CHAPTER III

RESULTS AND DISCUSSION

3.1 Vesicle preparation and polymerization

Diacetylene monomer was prepared in the form of vesicles in water using a sonicator. The sonication of 10,12-pentacosadiynoic acid (PCDA) in water at 75-85 °C afforded semitransparent or transparent hydrocolloid without discernible lipid precipitate or suspension. After keeping the lipid colloid at 4 °C overnight, it was irradiated with UV light (254 nm) for 5 min at room temperature to give blue solutions, showing an electronic absorption band in the visible range with λ_{max} near 640 nm, indicating that the lipid vesicles readily undergo photopolymerization to form the corresponding polydiacetylene, poly-10,12-pentacosadiynoic acid, vesicles. A clear deep blue sol was obtained as a filtrate from a filtration through a filter paper (Whatman number 1, 11 μm) indicating that the sizes of the dispersed lipid vesicles prepared by this method were typically smaller than 11 μm. It is important to point out here that the cooling step after sonication is essential for photo-polymerization of the PCDA vesicles. When PCDA was irradiated without the cooling step, the blue color was not observed while the photopolymerization of PCDA vesicles was readily achieved after overnight refrigeration (Figure 3.1). Chilling PCDA reduces the kinetic energy and hence the molecular rotation and vibration allowing the lipid molecules to form tighter supramolecular assembly just exactly the same manner occurred in the crystallization process.

Figure 3.1 Appearance of PCDA hydrocolloid irradiated with UV light after a) stored at room temperature and b) stored in a refrigerator overnight.

To study the optimum chilling period necessary for the successful photo-polymerization, the electronic absorption at 640 nm of the irradiated lipid hydrocolloid were monitored as a function of chilling time. The electronic absorption reached the maximum after 1 hr of refrigeration (Figure 3.2) indicated that the crystallization of PCDA molecules within the lipid bilayer was completed within 1 hr.

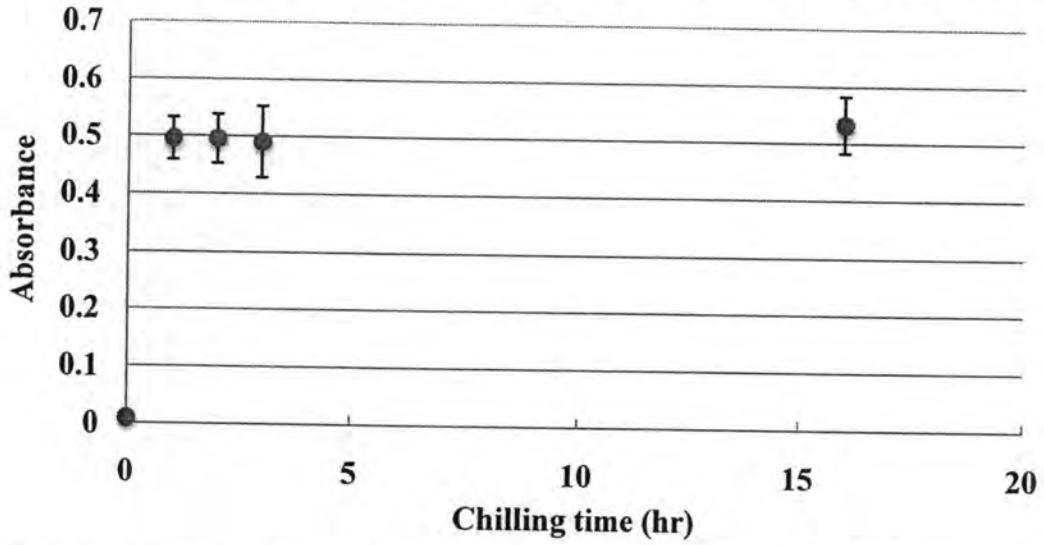


Figure 3.2 Adsorbance at 640 nm of the UV-irradiated PCDA hydrocolloid as a function of the chilling period.

In a photopolymerization, the irradiation dose which directly correlates on the exposure time can have a pronounced effect on the polymerization yield. For PCDA vesicles, increase of irradiation time from 1 to 40 minutes resulted in higher absorbance of the whole visible absorption band. The absorption band consisted of two maxima (λ_{max}), one at 638 nm and the other at 590 nm. The increase of the absorbance occured along with the hypsochromic shift of λ_{max} from 638 to 620 nm and 590 nm to 560 nm (Figures 3.3 and 3.4). The absorption at 620-638 nm produces blue color while the absorption at 560-590 nm produces red color. Hence, the PCDA hydrocolloid appeared as a purple color upon long UV exposure time. The amount of blue phase and red phase vesicle was determined by normalization of the absorbance at 590 with the absorbance at 630 nm. The normalized absorbance showed an increasing of red phase after 5 minutes (Figure 3.5). It appeared that the polymerization was complete within 5 minutes.[28] The 5 minute polymerization time was used in further experiments.

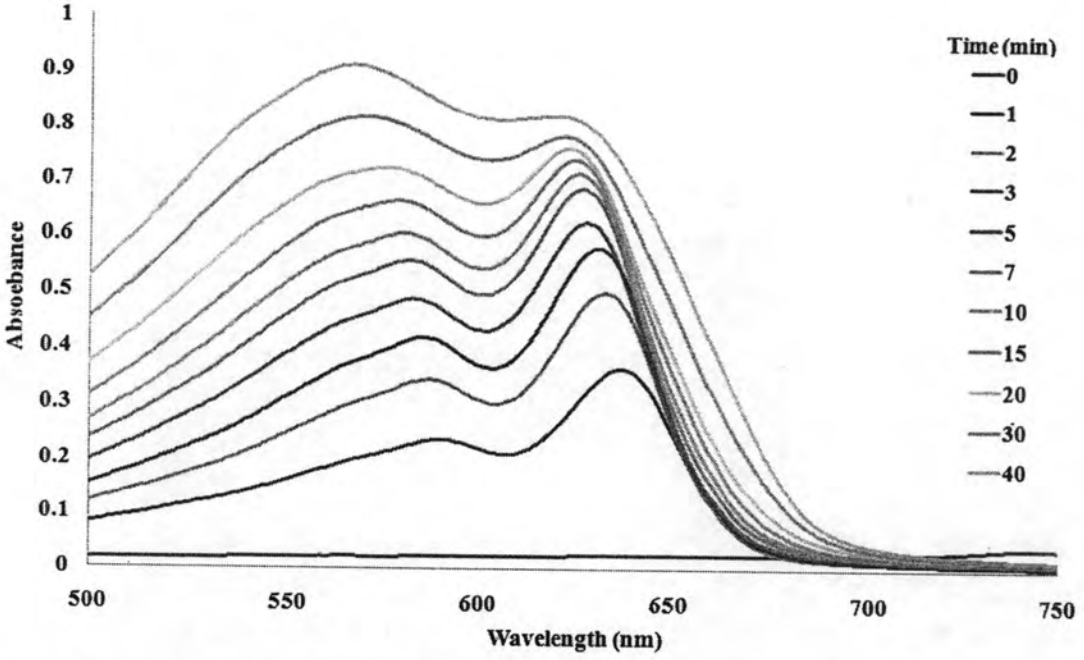


Figure 3.3 Electronic absorption spectra of UV-irradiated PCDA hydrocolliod at variable irradiation time.

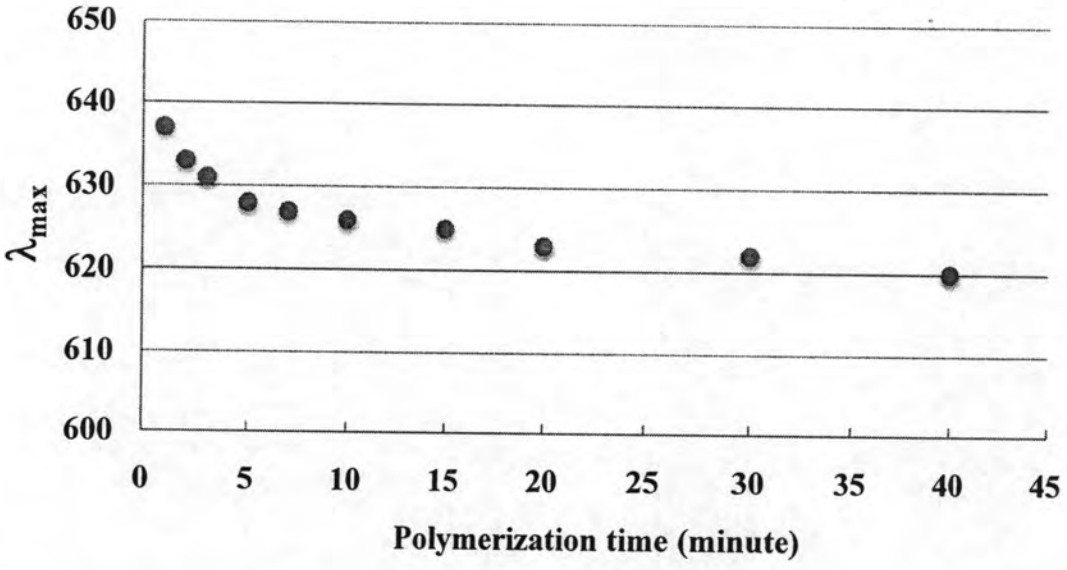


Figure 3.4 Shifting of the maximum wavelength of PCDA hydrocolloid along the UV-irradiation time.

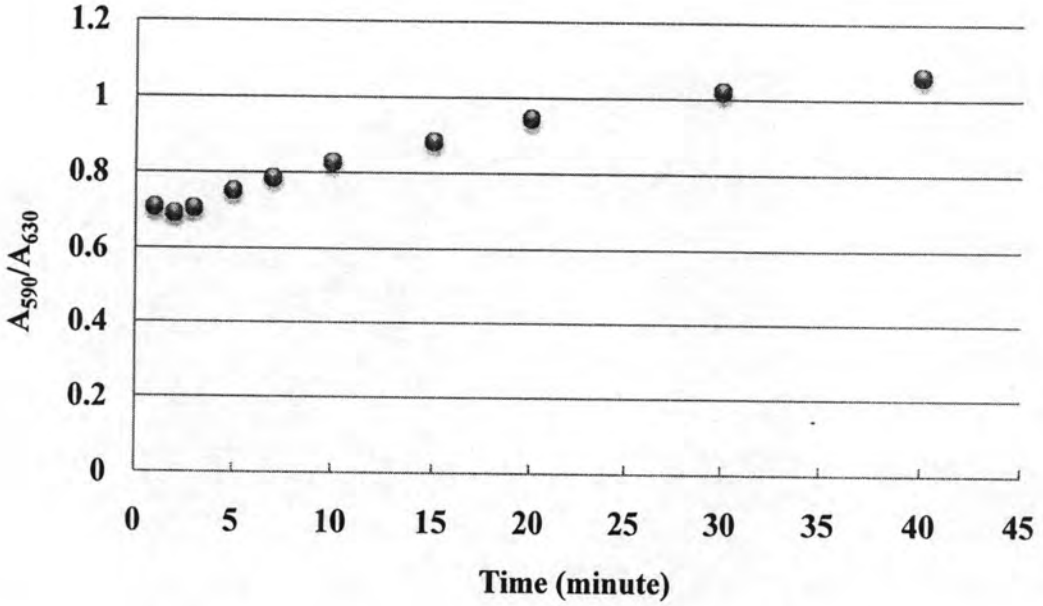


Figure 3.5 Plot of A_{590}/A_{630} of the UV-irradiated PCDA hydrocolloid as function of polymerization time.

3.2 Characterization of poly(PCDA) sol

Mean particle size and distribution

The average particle size of the vesicles determined by dynamic light scattering (DLS) was 70-200 nm. Transmission electron microscopy (TEM) images of an air dried sample of poly(PCDA) sol stained with uranyl acetate on a formvar grid showed spherical structure of vesicles with diameters around 50-70 nm agreeing well with the dynamic light scattering results (Figure 3.6).

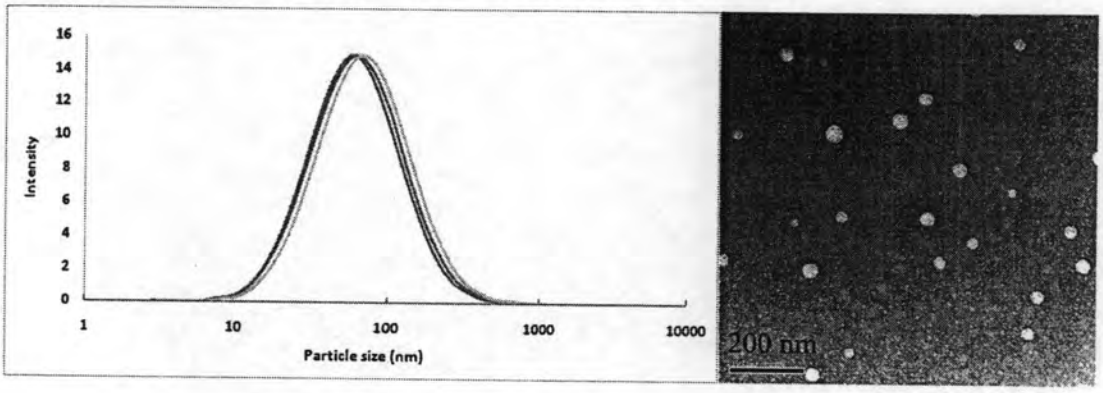


Figure 3.6 a) Three repetitive of dynamic light scattering spectra and b) TEM image of poly(PCDA) vesicles.

Electronic absorption spectra

Since the UV-irradiated PCDA hydrocolloid, or poly(PCDA) sol for short, is highly colored, its electronic absorption spectrum can be very characteristic and interesting. The electronic absorption spectrum of poly(PCDA) solution showed the major band with the λ_{max} between 630-640 nm (Figure 3.7) depending on the irradiation time and sample preparation as described previously. This band has been assigned to a HOMO-LUMO (π-π^*) transition of the electron in the conjugated ene-yne backbone of poly(PCDA).[20] The spectrum also contained a minor band with λ_{max} near 590 nm. The vibronic coupling has been suggested to account for this minor band.[52] Heating poly(PCDA) solution to 90 °C resulted in the irreversible color change from blue to a red and the λ_{max} was shifted from 640 to 540 nm. The mechanism of this color transition is described in the next section.

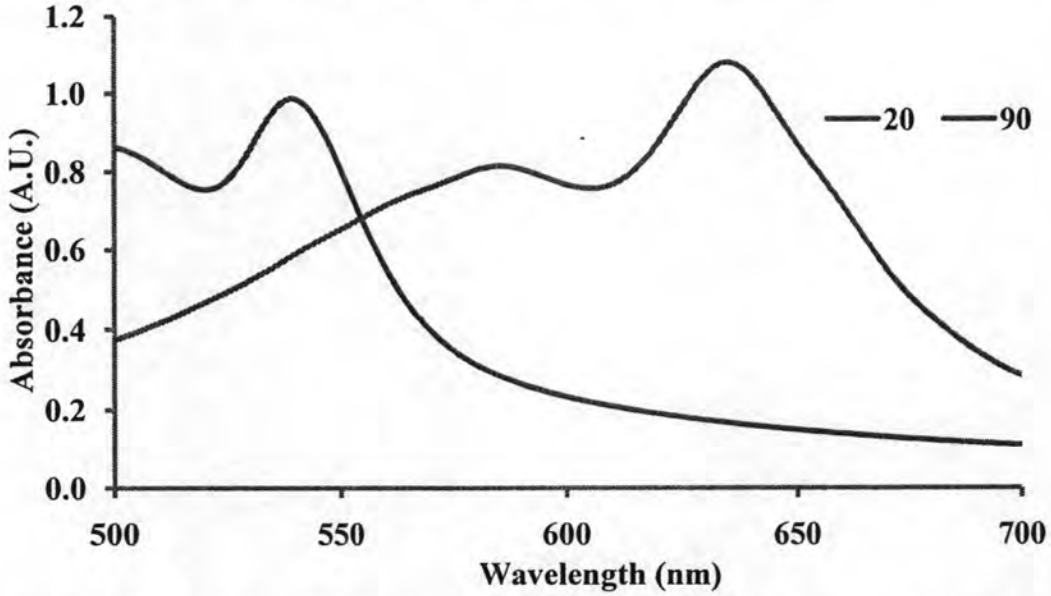


Figure 3.7 Absorption spectra of blue phase (20°C) and red phase (90°C) poly(PCDA) vesicles.

3.3 Mechanism of chromic transition of poly(PCDA) vesicles

Under an external stimulation, *e.g.* adding an organic solvent, increasing pH and raising temperature, poly(PCDA) veiscles undergo a drastic color transition from blue to red irreversibly. Optical absorption of blue and red forms of poly(PCDA) is a consequence of a π-π^* transition of electrons within the ene-eyne conjugated backbone. The absorption maxima of blue and red forms of poly(PCDA) vesicle solutions are generally observed near 635 and 540 nm, respectively.[20,28] Although it is widely believed that these transitions, so called solvatochromism,[1, 8]

alkalinochromism[34] and thermochromism,[21, 25-31,33] are related to the conformational change of the polymeric side chain, their mechanisms have not yet been clearly justified. Understanding the detailed mechanisms of these transitions can lead to logical design of suitable sensing materials for different applications.

To gain insight mechanism of these transitions, the change of electronic absorption spectra in the course of solvatochromic, alkalinochromic and thermochromic transitions of poly(PCDA) vesicles with reproducible size distribution were examined. The color transitions induced by these three types of stimulations appeared very similarly as the color change from blue to purple and to red. The spectroscopic profiles of these transitions were however interestingly different. The difference in these spectroscopic data has not yet been properly addressed in the literatures despite the long known chromism properties of the polydiacetylenes.

In the solvatochromism study, the gradual addition of absolute ethanol into an aqueous solution of blue poly(PCDA) vesicles (0.1 mM lipid) caused the absorbance at 635 nm to decrease while the absorbance at 540 nm increased (Figure 3.8a). In 45-50% (v/v) ethanol solution, the vesicle appeared as a purple color. The vesicle solution turned completely red when the medium contained more than 55% (v/v) of ethanol. In the case of alkalinochromism, a careful titration of poly(PCDA) vesicle solution with NaOH (1 M) solution showed very similar change of the absorption spectra, the increase of the absorbance at 540 nm with the expense of the absorbance at 635 nm (Figure 3.8b). The vesicle solution was purple when pH was 9.7-10.5 and became red at pH higher than 10.7. A single isobestic point at 550 nm was observed during both solvatochromic and alkalinochromic transitions implying quantitative conversion between these two forms, blue and red, of the vesicles.

