CHAPTER III

RESULTS AND DISCUSSION

In this work, the key component of thermochromic films with tunable color transition temperature (CTT) is the thermochromic agent, polydiacetylene (PDA) vesicles. Since the temperature induced color change of PDA vesicles is closely related to the interaction between the side chains of the ene-eyne conjugated backbone, the modification of this interaction through two different approaches is the main subject of this thesis.

The first approach involves a simple mixing of a widely used diacetylene lipid monomer, 10,12-pentacosadiynoic acid (PCDA), with a fatty acid of different aliphatic chain length at various mole ratios. The insertion of the fatty acid molecules into the vesicle lipid bilayers should moderate the perfect packing between the aliphatic chains of the diacetylene monomer and thus limit the topopolymerization as well as the interaction between the polymer side chains. This approach should provide a very convenient technique for tuning down the CTT and the experimental results should provide useful quantitative data for further applications and insight into packing pattern in mixed lipid vesicles.

The second approach deals with modification of the carboxylic head group of PCDA. The modification of the carboxylic head group should cause significant change in the orientation and strength of the hydrogen bonds between the headgroups. Two amide derivatives *N*-(2-aminoethyl)pentacosa-10,12-diynamide (AEPCDA) and *N,N'*-ethylenebispentacosa-10,12-diynamide (EBPCDA) derived from condensation of ethylenediamine with one and two equivalents of PCDA, respectively (Figure 3.1). Moreover, *N*-(2-stearamidoethyl)pentacosa-10,12-diynamide (SEPCDA) was synthesized by condensation reaction between *N*-(2-amonoethyl)stearamide and 10,12-pentacosadiynoyl chloride. These amide diacetylenes may polymerize to form PDA vesicles possessing CTT higher than PCDA. This chapter of thesis will elaborate first the synthesis of the amide lipids, then the preparation and study of thermochromism properties of the PDA vesicles and finally the preparation and study of the thermochromic films.

3.1 Synthesis of diacetylene lipid monomers

Synthesis of AEPCDA was acheived by dropping a solution of PCDA and DCC in chloroform into a large excess of ethylenediamine (5 equivalents). The reaction yielded AEPCDA as a major product (42% isolated yield) and trace amount of EBPCDA from the double substitution of PCDA on ethylendiamine as a minor product (Figure 3.1). Inverse addition of the reactants or using lower excess of ethylenediamine resulted in greater formation EBPCDA which was obtained intentionally in 52% yield by dropping a solution of 0.5 equivalents of ethylenediamine into the solution of PCDA and DCC in chloroform.

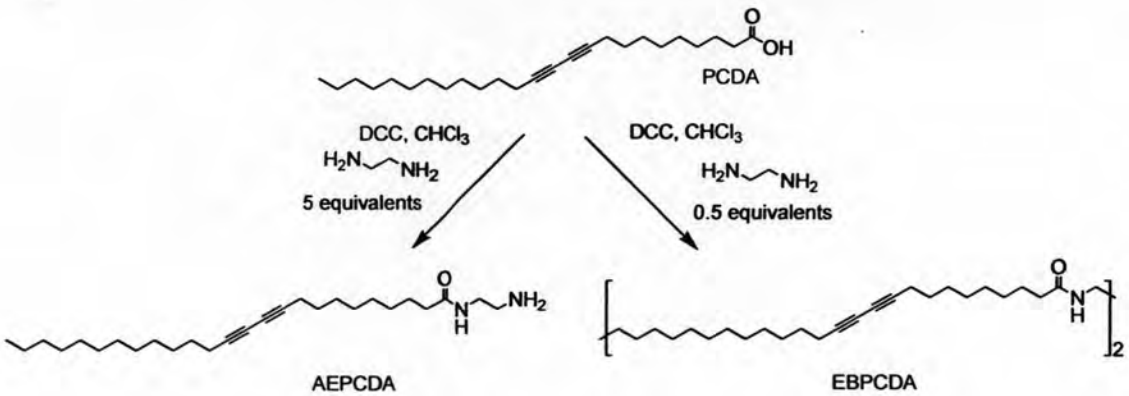


Figure 3.1 Synthesis of AEPCDA and EBPCDA lipids.

The synthesis of SEPCDA was acheived through a two-stepped acylation of ethylene diamine (Figure 3.2). The first step is the condensation of stearoyl chloride with a large excess of ethylenediamine (10 equivalents) in dichloromethane afforded a monosubstitution of stearoyl group on ethylendiamine, *N*-(2-amonoethyl) stearamide. The second step is the condensation of *N*-(2-aminoethyl)stearamide with 10,12-pentacosadiynoyl chloride generated *in situ* from the reaction of PCDA with oxalyl chloride. SEPCDA was obtained in 43% isolated yield.

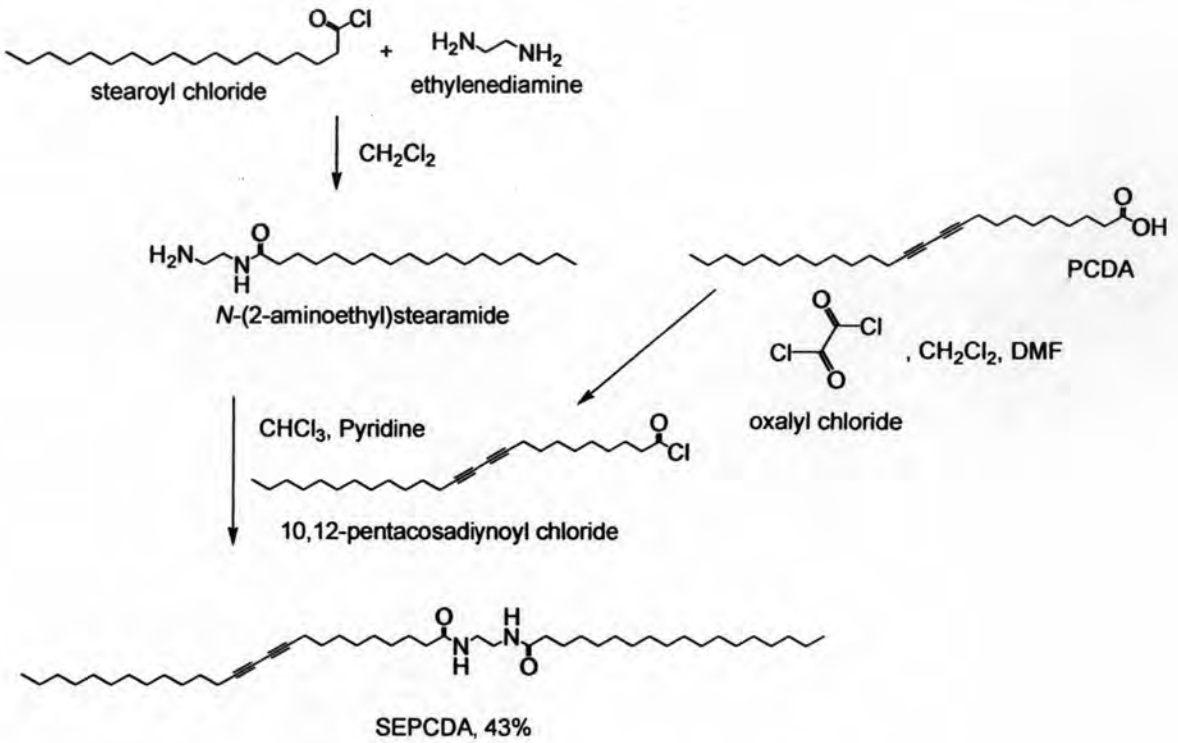


Figure 3.2 Synthesis of SEPCDA lipid.

^{1}H NMR spectra of AEPCDA, EBPCDA and SEPCDA are shown along with the spectrum of PCDA monomer (Figure 3.3). The signals in the spectra of the products most obviously distinctive to that of PCDA appear at δ 3.4 ppm. This is the signal of methylene protons (proton v) next to the amido nitrogen. The less distinctive signal is a broad signal at δ 6.2 ppm belonging to the amido N-H protons (proton u). Moreover the position of the methylene proton connected to the carbonyl group of the carboxylic group in PCDA (proton t) shifted slightly from 2.4 to 2.2 ppm upon conversion into the amido groups in the products. For AEPCDA, an extra distinctive signal observed at 2.8 ppm belongs to the methylene protons (proton w) next to the amino group. Most of the protons in the aliphatic chain in all three products give the signals in the range of 2.2-0.9 ppm. The patterns of these signals in the spectra of AEPCDA and EBPCDA are virtually identical but they are significantly different from that of SEPCDA attributed to the difference in aliphatic chain constituents.

