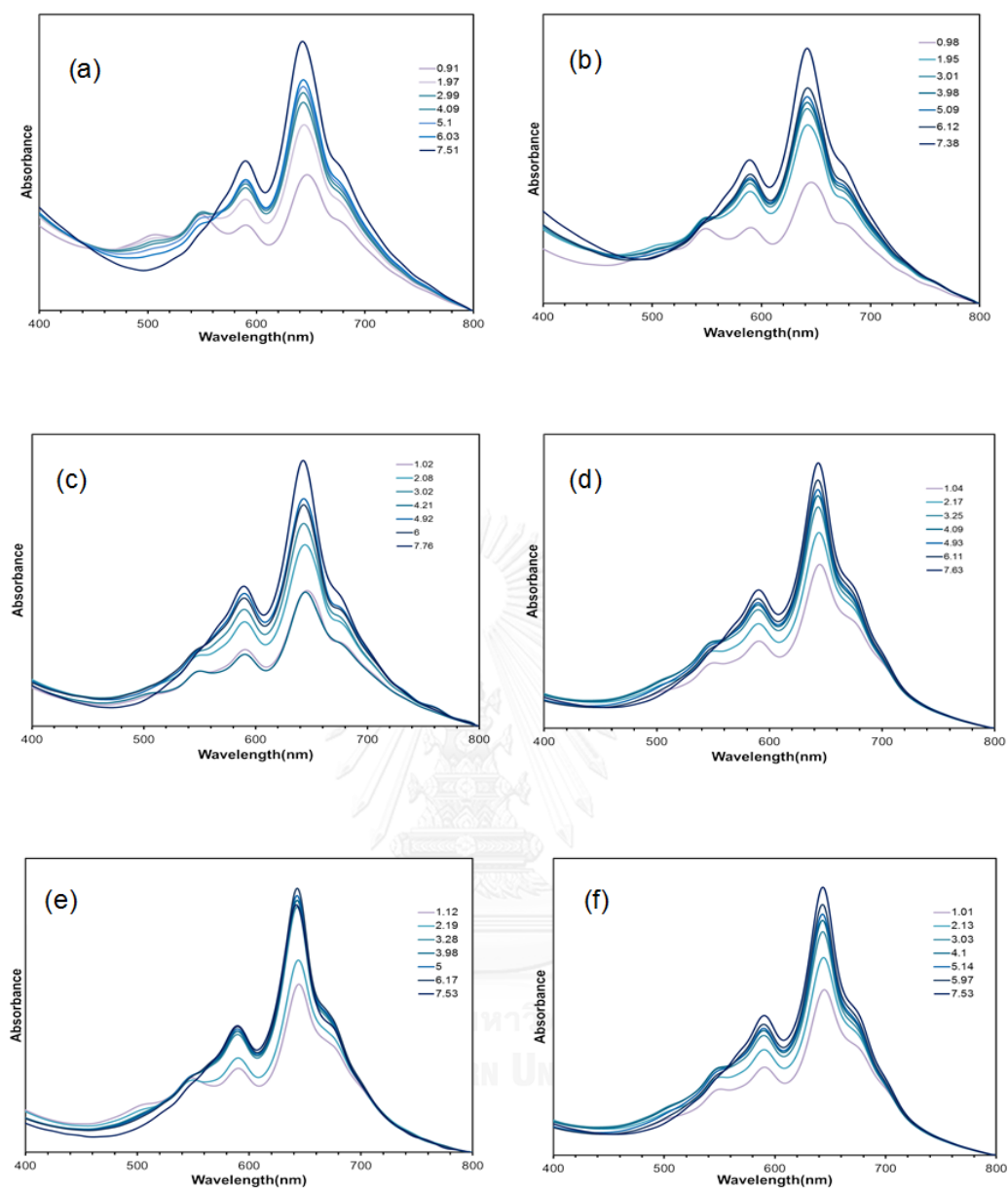
Fig. 4. 35. Absorption spectra upon increasing pH of poly(PCDA)/ZnO nanocomposites prepared with various sizes of ZnO (a) 65.31 nm (b) 174.56 (c) 224.42 nm (d) calcined 65.31 nm (e) calcined 174.56 nm and (f) calcined 224.42 nm

Fig. 4. 36. Colorimetric response to (a) HCl and (b) NaOH of poly(PCDA)/ZnO nanocomposites prepared with various sizes of ZnO

The color photographs upon variation of pH of poly(PCDA)/ZnO nanocomposites obtained by difference sizes of ZnO are illustrated in Fig. 4.37. The color transition upon variation of pH is slightly observed. In acidic condition, the nanocomposites are purple at pH around 1. In basic condition, colorimetric response of the poly(PCDA)/ZnO nanocomposites is not clearly observed.