Thermochromic transition was studied by gentle heating of poly(PCDA) vesicle solution from 20 to 90 °C. The absorption spectrum was recorded 10 minutes after the temperature had reached the specified temperature. Unlike in the solvatochromism and alkalinochromism, the thermochromic transition showed hypsochromic shift of the λ_{max} (Figure 3.8c). For example, at 60 °C the vesicle solution adopted a purple color with the maximum absorption at 612 nm. At 80 °C or higher, the color of the vesicle solution completely changed to red with the absorption maximum at 540 nm. The hypsochromic shift in thermochromism is most likely to associate with the microscopic movement of the methylene side chain to relieve part

of the strain present in ene-yne conjugated backbone resulting in valence band lowering and π-π^* gap widening.[21, 53-56] This process is however driven mainly by the entropic gain rather than the enthalpic gain from the strain relief as the transitions from the blue to purple colors were essentially reversible.

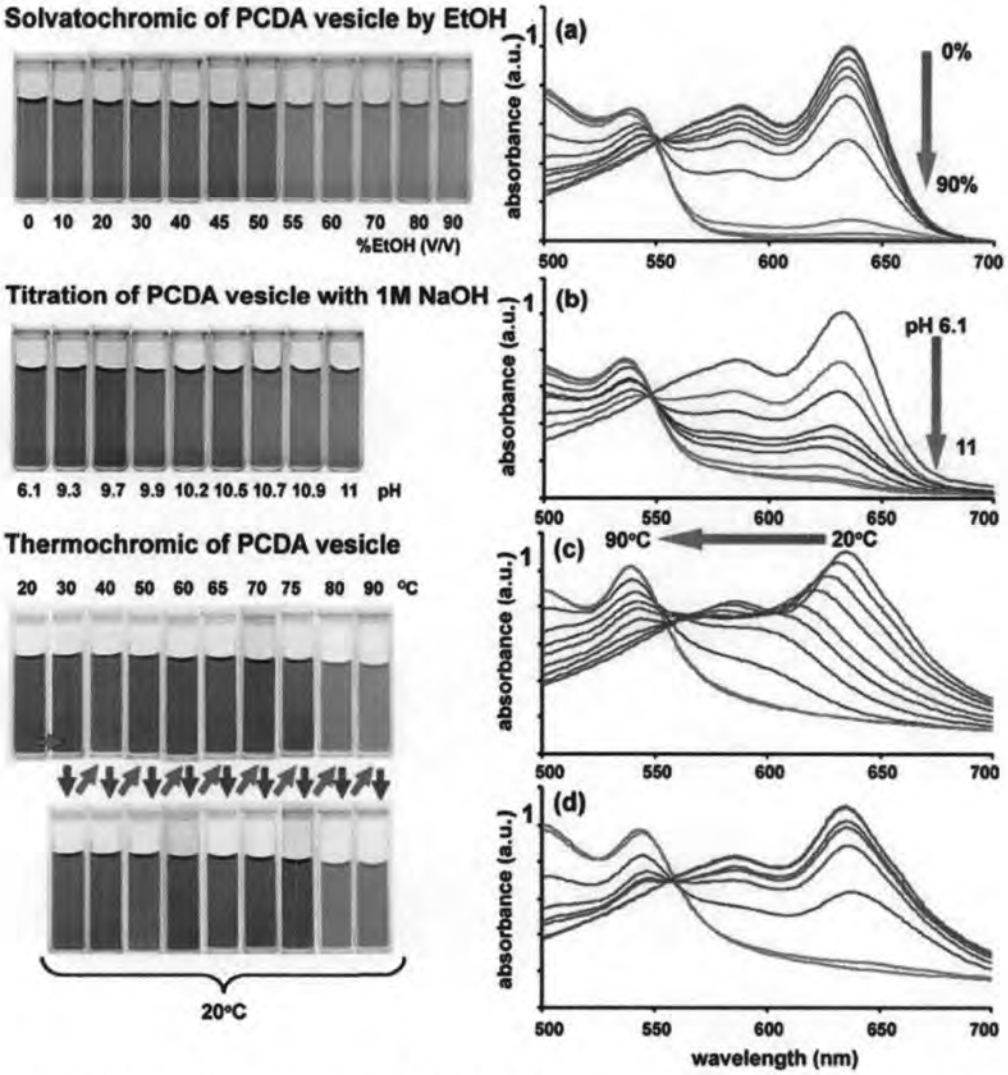


Figure 3.8 Absorption spectra of poly(PCDA) vesicle aqueous solution a) in the presence of various concentrations of ethanol, (b) during titration with NaOH (c) heating and (d) cooling to 20°C

Evidently, the hypsochromic shift of the absorption spectra, recorded during the heating and cooling cycles, returned to almost its original λ_{max} by cooling the solution to 20 °C after being heated up to 65 °C (Figure 3.8d). The purple vesicles observed in the thermochromism are thus a series of thermodynamically unstable transition forms. At 80 °C or higher, the thermal energy is not only enough to disturb

the hydrophobic interaction but also enough to break the hydrogen bonding between the carboxylic head groups (Figure 3.9) relieving all the backbone strain and turning all the vesicles into the red form.

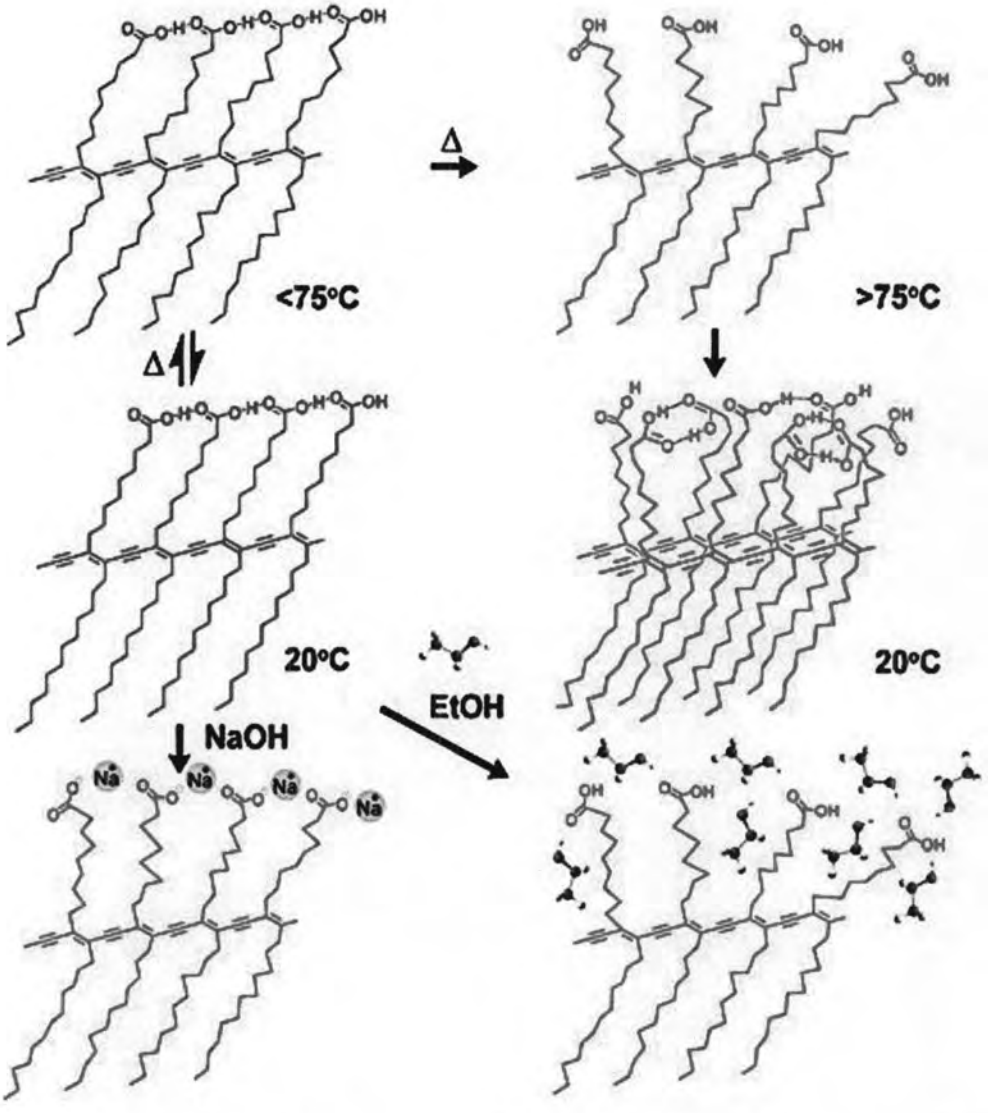


Figure 3.9 Proposed side chain movement in the chromic transitions of poly(PCDA) vesicles.

The relief of backbone strain was evidenced by the shift of the peaks in the raman spectra to lower energy upon the blue to red transition corresponding to the increase of the bond length. The double and the triple bond stretching peaks shifted from 1475 and 2103 to 1510 and 2129 cm^{-1}, respectively (Figure 3.10). The red vesicles appeared to lack the reversibility as there was no recovery of the absorption at 635 nm observed in the spectra after heating the vesicle solution to 80 °C or higher

(Figure 3.8d), indicating that the red form is a thermodynamically stable form. In the red form, not only the entropic gain but also significant enthalpy gain through the backbone strain relieving also contribute to overcome the enthalpy lost due to hydrogen bond breaking. Upon cooling, new sets of inter- and intra-chain hydrogen bonds are formed without reinstating the original backbone strain to foster the stabilization of the red form (Figure 3.9). It is of significance to note that the absorption spectra between 65 and 75 °C contain a little band at 540 nm indicating that some of the vesicles already turned into the red form at these temperatures. The vesicles with smaller sizes were noted to have slightly higher sensitivity to stimulants.[57] The size of the vesicles prepared in this work were Gaussian like distributed with an average diameter and polydispersity of 60 nm and 0.47, respectively. It is thus likely that the smaller vesicles turned red at the temperature lower than 80 °C. It is thus important to control the size distribution of polydiacetylene vesicles to ensure reproducible results when applying them in sensing applications and sharper responses should be obtained with vesicles having narrower size distribution.

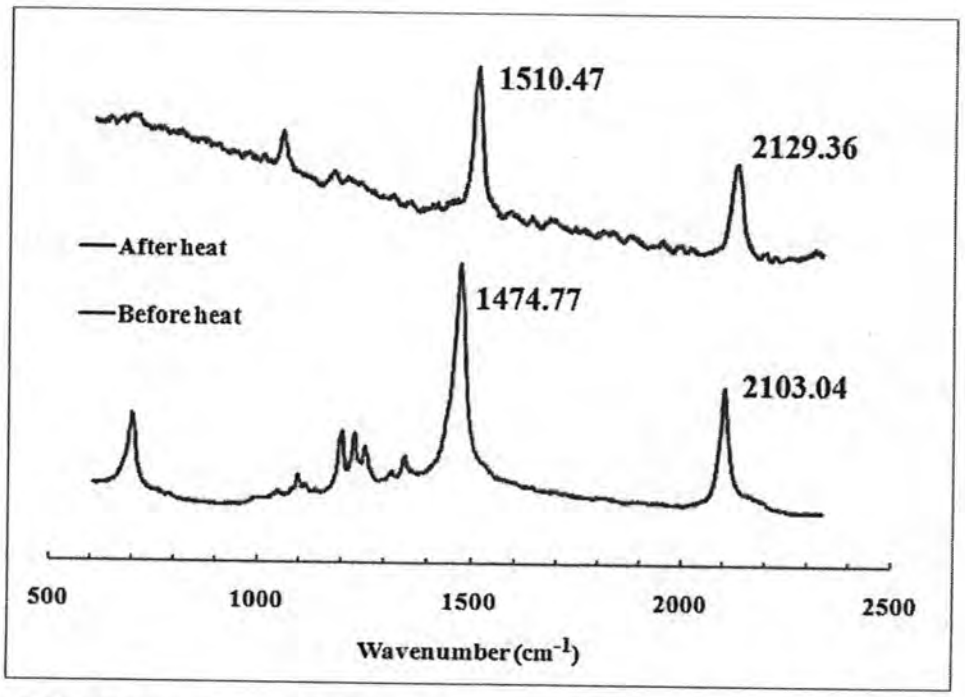


Figure 3.10 FT-Raman spectra of poly(PCDA) vesicles before and after being heated to 90 °C

Although the purple color was also observed in the solvatochromism and alkalinochromism, the gradual shift of λ_{max} to shorter wavelength was not. There was also no reversibility of the purple vesicles back to blue in the solvatochromism and alkalinochromism. The purple colors observed in the solvatochromism and alkalinochromism are thus actually the combination of the blue and red vesicles. As the vesicles interact with the solvent molecules or hydroxide ions at their interface, it is most likely that the molecular process in solvatochromism and alkalinochromism started immediately by the hydrogen bond breaking leading to the utmost side chain disarray and relief of backbone strain (Figure 3.9). In biochromism of polydiacetylene reported in a number of literatures,[40,58-62] the transition of the absorption spectra are very similar to those observed in solvatochromism and alkalinochromism. It is thus reasonable to propose that the mechanism for biochromism initiated by the interface interaction is more resemble to the solvatochromism and alkalinochromism than the thermochromism.

3.4 Layer-by-layer deposition of poly(PCDA) vesicles

The nanospherical vesicles or liposomes of polydiacetylenes homogeneously dispersed in aqueous media have been successfully used as colorimetric sensors.[63-70] Immobilization of polydiacetylene vesicles into thin films would enhance their storage stability and user-friendliness. Despite long and extensive research on polydiacetylene vesicles, reports on the fabrication of films containing these materials have just come to light in recent years. Monomeric diacetylene vesicles have been covalently fixed onto functionalized glass substrates followed by photopolymerization to form blue-phase polydiacetylene monolayer films.[71-72] This approach is useful when monolayer deposition is desired, but the fabrication of multilayer films with sufficient visible color by this technique is not generally practical. The transfer of self-assembled polydiacetylene Langmuir–Blodgett films to flat substrates is somewhat less complicated, but is not suitable for the assembly of vesicles that have spherical hydrophilic surfaces.

The polyelectrolyte multilayers (PEM) technique developed by Decher and coworkers emerged as an alternative method for the preparation of multilayer thin films.[73-78] Although based on a very simple adsorption process, PEM assembly has proven to be a very powerful method for immobilizing charged species onto a

substrate. In this technique, oppositely charged polyelectrolytes (polyanions and polycations) are assembled into thin films by sequential dipping of a substrate into polyelectrolyte solutions followed by rinsing steps. The electrostatic interaction between the adsorbed layer on the substrate and the oppositely charged polyelectrolytes in the solution leads to the adsorption of another polyelectrolyte layer and the reversal of the surface charge, allowing the deposition of the next layer. The PEM technique is well suited for the preparation of thin films on objects with various types of surface and shape. The thickness of the film can also be easily controlled by choosing the appropriate number of layers deposited, which is convenient for preparation of colorimetric sensing devices detectable by naked eyes.

Early use of the PEM technique to assemble diacetylene monomers or polydiacetylene chains with polyallylamine (PAH) resulted in thin films with an irreversible red color, which excluded them from being colorimetric sensors.[79,80] It is important to emphasize here that in order for polydiacetylene vesicles to be usable in sensing applications, the characteristic blue color of the vesicles must be maintained during the film preparation process. Michael and coworkers, have recently demonstrated that the assembly of phospholipid vesicles in PEM thin films was possible by dipping or spraying the vesicles onto a substrate.[81-82] They also demonstrated that the phospholipid vesicles conserved their spherical shape and could be used as bioreservoirs for drug release. The deposition of unpolymerized vesicles into thin films that were later photopolymerized has recently been reported.[16] However, no clear evidence indicates whether the spherical structure of the vesicles remained intact. To the best of our knowledge, the direct assembly of prepolymerized vesicles with retaining blue color has not yet been successful. The aim of this part of dissertation is to report the development of the layer-by-layer deposition technique for preparation of the PEM thin films with the blue color and the spherical structure of the polydiacetylene vesicles preserved (Figure 3.11). Poly(PCDA) vesicle sol was used as polyanionic solution and either acidic aqueous solution of chitosan or polyethyleneamine (PEI) was used to provide the polyanionic counterpart. The chromic responses of the PEM film to various stimuli such as ethanol, pH, and temperature in comparison with that of vesicle sol will also be presented.

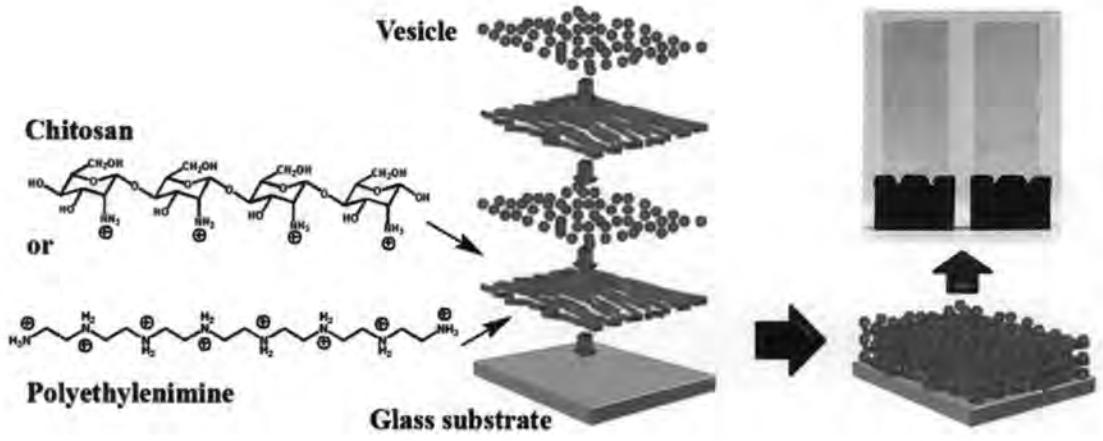


Figure 3.11 Schematic representation of layer-by-layer techniques for deposition of polydiacetylene vesicles.

3.4.1 Deposition of chitosan/poly(PCDA) vesicle film

Charge interaction between positive charge and negative charge of polymer was the major role of film deposition. The higher electrostatic interaction can be made by increasing positive charge and negative charge on both of cationic polymer and anionic polymer. For example, in standard condition of chitosan and poly(PCDA) vesicle deposition, the pH of vesicle was adjusted to 5.0 which chitosan/poly(PCDA) film was prepared but PEI/poly(PCDA) film cannot prepare in this condition.

In the initial study, chitosan was used as a cationic polymer. The chitosan solutions used for deposition were controlled by adjusting the pH value in the range of 3.0 - 9.0. At pH lower than 3.0 poly(PCDA) vesicles were precipitated probably by the protonation of the carboxylate head groups on the vesicle surface. At pH higher than 9.0 the poly(PCDA) vesicles changed the color from blue to purple due to its alkalinochromic properties. The chitosan/poly(PCDA) PEM film was successfully prepared by using a 0.1% w/w chitosan solution in acetate buffer pH 5. This condition was used to study the other parameter such as dipping time, vesicle concentration, pH of solution.

