



CHAPTER I

INTRODUCTION AND THEORY

1.1 Introduction

Temperature is one of the most important physical parameters affecting biological and chemical system. There are various circumstances in which the temperature history must be monitored and recorded, for examples, the need to know whether a frozen food product has been exposed to an unacceptable level of temperature during storage and distribution or whether a person traveling through a broader of hygienically controlled zone having a high fever. A disposable, economical and simple to use device such as irreversible colorimetric temperature sensing films can be very useful for such applications [1].

Polydiacetylenes (PDA) [2] are a class of ene-yne conjugated polymers possessing several interesting chromic properties. PDA exhibit dramatic color change upon exposure to various stimuli including light (photochromism) [3-5], heat (thermochromism) [6-10], mechanical stress (mechanochromism) [11-13], solvent/chemical environment (solvatochromism/chemochromism) [14-15] and binding of specific chemical/biological agents (affinochromism/biochromism) [16-18]. PDA can be prepared from topochemical polymerization of monomeric diacetylenes (DA) in numerous forms: bulk solid [23-25], self-assembled films [26-27] and vesicles suspended suspension in liquids [28-29]. Thermal sensing devices using PDA as colorimetric indicators have so far been developed based solely on the thermochromic property of PDA microcrystalline [19-20]. In this approach, the color transition temperature (CTT) of the devices relies mainly on the types of DA monomers used. It is desirable to have a simpler and more general way of tuning the CTT of the thermochromic devices without having to change the types of PDA for every designated temperature.

The objective of this thesis work is to search for a general method for fabrication of tunable thermochromic films from a single type of PDA. Poly(10,12-pentacosadiynoic acid), PPCDA, nanovesicles was selected as a thermochromic agent and polyacrylic-acrylate latexes were tested as a film matrixes. There are three important strategic features behind this design. First, the nano-sized vesicle of PPCDA was selected due to its high color intensity per weight of the diacetylene monomer. Second, the selection of polyacrylic-acrylate latexes as film forming matrixes was not only because of their excellent film

forming properties [30] but also because of their availability in aqueous media and their average particle sizes being in the proximity range of those of PDA vesicles (~100nm) [31]. The requirements for the aqueous media and the size of the particles are to ensure the compatibility and uniformity of the mixing between the vesicles and the latexes. Third, a nonpolar organic liquid was added into the blend to bring about the color transition by solvatochromism effect upon thermal induction. In the last strategy, the latex particles function as nanoreservoirs of the organic liquid which can be released from the latex at the temperature above the glass transition temperature (T_g) of the latex. The CTT of such system should be related to the T_g of the latexes used.

1.2 Theory

1.2.1 Polydiacetylenes

Topopolymerization of diacetylene monomer

Polydiacetylenes (PDA) is a class of conjugated polymers resulted from topopolymerization of diacetylene monomers via 1,4-addition reaction to form an ene-yne alternated polymeric chains upon UV irradiation (Figure 1.1)

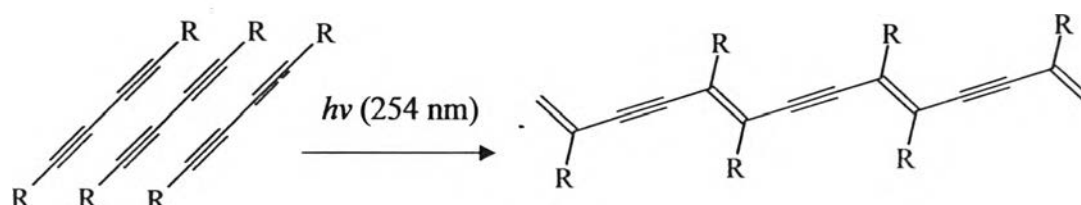


Figure 1.1 Schematic representation of polymerization of assembled disubstituted diacetylene monomers by irradiation with UV light.

