



CHAPTER III

RESULT AND DISCUSSION

3.1. Preparation and characterization of PPCDA vesicles

The PPCDA vesicles were prepared in water at a monomer concentration of 1.6 mM. The average particle size of PPCDA vesicles was observed by DLS and TEM techniques was 90-100 nm (Figure 3.1). The PPCDA vesicles was dissolved in water to obtain a blue solution which turned into red upon heating. The color transition temperature (CTT) of the PPCDA vesicle solution was observed at 65-70 °C (Figure 3.2). The blue phase PPCDA showed λ_{\max} at 635 and 590 nm while the red phase PPCDA has λ_{\max} at 540 and 495 nm (Figure 3.3). The colorimetric responses (%CR, for its description and calculation see section 2.3.3.6) of PPCDA solution at the CTT (65-70 °C) was 70-75% (Figure 3.4).

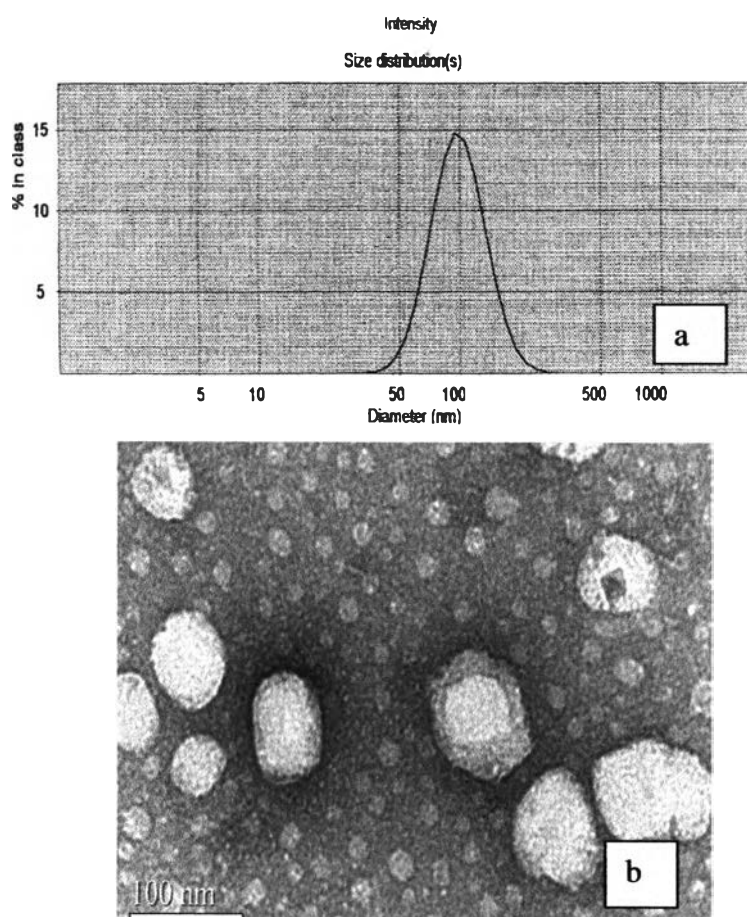


Figure 3.1 (a) Dynamic light scattering spectrum and (b) TEM micrograph of PPCDA vesicles.

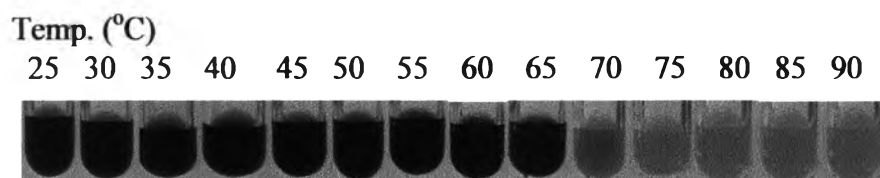


Figure 3.2 Thermochromism of aqueous suspension of PPCDA vesicle

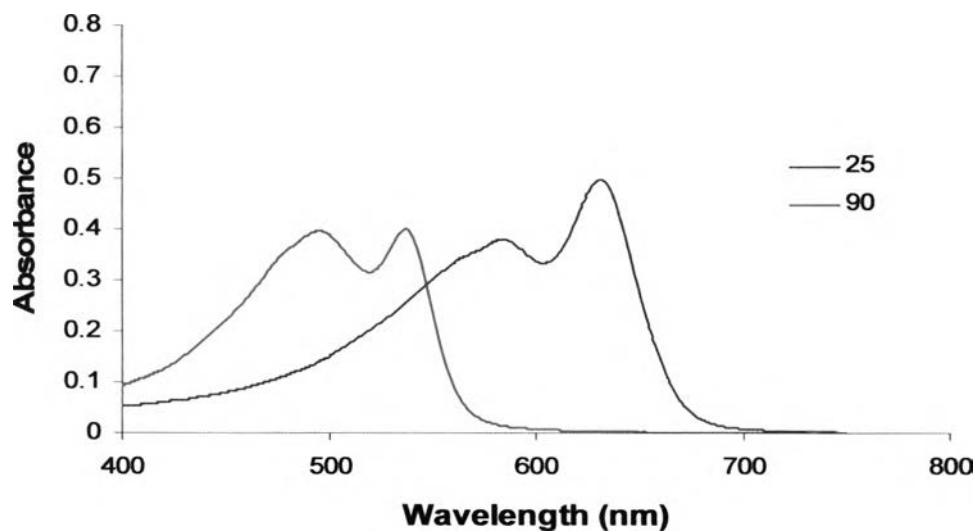


Figure 3.3 Visible spectra of the blue PPCDA vesicle solution at 25 °C and the red solution at 90 °C

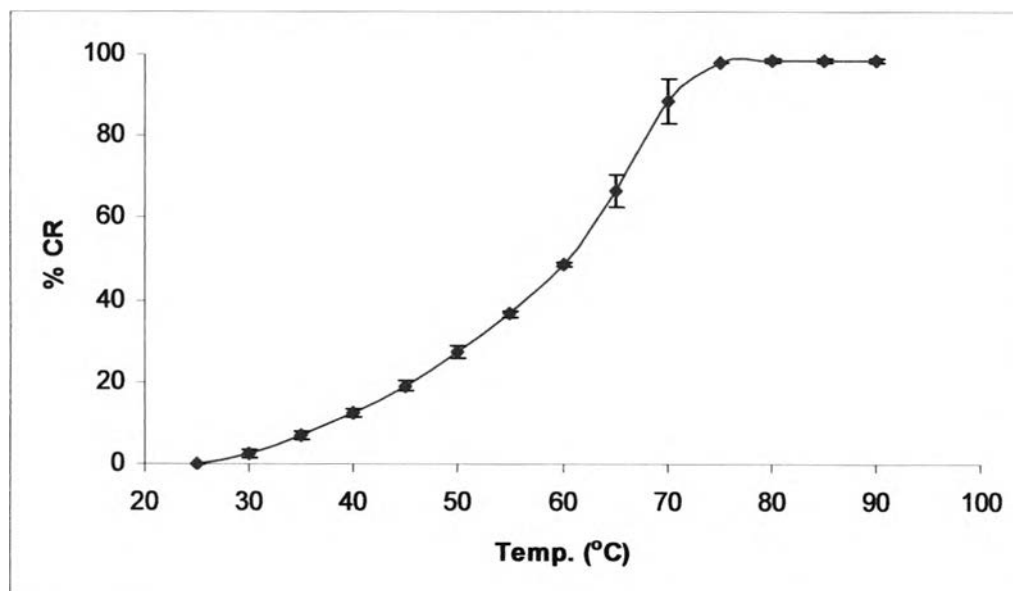


Figure 3.4 The colorimetric responses of PCDA vesicle solution upon increasing temperature