To investigate the maximum absorption of vesicles on multilayer films, the PEM films were prepared by varying the concentration of vesicle sol. After the preparation, the PEM films were dipped into an absolute ethanol solution to convert the blue to be red films of which the absorbance is more stable than the blue ones. The absorbance at 540 nm of the red 20-layered PEM films increased linearly with the

concentration of vesicle sol (Figure 3.12). When the concentration of vesicle sol was increased to 1 mM, aggregation of the lipid vesicles was observed that lead to dreadful precipitation of vesicle-chitosan complex during the dipping cycle. The maximum concentration poly(PCDA) sol investigated in this work was thus limited to 0.8 mM where the saturation of the electronic absorption has not been reached. The results suggested that the adsorption of vesicles of the PEM film increased with the the sol concentration.

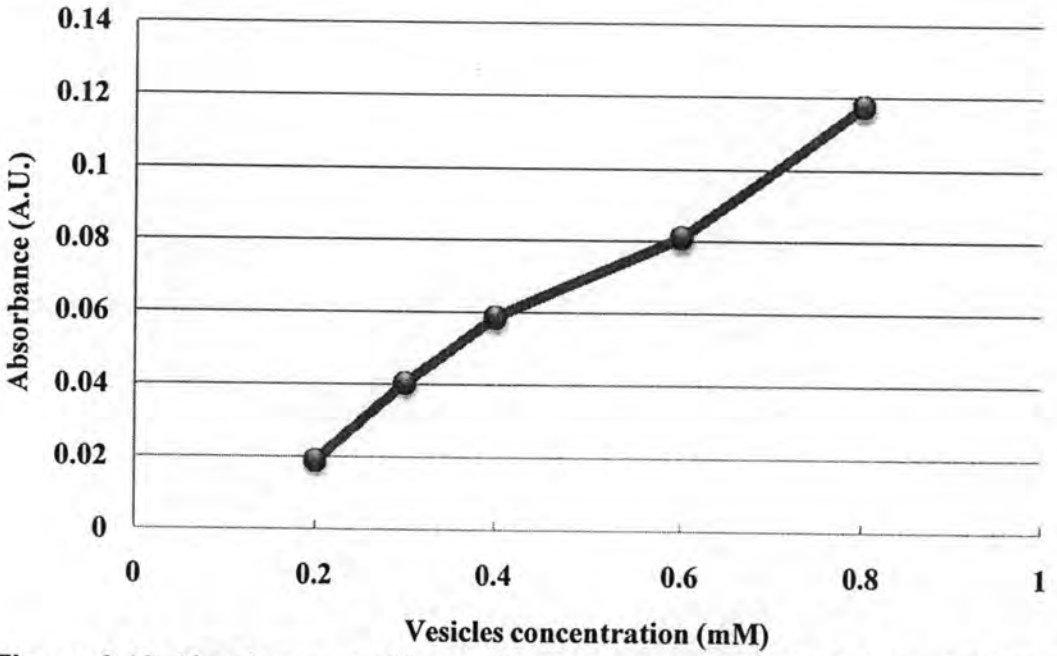


Figure 3.12 Absorbance at 540 nm of chitosan/poly(PCDA) 20-layered PEM films prepared from various concentrations of poly(PCDA) sol. Chitosan was 0.1%w/w and dipping time was 5 minutes.

The film growth in the preparation of chitosan/poly(PCDA) PEM film is a type of chemisorption. Theoretically, chemisorption on a substrate is dynamic process. The rate of adsorption is faster than the rate of desorption in the initial state and the adsorption and desorption rate become equal when the process reaches its equilibrium state. After reaching the equilibrium state, there is no net adsorption and the saturation of the film growth should be observed. To determine the dipping time required to allow the adsorption to reach the equilibrium, 10-layered films were prepared by varying the dipping time in each cycle. The physisorbed chitosan and poly(PCDA) was removed by three rinsing steps with excess water. The electronic absorbance showed that the film grew relatively fast during the first 10 minutes of the dipping period used in each adsorption step of the layer-by-layer deposition (Figure

3.13). The film growth became slower when the dipping time was greater than 10 minutes but, however, no saturation of the electronic absorbance observed indicating no saturation of the film growth. The unsaturation of the film growth maybe attributed to some slow physisorbtion occurred by coiling and folding of the polyelectrolyte chain, chitosan in this case, that is reported to be significant pitfall for the first few layers of some layer-by-layer depositions.

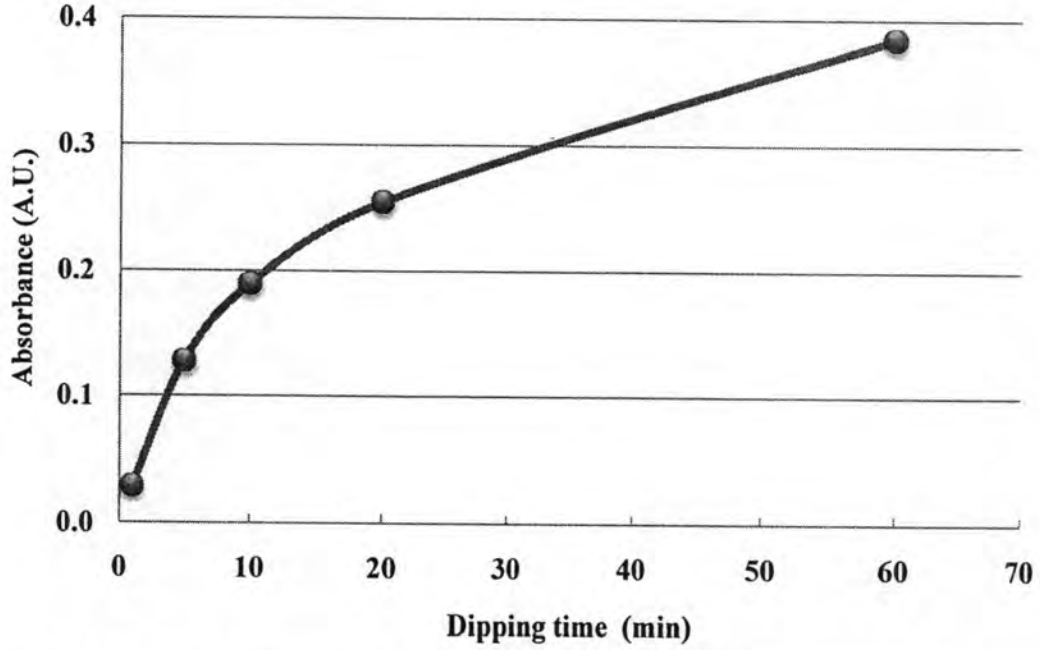


Figure 3.13 Electronic absorbance of 10-layered films at 540 nm prepared by varying the dipping time in each adsorption step of the layer-by-layer deposition.

The next experiment was thus performed by dipping chitosan and vesicle only 1 minute at the first 5 layers to prepare the uniform chitosan layer on the glass substrate for the next absorption. The sixth layer was varied absorption time to see the saturated absorption. The saturated absorbance of films was observed at 5 min of dipping time when using vesicle concentration 1 mM (Figure 3.14).

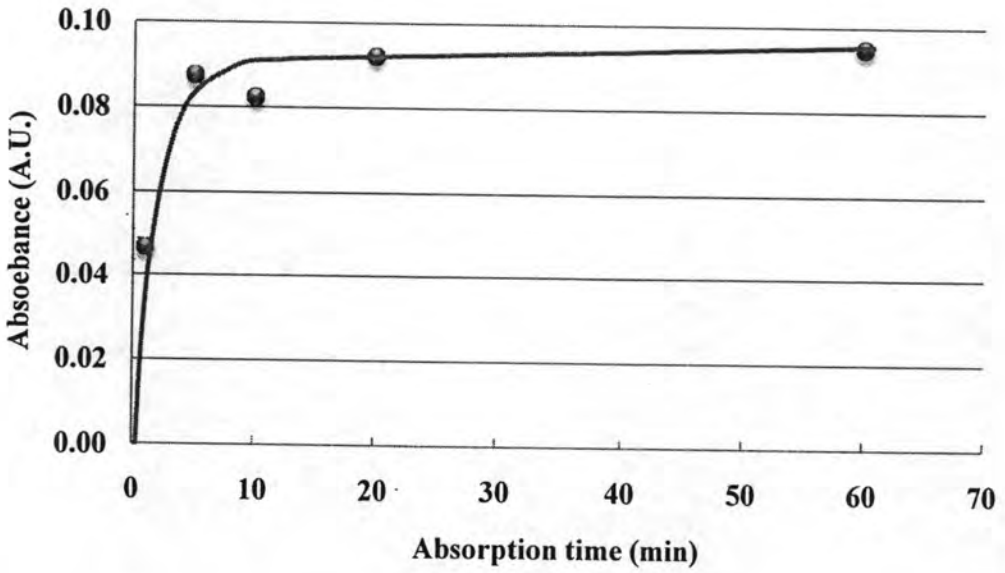


Figure 3.14 Electronic absorbance of six-layered films at 540 nm prepared by varying the dipping time in the sixth cycle of the layer-by-layer deposition.

3.4.2 Deposition of polyethylenimine/poly(PCDA) film

To prepare PEI/poly(PCDA) film, various conditioning preparations had been investigated. Increasing of the negative charge of vesicle by adjusting the pH of vesicle solution to pH 7.0 would prepare PEI/poly(PCDA) film. However, the PEI films cannot be prepared at this pH value (Table 3.1, entry a). The result was contrast with a hypothesis that highly negative charge should has stronger interaction. The non-deposition of film probably occurred by cationic polymer that deposit on film dissolved in high pH solution during the vesicle absorption.

The PEI/poly(PCDA) film was successfully prepared by increasing of an acidity of vesicle solution lower than pH 4.0 and use PEI concentration 10 mM (entries d-g). However, at low pH solution (pH 2.8) the vesicle solution was aggregated after second dipping cycles. The aggregation might occurred by strong electrostatic charge interaction between highly protonated PEI with vesicle. Reducing of PEI concentration from 10 mM to 1 mM can prepare PEI/poly(PCDA) film at the pH 2.8 condition (entry h).

Table 3.1 Preparation condition of LBL deposition of PEI films

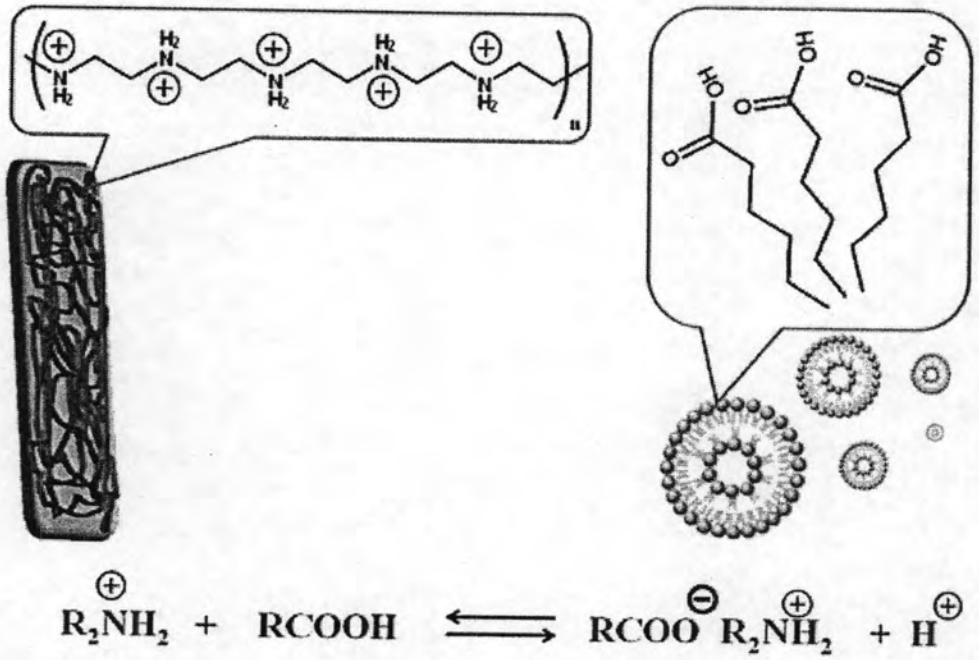
Entry	PEI (mM)	pH	vesicle (mM)	pH	Rinse buffer	pH	Film
a	1	4.0	1	6.7[a]	phosphate	5.0	X
b	1	3.0	1	5.0	HCl	3.0	X
c	10	2.6	1	5.5	HCl	3.0	X
d	10	2.6	1	4.0	HCl	3.0	O
e	10	2.6	0.5	3.0	HCl	3.0	O
f	10	3.7	1	4.0	HCl	3.9	O
g[b]	10	2.8	1	2.8	HCl	2.9	O
h	1	2.7	1	2.8	HCl	2.9	O

a) adjusted pH by 100 mM Na_2HPO_4

b) vesicle precipitate after the second dipping

O = preparable (observe by naked eye)

X = unpreparable



$$R_2\overset{\oplus}{N}H_2 + RCOOH \rightleftharpoons RCOO^{\ominus}\,R_2\overset{\oplus}{N}H_2 + H^{\oplus}$$

Figure 3.15 Proposed charge interaction derived from an ion exchange process responsible for the adsorption of chitosan and vesicles in the PEM film formation.

3.4.3 Effect of pH of the solutions used in the preparation of PEM films

From previous section, the PEM films can be prepared only when pH of all the solutions are acidic. In this section, the preparation of chitosan/poly(PCDA) and PEI/poly(PCDA) PEM films with all the solutions adjusted to 3 and 5. The 20-layed PEM films prepared at pH 3 showed the electronic absorbance at 639 nm significantly lower than those of the films prepared at pH 5 (Figure 3.16). The lower absorbance of the films prepared at pH 3 indicates the lower amount of poly(PCDA) vesicles adsorbed in each layer that may be attributed to the higher concentration of proton that increases the reversed reaction of the ion exchange process (Figure 3.15).

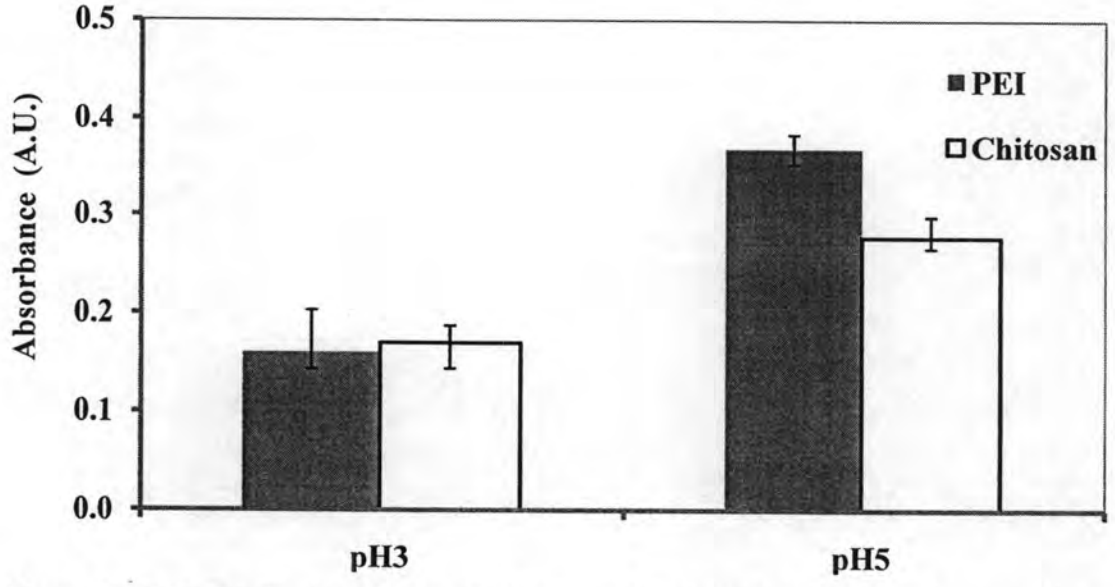


Figure 3.16 Electronic absorbance of 20-layered PEM films at 639 nm (the error bar calculated from 3 samples).

3.4.4 Characterization of the PEM films

Two types of PEM films, chitosan/poly(PCDA) and PEI/poly(PCDA) were prepared by a layer-by-layer assembly deposition. UV–vis absorbance at 635 nm was employed to monitor the layer-by-layer deposition. Linear relationships between the number of layers and the absorbance were obtained for both polycationic electrolytes (Figure 3.17), signifying a well-defined layer-by-layer deposition system.

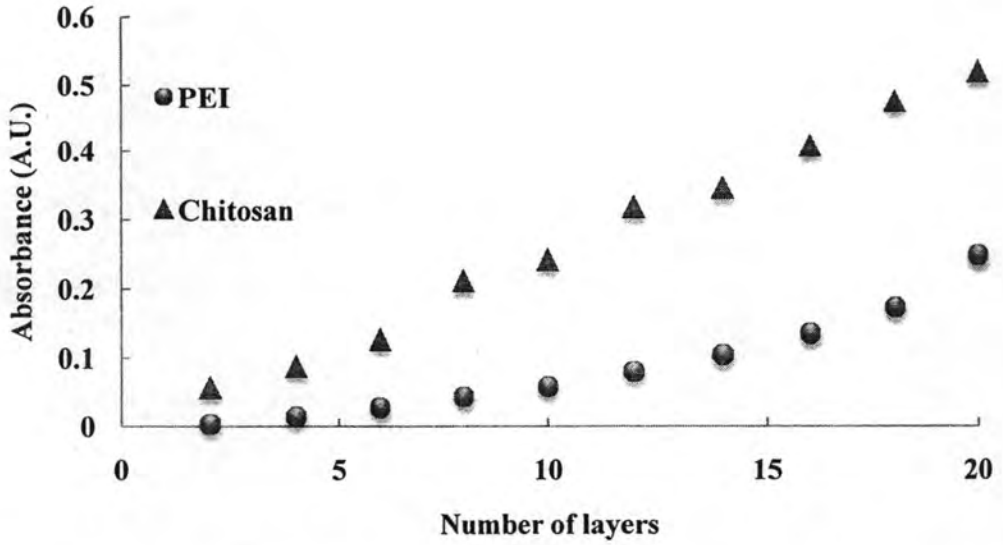


Figure 3.17 Electronic absorbance at 640 nm of chitosan/poly(PCDA) and PEI/poly(PCDA) films. Films preparation were carried out at pH 3 and 25 °C.

As mentioned previously that the average size of poly(PCDA) vesicles used in the layer-by-layer assembly was estimated from the vesicle sol using dynamic light scattering (DLS) and dry samples cast on glass slides using tunneling electron microscopy (TEM) and atomic force microscopy (AFM). The nano-sized vesicles had an average diameter of 60 nm obtained from the light-scattering data and TEM image (shown previously in Figure 3.6) agreed well with that observed from the AFM image (Figure 3.18a). The spherical vesicles were also observed in the AFM image of chitosan/vesicles PEM film (Figure 3.18b). The AFM image clearly shows, for the first time, that the intact polydiacetylene vesicles could be assembled into a PEM film.