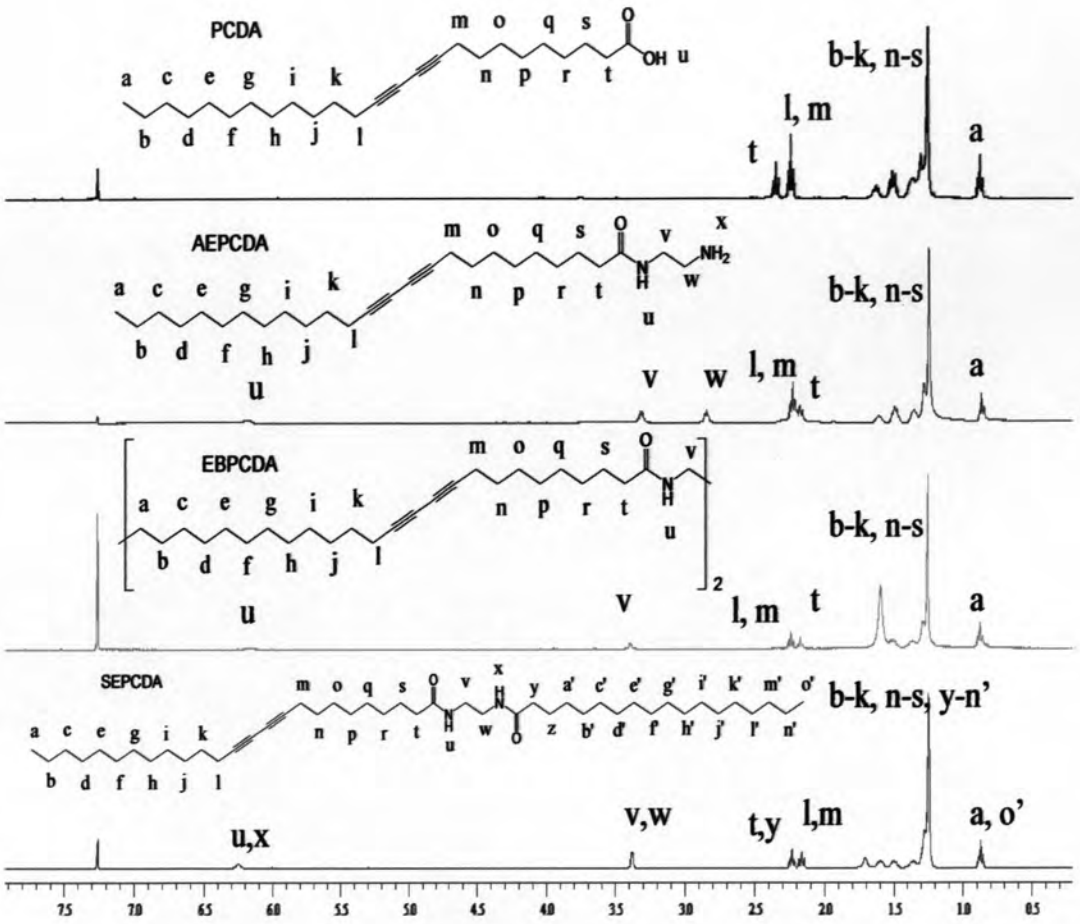


Figure 3.3 ^{1}H NMR spectra of PCDA, AEPCDA, EBPCDA and SEPCDA lipids.

ESI-Mass spectrometry was used to confirm the molecular weight of the synthesized lipids. MS spectrum of AEPCDA shows the signals at m/z = 417.6 and 400.4 corresponding to the $(M + H)^+$ molecular ion adduct and $(M - NH_2)^+$ fragment, respectively (Figure 3.4). The spectrum of SEPCDA confirms the signal at m/z = 683.9 and 400.4 corresponding to the $(M + H)^+$ molecular ion adduct and $(M - C_{18}H_{36}CONH_2)^+$ fragment, respectively (Figure 3.5).

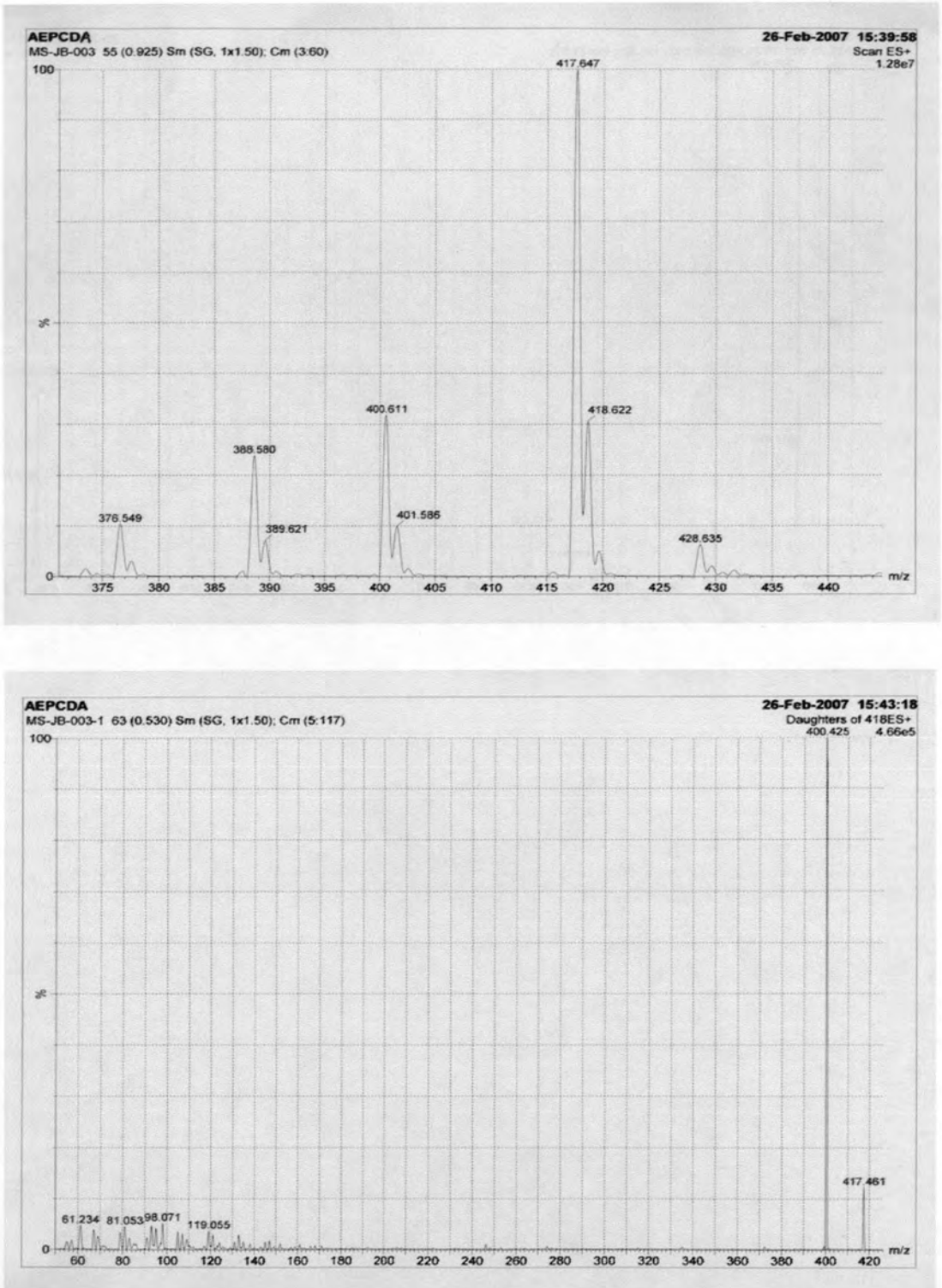


Figure 3.4 Mass spectrum of AEPCDA.

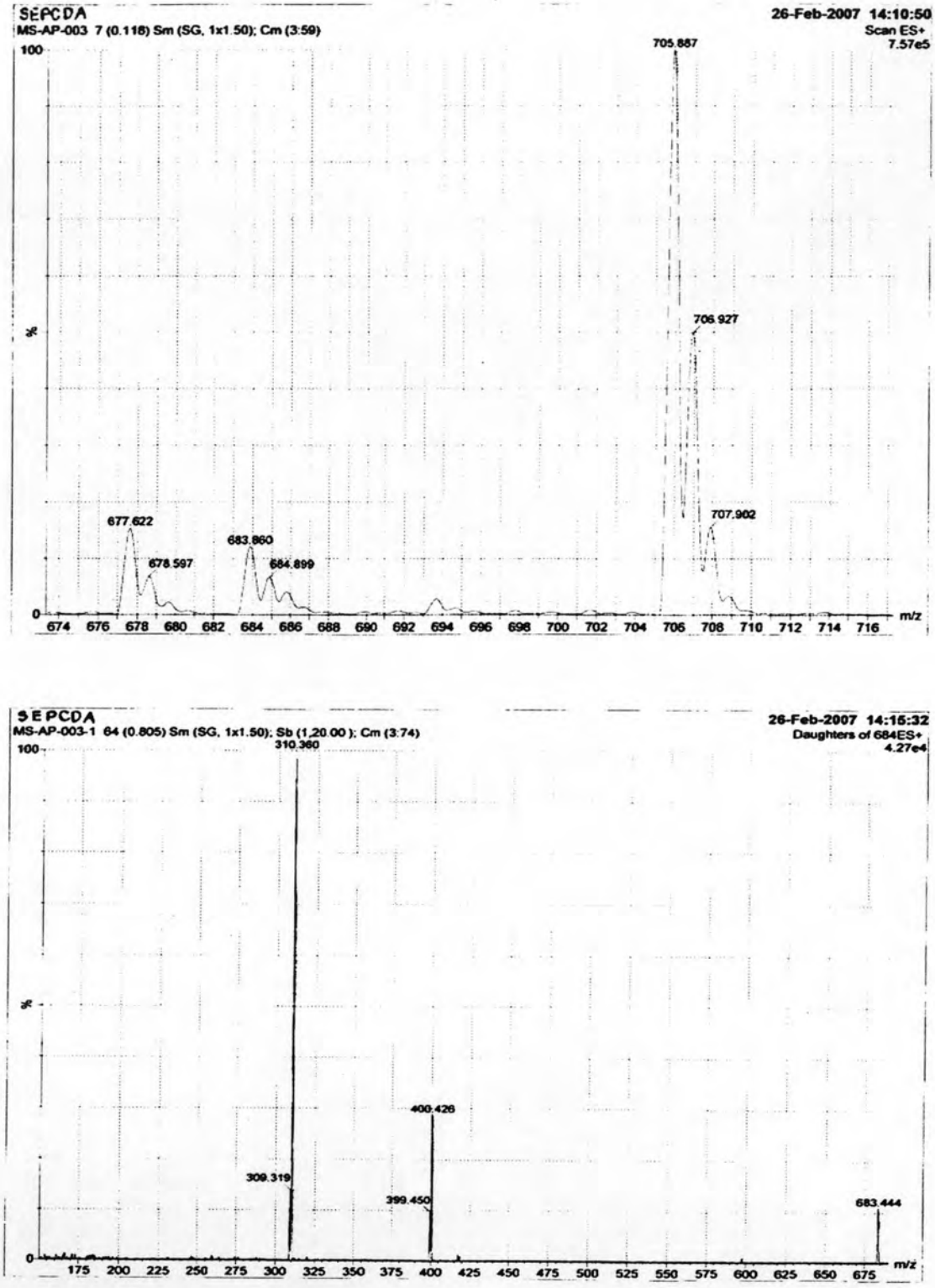


Figure 3.5 Mass spectrum of SEPCDA.