Fig. 4. 37. Color photograph upon variation of pH of poly(PCDA)/ZnO nanocomposites prepared with various sizes of ZnO.

Absorption spectra of poly(HDDA)/ZnO nanocomposites measured upon the decrease of pH are illustrated in Fig. 4.38. The color transition when adding H^{+} ion is clearly observed in all nanocomposites. Color transition from blue to purple occurs at pH ~5-6. The new peak at ~ 540 nm is detected and this peak continuously grows when further adding H^{+}ions. The complete blue-red transition is observed at pH ~ 3. The plot of %CR is illustrated in Fig. 4. 40a Similarly for all poly(HDDA)/ZnO nanocomposites, the color transition is observed at pH ~ 6 and the complete red phase takes place at pH ~ 3.
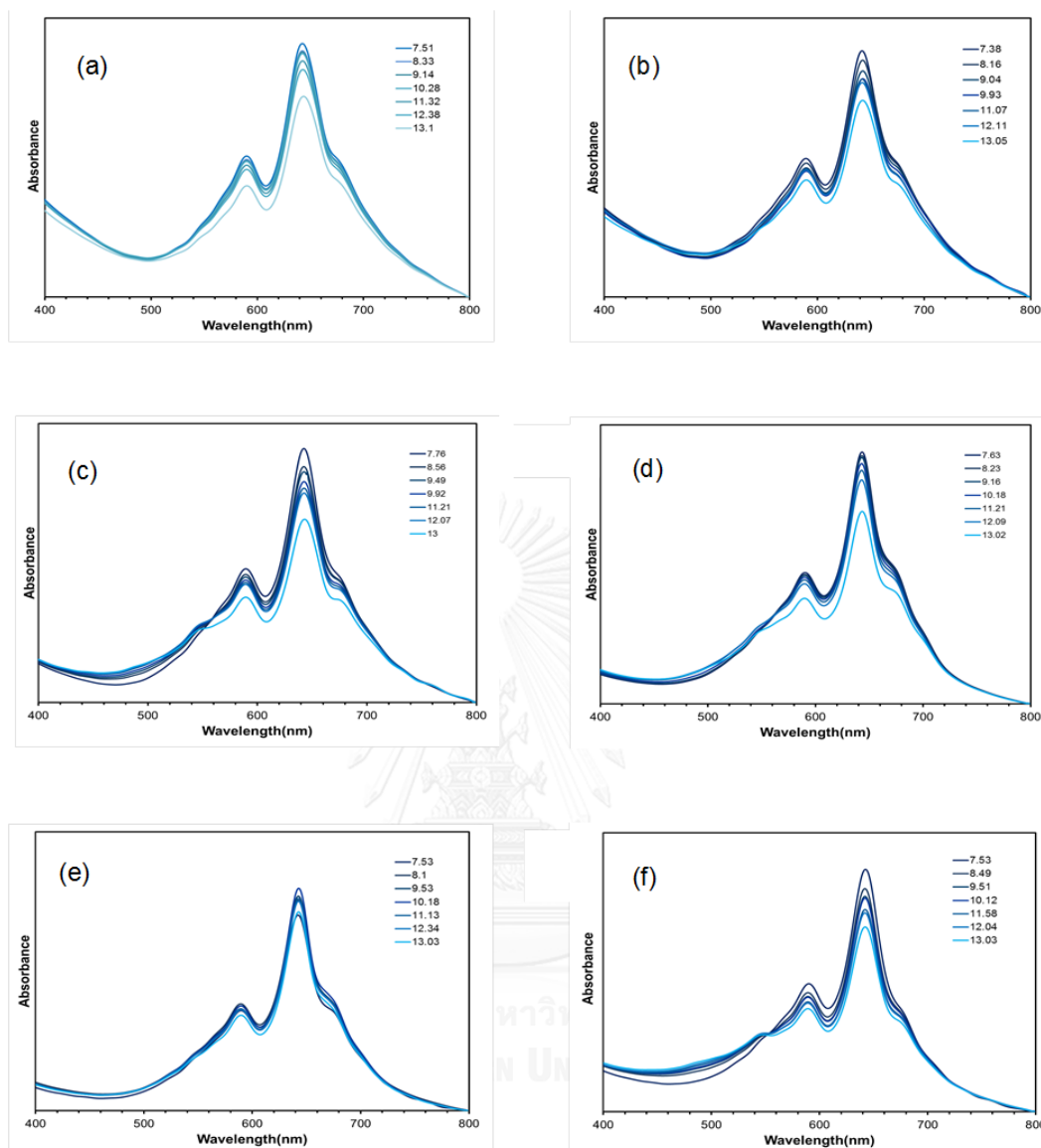
Fig. 4. 38. Absorption spectra upon decreasing pH of poly(HDDA)/ZnO

nanocomposites prepared with various sizes of ZnO (a) 65.31 nm (b)