3.2 Preparation and characterization of acrylic-acrylate latexes

The latexes were prepared from emulsion copolymerization of acrylate and methacrylic monomers using an anionic surfactant, Rhodapax CO-436 (E) as an emulsifier. Five monomers could be classified into two groups, a) conventional monomers: ethyl acrylate (EA) and methacrylic acid (MAA), b) crosslinking monomers: glycidyl methacrylate (GMA), n-methylol acrylamide (nMA) and ethylene glycidyl dimethacrylate (EGDMA) were used in this work.

3.2.1 Effects of comonomer ratio on the properties of latexes

In polymer physics, the glass transition temperature (T_g) represents the change of an amorphous polymer from glassy to rubbery state. The T_g of copolymers may be predicted from the constituents and the T_g of each homopolymer according to the following equation; $1/T_g = X_1/T_{g1} + X_2/T_{g2} + X_i/T_{gi}$ where X_1 , X_2 and X_i are mole fractions of homopolymer 1, 2 and i and T_{g1} , T_{g2} and T_{gi} are T_g (K) of homopolymer 1, 2 and i. In this work, the latexes were prepared from the copolymerization of the hard monomer, MAA, and the soft monomer, EA. The T_g of homopolymer of MAA and EA are 228 and -22 °C, respectively. The predicted T_g agreed well with the experimental values (Table 3.1, for thermograms see Appendix C1-C6). The comonomer ratio also affected other latex properties such as film hardness and minimum film forming temperature (MFFT) values. The T_g , hardness and MFFT values of the latexes increased with the hard/soft monomer ratio. Therefore, the variation of the co-monomer ratio can be utilized as a strategy for preparation of latexes with a wide range of predictable physical properties. This strategy was however limited for the synthesis of latexes with the predicted T_g lower than the polymerization temperature, which was 80-84 °C. The copolymers with predicted T_g values higher than the polymerization temperature tended to form gel during polymerization.

Table 3.1 Effects of the comonomer ratio on the properties of latexes.

Polyacrylic latexes	Predicted T _g (°C)	T _g observed by DSC (°C)	Pencil hardness	MFFT (°C)
EA35/E0.5	-22.1	-29.99	<6B	<5
EA30/MAA5/E0.5	-2.7	-1.1	5B	<5
EA25/MAA10/E0.5	19.74	14.38	3B	21
EA21/MAA14/E0.5	40.59	35.53	B	42
EA18/MAA17/E0.5	58.29	50.74	F	72
EA13/MAA22/E0.5	117.01	124.78	cracking	>100
EA2/MAA30/E0.5	165.59		gelation	

EA = ethyl acrylate, MAA = methacrylic acid monomer, E = Rhodapax CO-436 emulsifier; %NV = 35-36%, pH = 2.5-2.8, viscosity = 8-13 cPs

The MFFT is the temperature above which latex particles will deform and coalesce to form film. Factors affecting the MFFT values include the types of monomers, surfactants, latex particles size and the presence of plasticizers or stabilizers. As film formation at room temperature or lower is preferred in this work, the latexes with the MFFT below the room temperature are desirable. Since the MFFT and the T_g of latex film are interrelated, the latex with rather low T_g (< 10 °C) tends to form tacky films which may have an application as self adhesive labels on product packages. Adhesion between latex films and two types of substrates, glass and polyethylene plastic was evaluated. The tacky films with the MFFT below 5 °C showed excellent adhesions to both substrates (Table 3.2). At room temperature, the latexes with the MFFT above room temperature formed films with poor adhesion and poor film properties *i.e.* cracking and opaque.

Table 3.2 Effects of hardness properties of latex on adhesion on various substrates

Polyacrylic polymer	MFFT (°C)	Dry film appearance at room temperature	Adhesion on glass	Adhesion on polyethylene
EA35/E0.5	<5	clear and tacky	excellent	excellent
EA31/MAA5/E0.5/CA	5	clear and tacky	excellent	good
EA21/MAA14/E0.5/CA	26	clear and hard	good	fair
EA20/MAA15/E0.5/CA	29	clear and hard	fair	poor
EA15/MAA20/E0.5/CA	35	clear and cracking	poor	very poor
EA10/MAA25/E0.5/CA	43	opaque and cracking	very poor	very poor

excellent = no peel off, good = not more than 30% peel off, fair = no more than 70% peeled off, poor = 100% peeled off, very poor = not adhered to the substrate

3.2.2 Variation of monomer concentration

At constant monomer ratio (EA/MAA) and emulsifier concentration, the total dosage of the monomers in the formulation was varied from 35 to 49% w/w. The %NV determined after polymerization were in good agreement with the amounts of the initial monomers indicating that the polymerization proceeded virtually quantitative (Table 3.3). The viscosity tended to increase with the increasing amount of monomers. The latex particle size determined by dynamic light scattering (DLS) increased with the monomer concentration due to the larger numbers of monomeric molecules in each micelle of the emulsifier during polymerization (for DLS spectra see Appendix D1-D4). The minimum film forming temperature (MFFT) and hardness were also increased with the increasing concentration of the monomers. The higher MFFT observed for the latex with bigger particles is presumably due to the greater distances between the neighboring particles. However, once the film was formed, the bigger particles probably abided greater impact loading and thus the film hardness increased [53]. In this particular polymerization system, the nonvolatile content was limited at 45.5% as the gelation occurred at higher content.

Table 3.3 The effects of monomer concentration on latex properties.

Latexes	%NV	Viscosity (cP)	Particle size (nm)	MFFT (°C)	Pencil hardness
EA21/MAA14/E0.5	35	9	95.5	26	B
EA23/MAA14/E0.5	38.5	14	96.9	28	F
EA25/MAA17/E0.5	42	18	98.2	31	*F-H
EA27/MAA18/E0.5	45.5	25	105.3	35	*H
EA29/MAA20/E0.5	gelation during polymerization				

*The films were prepared in an oven at 100°C for 10 minutes.