3.2 Preparation and study of polydiacetylene vesicles

3.2.1 Preparation of polydiacetylene vesicles

All diacetylene monomers (PCDA, AEPCDA, EBPCDA and SEPCDA) were prepared in the form of vesicles in water by using sonicator bath (230 watt) at 75-85 °C. Only PCDA, AEPCDA and SEPCDA but not EBPCDA dispersed well in water to form a semitransparent or transparent colloids without discernible lipid suspension at this temperature range. Poorer dispersion of EBPCDA is probably due to its high melting point (125-130 °C). Dispersion of EBPCDA could be improved by preheating its suspension in boiling water prior to the sonication. After keeping the colloids of the lipids at 4 °C overnight and irradiated with UV light (254 nm) for 5 min at room temperature and filtered through filter paper (No.1) to give blue solutions indicating that the vesicle lipid readily undergoes photopolymerization to form ene-yne alternated polymer chains. The blue color of PCDA and SEPCDA were deeper than that of EBPCDA suggesting higher polymerized vesicle concentration of PCDA and SEPCDA comparing to EBPCDA. The blue color of the vesicle solution of AEPCDA changed to purple or red during 5 min of the irradiation period. Therefore, the UV irradiation of AEPCDA vesicle solution was conducted in an ice bath that provided a clear intense blue solution of poly(AEPCDA) vesicles.

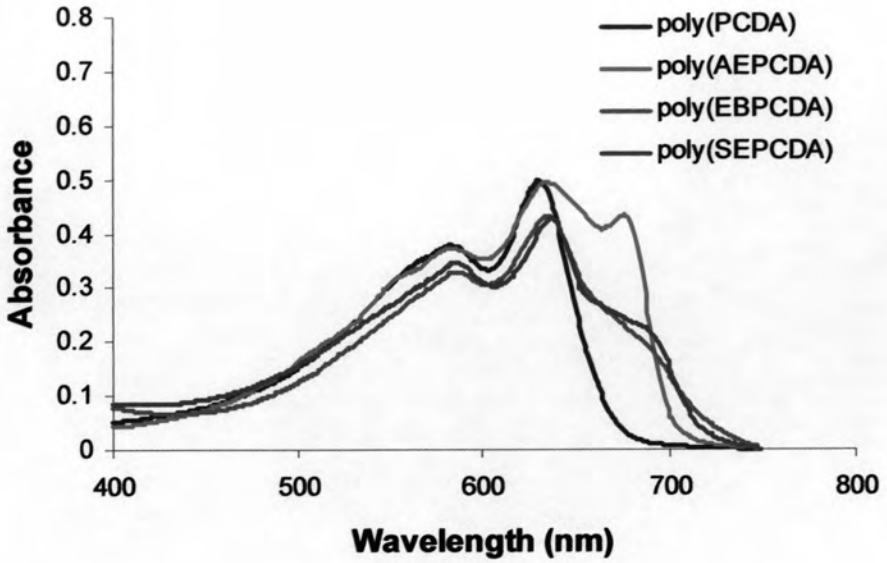
To study the efficiency of the vesicle formation at various lipid concentrations, the final concentrations of poly(PCDA) vesicles were compared with the initial PCDA concentrations. After photopolymerization, the blue poly(PCDA) vesicle solution was filtered to remove undesired lipid aggregate and the vesicle solution was freeze-dried to determine the content of poly(PCDA) vesicles. The experiment was performed in duplicate at each concentration. As the initial concentration of the monomeric lipid increased from 1.0 to 3.0 mM, the lower efficiency of the vesicle formation was obtained due to higher tendency of aggregation at higher lipid concentration. The results also show that the total transformation of PCDA into to poly(PCDA) can be obtained at 1.0 mM. Therefore, the lipid concentration of 1.0 mM was used and the quantitative conversion was assumed in all subsequent experiments unless specified otherwise.

Table 3.1 Correlation between the initial concentration of PCDA and final concentration of poly(PCDA) vesicles in solution

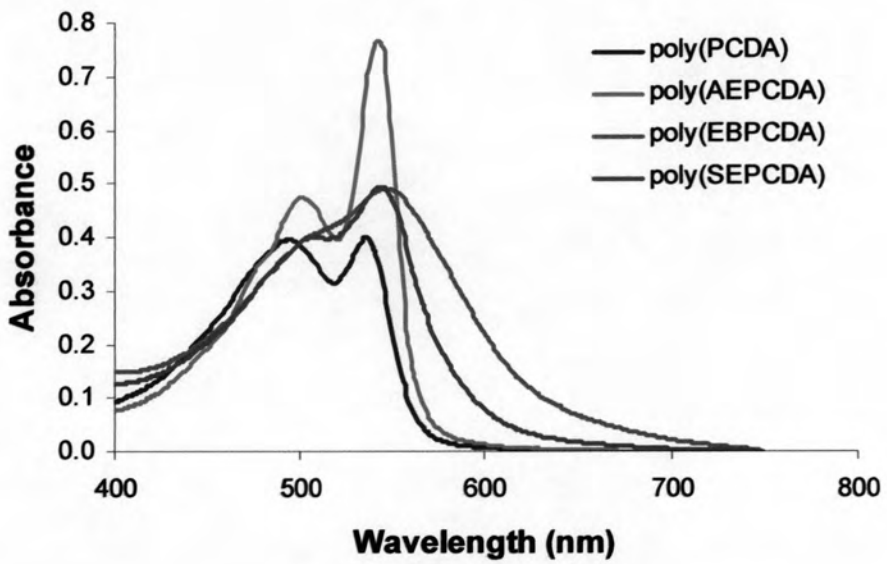
Initial concentration (mM)	Final concentration (mM)			Efficiency of vesicle formation (%)
	1st batch	2nd batch	Average	
1.0	1.02	1.15	1.09	109
1.5	1.20	1.12	1.16	77
3.0	1.54	1.66	1.60	53

3.2.2 Electronic absorption of polydiacetylene vesicle solutions

Since all PDA vesicle solutions prepared in this work are highly colored, the electronic absorption spectra of these solutions were recorded in the visible range 400-750 nm. For the sake of simplicity in comparison of the spectra, the absorbance of all solutions was arbitrarily set to zero at 750 nm. At 25 °C, all the vesicle solutions appeared blue and showed absorption band in the range of 500-700 nm (Figure 3.6a). When the temperature was raised from 25 to 90 °C, the color of the vesicle solutions change from blue to red and the absorption bands shift to 400-600 nm range (Figure 3.6b). Although the detail features of the absorption band of each PDA vesicles are quite different, they have quite similar λ_{max}, ~ 630 nm and ~ 540 nm for blue and red phase PDA (Table 3.2). The absorbance at these λ_{max} were used for the calculation of the colorimetric response (%CR).



(a)



(b)

Figure 3.6 Visible absorption spectra of polydiacetylene vesicle solution at a) 25 and b) 90 °C.

Table 3.2 λ_{max} for blue and red phase of polydiacetylene vesicles.

Type of polydiacetylene vesicles	λ_{max}	
	Blue phase	Red phase
Poly(PCDA)	631	537
Poly(AEPCDA)	635	544
Poly(EBPCDA)	636	548
Poly(SEPCDA)	638	545

Since the concentrations of the vesicles depend not only on the initial concentrations of the diacetylene monomer lipids but also on the condition of the vesicles prepared. It is thus desirable to have convenient means to determine the concentration or at least convey the terms of vesicle concentration in various experiments. The relationships between the absorbance of the blue and red phases and the concentration of poly(PCDA) lipid were thus investigated in the lipid concentration range of 0.02-0.10 mM (Figure 3.7). The exact concentration of poly(PCDA) vesicles was determined from the dry weight of the filtered solution. The absorbance of the poly(PCDA) vesicle solution obeys Beer's law with the slope of 5.8 $\times 10^3$ and 4.8 $\times 10^3$ M^{-1} for blue and red phase, respectively. This slope corresponds to the molar absorptivity (ε) of repeating unit in poly(PCDA) vesicles. Since the absorbance of the blue phase poly(PCDA) vesicles can be set to zero at zero concentration without significant effect to the correlation factor (R^2), it is quite convenient to be used for specifying in place of the concentration of poly(PCDA) vesicles, and presumably others, in further experiments.