174.56 (c) 224.42 nm (d) calcined 65.31 nm (e) calcined 174.56 nm
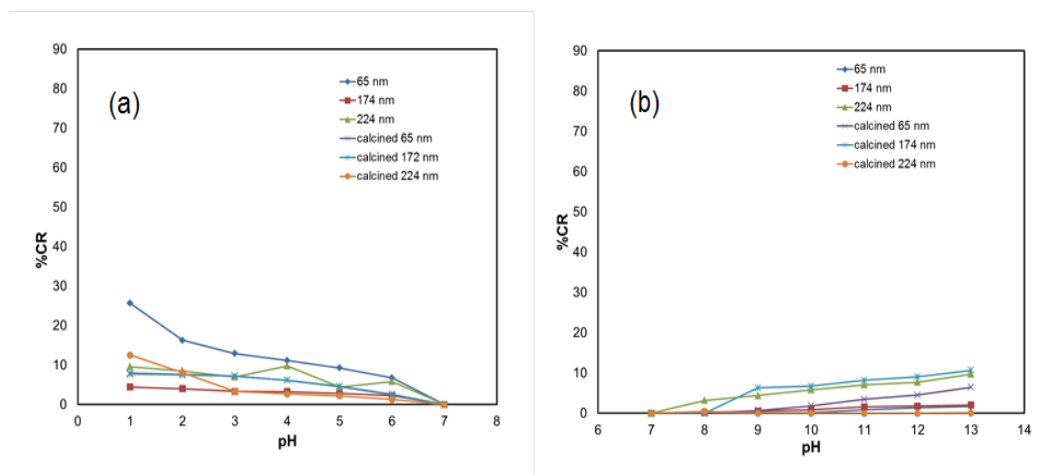
and (f) calcined 224.42 nm