The forms in which diacetylene monomer can be polymerized are bulk solid crystals, self assemble films such the Langmuir-Blodgett films, vesicles suspended in liquids. The PDA in the vesicle form is of interest as it allow greater access for characterization and fabrication. Diacetylene lipids are known to spontaneously organize into vesicle structure in aqueous media which can be further photopolymerized by UV light. One of the most commonly used lipid monomer for preparation of vesicles is 10,12-pentacosadiynoic acid (PCDA). PCDA monomer has a carboxylic group as a hydrophilic

head group, which can partially dissociate in water or form hydrogen bonds with water. The molecule also has a long hydrocarbon chain as hydrophobic tail. In water, PCDA molecules can be assembly in form of lipid bilayer vesicles to avoid the unlike interaction between hydrophobic tails with water molecules. The molecules assembled within the lipid bilayer vesicles are so well packed that they can be topopolymerized by UV irradiation to give poly(PCDA) (Figure 1.2). Thanks to their nano-sized structures, the lipid vesicles can be well dispersed in water and thoroughly polymerized unlike the bulk solid crystals. The typical size of poly(PCDA) vesicles prepared by sonication method is in the range of 50-200 nm.

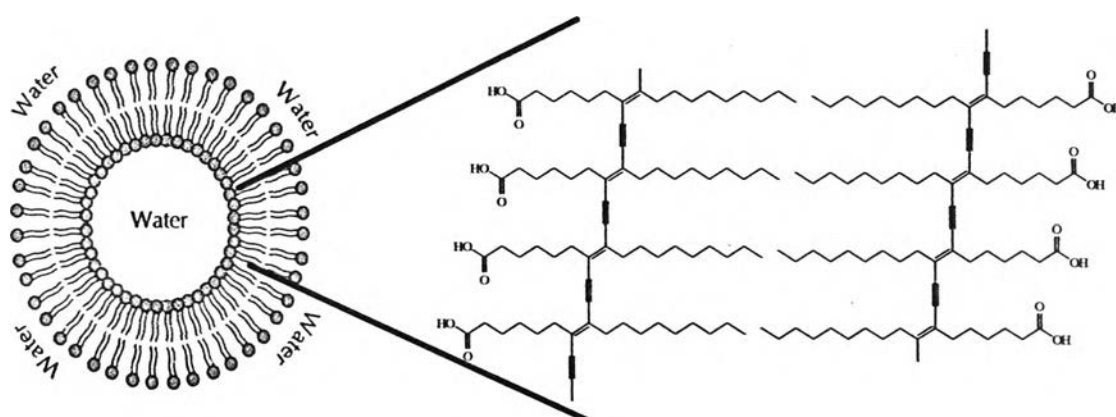


Figure 1.2 Schematic representation of polydiacetylene vesicles formed from a diacetylene lipid

Chromic properties and colorimetric responses

All polydiacetylenes are highly colored materials due to their extended ene-yne conjugated backbone. Optical absorption in poly(PCDA) occurs via a π -to- π^* absorption within the linear π -conjugated polymer backbone. Since the diacetylene monomers do not exhibit absorption in the visible region, the appearance of visible color and the optical absorption is the observation most frequently used to signify the topopolymerization. Upon polymerization, frequently the first chromogenically interesting state of the PDA appears blue in color, with an absorption maximum in the range of ~ 640 nm, although other features including a prominent vibronic side-peak are readily apparent.

Poly(PCDA) vesicles, if obtained under optimal conditions, appear as an intensely blue-colored solution. Typically, the main excitonic peak of the blue form occurs at ~ 640

nm associated with broad vibronic peak at ~ 590 nm (Figure 1.3a). The visible color change of poly(PCDA) from blue to red occurs in response to varieties of environmental perturbations, such as temperature, pH, solvent, mechanical stress and ligand-receptor interactions. The chromatic transitions involve a significant shift in absorption from low to high energy bands of the visible spectrum, where poly(PCDA) transforms from blue to red phase. The excitonic peak of the red form occurs at ~ 540 nm associated with broad vibronic peak at ~ 490 nm (Figure 1.3b).