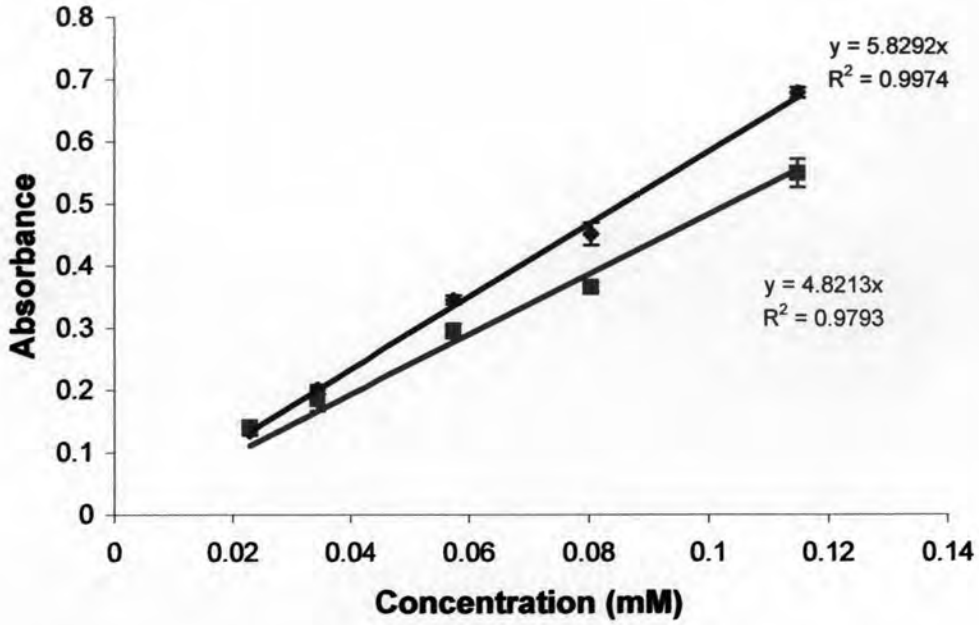


Figure 3.7 Relationship between visible absorbance and concentration of poly(PCDA) vesicles.

3.2.3 Particle size and microstructure of the PDA vesicles

Dynamic light scattering (DLS) spectroscopy was used for measuring the average particle sizes and size distribution of the PDA vesicles dispersed in the solution. The mean diameter of poly(PCDA), poly(AEPCDA) and poly(EBPCDA) vesicles were 73, 88 and 228 nm, respectively. Particle size distribution of these vesicles were shown in Appendix A.

Atomic force microscopy (AFM) and tunneling transmission electron microscopy (TEM) was utilized to observe the shape and size of the air-dried polydiacetylene vesicles. AFM and TEM images of poly(PCDA), poly(AEPCDA) and poly(EBPCDA) showed that the vesicle particles are mostly spherical (Figure 3.8). The typical particle sizes of non-aggregated poly(PCDA), poly(AEPCDA) and poly(EBPCDA) observed in the AFM images are 80-100, 30-60 and 40-80 nm, respectively. The AFM image of poly(EBPCDA) vesicles shows extensive aggregation of the vesicles which may explain a relatively bigger particle size measured by DLS. The size of poly(PCDA), poly(AEPCDA) and poly(EBPCDA) vesicles observed in TEM images are approximately 150-200 nm, 70-100 nm and 20-60 nm, respectively. In the TEM experiment, there was no significant aggregation of the vesicles observed in all three types of the PDA vesicles. Some discrepancies in

sizes measured by different techniques (DLS, AFM and TEM) are quite acceptable for soft nanomaterials such as lipid vesicles as long as the sizes are in the same order of magnitude since the condition of sample preparation can affect the individual particle size and aggregation state.

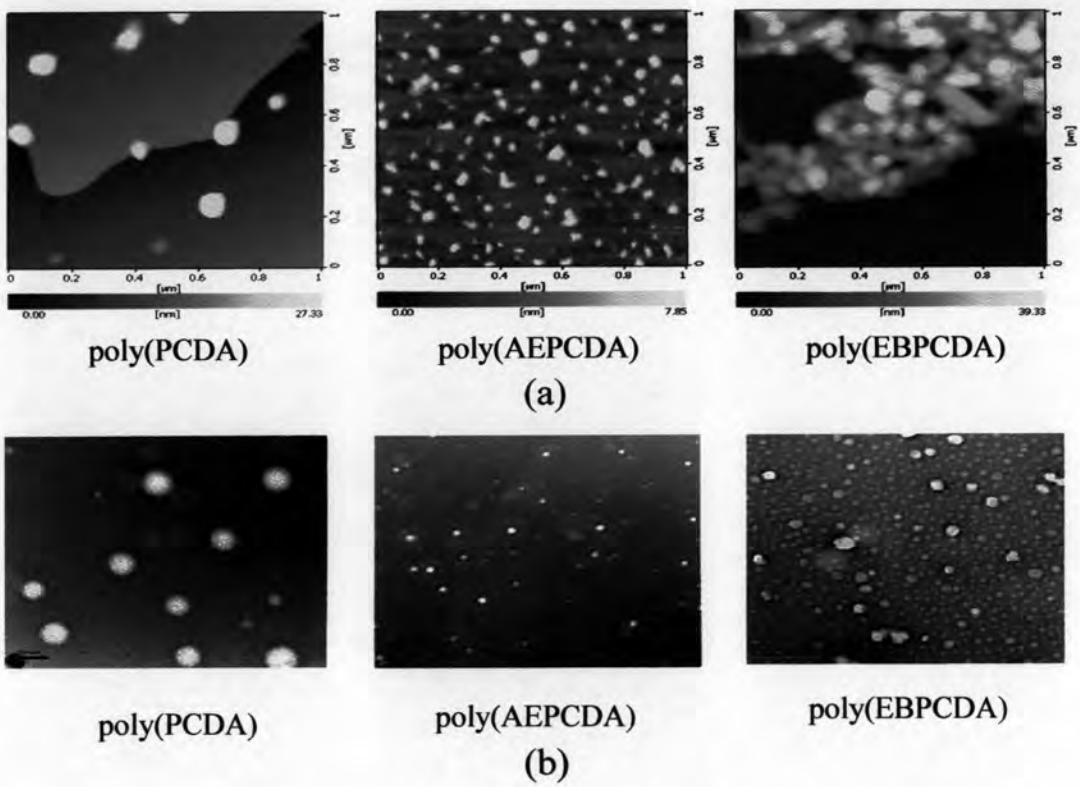


Figure 3.8 (a) AFM images and (b) TEM images of PDA vesicles on mica slide

3.2.4 Fourier transform infrared spectroscopy (FTIR)

To examine the nature of hydrogen-bonding among the headgroups, transmission FTIR spectroscopic analysed were executed for diacetylene monomers, PCDA, AEPCDA, EBPCDA and SEPCDA comparing to polydiacetylene vesicles, poly(PCDA), poly(AEPCDA), poly(EBPCDA) and poly(SEPCDA), respectively. From FTIR spectra, PCDA monomer had a peak position of hydrogen-bonded carbonyl stretching lower than poly(PCDA) vesicles, revealed that PCDA monomer showed relatively stronger hydrogen-bonding than poly(PCDA) vesicles. Whereas, AEPCDA monomer had a peak position of hydrogen-bonded carbonyl stretching higher than poly(AEPCDA) vesicles, indicated that poly(AEPCDA) showed stronger hydrogen-bonding than AEPCDA monomer that similar to in case of poly(EBPCDA) and poly(SEPCDA) vesicles that had stronger hydrogen-bonding than EBPCDA and

SEPCDA monomers, respectively (Figure 3.9). For other peak positions of diacetylene monomers and polydiacetylene vesicles showed slightly different. The peak positions of diacetylene monomers and polydiacetylene vesicles were summarized in Table 3.3.

Table 3.3 Changes in peak positions of diacetylene monomers.

Diacetylene monomers and polydiacetylene vesicles	Carbonyl stretching in carboxyl group ($\upsilon C=O, cm^{-1}$)	Carbonyl stretching in amide group ($\upsilon C=O, cm^{1}$)
PCDA	1694	-
Poly(PCDA)	1696	-
AEPCDA	-	1644
Poly(AEPCDA)	-	1643
EBPCDA	-	1643
Poly(EBPCDA)	-	1641
SEPCDA	-	1642
Poly(SEPCDA)	-	1641

From the results, only monomer of PCDA showed relatively stronger hydrogen-bonding than polymerized vesicles of PCDA, expect that PCDA prefers forming dimeric that have stronger double hydrogen-bonding than hydrogen-bonding in poly(PCDA) vesicles while AEPCDA, EBPCDA and SEPCDA monomers showed weaker hydrogen-bonding than polymerized vesicles.