The absorption spectra upon increasing pH of poly(HDDA)/ZnO nanocomposites are shown in Fig.4.39. The color transition when adding OH- ions is clearly observed in all nanocomposites. A small peak around 540 nm is detected at pH ~ 11, corresponding to red phase. When further increasing pH, the red phase peak continuously grows while the absorbance of blue phase continuously drops. Poly(HDDA)/ZnO nanocomposites prepared using as-received ZnO of all sizes and calcined 65 nm-ZnO change color when increasing pH to ~ 11. With calcined 174 nm-ZnO, the nanocomposite changes color at pH ~ 13. For the poly(HDDA)/ZnO prepared with calcined 224 nm-ZnO, the as-prepared nanocomposite is purple. The plot of %CR is shown in Fig. 4.40b. When compare between the nanocomposite prepared using as-received ZnO and the one prepared with calcined ZnO i.e., 65 nm vs. calcined 65 nm, 174 nm vs. calcined 174 nm and 224 nm vs. calcined 224 nm, it is found that colorimetric response to base is more obvious for the nanocomposites prepared using as-received ZnO. For example, the nanocomposite of 65 nm-ZnO exhibits %CR of 65%. at pH 13 while the nanocomposite of calcined 65 nm-ZnO shows %CR of 68%.
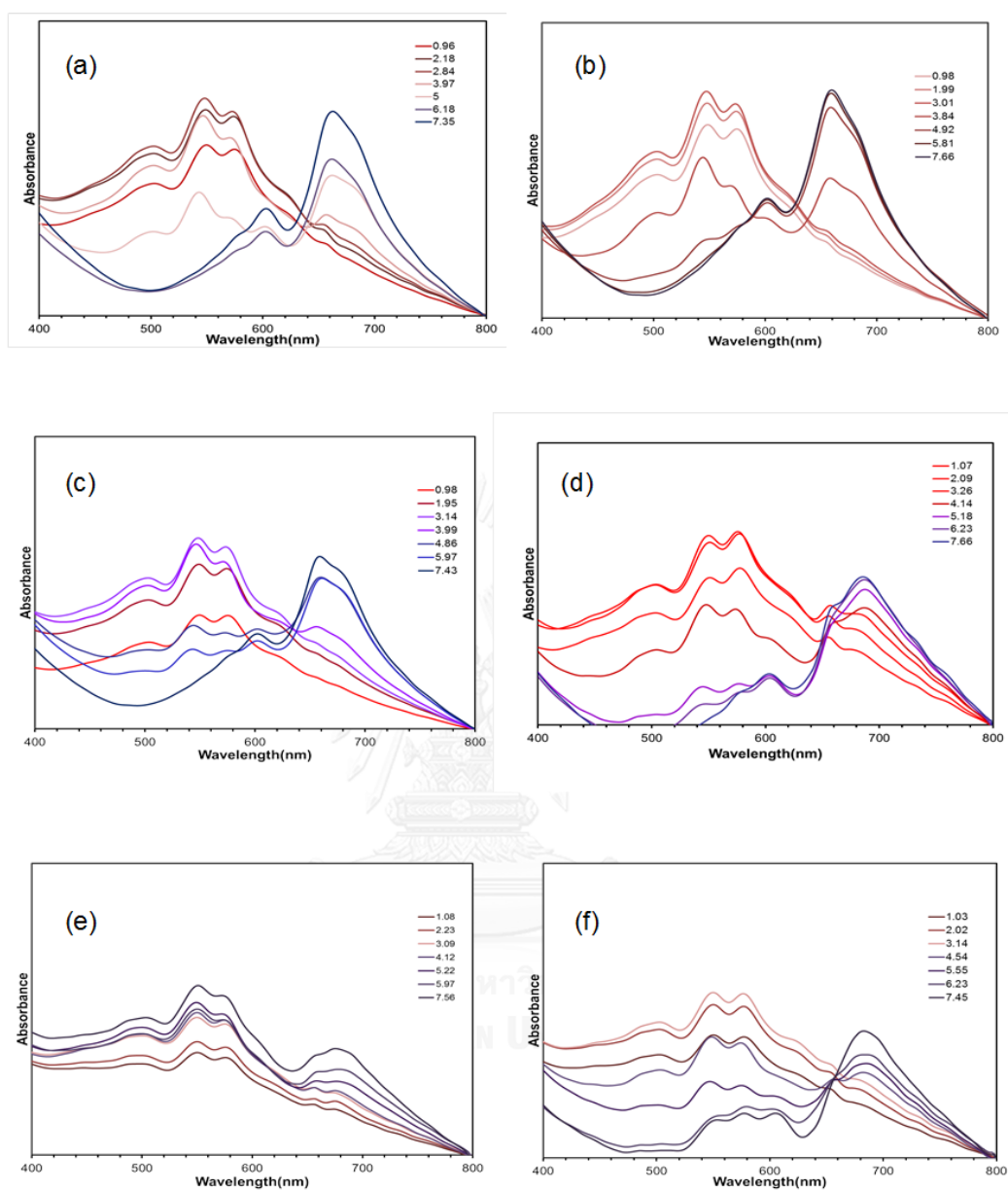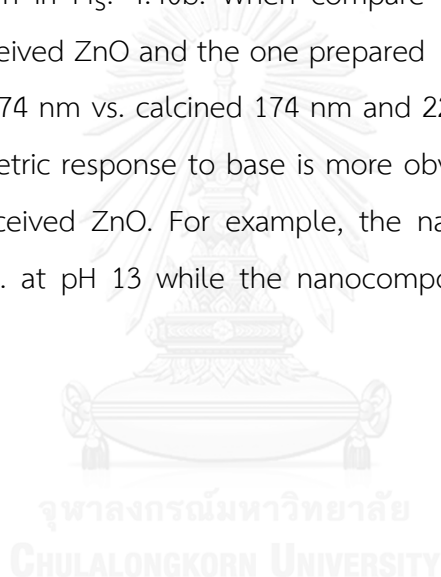
Fig. 4. 39. Absorption spectra upon increasing pH of poly(HDDA)/ZnO nanocomposites prepared with various sizes of ZnO (a) 65.31 nm (b) 174.56 (c) 224.42 nm (d) calcined 65.31 nm (e) calcined 174.56 nm and (f) calcined 224.42 nm

Fig. 4. 40. Colorimetric response to (a) HCl and (b) NaOH of poly(HDDA)/ZnO nanocomposites prepared with various sizes of ZnO