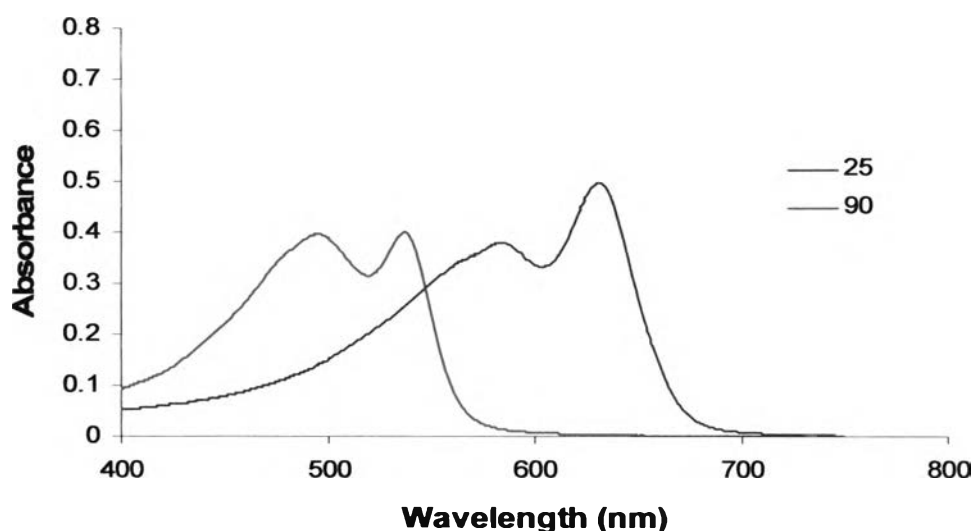


Figure 1.3 Visible absorption spectra of a) blue and b) red forms of poly(PCDA) vesicle solution

Generally, the blue phase of PDA does not exhibit any fluorescence while the red phase tends to exhibit some fluorescence. Fluorescence band, typically peaked at ~ 540 nm, has been observed for the red form [32]. This is believed to be due to energy shifts in the lowest-lying excited states during the color transition such that the very lowest excited state has the same symmetry as the ground state.

The mechanism behind these color transitions is not yet fully consented. Previously, it was proposed that the chromatics transition involve a transformation from the ene-yne structure to a butatrienic structure (three sequential double bonds) [33]. The absorption properties of the backbone were also found to depend sensitively to the planarity of the backbone. The molecular orbitals in the π -conjugated PDA backbone at the ground state are

presumably in the planar configuration (Figure 1.4). Energy levels are affected by the overlap of these orbitals and this overlap can be altered by rotation about one of the C-C bonds in the backbone. The red phase may consist of a non-planar backbone configuration in conjunction with rotated and/or distorted alkyl side chains. Theoretical calculations indicate that a rotation of only a few degrees about this bond dramatically changes the π -orbital overlap [34], causing a significant blue shift of the absorption spectrum.

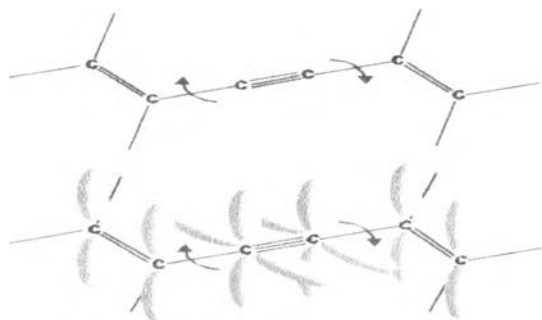


Figure 1.4 Schematic diagram of the molecular orbitals in the π -conjugated PDA backbone in the planar configuration

Rotation about the single bond necessitates changes in the conformation of the pendant side groups, and thus there exists a sensitive interplay between them. The side groups have a preferred packing arrangement which dominates the intermolecular arrangement in the unpolymerized form. During the polymerization, the extended backbones form in a strained configuration because of the geometric restriction imposed by the side group arrangement. Essentially, the packing energy of the side groups creates a barrier that prevents the backbone from adopting a more relaxed form. The subsequent application of heat, stress, or other stimuli leads to side chain fluctuations or reconfigurations and allows the backbone to adopt a more relaxed conformation that involves rotation about the C-C backbone bonds, and thus lead to changes in the optical absorption spectrum.

In the absence of the pendant side groups, there would be, hypothetically, a monotonic and reversible change in the energy of the polymer backbone as the C-C bond angle changes [34, 35]. The torsional mobility of the polymer backbone is restricted by pendant side group interaction as well as interactions between the head groups [35]. The

degree of reversibility of the transition likely depends on the height of the energy barrier and the total energy difference between the two conformations.

The color change of PDA vesicles can be quantified by measuring the absorbance differences between the vesicles before and after the addition of an analyte of interest. This information is often converted to a percentage, termed the Colorimetric Response (CR). A quantitative value for the extent of blue-to-red color transition is given by the colorimetric response (%CR) which is defined as

$$\%CR = [PB_0 - PB / PB_0] \times 100$$

Where $PB = A_{\text{blue}} / (A_{\text{blue}} + A_{\text{red}})$; A_{blue} and A_{red} are the absorbance of the blue and the red phase at 630 and 540 nm of the visible spectrum.