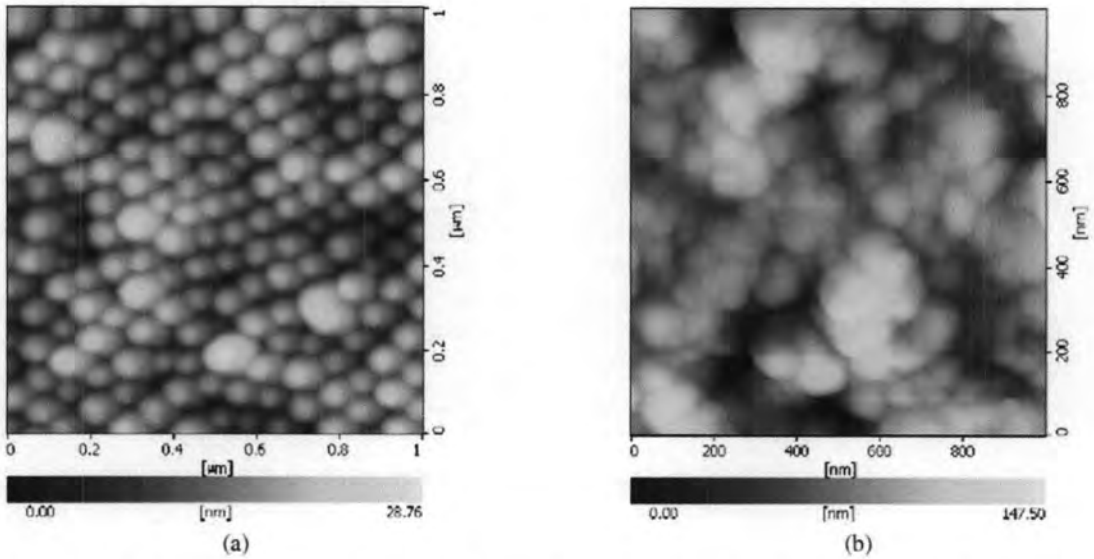


Figure 3.18 AFM images of (a) poly(PCDA) vesicles dried on a glass slide and (b) chitosan/poly(PCDA) vesicles in a 20-layered PEM film.

The visual appearance of the resulting chitosan/vesicles and PEI/vesicles PEM films was very smooth and uniform, with a deep blue color intensifying as a function of the number of deposited layers. The blue films immediately and irreversibly turned red when they were dipped into 95% ethanol. The visible absorption spectra of the blue and red films showed the maximum absorption at 635 and 540 nm, respectively (Figure 3.19). This irreversible color switch is probably related to the irrecoverable perturbation of the intramolecular hydrogen bonds between the carboxylic head groups of the polydiacetylene side chains, which reduced the conjugation length or relieved the mechanical stress on the polydiacetylene backbone.[83]

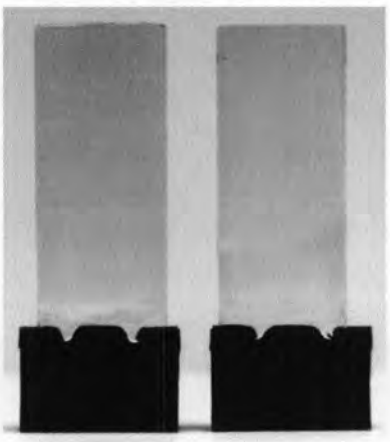


Figure 3.19 Color photographs of typical 20-layered chitosan/poly(PCDA) PEM films on glass substrates before (blue) and after (red) the films were dipped into 95% ethanol.

3.4.5 Chromic properties of PEM films comparing with the vesicle solution

For the PEM films containing vesicles to be used as colorimetric sensors, the chromic properties of poly(PCDA) vesicles must be conserved in the films. Solvatochromism, pH sensing, and thermochromism of the films were assessed in comparison with those of vesicles dispersed in water to demonstrate the essential chromic properties of poly(PCDA) vesicles in the PEM films. In a solvatochromism study, exposing the PEM films to the aqueous solution containing increasing percentages of ethanol resulted in an irreversible color switch from blue to red and an increase of %CR. The color transitions for the chitosan/ poly(PCDA) and PEI/ poly(PCDA) films were completed when the aqueous solution contained ethanol 62 and 68% (w/w), respectively (Figure 3.20). The color change of the poly(PCDA) sol was however completed at significantly lower ethanol content (47% w/w). As the electrostatic nature of the PEM films tends to repel less hydrophilic solvents, the shift in the colorimetric response of the vesicles embedded in the PEM films compared to the vesicles dispersed in water is not surprising.[84-86] The drastic change in %CR of the PEM films concurs with the sharp color change from blue to red, easily observed by naked eyes.

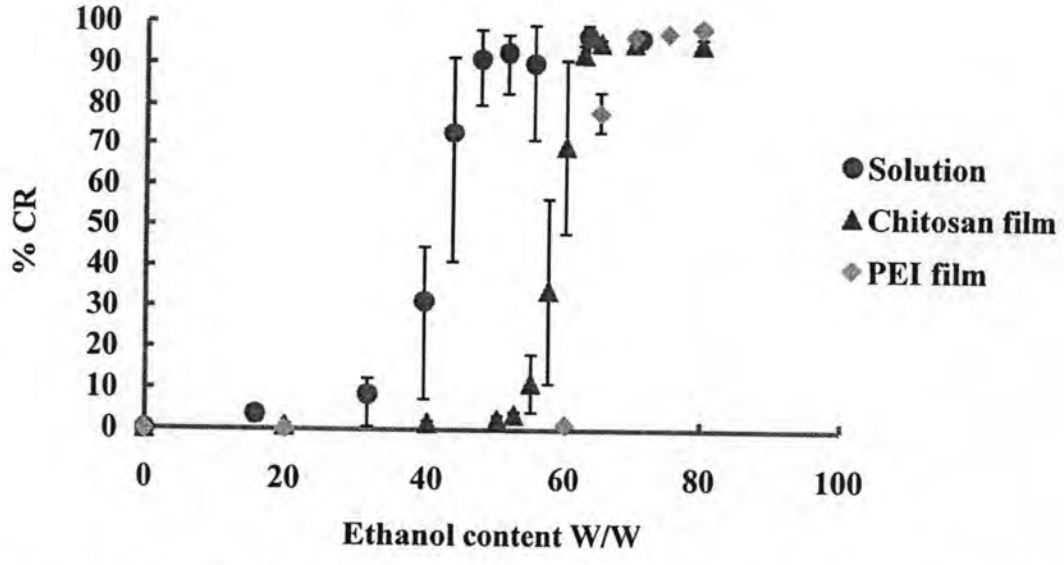


Figure 3.20 The colorimetric response (%CR) as a function of EtOH content for poly(PCDA) sol, chitosan/poly(PCDA) PEM film and PEI/poly(PCDA) PEM film. The experiments were carried out at pH 6 and 25 °C.

Another important stimulus known to trigger the color change of the blue phase polydiacetylenes is pH. The response of the PEM films containing poly(PCDA) vesicles to the surrounding pH was evaluated in comparison to that of poly(PCDA) sol. While the color transition of the free vesicles was completed at pH 8.3 (Figure 3.21), the chitosan/poly(PCDA) and PEI/poly(PCDA) PEM films showed slightly higher transition pH (~9.0). This difference is probably resulted from the lower acidity of the poly(PCDA) vesicles in the highly charged environment of the PEM film. The color change of the PEM films can be easily observed by naked eyes as shown in Figure 3.22.

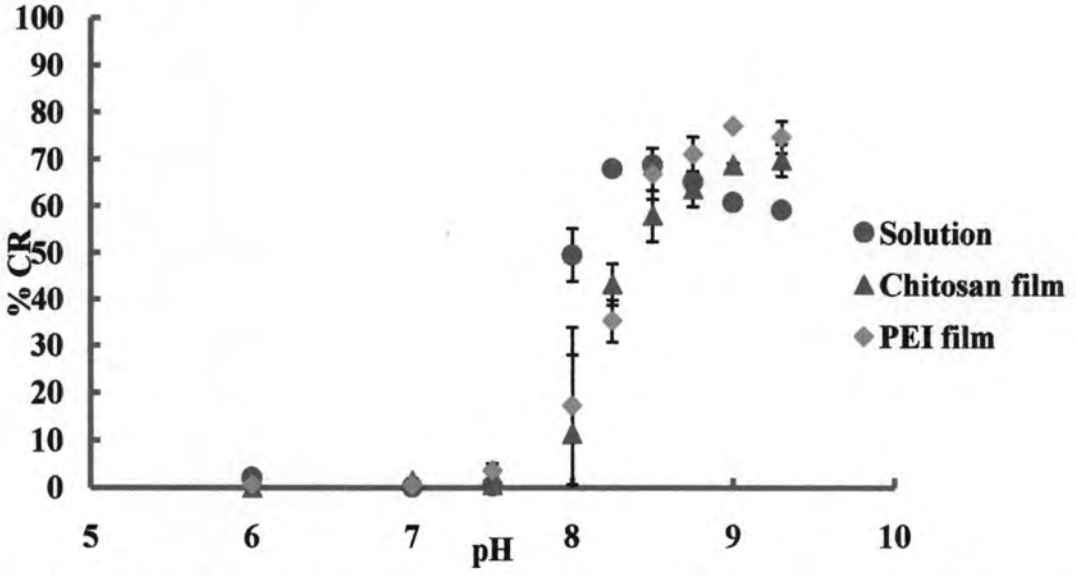


Figure 3.21 The colorimetric response (%CR) as a function of pH for poly(PCDA) sol, chitosan/poly(PCDA) PEM film and PEI/poly(PCDA) PEM film. The experiments were carried out in water at 25 °C.

Figure 3.22 Color photographs of 12-layered chitosan/poly(PCDA) films in various pH phosphate buffer (100 mM).

Last, the thermochromic properties of the immobilized poly(PCDA) vesicles in the PEM films were studied with a variable temperature UV–vis spectrometer. The %CR of the PEM films and the vesicles dispersed in aqueous media increased almost linearly with the temperature in the range of 25–70 °C and the color transition was completed around 68 °C (Figure 3.23). Notably, the %CR of the vesicles dispersed in water dropped after the color transition was completed. The decrease in %CR was observed along with a decrease of both blue and red absorbances, suggesting aggregation and precipitation of the vesicles at high temperature. At high temperature, the PEI/ poly(PCDA) film showed also significantly lower %CR than that of chitosan/ poly(PCDA) films corresponding to the opaque film observed in the PEI/vesicle film. These results suggest another favorable feature of chitosan/ poly(PCDA) PEM films. Poly(PCDA) vesicles dispersed in water generally aggregate and precipitate within a month. This short shelf life is one of the major obstacles to the use of the vesicles in real applications. However, the blue-phase PEM films prepared in this study can be kept in water for over a year without significant change in their appearance. This greater storage stability of the films certainly increases the practical value of the vesicles in real applications as sensing devices.

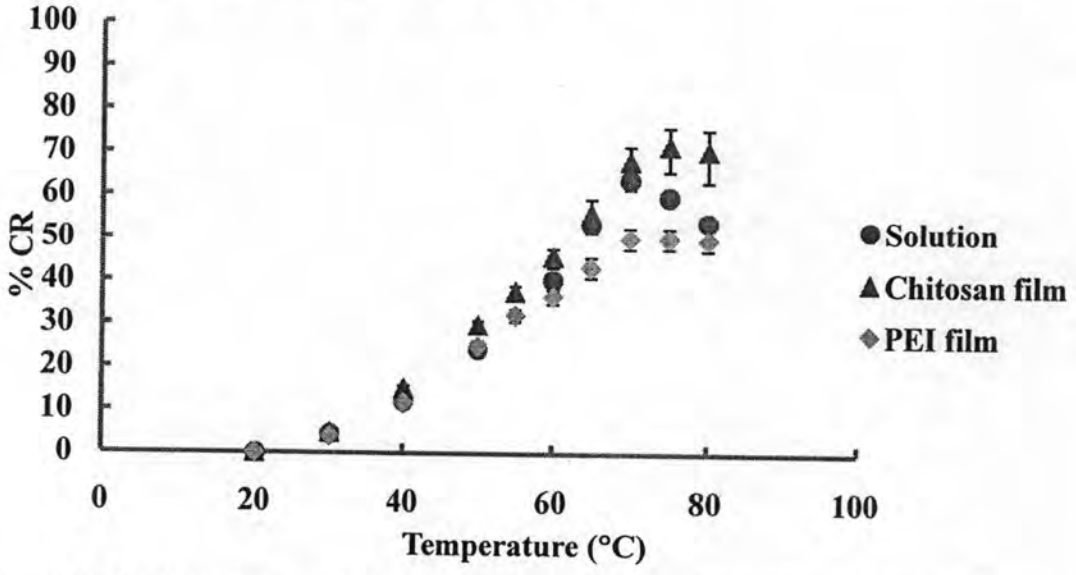


Figure 3.23 The colorimetric response (%CR) as a function of temperature for poly(PCDA) sol, chitosan/poly(PCDA) PEM film and PEI/ poly(PCDA) PEM film. The experiments were carried out in water at pH 6.

3.5 Development of metal ion sensor from poly(PCDA) vesicles

Contamination of natural water and soil by heavy metal ions has been one of most serious environmental problems. To control and prevent the contaminants spreading through ecological food chain, promptly and thoroughly field tests are necessary. An appropriate detecting system should be simple to use and inexpensive as the extensive on-site test can involve a vast field area and myriad numbers of samples. The color change of poly(PCDA) vesicles is easy to be observed by naked eyes that may be developed into an instrumentless detecting system.

3.5.1 Responses of poly(PCDA) sol to transition metal ions

Poly(PCDA) vesicles contain carboxylic groups on their surface which are potentially capable of binding transition metal ions. The idea of using of poly(PCDA) vesicles for metal ion detection relies on the color change induced by the metal ion binding of the carboxylate groups on the vesicle surface. To investigate the color change of poly(PCDA) induced by metal ion, the poly(PCDA) vesicle was synthesized with a final pH of 6.8 and 7.8. Upon addition of Hg^{2+}, the vesicle sol did not show significant change while the addition of Pb^{2+} and Zn^{2+} ion caused some precipitation (Figure 3.24). Pb^{2+} ion also induced a slight color change observed as bluish purple precipitate. The precipitation is probably caused by aggregation through metal-vesicle complexation. The result is quite encouraging that poly(PCDA) may be developed into colorimetric Pb^{2+} ion sensor if there is a way to prevent the vesicles from aggregation that can allow Pb^{2+} ion to extensively interact with an individual vesicle to bring about the more pronounce color change.

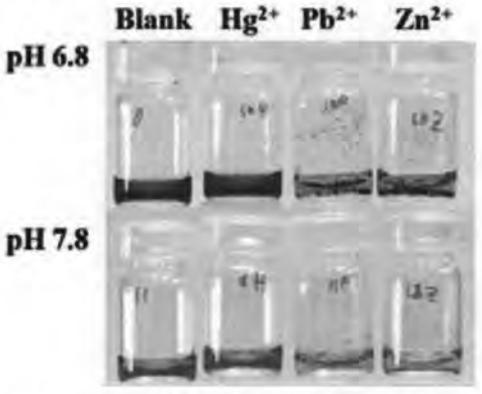


Figure 3.24 Color photographs of poly(PCDA) sol (0.5 mM) in the presence of Hg^{2+}, Pb^{2+} and Zn^{2+} (100 mM).

Lead ion contamination occurs in a variety of natural and anthropogenic sources, and it causes serious environmental and health problems. It is thus of interest to have a naked eye detection method for lead ion. In the following sections of this dissertation, the development of novel lead ion sensing system based on chromic properties of poly(PCDA) will be described.

3.5.2 Synthesis of triethylene glycol ester of 10, 12-pentacosadiyne

As ethylene glycol chain has been report that it can form ion chanel in lipid membrane, increase a fluidity of membrane permeation by reducing membrane crystalinity and widely used for preventing aggregation in many nano particulate systems,[87] triethyleneglycol ester of 10, 12-pentacosadiynoate (TEGPCDA) was thus synthesized in this work and used in the preparation polydiacetylene vesicles.

The synthesis of TEGPCDA was accomplished by condensing triethylene glycol with the acid chloride generated in situ from PCDA (Figure 3.25). The desired product was isolated by column chromatography as a white solid with 73% yield.

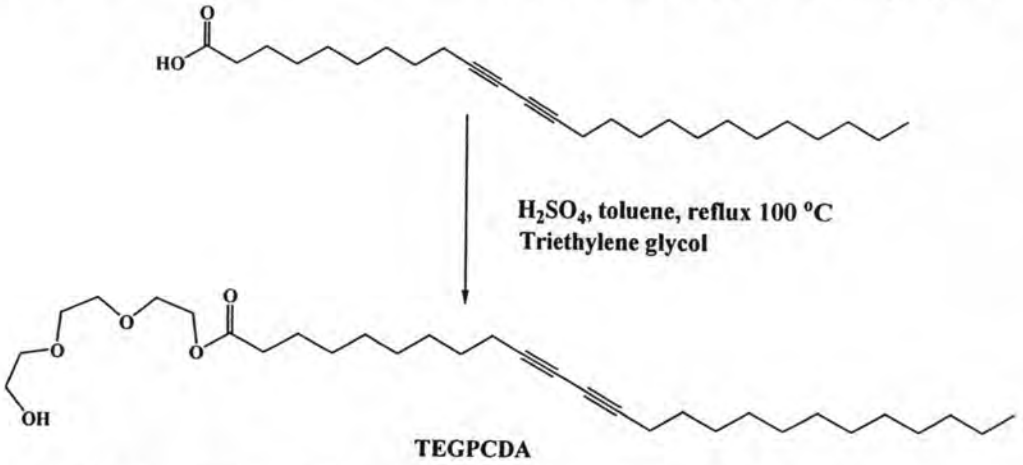


Figure 3.25 Synthesis of triethylene glycol ester of 10,12-pentacosadiynoic acid (TEGPCDA)

The TEGPCDA was characterized by ^{1}H-NMR spectroscopy. A triplet signal corresponding to the methylene group adjacent to the oxygen atom of the ester group appeared at δ 4.19 ppm (Figure 3.26). The integral ratio of the signal of the methylene protons adjacent to the carbonyl group, methylene protons adjacent to the hydroxyl group and those next to the the esterate oxygen was 1:1 indicating the monosubstituted product. Mass spectrum also showed the molecular ion peak at 507.5 m/z corresponding to the $[MH]^+$ (Figure 3.27).