The color photographs upon variation of pH of poly(HDDA)/ZnO nanocomposites obtained by using difference sizes of ZnO are illustrated in Fig. 4.41. The colorimetric response to both acidic and basic conditions can be clearly observed.
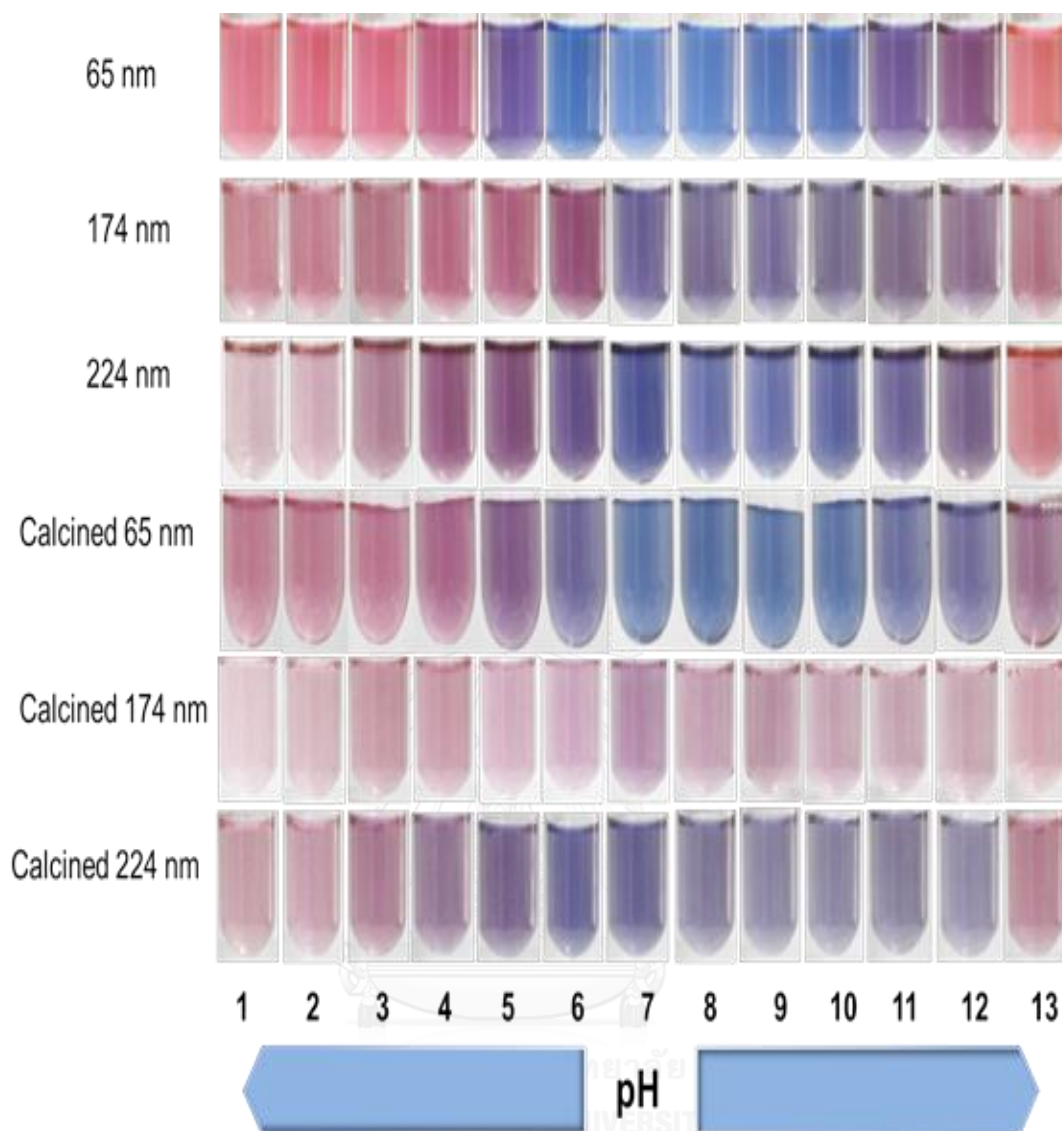
Fig. 4. 41. Color photograph upon variation of pH of poly(HDDA)/ZnO nanocomposites prepared with various sizes of ZnO nanoparticles