Thermochromism of polydiacetylene is generally accepted that the red form of the polymer arises from reduced effective conjugated length of the ene-yne polymer backbone. This arises from a planar to nonplanar conformation of the conjugated system. It is also generally accepted that the effective conjugated length is influenced by the pendant side groups. Several studies have suggested that the pendant side chains become entangled and undergo an order to disorder transition as film changes from the blue to red form. Others have suggested that a *gauche* to *trans* conformational transition of the methylene groups pendant to the polydiacetylene backbone strains and results in the color change.

The polymer backbones, composed of conjugated double and triple bonds, are planar in the blue phase films. Upon heating the side chains clearly reorganize into a near-perfect hexagonal packing. This fact, coupled with the increased intensity and low-frequency shift in the FTIR spectra, strongly suggests that the alkyl side chain bonds have more *trans* or planar character in the red phase. Hydrogen bonding may lock the headgroups such that the *gauche-trans* conformational change of alkyl side chain imposes a strain on the polymer backbone. Theoretical calculations have indicated that very slight rotations around the C-C bond of the polymer backbone (5°) are enough to produce a dramatic decrease in the π -electron conjugation length, predicting the blue shift in the visible absorption spectra. Thermochromism of PDA, the change is understood to be a first order phase transition and trends to occur in the range of 70-150 °C. The specifics of the absorption spectrum, transition temperature, and so forth vary somewhat with the nature of pendant side-groups and the form of the PDA (bulk crystal, film, vesicle, *etc*).

Mechanochromism of polydiacetylene much presented as an optical transducer of side chain disordering such as film defects or shear forces. The blue shift in the spectra is caused by breaks in the π -orbital overlap that shorten the conjugation length. Much of the results presented above clearly indicate that the shear forces experienced by the scanning probes are due to an interaction with the side chains that alters the side chain orientation with respect to the original plane of the all-trans blue form. Out of plane rotations of the side chains disrupt the π -orbital overlap or conjugation length, causing a blue shift of the absorption.

Applications of polydiacetylenes

The application for PDA are numerous, particularly in the area of sensors such as temperature sensors, biological sensors and chemo sensors. Poly(PCDA) is one of the most studied and applied in the field of sensors. The forms in which poly(PCDA) can be applied are numerous e.g. solutions, micro crystals and films.

1.2.2 Acrylic-acrylate latexes

Emulsion polymerization of acrylic-acrylate monomers

Emulsion polymerization is one of several processes by which a variety of unsaturated organic carbon compounds can be polymerized. This polymerization, which is an addition type, is carried out in liquid medium, which is almost always aqueous and produces milky fluid called latex. There are four basic ingredients required for an emulsion polymerization. These are (1) the monomer, (2) the dispersion medium, (3) the emulsifier, and (4) the initiator. When correct amounts of the ingredients are mixed properly in a suitable container within a certain temperature range, an emulsion of monomer droplets is formed in the continuous dispersion medium. The initiator causes the monomer molecules to polymerize. When the polymerization is complete, a stable emulsion of polymer particles will remain [36].

The major polymerizable component of an emulsion polymerization is a monomer which has limited water solubility. The monomers frequently used in emulsion polymerization are the vinyl type, $\text{CH}_2=\text{CHX}$. X maybe C_6H_5 (styrene), CN (acrylonitrile), O_2CCH_3 (vinyl acetate), Cl (vinyl chloride) or CO_2R (acrylates or acrylic acid for R being

alkyl or hydrogen atom, respectively). There are also di-substituted vinyl monomer, $\text{CH}_2=\text{CR}_1\text{R}_2$; for methyl methacrylate, R_1 is CH_3 and R_2 is CO_2R [37].

A source of free radicals, an initiator, is needed for addition emulsion polymerization. Most initiators used in emulsion polymerization are water-soluble e.g. potassium peroxodisulfate ($\text{K}_2\text{S}_2\text{O}_8$) and ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$). Persulfate produces sulfate radical as a result of bond scission; the activation energy for this process is quite high, so persulfate is usually employed at high temperatures above 50°C . A side-product of persulfate decomposition is HSO_4^- , produced by reaction of $\text{S}_2\text{O}_8^{2-}$ with water. Since HSO_4^- alters pH, which can drastically reduce initiator efficiency, buffer thus should be used with this initiator if controlled conditions are desired.