3.2.3 Addition of crosslinking agents

The latexes prepared with a mixture of GMA, NMA and EGDMA crosslinking monomers produced thermosetting latexes with lower MFFT but higher hardness comparing to the uncrosslinked polymer latexes. The lower MFFT value is attributed to the enhancement of the interfacial adhesion and bond formation among active functional groups of the crosslinking monomers residing on the surface of the latex particles. The extensive crosslinking network within the thermosetting film also leads to the higher hardness and T_g values of the films (Table 3.4).

Table 3.4 Effects of crosslinking agent on the properties of latexes and their films.

Polyacrylic latexes	T_g (°C)	MFFT (°C)	Pencil hardness	Viscosity (cP)
EA21/MAA14/E0.5	35.53	42.5	*B	9
EA21/MAA14/E0.5/CM2.76	42.15	26	2H	8
EA25/MAA10/E0.5	14.38	21	4B-3B	12
EA25/MAA10/E0.5/CM2.76	21.26	15	2B	11

*The films were prepared in an oven at 100 °C for 10 minutes; CM = crosslinking monomers *i.e* GMA= 0.21, NMA= 0.48 and EDGMA= 2.07; %NV = 35-36%, pH = 2.5-2.8

3.2.4 Variation of emulsifier concentration

The relationships between the latex particle size and the concentration of the surfactants used during emulsion polymerization were studied. In the presence of high concentration of the emulsifiers where there are plenty of emulsifier molecules available for stabilization of new emulsion droplets in the system, the monomer molecules tend to form new monomer droplets latex particles rather than going into the old monomer swollen particles. The increase of the emulsifier concentration tended to reduce latex particle size which in turn increased the latex viscosity (Table 3.5). With the same solid content, the smaller particle size translates into the greater particle density and thus the increased viscosity. The film hardness and MFFT values decreased with the increasing amount of emulsifier used also associate to the change in the latex particle size. The lower film hardness in relation to the smaller latex particle sizes has been observed and explained in section 3.2.2.

Table 3.5 The effect of emulsifier concentration on latexes properties.

Polyacrylic latexes	Latex particle size (nm)	Viscosity of latex (cP)	Pencil hardness	MFFT (°C)
*EA21/MAA14/E0.3/CM2.76	118	8.2	2H-3H	30
EA21/MAA14/E0.4/CM2.76	105	9.1	2H	28
EA21/MAA14/E0.5/CM2.76	94.1	10.5	2H	27
EA21/MAA14/E0.75/CM2.76	90.8	17.5	H	26
EA21/MAA14/E1.5CM2.76	88.1	250	H	24

%NV = 35-36%, pH of latexes = 2.5-2.8

3.2.5 Addition of ammonia

The pH value of poly(acrylic-acrylate) latex was varied by addition of aqueous ammonia solution. At higher pH, the carboxylic groups in the latex particles ionized to form carboxylate anion causing charge repulsion between the polymeric chains and thus the latex particles became swollen. The entanglement of loosen polymeric chains among the swollen particles tended to be greater than that among the tight and smooth particles leading to higher viscosity of the latex (Table 3.6). The MFFT was slightly lower and the film hardness was slightly higher at higher pH. The greater interaction

between neighboring particles is also responsible for the improved film quality as the dry film appeared smoother.

Table 3.6 Effects of ammonia solution on latex properties.

Polyacrylic latexes	pH	Viscosity (cP)	Film appearance	MFFT (°C)	Pencil hardness
EA21/MAA14/E0.5/CM	2.8	10.5	patchy	26	H
EA21/MAA14/E0.5/CM/Am5	3.3	24.7	patchy	26	H
EA21/MAA14/E0.5/CM/Am10	3.7	53.9	patchy	25	H
EA21/MAA14/E0.5/CM/Am15	4.8	1,247	smooth	25	H
EA21/MAA14/E0.5/CM/Am20	5.6	7,800	smooth	25	F-H
EA21/MAA14/E0.5/CM/Am25	6.4	80,200	smooth	24	F

%NV = 35-36%, Am = 2.5% ammonia solution

3.2.6 Addition of texanol (a coalescing agent)

Texanol (2,2,4-trimethyl-1,3-pentanediol monoisobutyrate) is one of the most popularly used hydrophobic coalescing agents for latex industry. The molecules of texanol can penetrate into the latex particles and dwelled inside their hydrophobic part. The latexes containing texanol thus appear homogeneously dispersed similar to the pure latexes. DLS spectroscopy (for spectra see Appendix D5-D10) showed that the size of the latex particles increased with increasing amount of texanol (Table 3.7) confirming the lodging of texanol inside the latex particles. The swollen particles are probably also responsible for higher viscosity of the latexes. The coalescing agent is generally used for improving the film formation of the latex by decreasing the MFFT value as it is also true for texanol. The latex films containing texanol also showed lower T_g and hardness.

Table 3.7 Effects of texanol on latex properties.

Polyacrylic latexes	Latex particle size (nm)	Properties of latex films			
		Tg (°C)	Pencil hardness	MFFT (°C)	Viscosity (cP)
EA21/MAA14/E0.5/ CM2.76	88.6	42.15	2H	26	8.2
EA21/MAA14/E0.5/ CM2.76/Tx5	94.1	23.00	H	19	18.5
EA21/MAA14/E0.5/ CM2.76/Tx10	95.5	2.10	F	14	125.6
EA21/MAA14/E0.5/ CM2.76/Tx15	96.9	-9.12	B	6	195
EA21/MAA14/E0.5/ CM2.76/Tx20	98.2	-29.90	2B	3	485
EA21/MAA14/E0.5/ CM2.76/Tx25	105.3	-42.60	3B	<0	1,350

Tx = texanol (coalescing agent), %NV of latex = 35-36%

3.3 Color transition temperature (CTT) of the latex films containing PPCDA vesicles (thermochromic film)

The main objective of this thesis is to obtain thermochromic films with tunable color transition temperature (CTT) from a single thermochromic agent. In this work, nano-sized vesicles of PPCDA were used as a thermochromic agent and varieties of EA-MMA copolymer latexes were used as matrixes. PPCDA generally changes its color from blue to red at a narrow temperature range of ~ 70 °C. To obtain films changing color at temperatures outside this range, the latexes should serve not only as a good film forming matrix, but also as an active agent which provide extra mechanisms for color change of PPCDA. The investigation for suitable latexes and conditions for mixing between PPCDA and the latexes as well as the proposed mechanism for color transition of the films are discussed as follows.

3.3.1 Latexes with variation of monomer ratio

Upon mixing PPCDA vesicles with the latexes of various hard/soft monomer ratios, the CTT of the resulting films cast on glass substrate evidently increased with the proportion of the hard monomer, MMA (Table 3.8). In section 3.2.1, the T_g and hardness of the latexes were found to increase with the proportion of the hard monomer. The change of CTT should thus be related to the change of T_g .