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

In this work, two types of DA monomers with different alkyl chain length i.e., 10,12-pentacosadiynoic acid (PCDA)and 5,7-hexadecadiynoic acid (HDDA), were used for preparing the PDA/ZnO nanocomposites. ZnO concentrations were varied at 5, 10, 15, 20, 30 and 50wt%. As received ZnO with sizes 65.31 nm, 174.56 nm, 224.42 nm were used along with the calcined ZnO with sizes 65.31 nm, 174.56 nm, and 224.42 nm. The colorimetric responses to temperature and pH of PDA/ZnO nanocomposites were investigated. The results could be concluded as follows;

5.1.1. Effects of ZnO concentration on colorimetric response of PDA/ZnO nanocomposites

In the system of poly(PCDA)/ZnO, the nanocomposites prepared with various ZnO concentrations exhibit blue phase after polymerized. The aqueous suspensions with 30-50 wt% ZnO are easy to precipitate. The concentration of the nanocomposite verified by absorbance spectra and color photograph is found to decrease with increasing ZnO amount. When thermochromism is investigated, it is found that the color transition temperature and thermal stability of the nanocomposite increase when the concentration of ZnO is increased. For colorimetric response to pH, it is found that the nanocomposites change color in acidic condition. The response to acidic pH is more sensitive when ZnO concentration increases.

For poly(HDDA)/ZnO, the nanocomposite prepared with 5 wt% ZnO is purple after polymerized. At 10-50wt% ZnO, the nanocomposites are blue after polymerized. The concentrations of nanocomposite prepared using various ZnO

amounts are similar. Thermochromic study shows that color transition of all nanocomposites occurs at 60oC and thermal stability can be observed after cooling to room temperature. Increasing of ZnO concentration leads to a decrease in thermal stability of the nanocomposite. For pH response, color transition upon variation of pH is clearly observed in all nanocomposites. At decreasing of pH, the nanocomposite changes color at pH ~ 5 and a complete transition occurs at pH ~ 3. For basic pH response, the nanocomposite changes color at pH ~ 11 and a complete transition occurs at pH ~ 13.

5.1.2. Effects of ZnO size on colorimetric response of PDA/ZnO nanocomposites

Poly(PCDA)/ZnO nanocomposites prepared with as-received ZnO of sizes 65.31 nm, 174.56 nm, 224.42 nm and calcined ZnO of sizes 65.31 nm, 174.56 nm, 224.42 nm exhibit deep blue color after polymerized. When subjected to heat, color transition temperatures of all nanocomposites are similar. However, when decrease to room temperature, the nanocomposites prepared with 65-calcined 65.31 nm. ZnO exhibit completely reversible behavior while the ones prepared with calcined 174.56 nm and calcined 224.42nm-ZnO are partially reversible. Colorimetric response to acidic pH is detected around pH ~ 1. However, under basic condition, color transition cannot be observed.

Poly(HDDA)/ZnO nanocomposites prepared with various ZnO sizes exhibit blue phase after polymerized. The exception is the nanocomposite prepared with calcined ZnO of size calcined 224.42nm, which is purple due to coexistence of pure poly(HDDA) and poly(HDDA)/ZnO. Thermochromic behavior of all nanocomposites are simillar. Partially reversible thermochromism is observed. When subjected to heating-cooling cycles, thermal stability is found to decrease with increasing ZnO size. The colorimetric response to acid and base is clearly observed. The nanocomposites exhibit color transition around pH ~ 6 and a complete color transition occurs around pH ~ 3. In basic condition, the nanocomposites change color around pH ~ 11. When compared between an as-received ZnO and its calcined one,

the nanocomposite prepared with the as-received ZnO is more sensitive to the basic condition.

5.2. Recommendations for future work

1. Study effects of ZnO concentration and size on colorimetric response of poly(PDA)/ZnO nanocomposite subjected to other stimuli.

2. Study effects of ZnO concentration and size on colorimetric response of poly(PDA)/ZnO nanocomposite film subjected to external stimuli.

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VITA

Miss Sarntmon Pengoubol was born on September 14, 1989 in Songkhla, Thailand. She finished her Bachelor's Degree in Materials Science from the Department of Physics, Faculty of Science, Thammasart University. She continued a furtuther study in Master's degree in the field of Ceramic Technology at Chulalongkorn University and graduated in 2014.

Acadamic Conference presentations

Pengoubol, S., Traiphol, N. "Effects of ZnO concentration on Thermochromism of Polydiacetylene/ZnO nanocomposites" 9th The Mathematics and Physical Science Graduate Congress (MPSGC) at the University of Malaya in Kuala Lumpur, Malaysia (Poster presentation)

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