Surfactant is used to stabilize the latex particles from aggregation. There are three basic types of surfactants: (a) electrostatic stabilizers such as anionic or cationic soaps, which prevent coagulation by electrostatic repulsion from the charges located on the particle surfaces and their associated electric double layers, (b) polymeric (steric) stabilizers such as partially hydrolyzed poly (vinyl acetate), which stabilize the particles through the entropic repulsion caused by trying to pack two chains in the same space, and (c) electrosteric stabilizers, such as polyelectrolytes.

Other ingredients commonly added as modifiers in commercial emulsion polymerization are chain transfer agent to control molecular weight, buffers to control pH and initiator efficiency. Electrolytes may also be added to induce particle size monodispersity. It is also common to add a chaser to reduce residual monomer at the end of polymerization process. Typically, a chaser may be a shot of redox initiator added later in the polymerization batch.

It is convenient to divide emulsion polymerizations into the three stages or intervals (Table 1.1) [38]. Interval I is characterized by an increasing in the number of particles and the rate of the reaction. It is normally completed early in the course of a batch reaction; conversion of 2-10% is typical. The explanation of this phenomenon is based on the new surface area formed by the growing monomer-swollen polymer particles. The expanding particles provide a new hydrophobic surface for emulsifier adsorption. This emulsifier is extracted from the water, which causes the dissolution of micelles to maintain the micelle-solution equilibrium (Figure 1.6). Nucleation stops when the surface area of the previously formed particles plus that of the monomer droplets is adequate for the adsorption of all

emulsifier. When all the emulsifier molecules from the micelles are fully adsorbed, the particle nucleation ceases constituting the end of Interval I and the beginning of Interval II. Three possible phases, an aqueous phase, latex particles and monomer droplets, are present in this interval. The latex particles maintain constant monomer/polymer ratio by combining monomer droplets to the growing latex particles. The monomer concentration within a latex particle (C_p), number density of the latex particles (N_c) and the reaction rate do not change during Interval II. As the polymerization progresses and the monomer is consumed, the monomer droplets eventually become exhausted and disappear that is when the final stage of the reaction, Interval III, begins. Only latex particles and aqueous phase are present during this final period.

Table 1.1 Qualitative details of the three intervals of an emulsion polymerization

Interval	Typical% conversion range	Micelles	Monomer droplets	Number of latex particles	Particle size	Comments
I	0-10	decrease	increase	increase	increase	Nucleation
II	10-40	absent	decrease	constant	increase	C_p constant
III	40-100	absent	absent	constant	roughly constant	C_p decrease

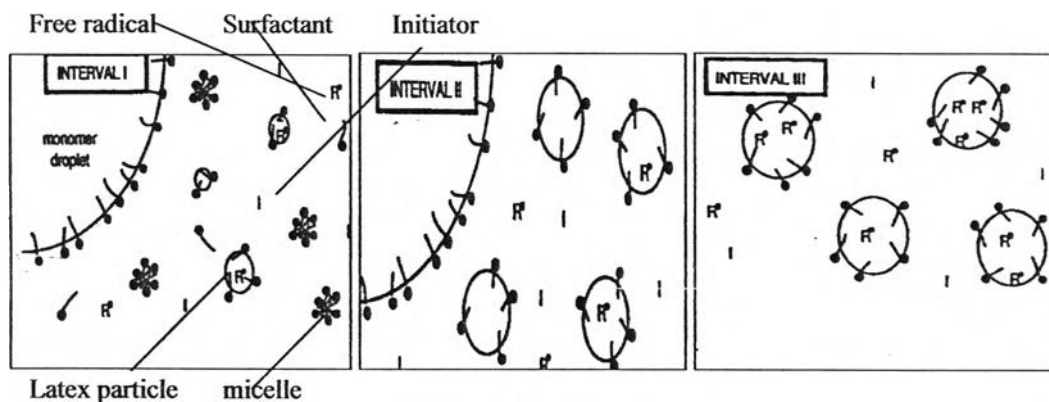


Figure 1.5 A simple illustration of the three intervals of an emulsion polymerization

Acrylic monomer, such as ethyl acrylate, methacrylic acid and vinyl monomer, polymerize only by addition processes. In addition polymerization, after chain initiation has begun there follows the successive addition of a large number of monomer molecules to the

growing polymer chain called propagation. Eventually, this growth ends by a termination step. The process of the addition polymerization is shown generally as:



Addition polymerizations are further characterized by the type of initiator used. They can be induced by free radical, ionic, or high-energy mechanisms. These mechanisms, however, are quite similar, including initiation, propagation and termination steps.