Table 3.8 Effects of monomer ratio in the latexes on the CTT

Latexes	Properties of thermochromic films			Property of latexes
	CTT (°C)	Pencil hardness	Film appearance	T_g observed by DSC (°C)
EA35/E0.5	5 \pm 2	<6B	blotchy	-29.99
EA30/MAA5/E0.5	25 \pm 2	5B	blotchy	-1.1
EA25/MAA10/E0.5	35 \pm 2	4B-3B	blotchy	14.38
EA21/MAA14/E0.5	55 \pm 2	B	cracking	35.21
EA18/MAA17/E0.5	57 \pm 2	F	cracking	49.67

PPCDA/Latexes = 0.3% (w/w of solid)

Since the CTT observed for all films were significantly higher than the T_g values of the latexes but lower than the CTT of PPCDA, the color change of PPCDA in the latex films was thus likely to be involved not only the thermochromism, but also the mechanochromism, the color transition caused by mechanical stress. At the temperatures higher than T_g , the latex films changed from glassy to rubbery state in which the polymeric chains became mobile. The movement of these mobile polymeric chains might cause mechanical stress to the nearby PPCDA vesicles in the blend.

Although the variation of hard/soft monomer ratio provides a very logical approach toward the CTT tenability of the thermochromic films, the films obtained in this experiment were not of good quality. Some of the tested latex cast on glass cracked during leaving for air drying to form film.

3.3.2 Latexes with variation of monomer concentration

As mentioned in section 3.2.2, the hardness of the films (and presumably their T_g) increased with the concentration of the monomers used in the latex preparation or %NV of the latexes. It would be interesting to see if the variation of the monomer concentration can affect the CTT of the thermochromic films. The CTT of the thermochromic films showed good correlation to %NV of the latexes (Table 3.9). The higher the nonvolatile content, due to higher monomer concentration, the higher CTT was observed. The variation of the monomer concentration in the latex preparation however, provided rather narrow range of tunability of the CTT (37-57 °C) and this approach was also severely limited by the film forming properties as some cracking films obtained, especially for the harder films prepared from high %NV latexes.

Table 3.9 Effects of monomer concentration in the latexes on the CTT

Composition	Property of latexes		Properties of thermochromic films	
	%NV	CTT (°C)	Film appearance	Pencil hardness
EA25/MAA10/E0.5	35	37 ± 2	blotchy	4B-3B
EA27/MAA11/E0.5	38.5	45 ± 2	blotchy	3B
EA29/MAA13/E0.5	42	48 ± 2	blotchy	2B
EA31/MAA14/E0.5	45.5	57 ± 2	cracking	B

PPCDA/Latexes = 0.2% (w/w of solid)

3.3.3 Latexes with cross linking monomers

From the previous sections, it is reasonable to contend that the CTT of the thermochromic films are highly dependent to the T_g of the latex films and the good film properties can be obtained from the latexes with low MFFT. Since the T_g and MFFT values are generally correlated, it seems improbable to obtain high CTT films with acceptable film quality from the conventional latexes.

The crosslinking monomers (CM) are known to be used in formulation of unconventional thermosetting latexes. In comparison with the conventional non-crosslinked latexes, the thermosetting latexes having lower MFFT value form films at lower temperature but the resulting films possess higher hardness and T_g values (refer

to section 3.2.3). Addition of crosslinking monomers might provide an approach to obtain films with higher T_g , required for the preparation of high CTT films, without scarifying the film forming properties.

The CTT of thermochromic films prepared from the conventional latexes and the thermosetting latexes were compared. The thermosetting latexes showed higher CTT than those of the conventional non-crosslinked latexes (Table 3.10). It is also interesting to note that the effect of hard/soft (MAA/EA) monomer ratio on the CTT was still observed in the thermosetting films. The EA21/MAA14/E0.5/CM2.76 gave films with higher CTT than that of EA25/MAA10/E0.5/CM2.76.

While smooth films are preferred, the blotchy films are acceptable for further development. Since the mixture of EA21/MAA14/E0.5/CM2.76 latex with PPCDA vesicles forms an acceptable film with CTT very close to the intrinsic CTT value (~ 70 °C) of PPCDA, it is a very good candidate for further design in the preparation of the thermochromic films with lower CTT.

Table 3.10 Effects of cross linking monomers in the latexes on the CTT

Thermochromic films	CTT (°C)	Pencil hardness	Film appearance
EA21/MAA14/E0.5	57 ± 2	B	cracking
EA21/MAA14/E0.5/CM2.76	70 ± 2	H	blotchy
EA25/MAA10/E0.5	37 ± 2	3B	blotchy
EA25/MAA10/E0.5/CM2.76	45 ± 2	B	blotchy

PPCDA/Latexes = 0.3% (w/w of solid)

The thermochromism of the film prepared from a mixture of PPCDA vesicles and EA21/MAA14/E0.5/CM2.76 latex was evaluated by visual observation and UV-vis spectroscopy. The CTT of the latex film was observed around 65-70 °C close to the CTT of PPCDA vesicle solution (Figure 3.5). The colorimetric response (%CR) determined from the visible spectra of the film at various temperature indicated that the temperature of 65-70 °C caused the color change on the film and vesicle solution at about the same level corresponding to the %CR of 70-75% (Figure 3.6).

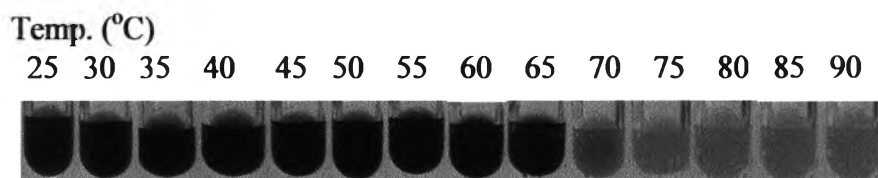


Figure 3.5 The relationship between %CR and temperature of EA21/MAA14/E0.5/CM2.76 latex films containing PPCDA vesicles.