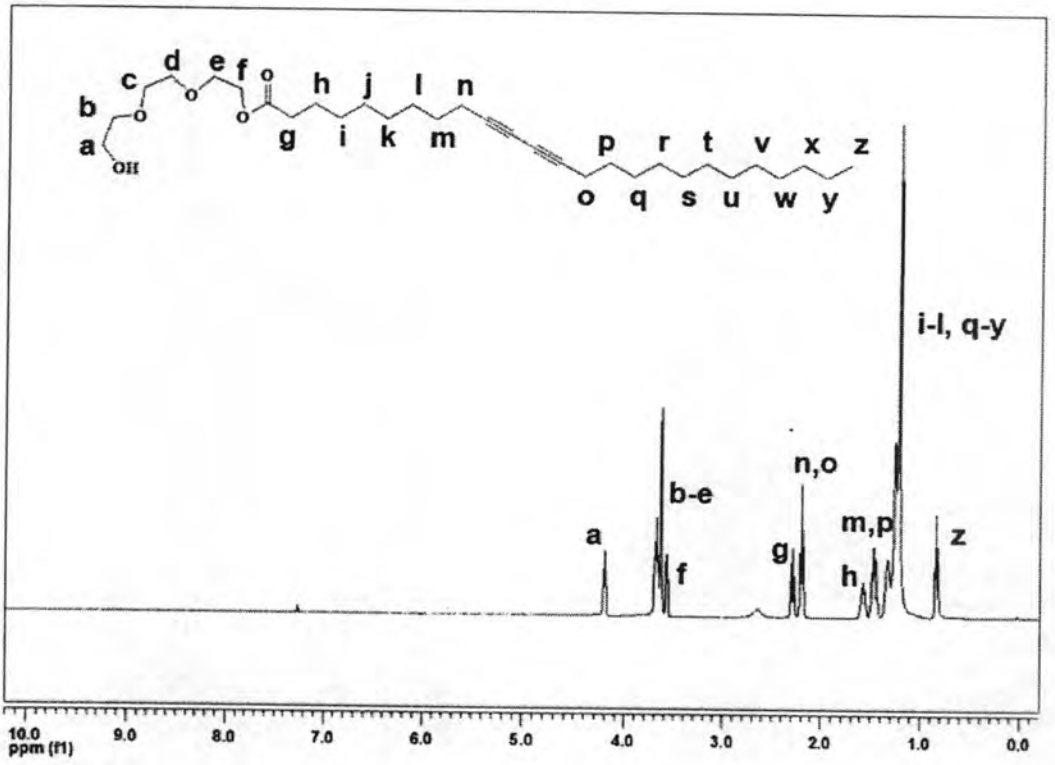


Figure 3.26 ^{1}H-NMR spectrum of TEGPCDA in $CDCl_3$.

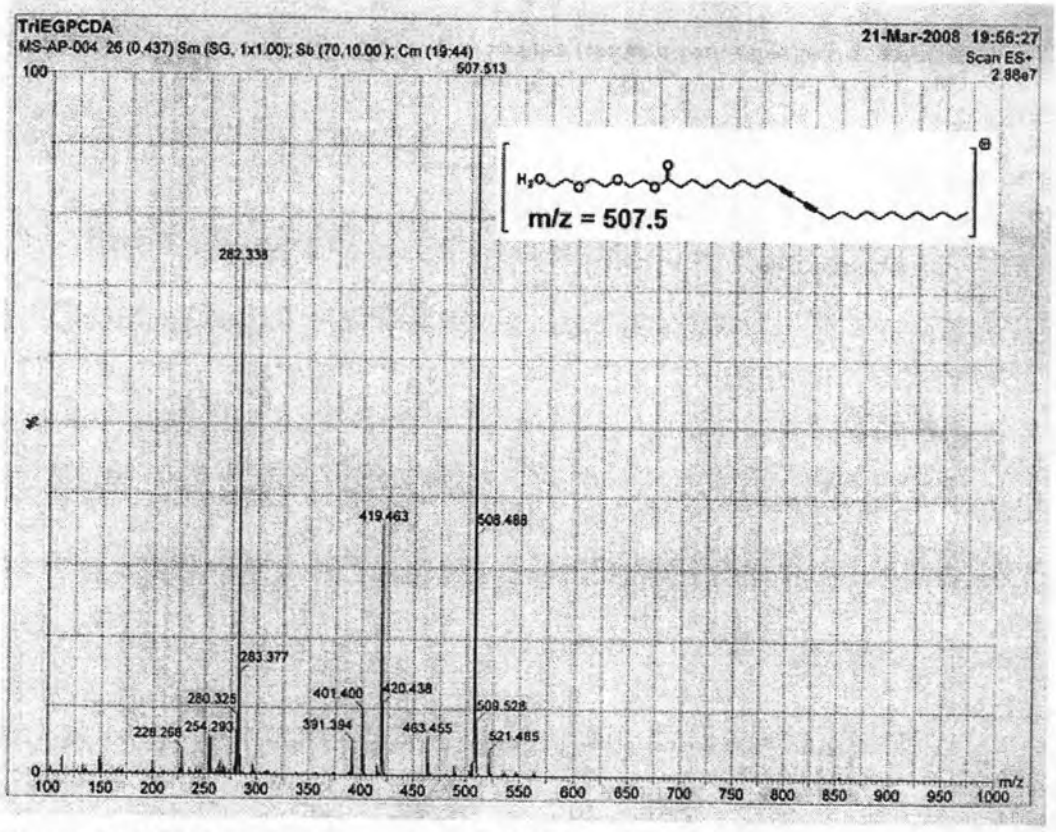


Figure 3.27 ESI-MS spectrum of TEGPCDA using positive ionization mode.

3.5.3 Molecular assembly of TEGPCDA mixed with PCDA

Molecular assembly of TEGPCDA with PCDA in aqueous media was studied using varying content of TEGPCDA in the mixed lipids from 0-100% mole. After sonication, the lipid suspension appeared as white cloudy sol. Upon refrigeration overnight, the sol containing 50% and 80% mole of TEGPCDA showed serious aggregation to form apparent precipitates (Figure 3.28a and b). The dependence of aggregation on the lipid ratio is quite interesting but further study is needed before any reasonable hypothesis can be drawn.

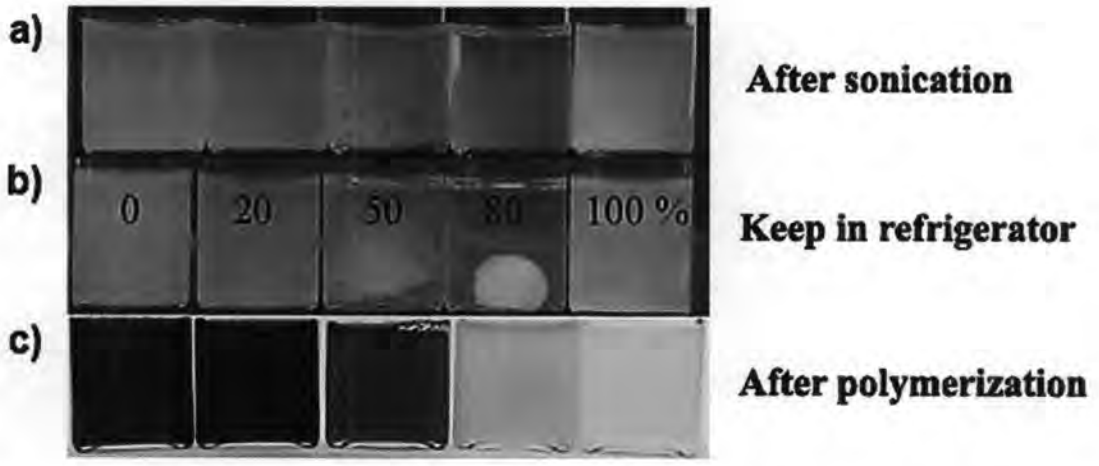


Figure 3.28 Color photographs of TEGPCDA and PCDA mixed lipid suspension (total lipid concentration is 1mM) in Milli-Q water a) right after sonication at 70 °C, b) after refrigeration for overnight and c) after UV irradiation for 5 min.

Although forming a stable sol, pure TEGPCDA assembly did not polymerize into blue polydiacetylene upon UV irradiation. Photo polymerization was possible for the mixed lipid assembly containing 20% and 50% mole of TEGPCDA but not for the one containing 80% mole. The unpolymerizability of pure TEGPCDA indicates that the packing parameters of TEGPCDA molecules in the assembly do not match the topological requirement for the formation of polydiacetylene. Generally, for successful topopolymerization, the molecules of diacetylene lipid are required to pack tightly that is usually assisted by the hydrogen bonding between their head group. The conversion of the strong hydrogen bonding carboxylic group into the non-hydrogen bonding ester group is hence probably the main contributor to the inability to polymerize. As the mixed lipid containing 80% mol of TEGPCDA also cannot polymerize and the blue color of polymerized mixed lipid containing 50% mole of TEGPCDA is considerably paler than those from the pure PCDA and mixed lipid

containing 20% mole of TEGPCDA, it is thus reasonable to assume that the mixing lipids assembled in a block wise fashion and only the PCDA block can polymerize to form ene-yne conjugate (Figure 3.29).

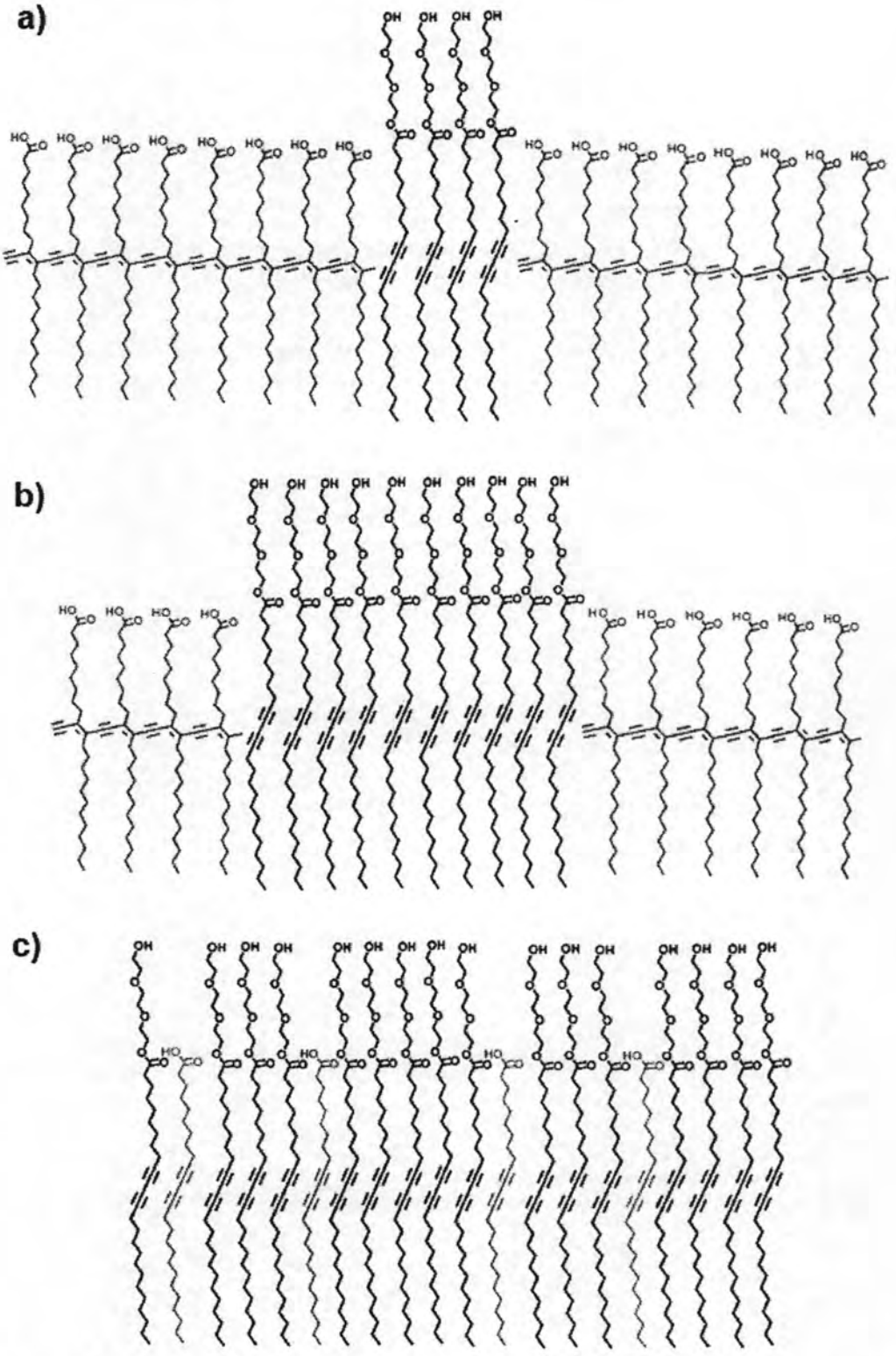
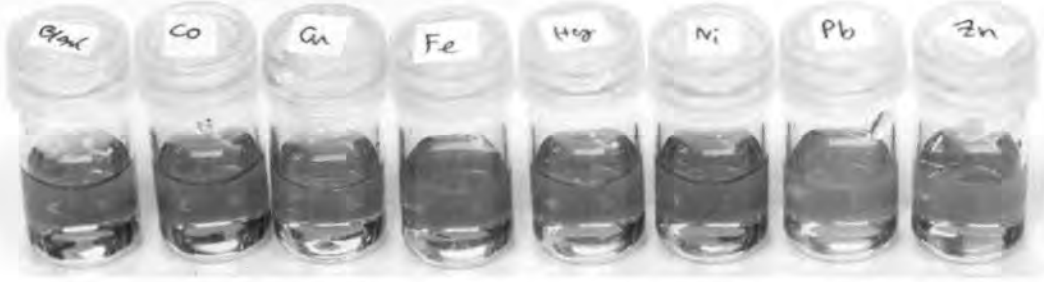


Figure 3.29 Proposed assemblies of TEGPCDA/PCDA mixed lipid containing a) 20% TEGPCDA b) 50% TEGPCDA and c) 80% TEGPCDA

3.5.4 Color change of TEGPCDA/PCDA assembly induced by Pb^{2+}

The metal ion induced color change of the polymerized mixed lipid sol containing 20:80 mole ratio of TEGPCDA/PCDA was investigated. Upon addition of 5 mM of various metal salts *i.e.* $CoCl_2$, $CuSO_4$, $FeSO_4$, $Hg(OAc)_2$, $NiSO_4$, $Pb(NO_3)_2$, and $Zn(OAc)_2$. Among the metal ion tested, the distinct color change of the sol from blue to red was observed only for Pb^{2+} (Figure 3.30).



Control Co^{2+} Cu^{2+} Fe^{2+} Hg^{2+} Ni^{2+} Pb^{2+} Zn^{2+}

Figure 3.30 Color photograph of polymerized mixed lipid sol containing 20:80 mole ratio of TEGPCDA/PCDA, with total lipid concentration of 0.1 mM, 20 minutes after the addition of 5 mM metal ions.

3.5.5 Colorimetric response induced by Pb^{2+} ion

For further study of the colorimetric response of poly(TEGPCDA/PCDA) sol to Pb^{2+}, TEGPCDA/PCDA mixed lipid sol was preparared using total lipid concentration of 0.5 mM. At 0.5 mM of total lipid concentration, the homogeneous sol was obtained with the TEGPCDA content of 0-30% mol but not of 50% mol. Only the TEGPCDA/PCDA mixed lipid sol containing 0-30% mol were polymerized and used for further evaluation of the Pb^{2+} induced colorimetric responses. The mixed lipid sol were irradiated with UV irradiation for 30 minutes to afford the transparent deep blue sol of poly(TEGPCDA/PCDA) (Figure 3.31).

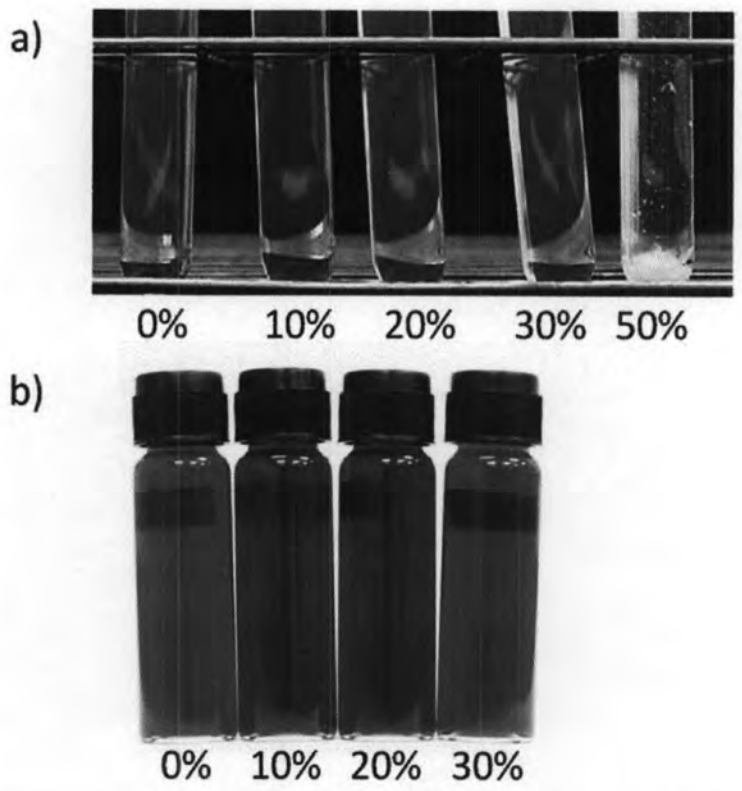


Figure 3.31 Aqueous suspension of TEGPCDA/PCDA mixed lipid (0.5 mM) containing various content of TEGPCDA: a) after sonication for 30 minutes and b) after UV irradiation for 5 minutes.

The colorimetric response of TEGPCDA/PCDA vesicle with lead ion was studied in term of kinetic. The colorimetic response of 20 and 30% TEGPCDA/PCDA vesicle were increasing to 25% and 17% respectively after addition 1 mM lead ion in a minute. The colorimetric response also increase to 45% in both of 20% and 30% TEGPCDA /PCDA vesicle at 20 minute while PCDA vesicle is only 8% (Figure 3.32).