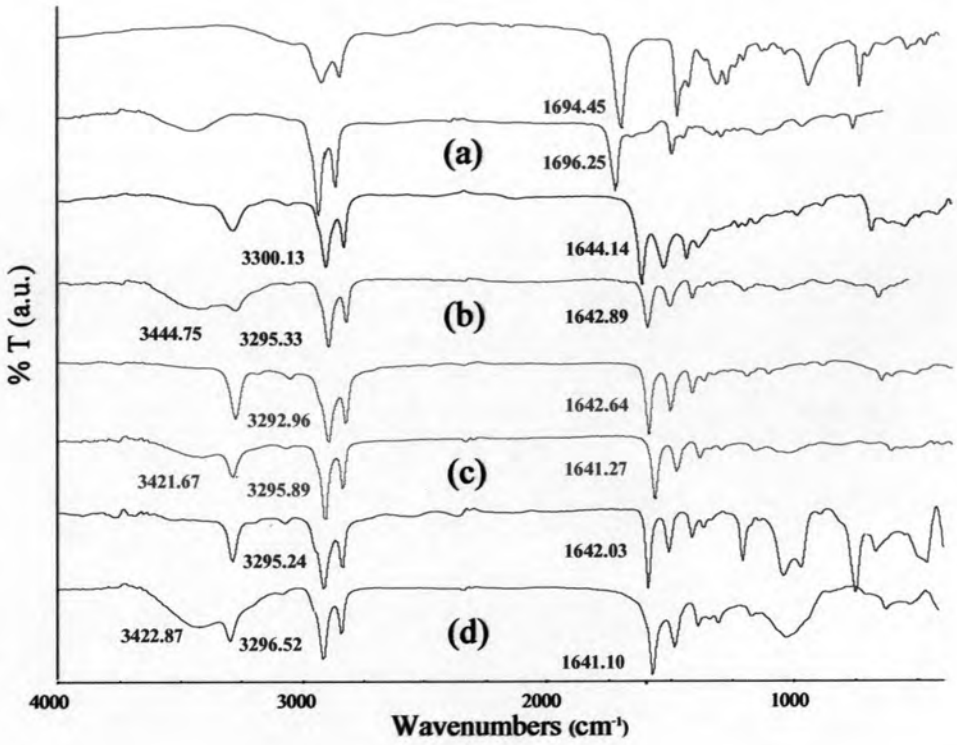


Figure 3.9 FTIR spectra of (a) PCDA and poly(PCDA) vesicles, (b) AEPCDA and poly(AEPCDA) vesicles, (c) EBPCDA and poly(EBPCDA) vesicles and (d) SEPCDA and poly(SEPCDA) vesicles.

3.3 Thermochromism of polydiacetylene vesicles and films

3.3.1 Color transition of four types of PDA vesicle solutions

The color of PDA vesicle solutions *i.e.* poly(PCDA), poly(AEPCDA), poly(EBPCDA) and poly(SEPCDA) changed from blue to red (Figure 3.10) when the temperature is raised from 25 to 90 °C with their maximum absorption undergoes gradual shifts from 630 to 540 nm (Figure 3.11).

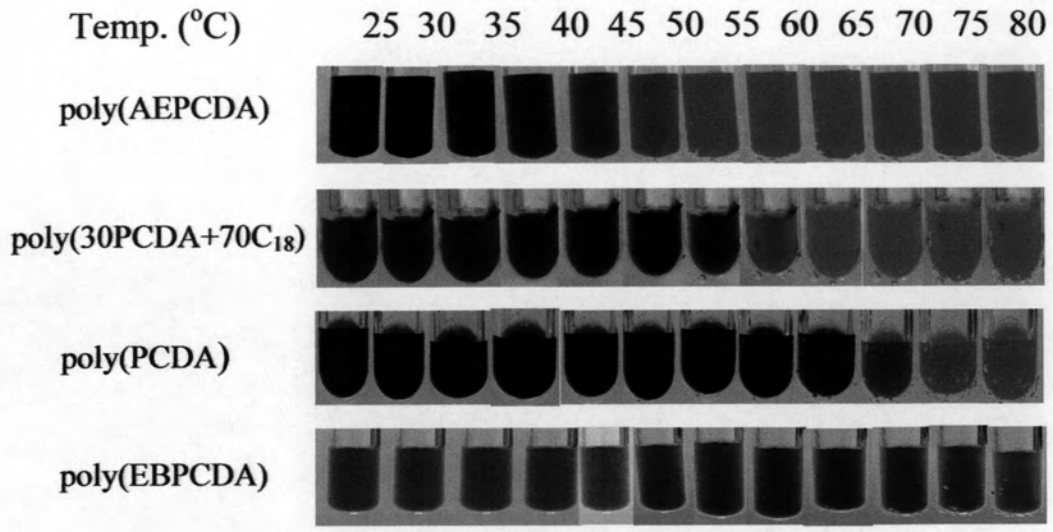


Figure 3.10 Thermochromism of the polydiacetylene vesicle solution prepared from PCDA, AEPCDA,EBPCDA and SEPCDA at various temperatures.