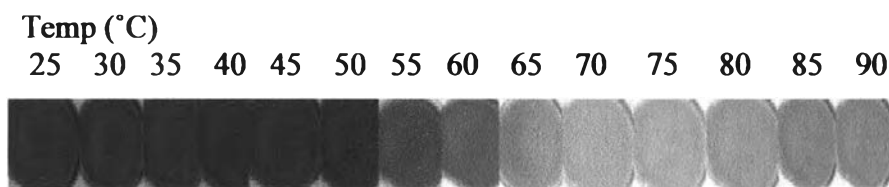


Figure 3.6 Thermochromism of the EA21/MAA14/E0.5/CM2.76 latex film containing PPCDA vesicles 1:0.3 % w/w by solid

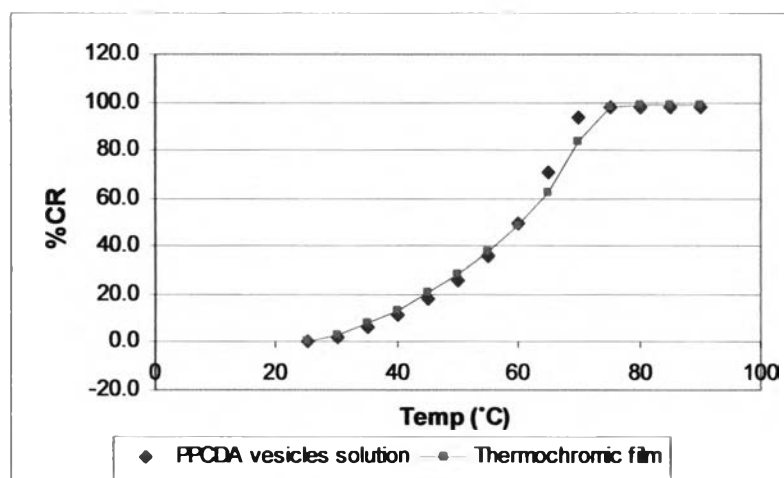


Figure 3.7 The 1.6 mM of PPCDA vesicles solution versus thermochromic film of PPCDA/Latexes 0.3% (w/w of solid).

3.3.4 Variation of emulsifier concentration.

It is known that the size of the latex particles prepared from emulsion polymerization reduces while the latex viscosity increases with the increasing amount of the emulsifier used [53]. The smaller latex particles along with the increased viscosity should improve the film quality of the latexes. The latexes were thus

prepared with different amount of the emulsifier (E). The increase of emulsifier concentration used in the latex preparation indeed reduced the size of the latex particles and increased the viscosity of the latex as already discussed in section 3.2.4 and provided better film forming properties of the latexes as expected when the emulsifier concentration was increased to 1.5% w/w (Table 3.11). The CTT of thermochromic films was also slightly affected by the emulsifier concentration and the CTT clearly decreased when the dosage of the emulsifier was higher than 0.5% (w/w). For further development the dosage of the emulsifier was fixed at 0.5% (w/w) because it is the highest level of the emulsifier that can be used without lowering the CTT.

Table 3.11 Effects of the emulsifier concentration used in the latexes on the CTT

Thermochromic films	Properties of latex	Properties of thermochromic films	
	Viscosity (cP)	Film appearance	CTT (°C)
EA21/MAA14/E0.3/CM2.76	8.2	blotchy	72 ₊₂
EA21/MAA14/E0.4/CM2.76	9.1	blotchy	72 ₊₂
EA21/MAA14/E0.5/CM2.76	10.5	blotchy	72 ₊₂
EA21/MAA14/E0.75/CM2.76	17.5	blotchy	67 ₊₂
EA21/MAA14/E1.5/CM2.76	250	Almost smooth	60 ₊₂

PPCDA/Latexes = 0.3% (w/w of solid)

3.3.5 Variation of pH of the latexes

As mentioned in section 3.2.5, another way to increase the viscosity of the latexes is to increase pH by addition ammonia solution. The high viscosity latexes (1,247 cps or higher) gave smooth film on glass substrate. The addition of ammonia to the latexes reduced the CTT value of the thermochromic films only slightly. This strategy can thus be used for preparation of thermochromic films with high CTT (~ 70 °C).

Table 3.12 Effects of addition of ammonia in the latexes on the color transition temperature

Thermochromic films	Properties of latexes		Properties of thermochromic films	
	Viscosity (cP)	pH	Film appearance	CTT (°C)
EA21/MAA14/E0.5/CM2.76	10.5	2.8	blotchy	70+2
EA21/MAA14/E0.5/CM2.76/Am5	24.7	3.3	blotchy	70+2
EA21/MAA14/E0.5/CM2.76/Am10	53.9	3.7	blotchy	70+2
EA21/MAA14/E0.5/CM2.76/Am15	1,247	4.8	smooth	69+2
EA21/MAA14/E0.5/CM2.76/Am20	7,800	5.6	smooth	69+2
EA21/MAA14/E0.5/CM2.76/Am25	80,200	6.4	smooth	69+2

PPCDA/Latexes = 0.3% (w/w of solid)

3.3.6 Addition of texanol

Texanol (3-hydroxy-2,2,4-trimethylpentyl isobutyrate) is well hydrophobic coalescing agent used in latexes. As a coalescing agent, texanol improves the film forming properties while reduces T_g and hardness of the latex films. It would thus be of interest to test if texanol may be used conveniently for tuning down the CTT of the thermochromic films. Upon the addition of texanol, the CTT of the films decreased with amount of texanol added (Table 3.13). The CTT could be tuned from over 70 °C down to below 10 °C by addition of texanol at 25% (w/w). Furthermore, with the addition of texanol over 20% (w/w), smooth films were obtained. These results are very promising as the thermochromic films with a wide range of CTT could prepared from a single formula of the latex and a single type of polydiacetylene.

Table 3.13 Effects of texanol on CTT of the thermochromic films

Thermochromic films	Visually observed CTT (°C)	Dry film appearance on glass substrate	Pencil hardness
EA21/MAA14/E0.5/CM2.76	72 ₊₂	blotchy	2H
EA21/MMA14/E0.5/CM2.76/Tx5	62 ₊₂	blotchy	H
EA21/MMA14/E0.5/CM2.76/Tx10	42 ₊₂	blotchy	F
EA21/MMA14/E0.5/CM2.76/Tx15	27 ₊₂	blotchy	B
EA21/MMA14/E0.5/CM2.76/Tx20	12 ₊₂	almost smooth	2B
EA21/MMA14/E0.5/CM2.76/Tx25	7 ₊₂	smooth	3B

PPCDA:Latexes = 0.3% (w/w of solid)

Texanol is an organic liquid which can cause color change of PPCDA vesicles by solvatochromism in the presence of surfactant. Texanol mixed with the latex however, did not cause the color transition of the vesicles. The result confirmed that texanol is trapped within the hydrophobic part inside the latex particles. It is however expected that texanol maybe released out to come into contact with PCDA vesicles to cause solvatochromism at the temperature higher than T_g of the latex films. To prove this hypothesis, it was necessary to show that the lowering of CTT upon addition of texanol was not due solely to mechanochromism as already proposed in section 3.3.1. In section 3.3.1, lowering of T_g by decreasing hard/soft monomer ratio in the latex preparation can induce mechanochromism to participate in the color transition of the thermochromic films. The CTT of thermochromic films with and without texanol having T_g close to each other were compared. The CTT of thermochromic films consisting of texanol showed significantly lower CTT comparing to the thermochromic films formulated from the latexes without texanol despite having similar T_g (Table 3.14). The solvatochromism should thus play a part in further lowering the CTT.