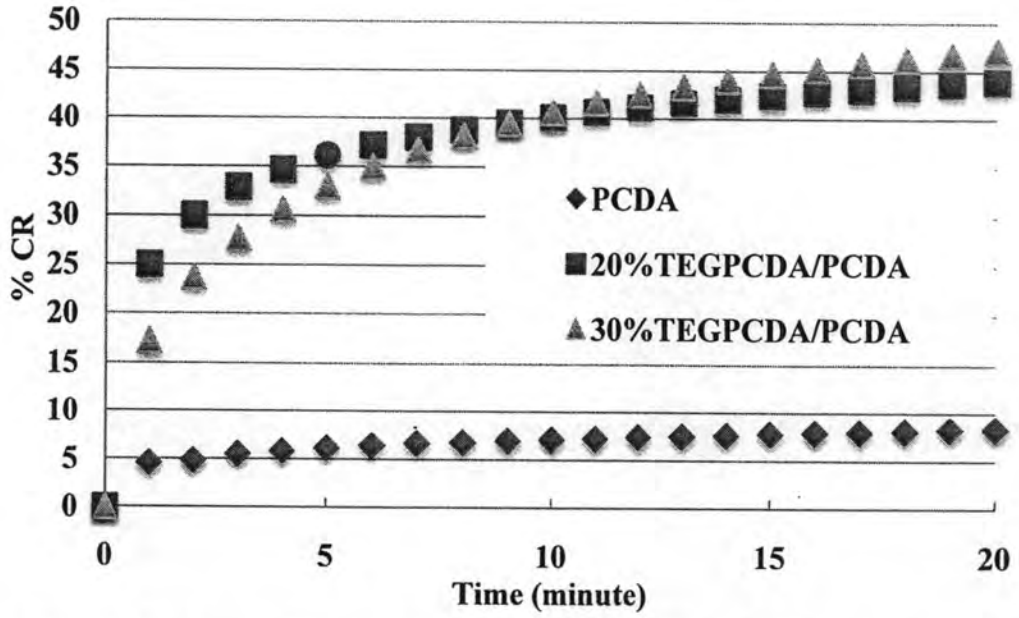


Figure 3.32 Colorimetic response of 50 μM TEGPCDA/PCDA vesicle with 1mM Pb^{2+} ion as function of time (PCDA for control experiment).

It has been reported that the appropriate pH range for Pb^{2+} -carboxylate interaction is 5 - 7.[89] Time dependence of the colorimetric resonse of poly(20%TEGPCDA/PCDA) was studied under a controlled pH of 6.0 using an acetate buffer (10 mM) in comparison to the uncontrolled pH media (water). (Figure 3.33). The colorimetric response of 20%TEGPCDA/PCDA in buffer gave higher %CR than in water system which were 52% and 45% at 25 minuted respectively.

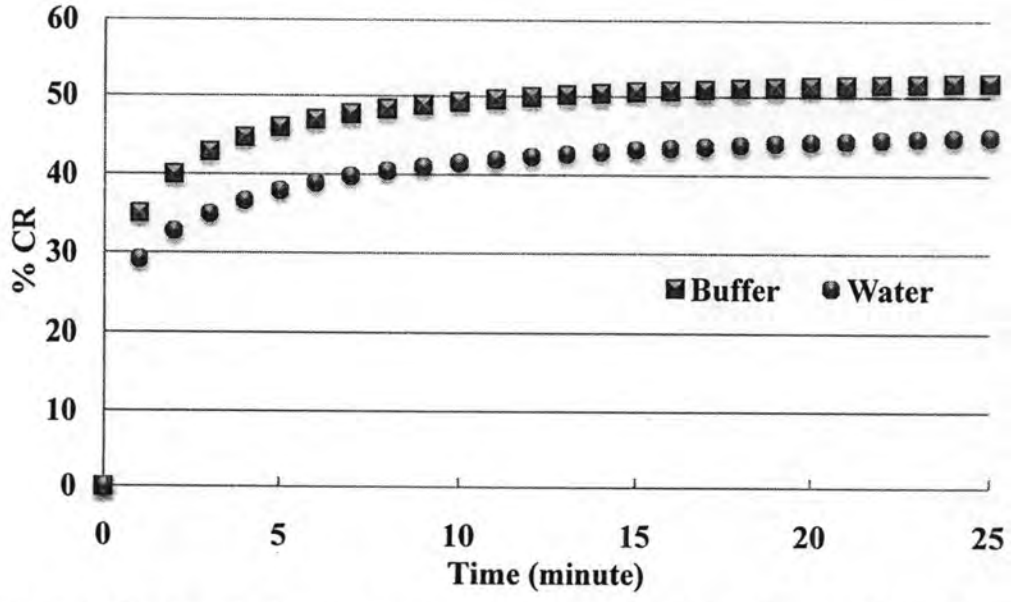


Figure 3.33 The colorimetric response of embedded 20% TGPCDA/PCDA vesicle after additional Pb^{2+} 1000 μM in pH 6 acetate buffer solution (10 mM) and water.

The colorimetric responses of 20%TEGPCDA/PCDA to various concentrations of Pb^{2+} were also determined in the presence and absence of the acetate buffer. Again, the colorimetric responses obtained from the system containing buffer was higher than those pure from the unbuffered system (Figure 3.34). In the presence of acetate buffer, the colorimetric response as high as 40% was observed with the concentration of Pb^{2+} as low as 50 μM.

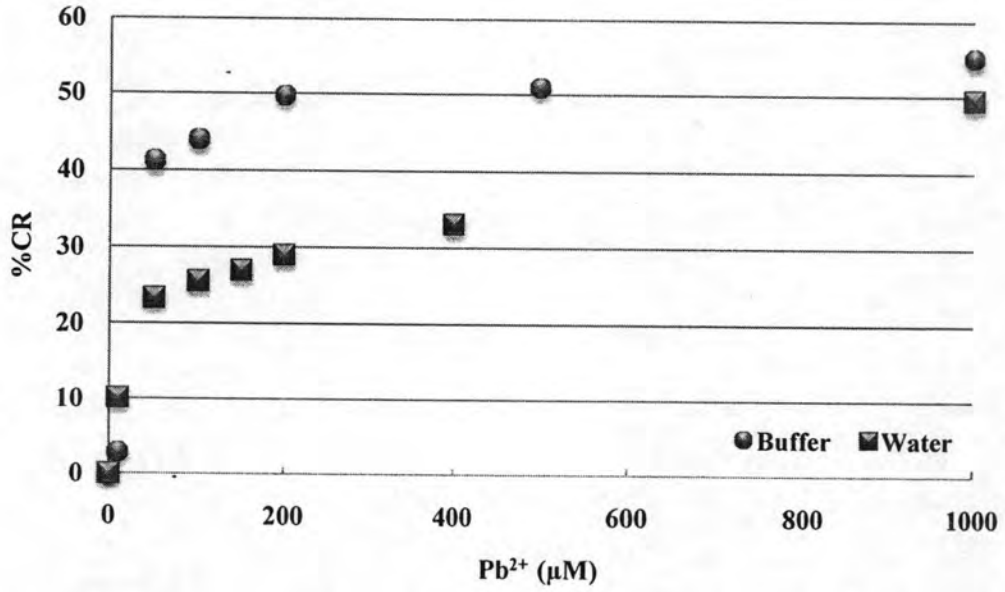


Figure 3.34 The colorimetric response of embedded 20% TEGPCDA/PCDA vesicle after additional Pb^{2+} in water and 10 mM, pH 6 Acetate buffer solution at 25 minute.

The titration of 10, 20, 30% of TEGPCDA/PCDA mixed vesicle with lead ion were studied in acetate buffer solution. The 30% TEGPCDA/PCDA gave the highest colorimetric response with the lead ion. The PCDA vesicle also gave the colorimetric response lower than the TEGPCDA/PCDA vesicle in the range of 50 to 200 μM of lead ion (Figure. 3.35). The sensitivity on lead ion of the 30% TEGPCDA/PCDA vesicle was 50 μM which was higher than the sensitivity of normal PCDA vesicle.

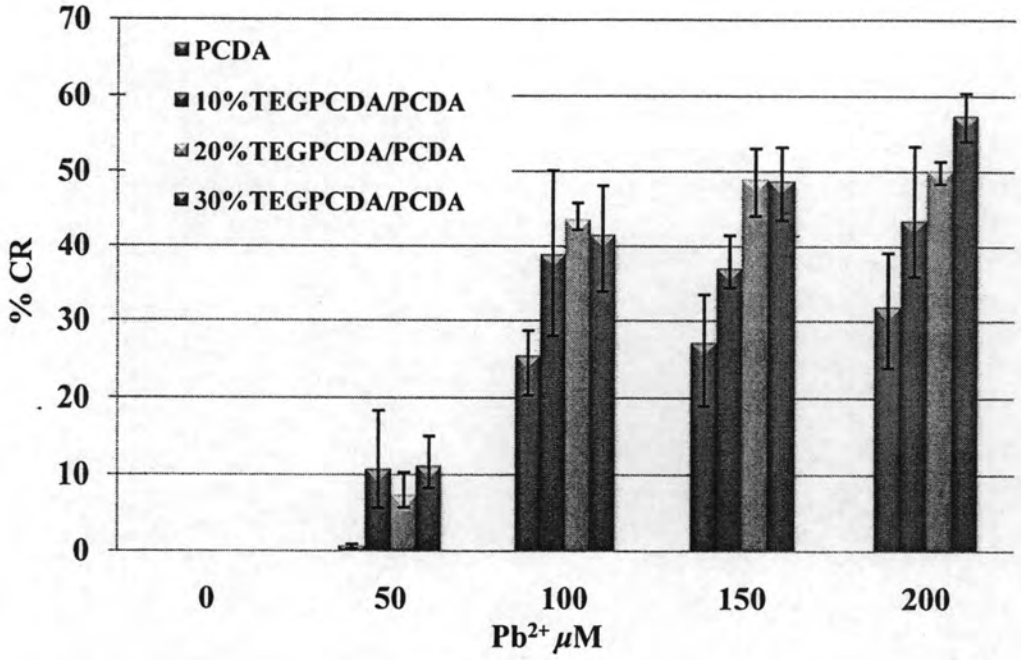


Figure 3.35 The colorimetric response of poly(TEGPCDA/PCDA) sol (50 μM of total lipid) after addition of Pb^{2+} in 10 mM acetate buffer solution pH 6.

The 30%TEGPCDA/PCDA vesicles was more selective towards lead ion than the other metal ions. The colorimetric response of 1 mM Pb^{2+} was 55% while other ions were lower than 3% (Figure 3.36). The sensing application of TEGPCDA/PCDA mixe vesicles was successfully achived to qualitatively detect of lead ion in range of 50 to 1000 μM.

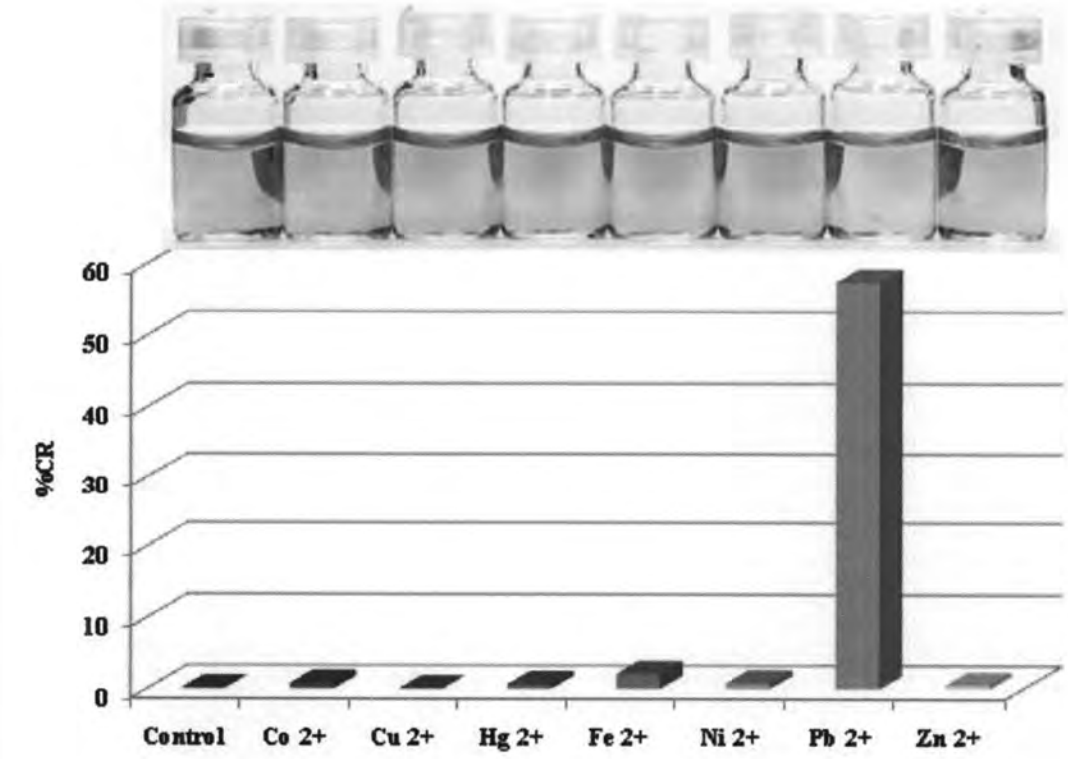


Figure 3.36 The colorimetric response of 30%TEGPCDA/PCDA vesicle after additional 1 mM of various metal ions in 10 mM acetate buffer solution pH 6.0.

3.6 Thermochromism of TEGPCDA/PCDA vesicles

Thermochromism of the embedded TEGPCDA/PCDA vesicle was studied by giving the gentle heating from 20°C to 90°C. The absorbance at 540 nm was used to recognize the red phase of polydiacetylene that occurred along the heating process. The absorbance at 540 nm of PCDA vesicle was increased during heating process and reached the maximum absorption at 80°C. The increasing of absorption had only one transition at 80°C (green line, Figure 3.37). Increasing of the absorption of embedded 20% TEGPCDA/PCDA vesicle showed two transitions which appeared the first transition at 45°C and the second transition at 75°C (blue line) while the mixing of TEGPCDA and PCDA vesicle at 20:80 mole ratio has only one transition at 80 °C (red line). The new transition at 45°C in case of an embedded vesicle was the evidence of an incorporation of TEGPCDA into PCDA mix vesicle.

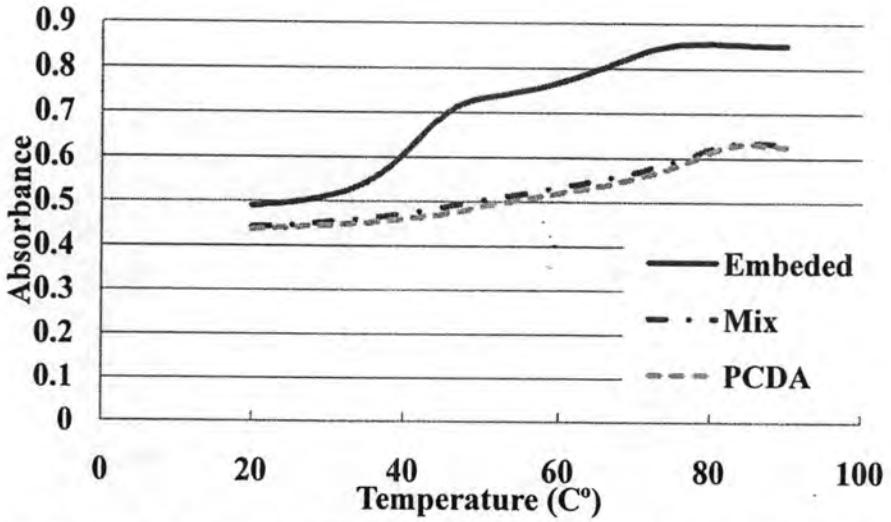


Figure 3.37 The visible absorption of an embedded 20% TEGPCDA/PCDA vesicle (blue line), a mixing of TEGPCDA (20% mole) with PCDA vesicle (red line) and PCDA vesicle (green line) at 540 nm along the heating.

Further study of the effect of TEGPCDA on thermochromic properties with a series of 10, 20 and 30% mole ratio of TEGPCDA in TEGPCDA/PCDA vesicle showed an increasing of absorbance at 40-45°C which related with the amount of TEGPCDA in mixed vesicle (Figure 3.38). The first derivative of the absorbance showed two temperature transitions of mix lipid PDA vesicle at 40-45 C° and 65-70 C° (Figure 3.39). Suggest that an assembly of TEGPCDA with PCDA was block polymer. This method can be applied to use as a tool for identify the amount of TEGPCDA incorporated in TEGPCDA/PCDA mix vesicle.

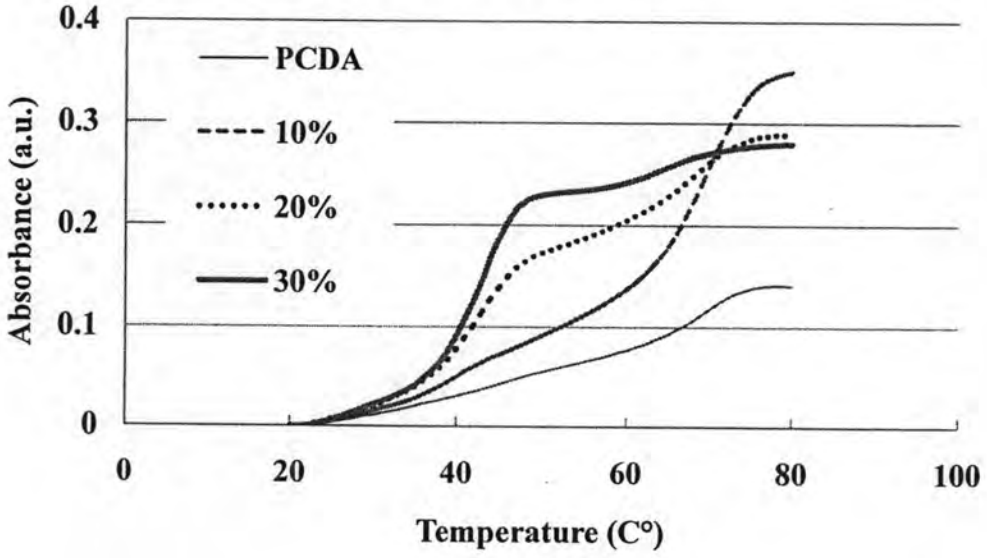


Figure 3.38 Absorption of an embedded TEGPCDA/PCDA vesicle at 540 nm along the heating (the absorbance at 20°C in each spectrum was normalized to zero).