A free radical is an extremely short-lived, highly energetic molecular fragment containing a single, unpaired electron. It readily reacts with the unsaturated double bond of a monomer molecule to begin a polymer chain growth. Radicals generally arise either by absorption of sufficient vibration energy by initiator precursors or by chemical reaction of a precursor with reducing agents involving a one electron transfer. When the radical reacts with a monomer molecule a larger free radical is formed which, in turn, reacts with another monomer molecule, thus propagating the polymeric chain. While individual monomer addition reactions are almost instantaneous, the polymerization may take several hours to complete in the reaction mixture depending on the method and the temperature of polymerization. Growing polymer chains are finally terminated (free electrons coupled) in a variety of ways including disproportionation, biradical coupling, and one or more chain transfer mechanisms [39,40].

Parameters affecting the molecular weight and particle size

The concentration of the monomer in the emulsion can have a marked influence on the behavior of a polymerization. According to the Smith-Ewart concept the monomer-to-water phase ratio should have no influence on the rate of polymerization and number of particles. In practice this is usually not the case, though with some monomers the effect may be more marked than with the others, depending mainly on the solubility of the monomer in water and in the polymer particle. Increasing the monomer-to-water ratio increases the rate of polymerization which results the increasing of molecular weight and larger particles [39,41].

The size of latex particles is also depended on the concentration of the emulsifier. As the concentration of the emulsifier is lowered, the number of latex particles formed is decreased. Consideration of the kinetic data would indicate that this should lead to an increase in the particle size. The increase of particle size causes difficulty coalescence and

lead to increase MFFT values [39]. Increasing the initiator concentration also increases the number of free radical and the nucleation leading to the decrease of the particle size. The reaction time is the growth period of particle [41]. Increasing the reaction time increases the particle size as the conversion of monomer to polymer increases.

Another method of modifying the latex particle size and its distribution is by employing a seeding technique. Seeding can be achieved by adding a further quantity of monomer and catalyst to a latex (called seed latex) after the onset of the diffusion or growth period, Interval II. Since the number of particle is fixed, the particles will grow to a larger size. This technique may be seen also as a way of extending the period of diffusion [39].

Application of latexes

Applications of acrylic-acrylate latexes include (1) use as binder for paint coating, such as decorative paint, roof tile paint, textile printing, wood paint *etc.* (2) use for clear coating on various substrates such as wood, roof tile *etc.* (3) use as sealer in cement for improving water, alkali and chemical resistance.

1.2.3 Analysis of particle size and microstructure

Dynamic light scattering

Dynamic light scattering (DLS) is a well established technique for measuring particle size over the size range from a few nanometers to a few microns. The concept uses the idea that small particles in a suspension move in a random pattern. According to Einstein's developments in his kinetic molecular theory (applied to heat), molecules that are much smaller than the particles can impart a change to the direction of the particle and its velocity. Thus water molecules (0.00033 microns) can move polystyrene particles as large as a couple of microns. The combination of these effects is observed as vibrations and an overall movement of the particles. When a coherent source of light (such as a laser) having a known frequency is directed at the moving particles, the light is scattered, but at a different frequency. The change in the frequency is quite similar to the change in frequency or pitch one hears when an ambulance with its wailing siren approaches and finally passes. The shift is termed a Doppler shift or broadening, and the concept is the same of light when it interacts with small moving particles. For the purposes of particle measurement, the shift in light frequency is related to the size of the particles causing the shift. Due to their higher average velocity, smaller particles cause a greater shift in the light frequency than larger

particles. It is this difference in sizes frequency of the scattered light among particles of different sizes that used to determine the sizes of the particles present.

Scanning electron microscopy

Scanning electron microscopy (SEM), a finely focused beam of high-energy electrons is scanned across the surface of a sample. The electrons scatter at the electron in the near surface region of the sample in various different ways. The predominant process is inelastic scattering. An incoming primary electron transfers some of its energy to an electron of the sample. In most cases, upon scattering, the electron loses only a small amount of energy. This process occurs repeatedly until it has essentially lost its all energy and a cascade of excited low-energy secondary electrons has been created. A considerable number of these secondary electrons travel back to the surface. Hence, an image of the sample topography is obtained by recording the number of these electrons for each position of the incoming beam. If the sample under investigation is ferromagnetic, the emitted electrons are spin-polarized. The spin of these secondary electrons points preferentially in the opposite direction of the magnetization vector. Thus, by measuring the spin polarization along a certain direction in a spec, a map of the magnetization component in this direction is obtained.