Table 3.14 Comparison of the CTT of the thermochromic films having similar T_g formulated from the latexes with and without texanol

Thermochromic films	T_g of latexes ($^{\circ}\text{C}$)	CTT ($^{\circ}\text{C}$)
EA31/MMA4/E0.5/CM2.76	- 1.1	48 \pm 2
EA21/MAA14/E0.5/CM2.76/Tx5	2.1	40 \pm 2
EA35/E0.5/CM2.76	- 8.59	38 \pm 2
EA21/MAA14/E0.5/CM2.76/Tx10	- 9.12	25 \pm 2

PPCDA:Latexes = 0.3% (w/w of solid)

3.3.7 Variation of PPCDA concentration.

The effect of PPCDA content to the CTT of the thermochromic film was studied. The CTT increased slightly with the amount of PPCDA used in the latex mixture (Table 3.8). However, the variation of PPCDA concentration is probably not practical for making thermochromic films with variation of CTT since the variation of CTT was rather narrow (65-75 $^{\circ}\text{C}$) and the resulting films possessed different color intensities.

Table 3.15 Effects of PPCDA vesicles content in the latex mixture on the color transition temperature.

PPCDA vesicle/Latex (% w/w of solid)	CTT ($^{\circ}\text{C}$)
0.1	65 \pm 2
0.2	70 \pm 2
0.3	73 \pm 2
0.4	75 \pm 2

Latex = EA21/MAA14/E0.5/CM2.76

3.4. Stability of the thermochromic films

The storage stability of thermochromic films on various substrates were studied by recording the storage period required for the color of the films changing from blue to violet. Two types of latexes with different T_g , EA21/MAA14/E0.5/CM2.76 ($T_g = 42.15$ $^{\circ}\text{C}$) and EA25/MAA10/E0.5/CM2.76 ($T_g = 21.26$ $^{\circ}\text{C}$) were used as representatives in this study. While there was no significant

difference in the stability between two types of latexes, the stability of the film color was greatly influenced by the substrates used for the latex to be cast on (Table 3.16). The glass substrate provided the longest storage stability at room temperature ($\sim 30^{\circ}\text{C}$) of over six month without observable color change of the films. The hard type polyethylene plastic substrate maintained the blue color for about three months but the color of the films on soft type PE plastic substrate changed from blue to violet after two days of storage. The interaction of the PPCDA vesicles with the hydrophobic plasticizers in the plastics is probably responsible for the low stability on the plastic substrates.

Table 3.16 Storage stability of thermochromic films on various substrates

Latex	Stability period on various substrates		
	Glass	Hard PE plastic	Soft PE plastic
EA21/MAA14/E0.5/ CM2.76	no color change within 6 months	Color changed from blue to violet after 3 months and maintained in violet color for 4 months	Color changed from blue to violet after 2 days and maintained in violet color for 4 months
EA25/MAA10/E0.5/ CM2.76			

PPCDA:Latexes = 0.2% (w/w of solid)

3.5 Supporting evidences for the proposed mechanisms of color transition in the thermochromic films

Some experimental data in section 3.3.1 and 3.3.6 already suggested that two extra mechanisms, thermally induced mechanochromism and solvatochromism, take parts in reducing the CTT of the thermochromic films. Simple drawing models of both mechanisms are illustrated in Figure 3.8. At the temperature significantly higher than the T_g values of the latex films, the polymeric chains packed within the latex particles become mobile and the movement of these polymeric chains can assert the mechanical stress on the attached vesicles resulting in the mechanochromism. In the presence of texanol, the thermally induced solvatochromism should also comes into operation as texanol stored inside the latex particles can be released when the temperature is raised beyond the T_g of the latex films.

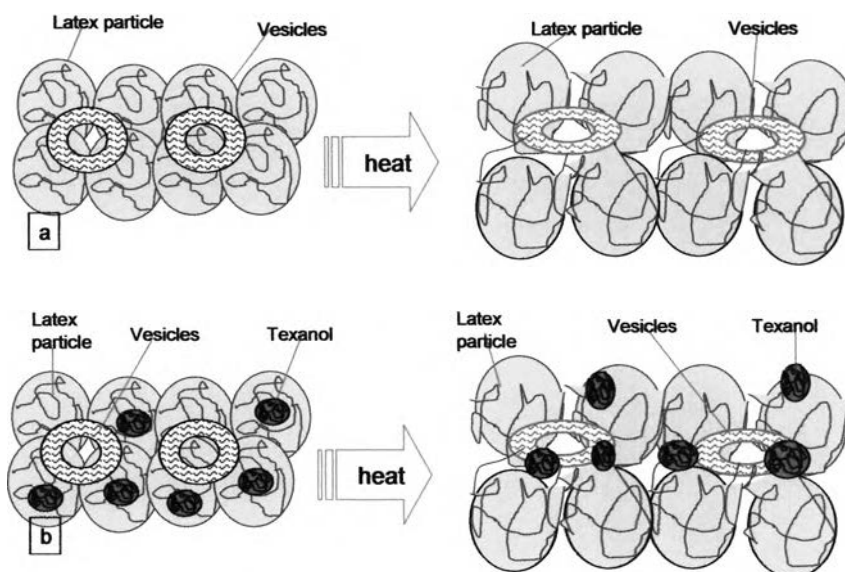


Figure 3.8 Models for thermally induced a) mechanochromism and b) solvatochromism.

According to the two proposed mechanisms, it would be interesting to see how two types of nano-particles, the latex particles and the polydiacetylene (PPCDA) vesicles arrange in the thermochromic films. The submicron-scaled morphology of the films was analyzed by scanning electron microscopy (SEM). The SEM micrograph of the dry latex over a glass slide showed well dispersed latex particles (Figure 3.9a) while aggregation and fusion of the particles were clearly observed in the dry sample of the mixture of the latex and the vesicles (Figure 3.9b). Unfortunately, it was not possible to clearly see PPCDA vesicles by SEM technique.