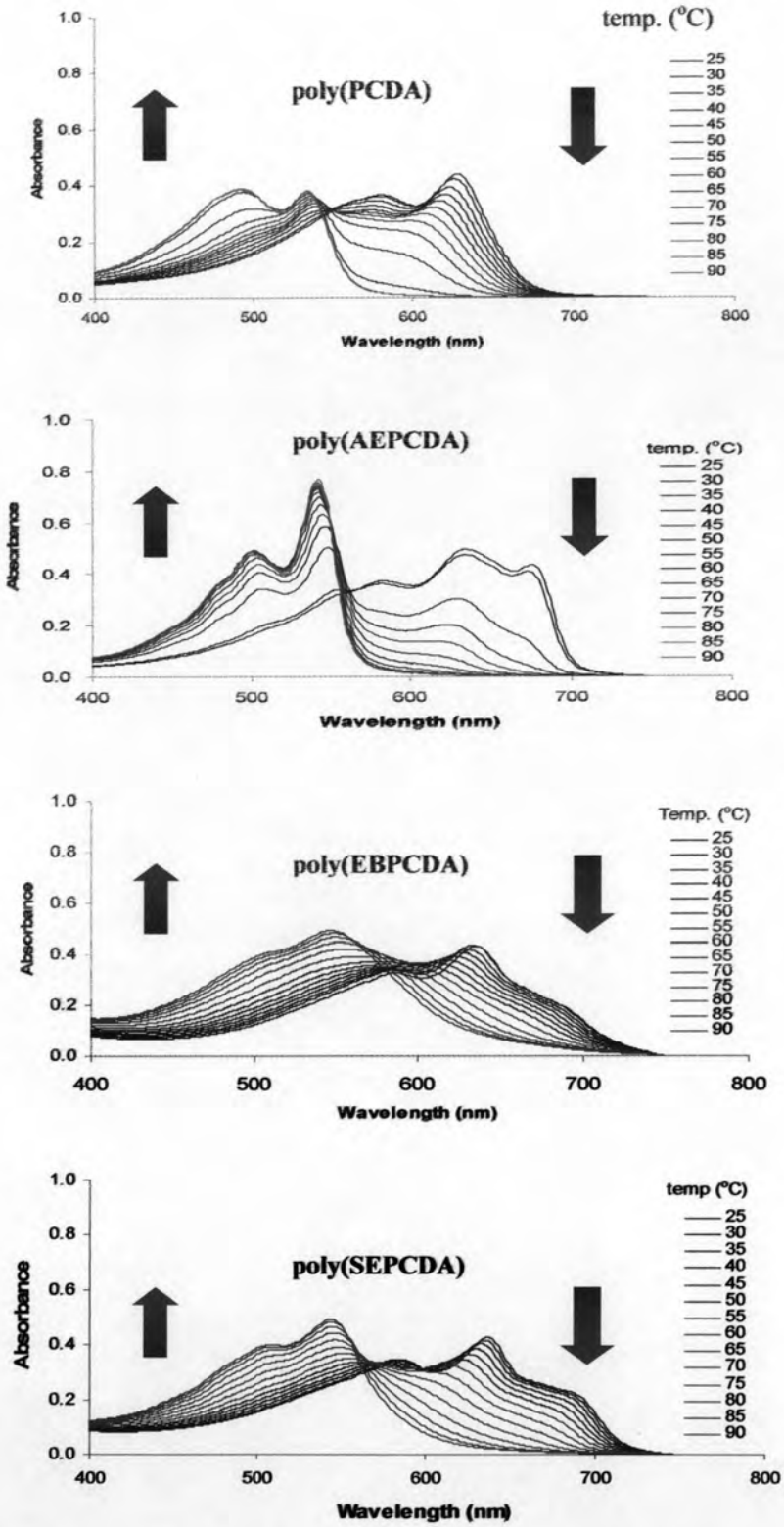


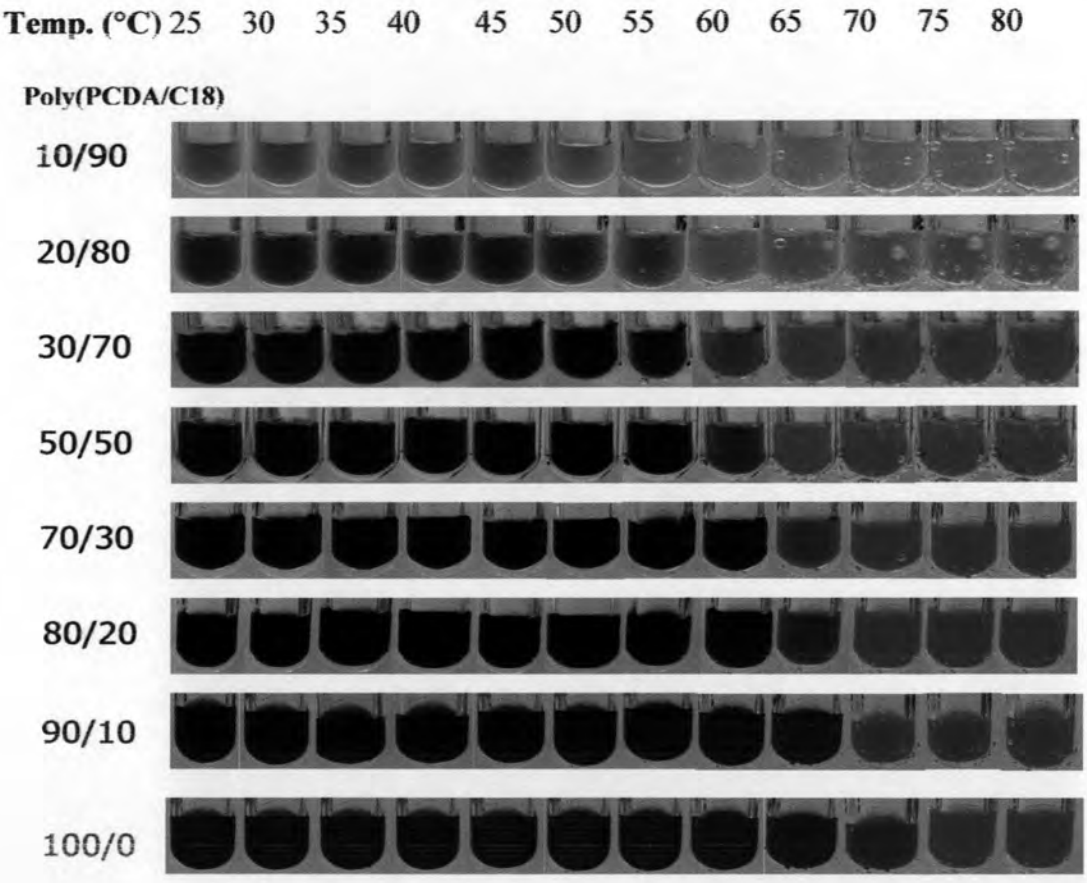
Figure 3.11 Visible absorption spectra of PDA vesicle solution prepared from PCDA, AEPCDA,EBPCDA and SEPCDA at various temperatures.

The color transition of these vesicles from blue to red indicating the increases of the energy gap between the ground and excited states, presumably the HOMO and LUMO of the π-conjugated backbone of PDA. The increase in the energy gap of PDA is generally interpreted as the reduction of the conjugation length due to the twisting of the single bonds between the double and triple bonds. Another theory proposed for explanation of the increase of the energy gap is the relief of mechanical strain in the conjugated backbone. Both theories however involve the weakening or lost of the hydrogen bonding between the functional group of the side chain. The color transition temperatures (CTT) observed were in the following order: poly(AEPCDA) < poly(PCDA) < poly(EBPCDA) ~ poly(SEBPCDA), suggesting the same order for the strength of hydrogen bonding between the head groups of the PDA vesicles. The stronger hydrogen bonding between the head groups of poly(EBPCDA) and poly(SEBPCDA) can be attributed to the simultaneous hydrogen bonding between two amide groups in each monomer molecule. The weaker hydrogen bonding between the head groups of poly(AEPCDA) was harder to envisage since its monomer lipid also contains two functional groups, amido and amino, that can form hydrogen bonds. One possible explanation may be that the optimum geometrical orientations for the hydrogen bonding of the two different functional groups are not the same.

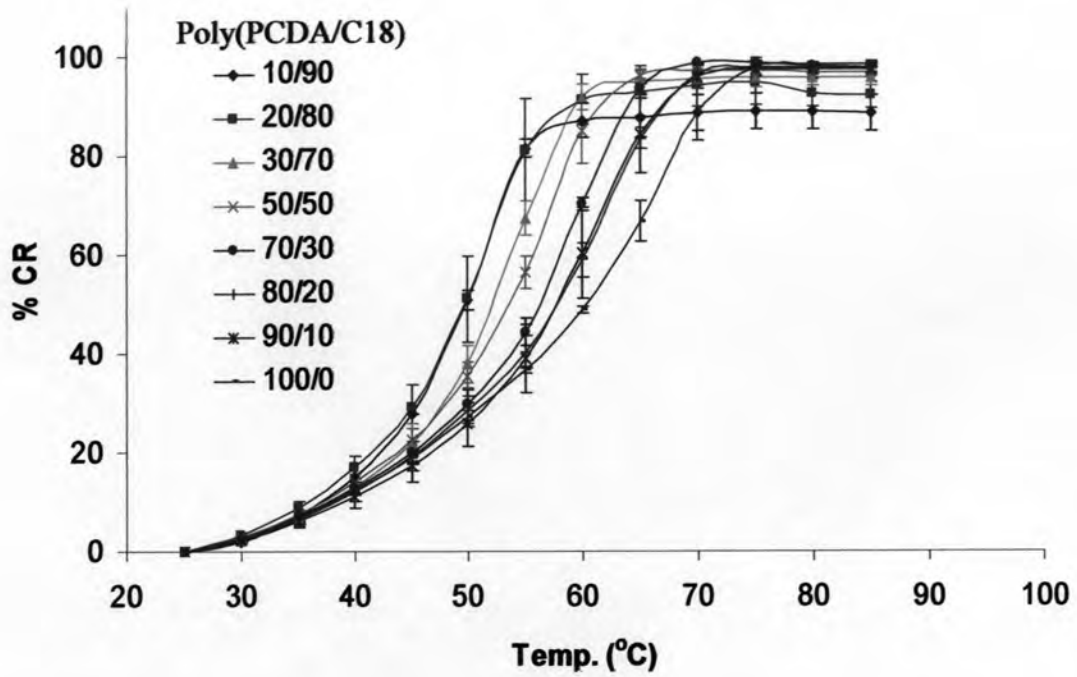
3.3.2 Lowering of CTT by mixing of fatty acids with PCDA

Mixing of PCDA with a long chain fatty acid in the preparation of vesicles is expected to lower the CTT of poly(PCDA) by interrupting the continuity of the topopolymerization and weakening the interaction between the side chains of poly(PCDA). Fixing the mole ratio of the fatty acid at 0.3, four types of fatty acids *i.e.* hexanoic, tetradecanoic, octadecanoic and oleic acids were tested. The CTT of poly(PCDA) vesicles containing hexanoic, tetradecanoic and oleic acids were not significantly different from that of pure poly(PCDA) vesicles. Octadecanoic acid (stearic acid) however lowered the CTT of poly(PCDA) vesicle by about 5 °C. For mixing of stearic acid (C_{18}) and PCDA had the lowest transition temperature (% CR of mixed vesicle solution was shown in Appendix C). Therefore , mixed vesicle solution of PCDA and stearic acid (C_{18}) was chosen for study optimized ratio. Mixed vesicle solution was prepared at a concentration of 1.0 mM at C_{18} molar ratios 0.1, 0.2, 0.3, 0.5, 0.7, 0.8 and 0.9. Under UV irradiation, those sonicated suspensions in

aqueous solution show an intense blue color at molar ratio 0.5 downward and gradually decreased when C_{18} molar ratio was increased, indicating that PCDA in the mixed lipid vesicles readily undergoes photopolymerization to form an ene-yne alternated polymer chain. The color transition changed from blue to red of their poly(PCDA+C_{18}) at various ratios when the temperature is raised from 25 to 90 °C with their maximum absorption undergoes gradual shifts from 630 to 540 nm (Appendix B). Transition temperature range observed by eyes of poly(PCDA+C_{18}) vesicle solution at various ratios and colorimetric response (%CR) obtained from spectrometer was shown in Figure 3.12.



(a)



(b)

Figure 3.12 Thermochromism of poly(PCDA+C_{18}) vesicle solution at various ratios recorded by (a) photography and (b) colorimetric responses.

Since the color of polydiacetylene vesicle solution prepared from the 10PCDA/90C_{18} mixed lipid at the total lipid concentration of 1.0 mM was rather pale, the total concentration of mixed lipid was thus raised to 10.0 mM. The color intensity of poly (10PCDA/90C_{18}) vesicle solution increased significantly when the total lipid concentration was increased from 1.0 to 10.0 mM (Figure 3.13). However, using the calibration line in Figure 3.5, the concentration of PCDA repeating unit was estimated to be 0.7 mM significantly lower than 1.0 mM of the initial concentration of PCDA. The loss of PCDA was also evident by considerable lipid aggregate observed after sonication. Another undesirable feature observed from the use of high lipid concentration is the turbidity of the vesicle solution even after filtration. These results agree well with the conclusion about the optimum lipid concentration surmised in section 3.2.1. Thus far, among all the mixed lipid vesicles, PCDA mixed with stearic acid at 30:70 mole ratio with the total lipid concentration of 1.0 mM provides the most satisfactory lowering effect on CTT and color intensity.