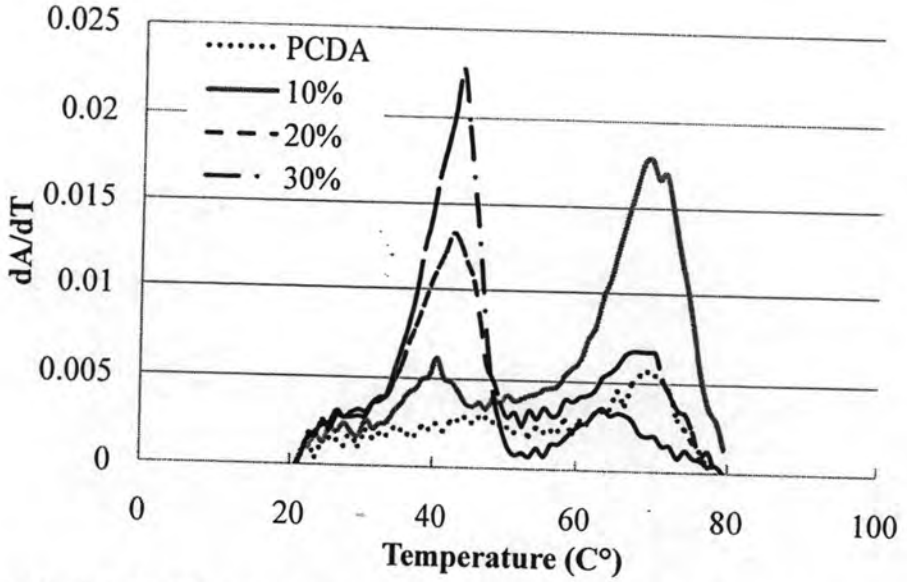


Figure 3.39 The *dA*/*d*T of absorption of an embedded TEGPCDA/PCDA vesicle at 540 nm along the heating.

To provide a mechanism of the new transition temperature at 40-45 °C, turbidity of TEGPCDA suspension and monomer suspension of PCDA were investigated by followed the absorption at 540 nm during heating process. In case of TEGPCDA, the result showed the sharply decreasing of an absorbance at temperature higher than 40°C which demonstrated an increasing of TEGPCDA solubility or the increasing of light scattering of TEGPCDA suspension (Figure 3.40). The decreasing of the absorbance was reversible and reproducibility. The temperature dependence of TEGPCDA might be related with the new transition at 45 °C of the embedded TEGPCDA/PCDA vesicle.

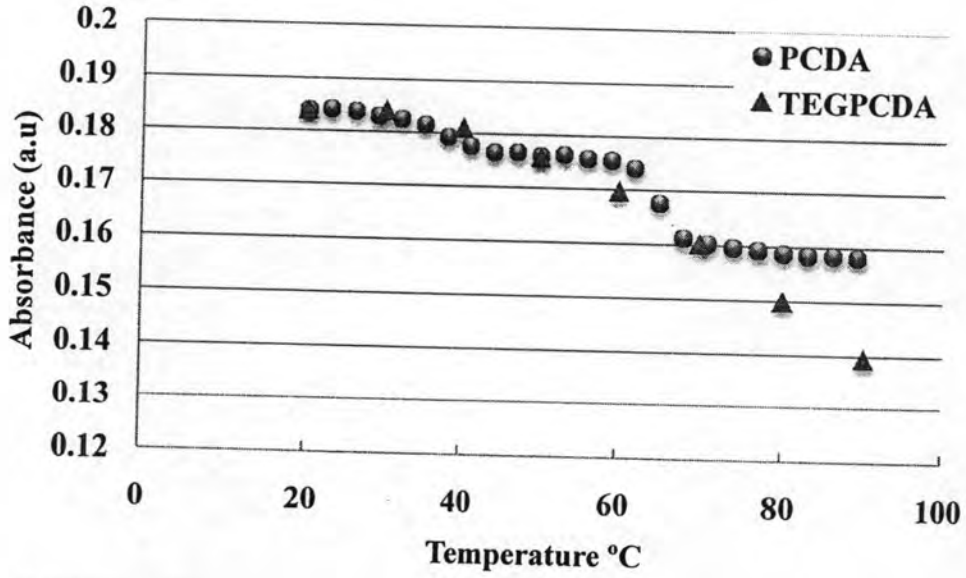


Figure 3.40 Turbidity of PCDA and TEGPCDA suspension at 540 nm along the heating cycles (normalized absorbance).

On the other hand, PCDA suspension showed two transition temperatures. The sharply decreasing of absorption at 60° corresponded with the melting point of PCDA molecule which was 63°C. However there was a slightly decreasing of absorbance around 30 to 40°C that was not identified in this experiment. The experiment for mechanism clarity need further study.

3.7 Fabrications of polydiacetylenes as temperature sensitive labels

There are circumstances where an evidence for a real time temperature or temperature history of commercial products is considered necessary. An active label that can irreversibly turn its color upon an exposure to unsuitably high temperature give customers and vendors a good indication about the quality of some temperature sensitive products such as medicines, cosmetics and refrigerated foods. On the other hand, a reversible temperature sensing label can indicate the right serving temperature for less temperature sensitive products such as beverages and cooked foods.

Different products may require labels that can change their color at different temperatures. For examples, pasteurized milk may require a label which can change its color irreversibly around 10-15 °C while medicines and cosmetics may require a similar type of label but with a little higher transition temperature of around 40-45 °C to signify an inappropriate storage temperature. Another situation where an irreversible temperature sensing material can be useful is a label indicating cooking temperature which may require high color transition temperature of 70-80 °C. A material which can change color reversibly around 70-80 °C can also be useful for warning of hot surface or hot food.

As mentioned earlier, polydiacetylene is a unique class of material possessing distinct thermochromic property of which the color transition upon temperature change can be clearly seen by eyes. With different types of diacetylene monomers in hands, it would be of commercial interest to develop a general method to integrate them in a label form. The development in this part of dissertation involves four types of diacetylene monomers, PCDA, MPCDA, AEPCDA and EBPCDA. The chemical structures of the monomers and thermochromic properties of the corresponding polydiacetylenes are summarized in Figure 3.41. EBPCDA and AEPCDA were synthesized according to the method used in Boonyiseng's thesis.[51] MPCDA was

synthesized in 97% yield by an esterification of PCDA with MeOH by using thionyl chloride.

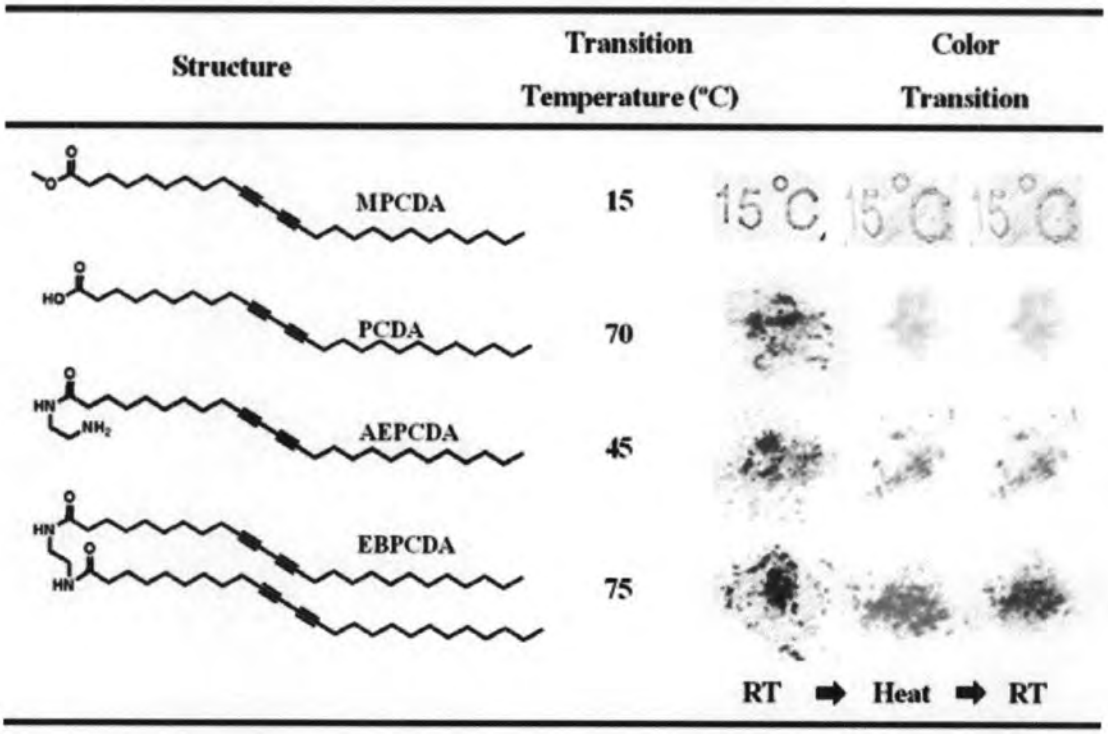


Figure 3.41 Structures of diacetylene monomers used in the development of temperature sensing labels and the thermochromic attributes of the corresponding polydiacetylenes.

In this work, three labeling platforms *i.e.* printing & writing ink, adhesive film and screen ink were developed.

3.7.1 Printing & writing ink

Printing ink is very actractive platform as it is convenient to be used for producing specifically designed labels. To be used as the printing ink, AEPCDA (12 mM) and EBPCDA (1mM) were prepared in the form of aqueous sols which were photopolymerized into the corresponding polydiacetylene sol. The sols were blue in color and appeared to be homogeneous with thermochromism properties (Figure 3.42).[51]

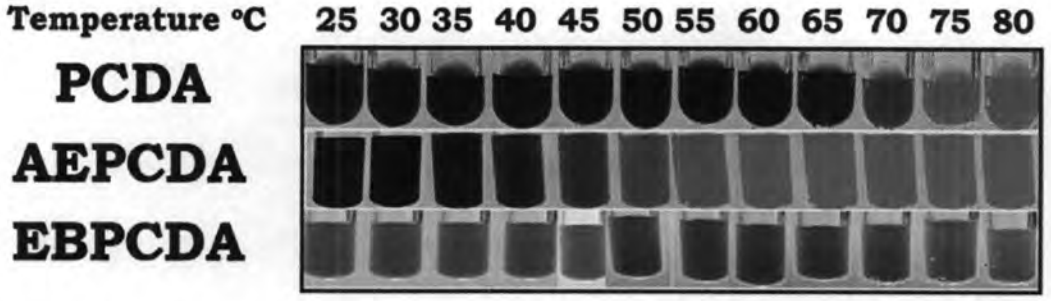


Figure 3.42 Color photographs of polydiacetylene sols undergoing thermochromic transition.[51]

Poly(EBPCDA) sol (1 mM) was filled into a empty black ink container of a ink-jet printer (C58 series, Epson). The printer was connected to a personal computer and a graphic image was printed on an A4 paper. The printed image was so light that required five times of repetition to obtain a blue image with barely acceptable level of color saturation. The image showed reversible thermochromic transition between blue and red color upon heating by a hair blower (Figure 3.43). Besides the pale color due to a rather low concentration of the sol, the ink jet head was also clogged badly after a few printing tests. These problems have dampened further development of the sols into the real usable ink for ink jet printer.

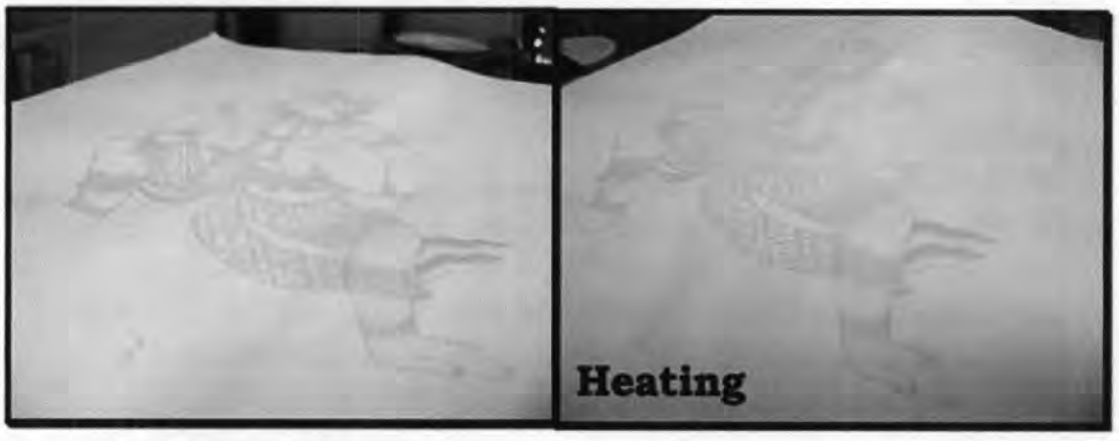


Figure 3.43 Graphic images, produced by 5 times reprinting from an inkjet printer using 1 mM poly(EBPCDA) sol as an ink, before and after heating with a hair blower.

To produce an image with good color saturation, the pigment content in the ink should be higher than 1% w/w that requires the concentration of the polydiacetylene sol of greater than 10 mM. However, the higher the concentration, the greater the risk of clogging is. In the subsequent experiment, a fountain pen was thus

used for the ink test in place of the inkjet printer to reduce the risk of clogging. Images and words with good blue color intensity were easily created by hand drawing and writing using the pen filled with 12 mM poly(AEPCDA) (Figure 3.44). The images exhibited irreversible thermochromic transition from blue to red color around 45 °C. The results exhibited that high concentration of polydiacetylene sol can be used as fountain pen ink. This is a prototype of an active marker for periodic on-site inspection of temperature sensitive products.

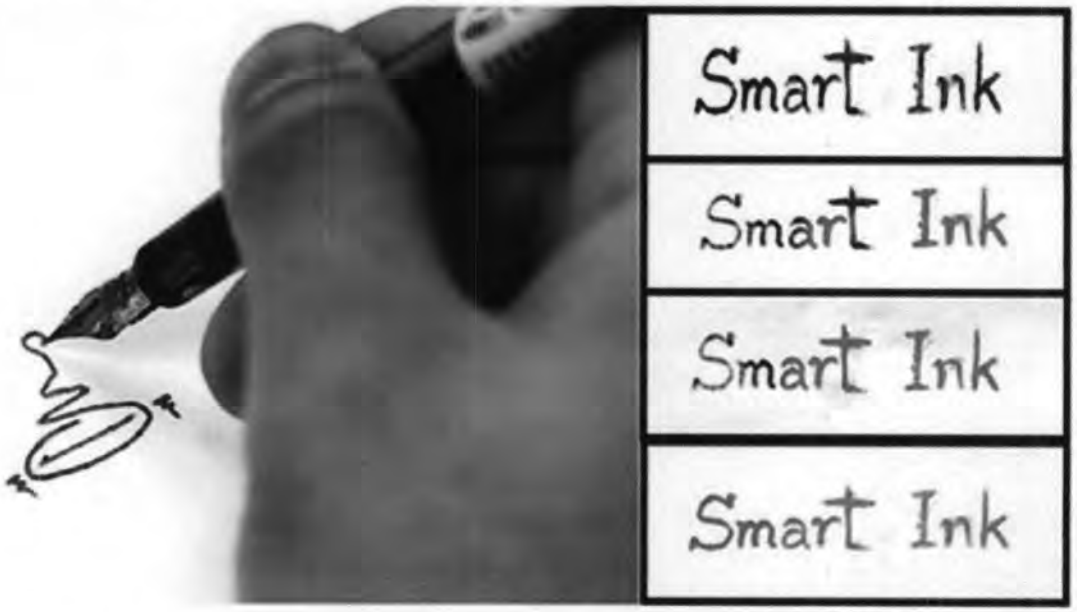


Figure 3.44 Images, produced by a fountain pen using 12 mM poly(EBPCDA) sol as an ink, before and after heating with a hair blower.

3.7.2 Polyvinyl alcohol films

Fabrication of polydiacetylene vesicles as thin films is interesting as ready-to-use temperature sensitive labels. To fabricate polydiacetylene vesicles into thin film, a water soluble polymer, polyvinyl alcohol (PVA), was used as a polymer binder. Preparation of polydiacetylene vesicles embedded in PVA film was previously studied.[89] In this work, the PVA films were prepared by allowing a mixture of the polydiacetylene sol (1 mM) and PVA solution (10 % w/w) evaporated on a smooth tray (Figure 3.45). Large area (30 × 35 cm^2) of smooth PVA film with good blue color saturation was obtaine. The film can be cut into a desired size and shape. The films containing poly(PCDA) and poly(AEPCDA) exhibited an irreversible thermochromic transition from blue to red color at 65 and 60 °C, respectively, while the film containing poly(EBPCDA) showed a reversible thermochromic transition from blue

to red color at 80 °C (Figure 3.46). The reversibility of the thermochromic transition of PVA film containing poly(EBPCDA) was highly stable that it can be repeated over hundred cycles (Figure 3.47)

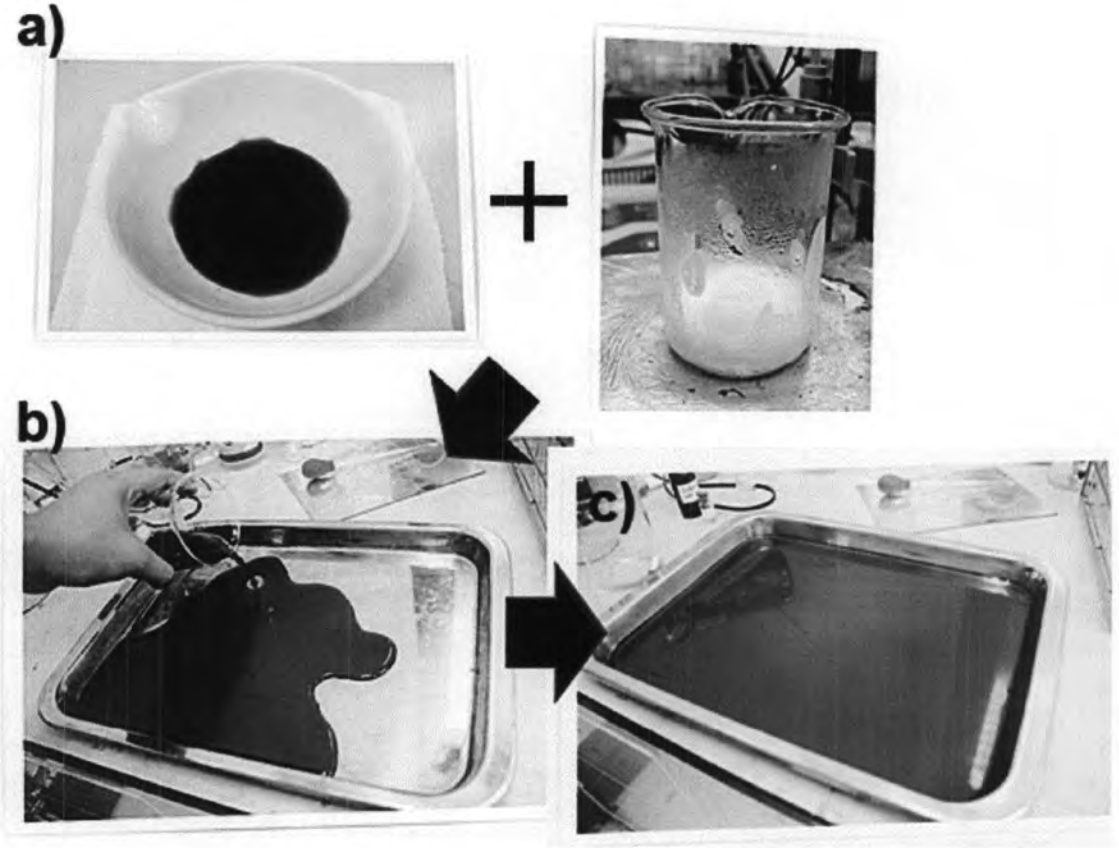


Figure 3.45 Pictorial illustration of preparation of PVA film containing polydiacetylene vesicles a) mixing of poly(PCDA) sol with PVA solution b) pour into a tray, c) stand for evaporation

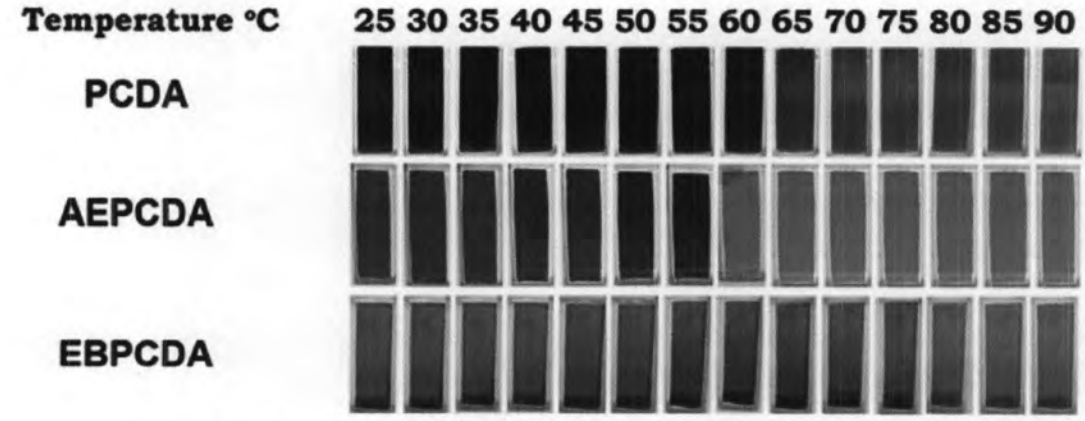


Figure 3.46 Color photographs of polydiacetylene /PVA film upon thermochromic transition.