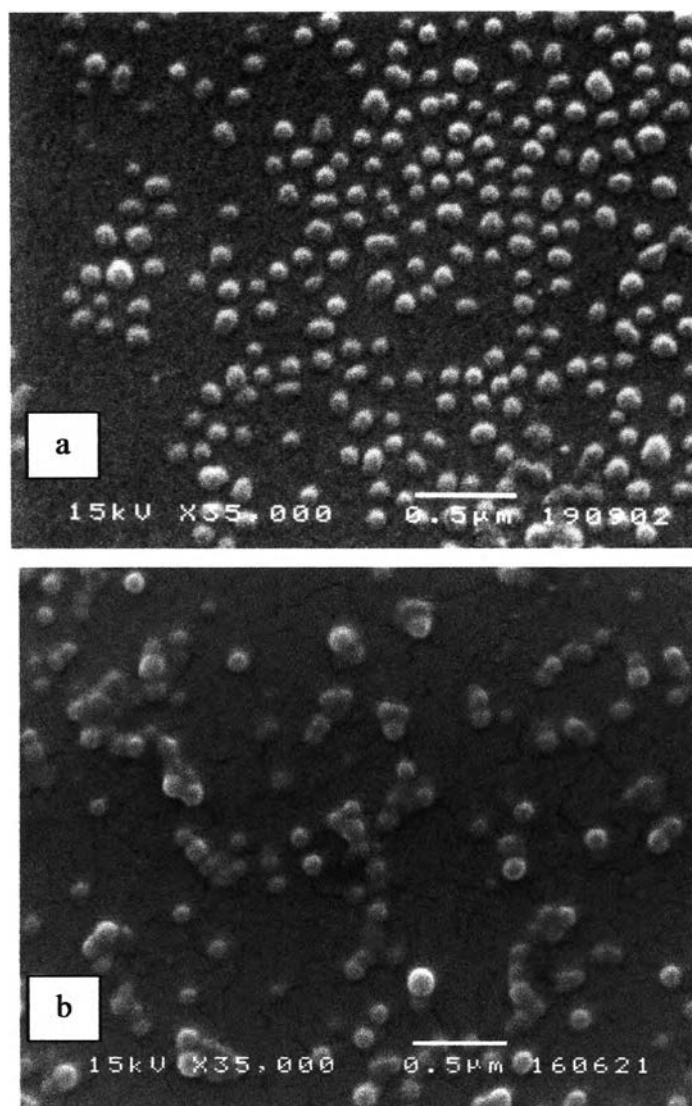


Figure 3.9 SEM micrographs of dry samples of (a) EA21/MAA14/E0.5/CM2.76 latex and (b) PPCDA vesicles mixed with EA21/MAA14/E0.5/CM2.76 latex at 1% w/w of solid.

TEM was used in the subsequent analysis as it is known to usually give satisfactory images of relatively soft nanoparticles such as lipid vesicles. The TEM micrographs of the vesicles, latex and the mixture were compared (Figure 3.10). The images reveal that upon mixing the vesicle with the latex, each vesicle is bounded by a few latex particles. Most of PPCDA vesicles are not broken under mixing and drying condition. The thermochromic films remained blue upon drying, which is the utmost important criterion for the sensing applications.

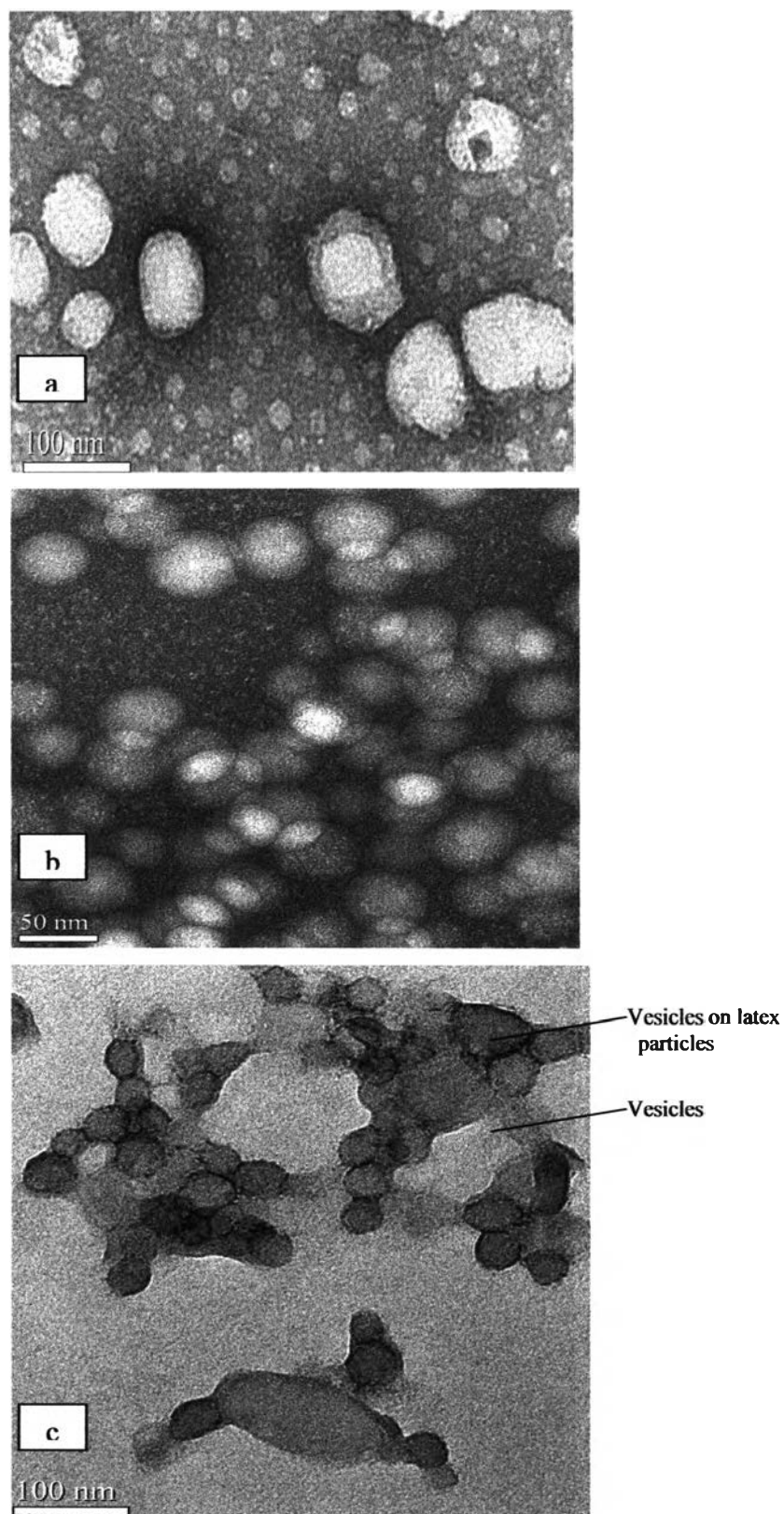


Figure 3.10 TEM images of dry samples of (a) PPCDA vesicles, (b) EA21/MAA14/E0.5/CM2.76 latex and (c) PPCDA vesicles mixed with EA21/MAA14/E0.5/CM2.76 latex at 4.5% (w/w of solid).

Differential scanning calorimetry (DSC) was also used to study the nature of blending between the latex and PPCDA vesicles in the thermosensing film. The DSC thermogram of the film prepared from the mixture of PPCDA vesicles and EA21/MAA14/E0.5/CM2.76 latex showed a single T_g onset at 49 °C (Figure 3.10) suggesting the miscibility of the blend supporting the interparticle interaction between the vesicles and the latex particles observed by TEM. It is also important to mention here that the T_g value of the latex film increased from 42 to 70 °C upon the addition of PPCDA vesicles at 4.5% w/w of solid. To verify the result, another DSC thermogram of a film, prepared from a mixture of two types of latexes with different particle sizes and T_g , was acquired for comparison (Figure 3.11). The thermogram clearly displays two T_g onset at 32°C and 61°C corresponding to the T_g of each latex component that indicated no interparticle interaction in such system. Segregation of the latex particles of different sizes was also clearly observed in the SEM micrograph (Figure 3.12).