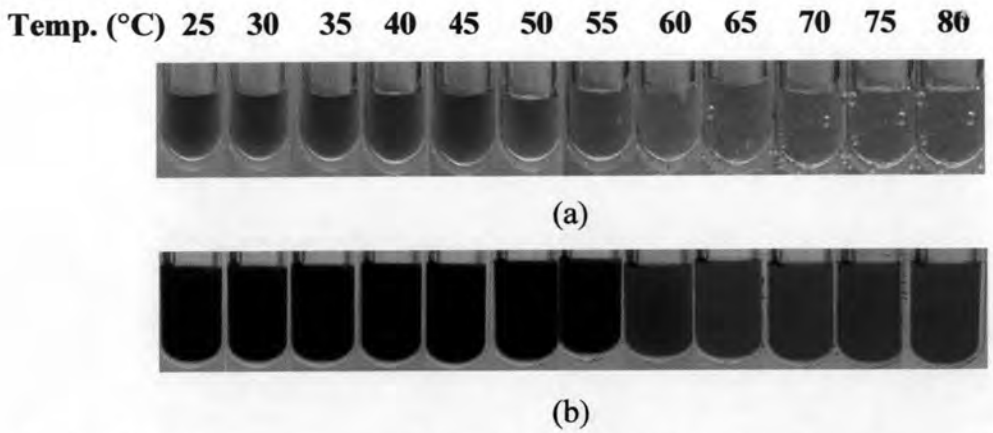
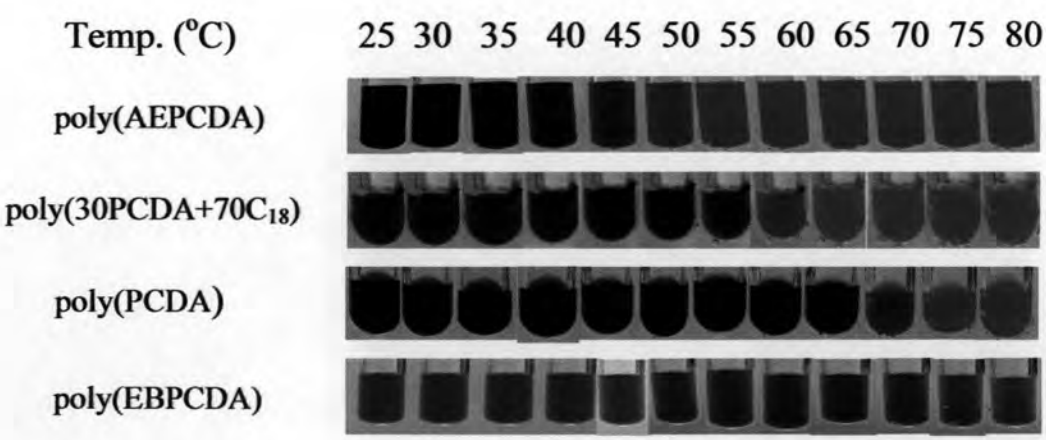
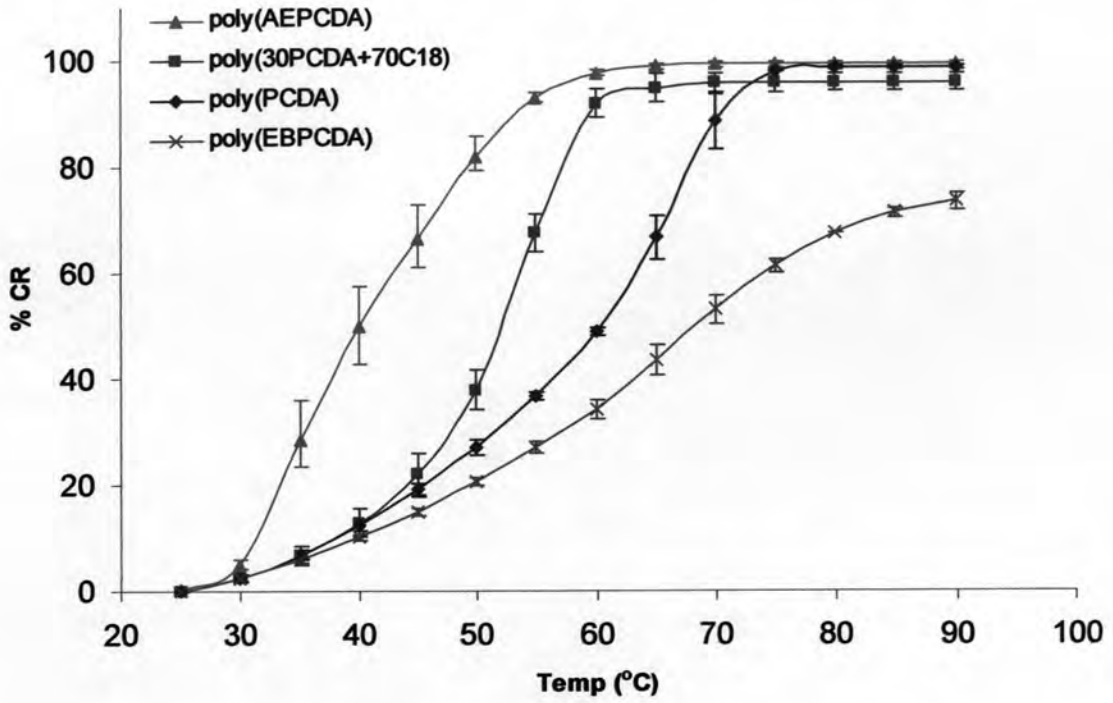


Figure 3.13 Thermochromism of poly(10PCDA+90C_{18}) vesicles prepared from different total lipid concentration: (a) 1.0 mM and (b) 10.0 mM.

3.3.3 The correlation between CTT observed by eyes and %CR

The photograph of color transition along with the colorimetric response (%CR) upon heating of the polydiacetylene vesicle solution prepared from PCDA, 30PCDA/70C_{18}, AEPCDA and EBPCDA are shown in Figure 3.14. The order of the CTT *viz.* poly (AEPCDA) < poly(30PCDA/70C_{18}) < poly(PCDA) < poly(EBPCDA) observed by eyes is the same to that observed from the change of %CR determined from UV-Vis spectrometer. However, it is not yet possible to define the %CR which corresponds to the CTT as each type of vesicle solution exhibits unique temperature sensitivity (the slope of the plot) and reaches different level of the final %CR.





(b)

Figure 3.14 Thermochromism of the polydiacetylene vesicle solution recorded by (a) photography and (b) colorimetric responses.

3.3.4 Reversibility of thermochromism

In the study of thermochromism of various polydiacetylene vesicles, reverse of color change from red back to blue was observed for poly(EBPCDA) vesicle solution. The degree of reversibility of the color transition of poly(EBPCDA) was thus monitored quantitatively using the colorimetric response. Barring the first heating-cooling cycle, the %CR of poly(EBPCDA) showed excellent reversibility for at least three cycles (Figure 3.15). The slight difference of %CR of the first cooling cycle from the original %CR of the unheated poly(EBPCDA) is probably due to some solvent memory of the vesicles. The observation of the color transition reversibility for poly(EBPCDA) but not for poly(PCDA) and poly(AEPCDA) suggests that either the two amide groups or two polymerizable diacetylene units of EBPCDA involve in keeping the polymeric side chain in position which can allow the return of their original packing.

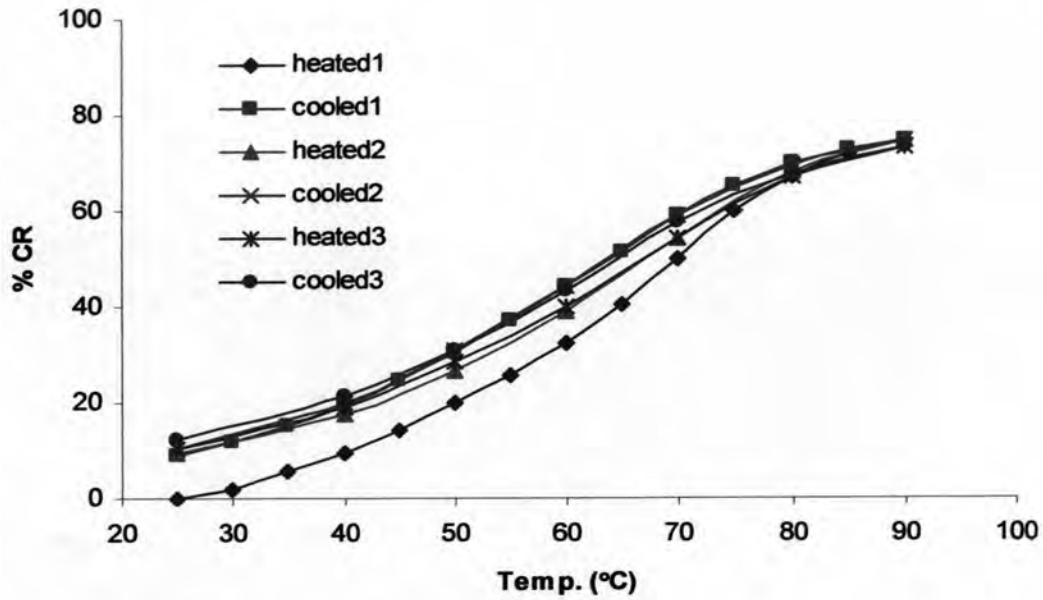


Figure 3.15 Reversibility of the colorimetric responses of poly(EBPCDA) vesicle solution subjected to three heating-cooling cycles

To decipher whether the two amide groups or two diacetylene units really responsible for the reversibility of poly(EBPCDA), another diacetylene analogue containing two amide groups but only one diacetylene unit, *N*-(2-stearamidoethyl)pentacosa-10,12-diynamide (SEPCDA), was synthesized and studied. Only the reversibility of the thermochromism of poly(SEPCDA) vesicle solution will be described here as the synthesis and some thermochromic properties of were already presented in the previous sections. The %CR of poly(SEPCDA) vesicles displayed greater solvent memory than that of poly(EBPCDA) vesicles in the first heating-cooling cycle. The second and third cycles however showed complete reversibility of the %CR (Figure 3.16). The results imply that the double hydrogen bonds between the diamide group are responsible for the reversibility of the thermochromism of both poly(SEPCDA) and poly(EBPCDA) vesicles while the polymerization of an extra diacetylene unit in EBPCDA is responsible for the lower solvent memory.