Transmission electron microscopy

The original form of electron microscope, transmission electron microscope (TEM), involves a high voltage electron beam emitted by a cathode and formed by magnetic lenses. The electron beam that has been partially transmitted through the very thin (and so semitransparent for electrons) specimen carries information about the inner structure of the specimen. The spatial variation in this information is then magnified by a series of magnetic lenses until it is recorded by hitting a fluorescent screen, photographic plate, or light sensitive sensor such as a CCD (charge-coupled device) camera. The image detected by the CCD may be displayed in real time on a monitor or computer.

1.3 Literature survey

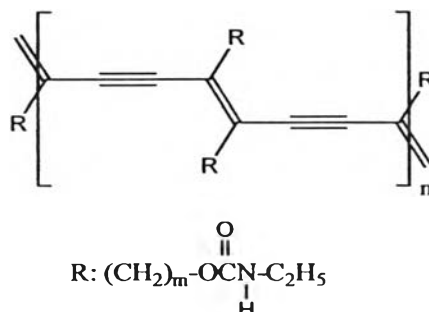
In 1998, Wu *et al.* [42] studied the effects of the acrylic thermosetting latexes which used methyl methacrylate (MMA)-butyl acrylate (BA) copolymer. The methacrylic acid (MAA) or hydroxyl ethyl methacrylate (HEMA) was incorporated to provide the latexes with carboxyl or hydroxyl functionality, respectively. A cycloaliphatic diepoxide (3,4-

epoxycyclohexyl methyl-3',4'-epoxycyclohexane carboxylate) was used to crosslink with hydroxyl and carboxyl functional latexes. The coating properties were evaluated in terms of water absorption, gel content, pencil hardness, and pull-off adhesion. In comparison with the coating at 25 °C without crosslinker, the water absorption of the crosslinked coating decreased substantially, while the gel content, pencil hardness, and pull-off adhesion of the coating increased. The decreased water absorption was due to the formation of ester bonds which reduced the polarity of the crosslinked coating. The increased gel content was due to the crosslinked network, which had lower entropy and was difficult to dissolve in the solvent. The increased adhesion may be attributable to the epoxy ring opening resulting in hydroxyl group, which promotes interfacial adhesion. Thus, the significant changes in coating properties can be attributed to the effect of the cross linking.

In 2004, Seda *et al.* [43] presented the study of homo and copolymers of acrylic latexes which synthesized by emulsion polymerization using methyl acrylate (MA), ethyl acrylate (EA), methyl methacrylate (MMA) and butyl acrylate (BA) monomers. The film structures of homo and copolymers were investigated and three of them [P(MMA/BA) 1:1, P(MMA:EA) 1:1.5, P(MMA/MA) 1:3] were indicated as appropriate binders for paint production. For latex characterization and determination of film formation properties, particle size and surface charge densities were determined and their thermal analyses were performed. The mechanical properties of the films were characterized by their hardness, flexibility, adhesion, gloss and UV resistance. The P(MMA:EA) 1:1.5 copolymer with T_g of 32.5°C and hardness of 5B was found to exhibit excellent film forming ability and have satisfactory mechanical properties, elongation and adhesion properties. The latex particle size was observed to be 78.4 and 177.7 nm for PMMA and PBA as the minimum and maximum average particle sizes. The film forming properties were influenced by the latexes particle size. Small particles were readily fused during film formation and induced to give a good dry film appearance.

In 1997, Lio *et al.* [44] studied thermochromism of polydiacetylene Langmuir-Schaefer film of 10,12-pentacosadiynoic acid (PCDA) and sialic acid derivatives of PCDA. It was found that the blue-colored film at 25 °C gradually changed to blue-purple at 50 °C and eventually complete converted to red at temperatures between 70 and 90 °C that color change from blue to red arises from reduction of the effective conjugated length of the polymer π - π backbone influenced by the pendant side groups.

In 2001, Tachibana *et al.* [45] polymerized crystals of diacetylene monomers containing urethane groups with different alkyl chain length in the side chain (PDA-mUEt, $m = 4, 5, 6$).



PDA-mUEt ($m = 4, 5, 6$)

The thermochromic reversibility depended on the alkyl chain length. PDA-5UEt showed full reversibility of the transition while PDA-4UEt was not fully reversible and PDA-6UEt was irreversible. No clear explanation for this results was provided.