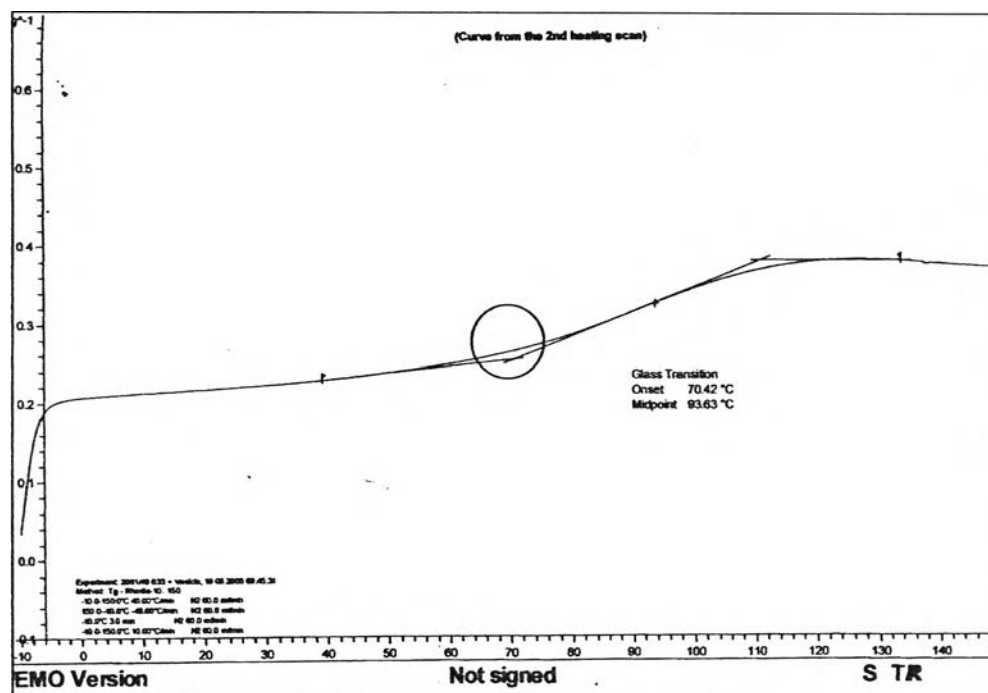


Figure 3.11 DSC thermogram of EA21/MAA14/E0.5/CM2.76 mixed with PPCDA vesicles at 4.5% w/w of solid.

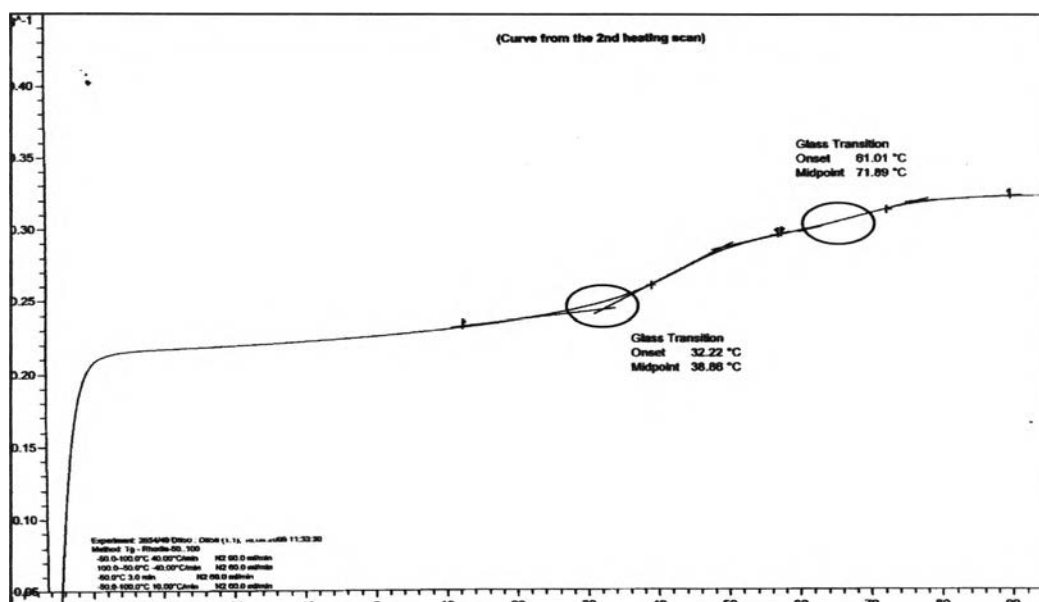


Figure 3.12 DSC thermogram of MMA31/BA4/E0.8/CM2.76 mixed with EA21/MAA14/E0.5/CM2.76 at 100% w/w of solid.

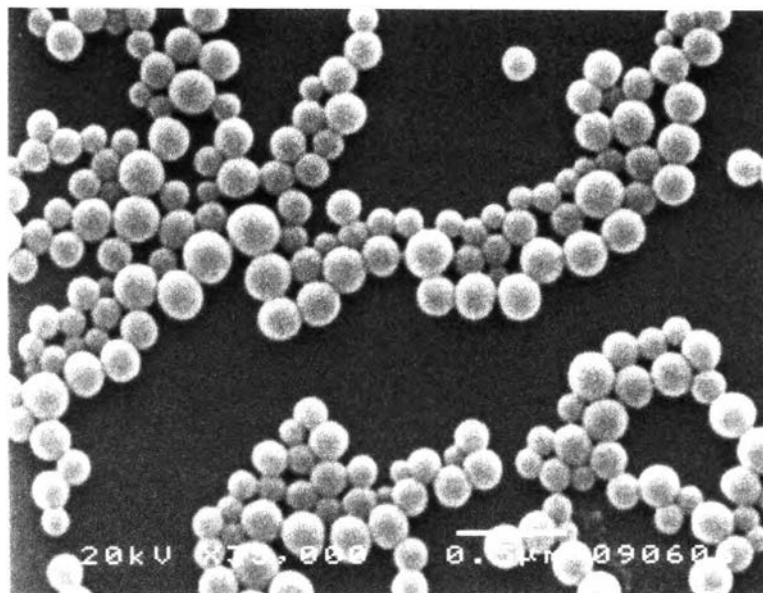


Figure 3.13 SEM images MMA31/BA4/E0.8/CM2.76 mixed with EA21/MAA14/E0.5/CM2.76 at 100% w/w of solid.