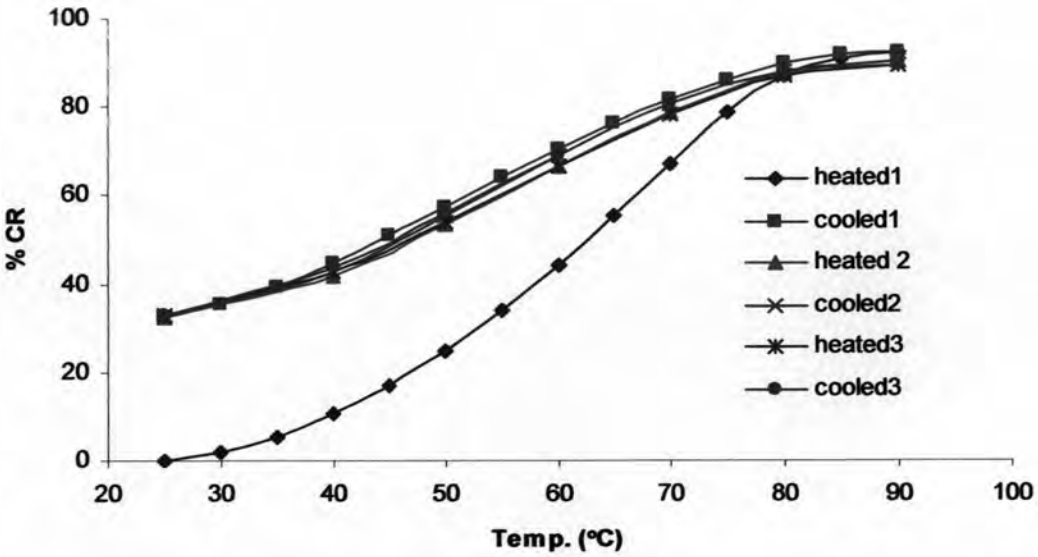


Figure 3.16 The reversibility of the colorimetric responses of poly(SEPCDA) vesicle solution subjected to three heating-cooling cycles.

3.4 Preparation and study of thermochromic films

3.4.1 Copoly(acrylic-acrylate) latex film

A copoly(acrylic-acrylate) latex was used as a film forming matrix for the polydiacetylene vesicles *viz.* poly(PCDA), poly(70PCDA+30C_{18}), poly(AEPCDA) and poly(EBPCDA). The films prepared from the latex mixed with poly(PCDA), poly(PCDA+C_{18}) and poly(EBPCDA) was blue while the film prepared from the latex mixed with poly(AEPCDA) appeared as a red film. (Figure 3.17). In fact, the mixture of the latex and poly(AEPCDA) also slowly turned into red color upon storing. The red color of this mixture may be attributed to the interaction of the protonated amine groups of poly(AEPCDA) with either the anionic head group of the surfactant used in the latex or the carboxylate anion of the copoy(acrylic-acrylate) latex. The prematurely red color of the mixture between the latex and poly(AEPCDA) making it unsuitable for thermal sensing application.

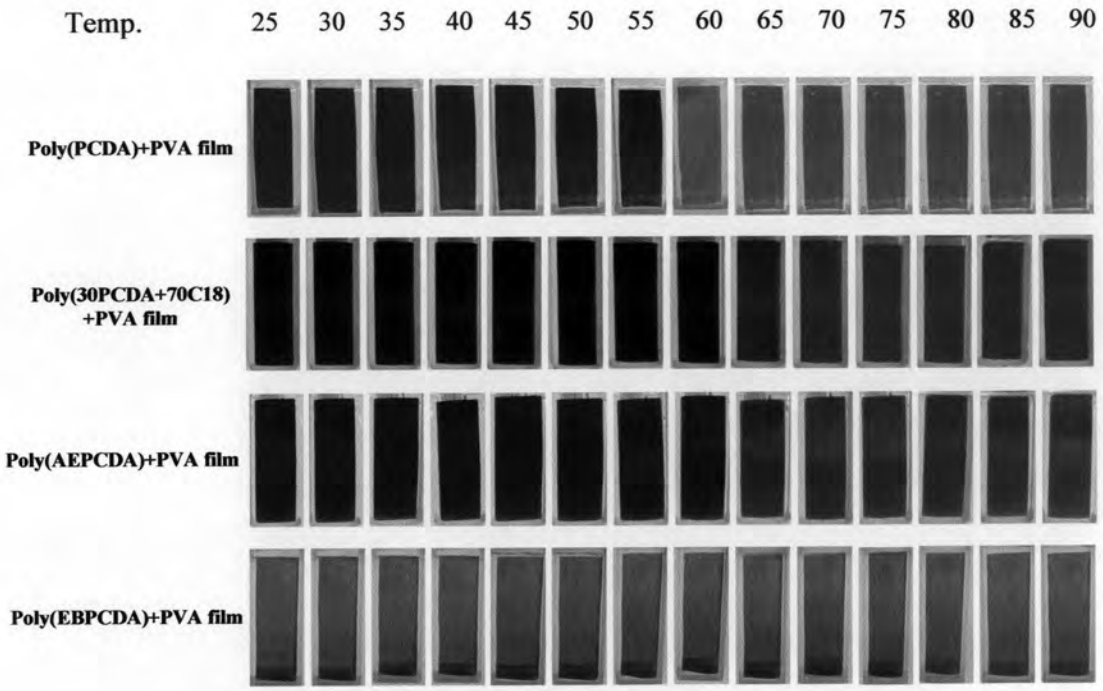
Poly(PCDA) Poly(PCDA+C_{18}) Poly(AEPCDA) Poly(EBPCDA)

Figure 3.17 Color of copoly(acrylic-acrylate) latex films containing polydiacetylene vesicles at room temperature.

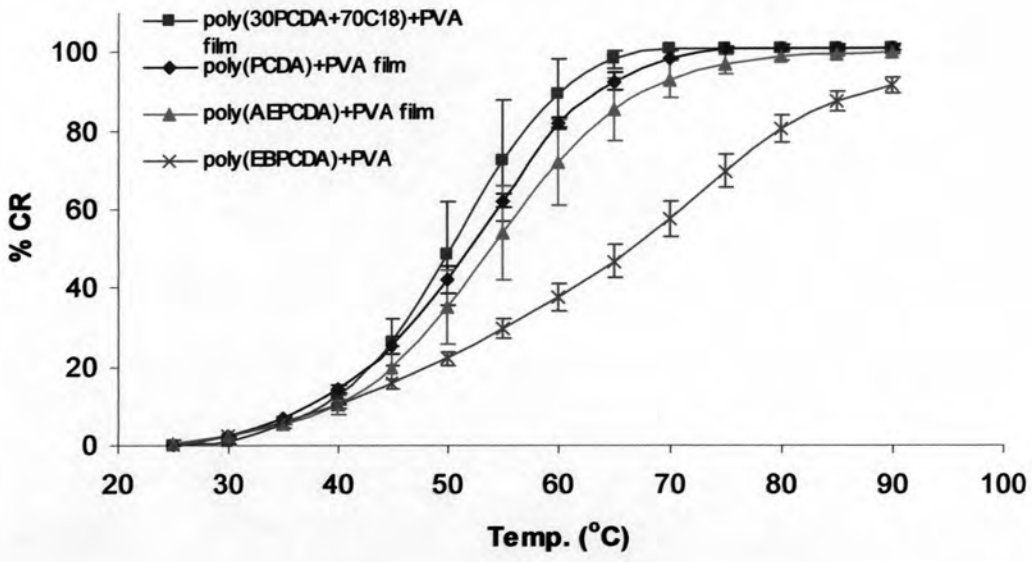
3.4.1 Polyvinyl alcohol film

Polyvinyl alcohol (PVA) was also tested as a polymeric film forming matrix. Pleasingly, PVA films containing vesicles of all polydiacetylene types *i.e.* poly(PCDA), poly(70PCDA+30C_{18}), poly(AEPCDA) and poly(EBPCDA) retained the desirable blue color at room temperature. This blue color is very important for their use as thermochromic films. Comparing to the copoly(acrylic-acrylate) films, the PVA films also showed superior film properties such as smoothness and toughness. The blue-colored films could be peeled from the glass Petri dishes used as their substrates to provide the translucent free standing films.

The thermochromic behaviors of the free standing PVA films containing polydiacetylene vesicles were recorded by photography and UV-Vis spectrometry reporting as %CR (Figure 3.18). The order of CTT of these films is poly(30PCDA/70C_{18}) < poly(PCDA) ~ poly(AEPCDA) < poly(EBPCDA). The thermochromism of poly(EBPCDA) vesicle embedded in PVA possesses its reversibility same as the solution.



(a)



(b)

Figure 3.18 Thermochromism of PVA films containing the polydiacetylene vesicles recorded by (a) photography and (b) colorimetric responses.

It is of significance to note that the CTT of poly(PCDA) vesicle embedded in PVA film appears at lower temperature than its solution while that of poly(AEPCDA) vesicles embedded in PVA film appears at higher temperature than its solution. The results may be caused by the relatively higher pH of PVA (~ 6.0) comparing to those

of the vesicles which are 5.8 and 4.9 for poly(PCDA) and poly(AEPCDA), respectively. The deprotonation of the lipid head groups by mixing with higher pH polymeric matrix probably increases the charge repulsion between the carboxylate head group in poly(PCDA) but decreases the charge repulsion between the protonated amine head group in poly(AEPCDA). The PVA matrix did not affect the CTT of poly(EBPCDA) because there is no acidic proton in EBPCDA besides pH values of PVA and poly(EBPCDA) vesicle solutions were similar.