In 2000, Burns *et al.* [46] presented a multi faceted research effort in the area of conjugated polymer surfaces, specifically polydiacetylene (PDA), and how they may be used to gain insight into molecular level tribology. The synthetic strategies were developed to produce stable, highly-ordered monolayers on atomically-flat substrates. The PDA film that was initially in the all-trans planar blue form, characterized by its visual color, was interrogated with AFM techniques and triggered the mechanochromic transformation to the fluorescent red form. The transformation was analyzed in detail and found to be dependent on the shear forces exerted on the pendant side chains. The shear forces perpendicular to the backbone direction were most effective in the transformation, which was also facilitated by defects and neighboring areas of the bare substrate. Overall, the transformation was the result of significant side chain rotation towards the substrate. Finally, this test presented preliminary modeling results that help correlating the molecular structure changes such as side chain rotation with the color changes of the PDA films.

In 2004, Robert *et al.* [47] presented high quality ultrathin PDA films using a horizontal Langmuir deposition technique. The number of stable layers in the film was controlled by altering the head group functionality. The films exhibited strong friction anisotropy that is correlated with the direction of the polymer backbone structure. Shear forces applied by atomic force microscope (AFM) or near-field scanning optical microscopy (NSOM) tips locally induced the blue-to-red chromic transition in the PDA

films. The results showed that spectroscopic ellipsometry could be used to monitor thermochromism in ultrathin poly(diacetylene) films. Spectroscopic ellipsometry revealed that trilayer films of poly-PCDA exhibited a partially reversible transition from blue to red form. The purple form appeared to be thermally distorted blue material. The purple form was present only at elevated temperatures and exhibited a large reversible shift in the absorption spectrum to shorter wavelengths. Only the red form exhibited significant fluorescence emission. From time resolved fluorescence experiments, an energy barrier of $17.6 \pm 1.1 \text{ kcal mol}^{-1}$ was determined for the irreversible transition from blue/purple to red form.

In 2004, Yan *et al.* [48] reported that a supramolecular assembly of phospholipid polymerized diacetylene vesicles functionalized with glycolipid could provide a molecular recognition function. The *Escherichia coli* glycolipid binding event led to a visible color change from blue to red, readily seen with the naked eyes and quantified by absorption spectroscopy. When *E. coli* was added into the mixed lipid vesicle functionalized with glycolipid in aqueous solution, the solution immediately changed to a purple, pink, or red color, depending on the incubation time, the component of the vesicle, and the amount of added *E. coli*. The color of the mixed vesicles (the molar fraction of dimyristoylphosphatidylcholine (DMPC):10,12-pentacosadiynoic acid (PCDA):dioctadecyl glyceryl ether- β -glucoside (DGG) is 5:5:0.2) in aqueous solution at pH 8.5 after addition of *E. coli* was changed from blue to red. The colorimetric response (CR) was quantified by the measurement of the percent change in the absorption of the blue form relative to the total absorption of the blue and red form.

In 2003, 2004, Ribi *et al.* [49] patented methods for preparation of materials containing PDA microcrystals for indication of expired product and cooked food.

In 2004, Disavo *et al.* [50] patented methods for preparation of thermochromic films that can change color at 40–45°F for indication of product expiration by using the composition comprised at 0.5–10% of thermochromic dye dispersed within 90–95% of a hardened matrix forming a thermoset for indication.

In 2005, Hay and 3M Co, Ltd. [51] patented the diacetylene monomers containing various side chains, mostly the derivatives of the diacetylene alcohols, and their syntheses. The polydiacetylenes prepared from these monomers can change color in the range of -10-

200 °C that maybe used for indication of expiration of food, pharmaceuticals and photographic films.

1.4 Objective and scope of this thesis

The objective of this research is to prepare films containing polydiacetylene vesicles that can change color at various temperature from a single type of diacetylene monomer. The thermochromic films were prepared from a mixture of poly(10,12-pentacodiynoic acid), poly(PCDA), and a variety of polyacrylate-methacrylic copolymer latexes. Various formulations of the latexes were prepared by emulsion polymerization by varying monomer concentrations, comonomer ratio, emulsifier concentration, addition of cross linking monomer, addition of ammonia solution and addition of texanol. The chromatic properties of the thermochromic films were studied by visual observation and confirmed by UV-Vis spectroscopy. The morphology and size distribution of both latexes and thermochromic films were studied by SEM, TEM and DLS techniques.