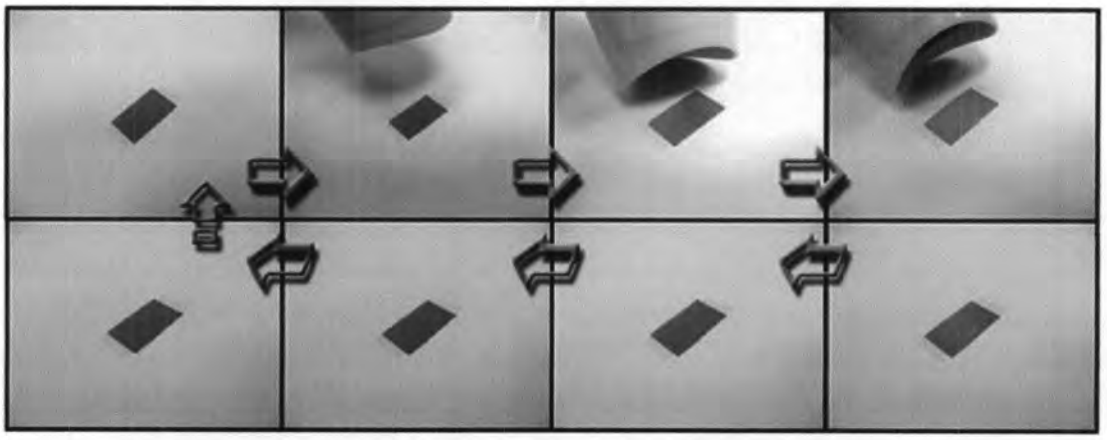


Figure 3.47 Color photographs showing the reversibility of thermochromic film fabricated from PVA containing poly(EBPCDA).

An example of application of reversible and irreversible thermochromic films fabricated from PVA containing poly(PCDA) and poly(EBPCDA) vesicles as dual active labels for frozen food is shown Figure 3.48. The irreversible film containing poly(PCDA) can be used to display that the food is cooked while the reversible film containing poly(PCDA) can be used to display that the temperature of the food has reduced to the temperature appropriate for serving.

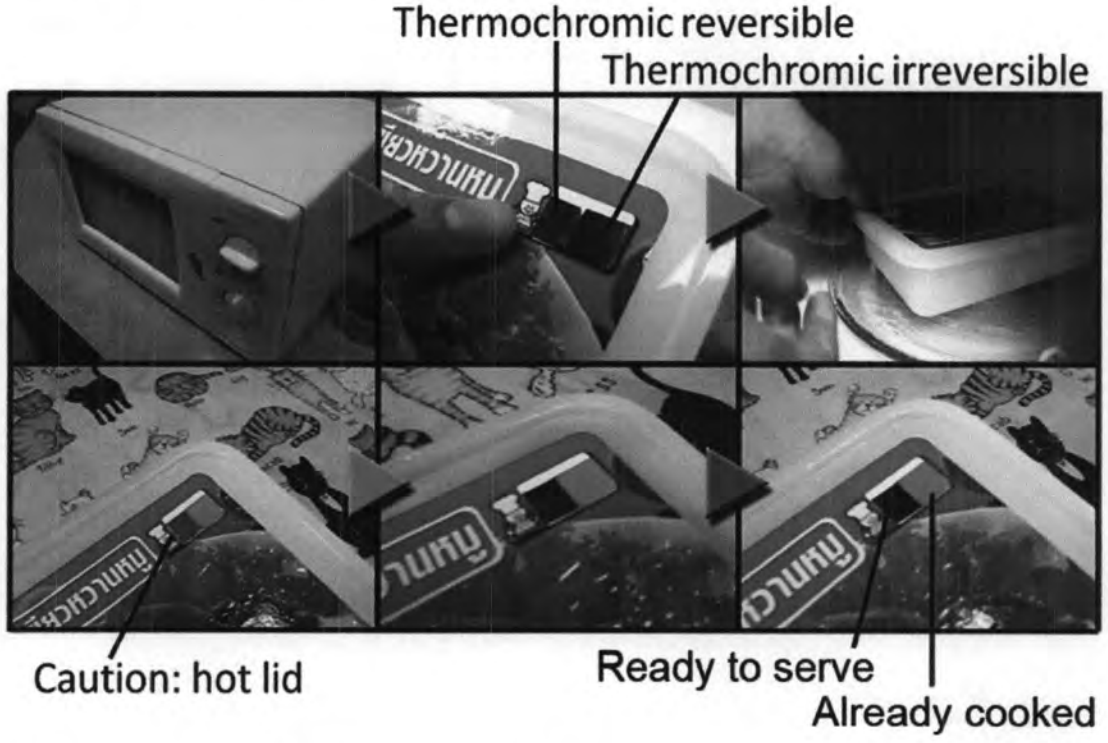


Figure 3.48 Example of ppplication of thermochromic PVA films containing poly(PCDA) and poly(EBPCDA) vesicles as dual active labels for frozen food.

Using PVA as a matrix has one major drawback that it is water soluble and thus it cannot tolerate to excessive contact of moisture. One solution to this problem is to apply thin layer coating of a water insoluble polymer on top of the PVA film. The nitrocellulose was used to cover PVA film for water resistant.

3.7.3 Polyvinyl chloride-based screening ink

A screening ink can be an alternative to the printing ink especially when a mass production of label of the same design is desired. To improve the moisture tolerant of the labeling image, a commercial polymeric resin in an organic solvent was selected as a matrix for formulation of screening ink. As polydiacetylenes also change color upon exposure to organic solvents, namely solvatochromism, the use of preformed polydiacetylene is precluded. It is thus interesting to apply a diacetylene monomer in the ink formulation and polymerize later after the screening process and the solvent is evaporated. The success of this method will however rely critically on the self-assembly of the diacetylene molecules during the evaporation of the solvent that is necessary for topological polymerization of the diacetylene unit.

The screening ink was developed by mixing PCDA monomer with a commercial screening resin composed of PVC and polyvinyl acetate as a major component (GPV0906, Chaiyaboon brothers co.,LTD). The viscosity of the screening ink increased with the amount of the screening resin used. If necessary, the resulting screening ink can be kept in a close container to prevent solvent evaporation. The screening ink was screened through a silk screen template on to a white PVC sticker sheet (Figure 3.49). White spirit can be used for reducing viscosity as necessary. After the screening process, the image was allowed to dry and then kept in a refrigerator overnight. The image was irradiated with UV irradiation to initiate topological polymerization of PCDA. The resulting image immediately turned blue with good color saturation. The blue poly(PCDA) image on a PVC sticker showed irreversible thermochromic transition from blue to red color at the temperature 70 °C (Figure 3.50) which may find application in curing industry.

The amount of diacetylene monomer used in screen ink that provided good blue color saturation observable by naked eyes were 5% w/w for PCDA and EBPCDA but 10% w/w for MPCDA. The higher amount of MPCDA required

suggested that MPCDA was less likely to self assembled and polymerized due to its lack of hydrogen bonding group.

For MPCDA, a topological polymerization of MPCDA was performed at temperature lower than 10 °C to avoid thermochromic transition during the polymerization process (Figure 3.51). The blue poly(MPCDA) image on a PVC sticker showed irreversible thermochromic transition from blue to red color at the temperature 10-15 °C .

Figure 3.49 Screening of temperature indicating screen ink

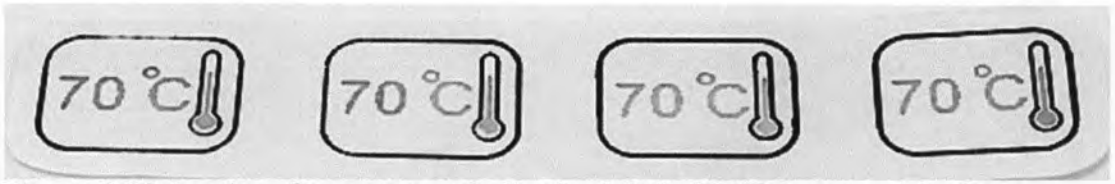


Figure 3.50 A color of temperature indicating label of PCDA screen ink after stimulated by heat (gradient heat was applied).

Figure 3.51 Polymerization of temperature indicating MPCDA screen ink in an ice bath.

Examples of applications on commercial products

All types of polydiacetylene in temperature indicating label can perform a thermochromic property as well as in solid polymer. A PCDA temperature indicating label can be use as smart packaging in various products such as frozen food, hot cup in convenience store. The label can show a heat level that was above 70 °C when it was cooking by microwave or hot water (Figure 3.52 and 3.53).

A MPCDA temperature indicating label can be use with product that has to store in refrigerator such as pasteurized milk, medicine and vaccine (Figure 3.54).

A temperature indicating screen ink can be apply in various type of packaging material such as PVC, PS, especially polyester (PET) which was a widely use in packaging industry (Figure 3.55).

The work in this section was done as a team of four and won the first runner up in Thailand innovation awards 2007 for innovation product and business plan.

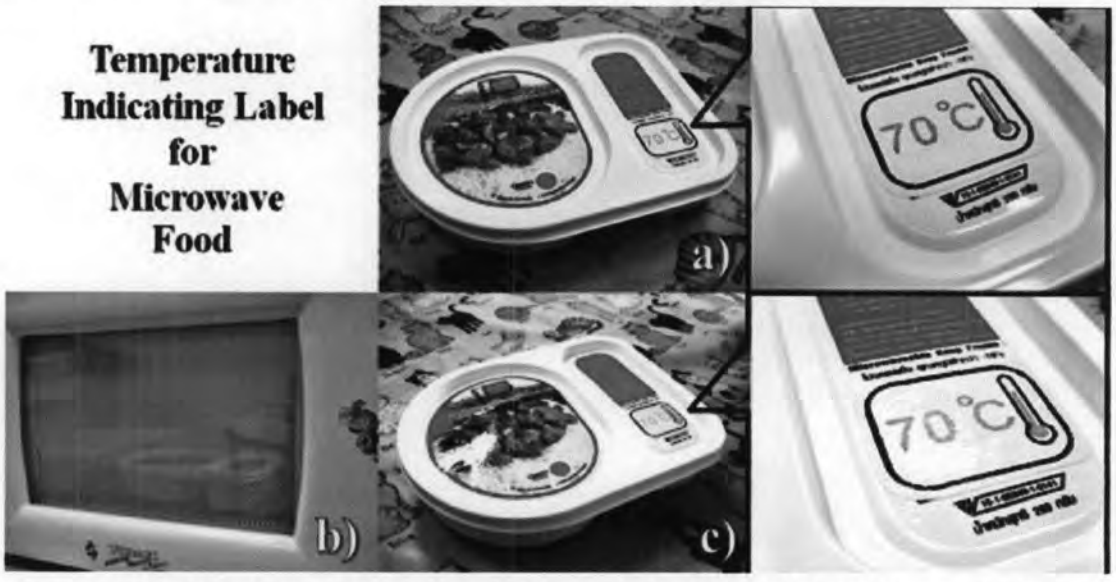


Figure 3.52 A using of PCDA temperature indicating label with frozen food. a) before cooking, b) microwave, c) after cooking.

Figure 3.53 Using of temperature indicating label with hot cup. (left) PCDA label before given heat, (middle) PCDA label after given heat, (right) EBPCDA label, (below) Color changing of PCDA label during addition hot water.

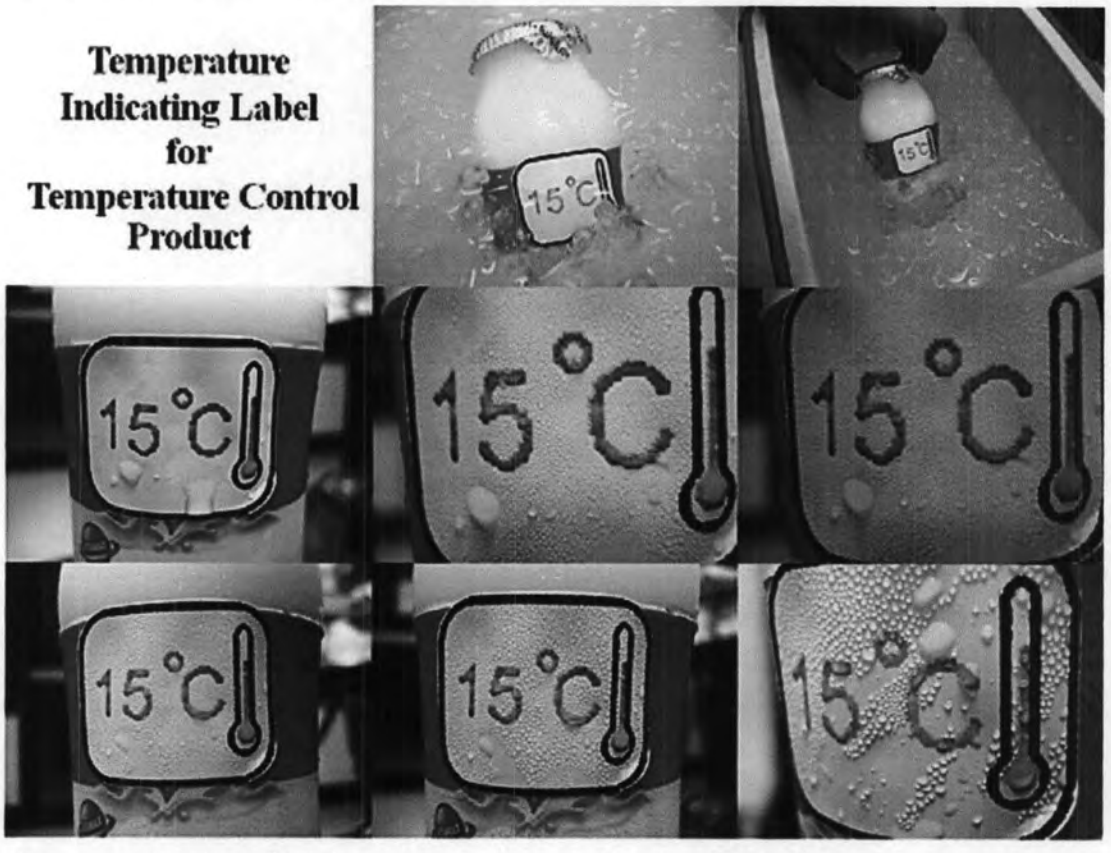


Figure 3.54 Using of MPCDA temperature indicating label with pasteurized milk. A color of label changed from blue to red when a storage temperature was above 15°C.

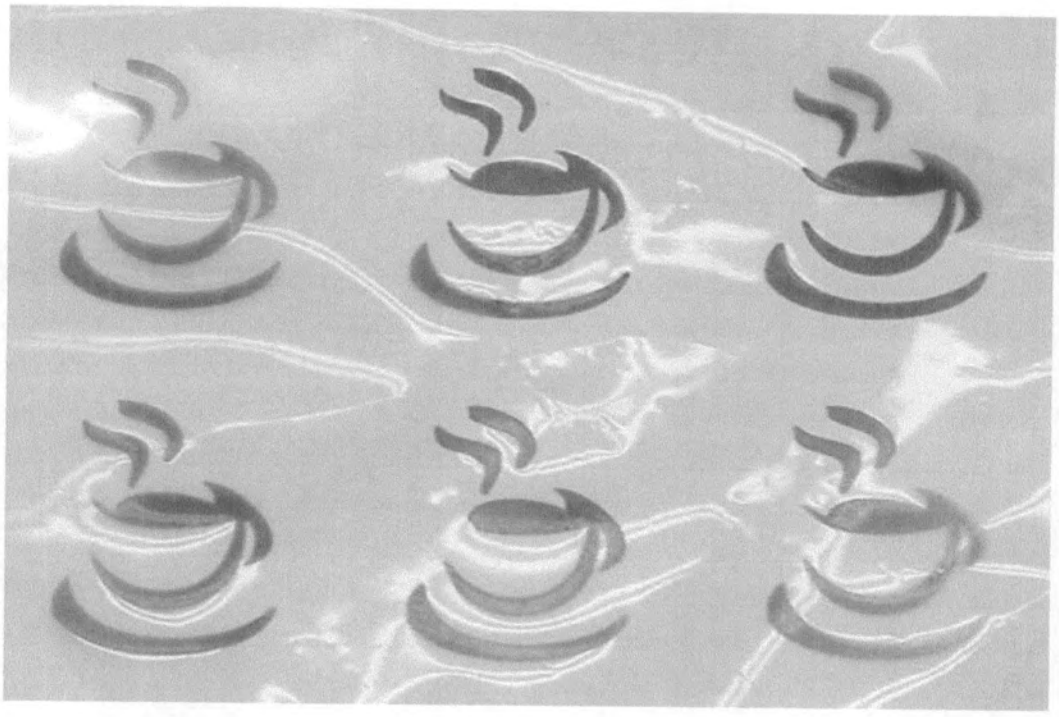


Figure 3.55 A temperature indicating label screening on polyester (PET) sheet.