



## CHAPTER II

### EXPERIMENTAL

#### 2.1 Chemicals

1. Ethyl acrylate monomer, commercial grade : Arkema (France)
2. Methacrylic acid monomer, commercial grade : Mitsubishi Rayon (Japan)
3. n-Methylol acrylamide (48%), commercial grade : Hapdong (Korea)
4. Glycidyl methacrylate, commercial grade : Mitsubishi Gas  
Chemical  
Company, Inc. (Japan)
5. Ethyleneglycol dimethacrylate, commercial grade : Rohm GmbH &  
KG, Chemische Fabrik  
(German)
6. Ammonium persulfate, commercial grade : Shanghai Ai Jian (China)
7. Alkyl phenol ethoxylates sulphate : Rhodia Thai Ltd. (Thailand)
8. 2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate : Eastman Chemical  
Singapore Pte, Ltd  
(Singapore)
9. Ammonia solution 26% : Asian Chemical (Thailand)
10. Formaldehyde solution : TOA Dovechem  
Industries Co., Ltd.  
(Thailand)
11. 10,12 Pentacosadiynoic acid : Lancaster Co., (USA)

#### 2.2 Equipments

1. 5-Necked round bottom reactor, 3 L capacity with Condenser
2. Brookfield viscometer : Brookfield Engineering,  
Model LVT (England)
3. pH meter : Mettler, Model Delta 340  
(Switzerland)

|  |  |
|--|--|
| 4. Oven                                  | : Binder, Model FD115/E2<br>(Germany)                  |
| 5. Bird Type Applicator (casting bar)    | : Sheen (England)                                      |
| 6. UV vis spectroscopy                   | : Model Cary 100 Bio                                   |
| 7. Scanning Electron Microscopy          | : JEOL, Model JSM-6400                                 |
| 8. Transmission electron microscopes     | : JEOL, Model TEM-2010<br>(Japan)                      |
| 9. Particle size                         | : Malvern 4700   |
| 10. Ultra sonicator                      | : Elma (Germany)                                       |
| 11. Minimum Film Forming Temperature Bar | : Rhopoint Instrumentation<br>Ltd. (England)           |
| 12. Water bath                           | : Heto CBN 18-30 (Thailand)                            |
| 13. Differential scanning calorimeter    | : Mettler Toledo DSC 822 <sup>c</sup><br>(Switzerland) |
| 14. Stirrer                              | : Sheen (England)                                      |
| 15. Balance 4 digit                      | : Satorious (England)                                  |

## 2.3 Procedures

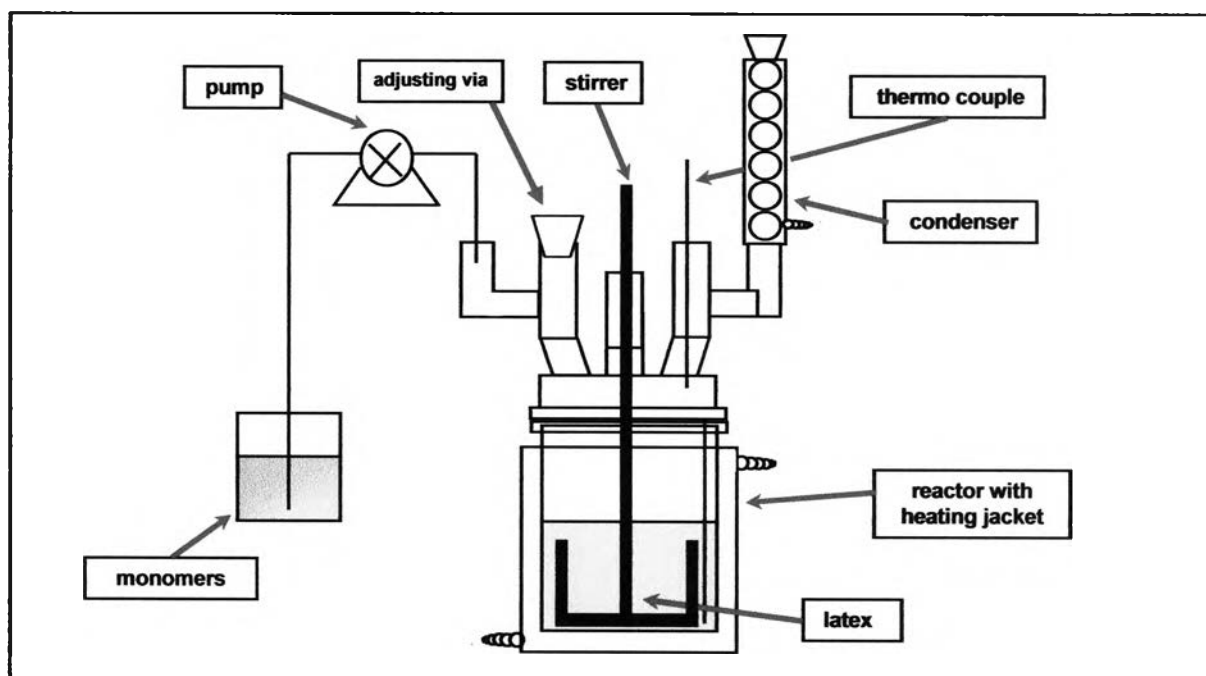
### 2.3.1 Preparation of PPCDA vesicle solution

10,12-pentacosadiynoic acid (PCDA, 17.9 mg) as a white solid was dissolved in chloroform (2 mL) in a test tube and the solvent was removed by rotating evaporator. A volume of milli-Q water was added to provide the lipid concentration of 1 mM. The suspensions were heated to 75-85 °C, followed by sonication in an ultrasonicating bath for 20 min when a semitransparent or transparent vesicle solution was obtained. The solution was kept at 4 °C overnight. The vesicles solution was irradiated with UV light (254 nm) for 5 min and filtered through filter paper no.1 to give clear intense blue-colored poly(PCDA) vesicles solution. The solution showed maximum visible absorption ( $\lambda_{\text{max}}$ ) at 630 nm.

### 2.3.2 Preparation of acrylate-methacrylic latexes

The acrylate-methacrylic latex was prepared by emulsion polymerization. Three different dosages of reagents: A) a monomer mixture, B) an aqueous solution of ammonium persulfate

initiator and C) an aqueous solution of Rhodapex CO-436 emulsifier, were utilized. Dosage C was prepared in a 3 L four-necked glass reactor. Dosage C was stirred by a mechanical stirrer at 40 rpm and then heated to 80 °C. Dosage B was added into the reactor when the reactor temperature had leveled off at 80-83 °C. After the addition of dosage B for 5 minutes, Dosage A was slowly fed into the reactor over 2 hours while keeping the reaction temperature in the range of 80-84 °C. The reaction mixture was kept under stirring within the temperature range of 80-86 °C for 3 hours. The latex was cooled down to room temperature and filtered through a 200 mesh filter.



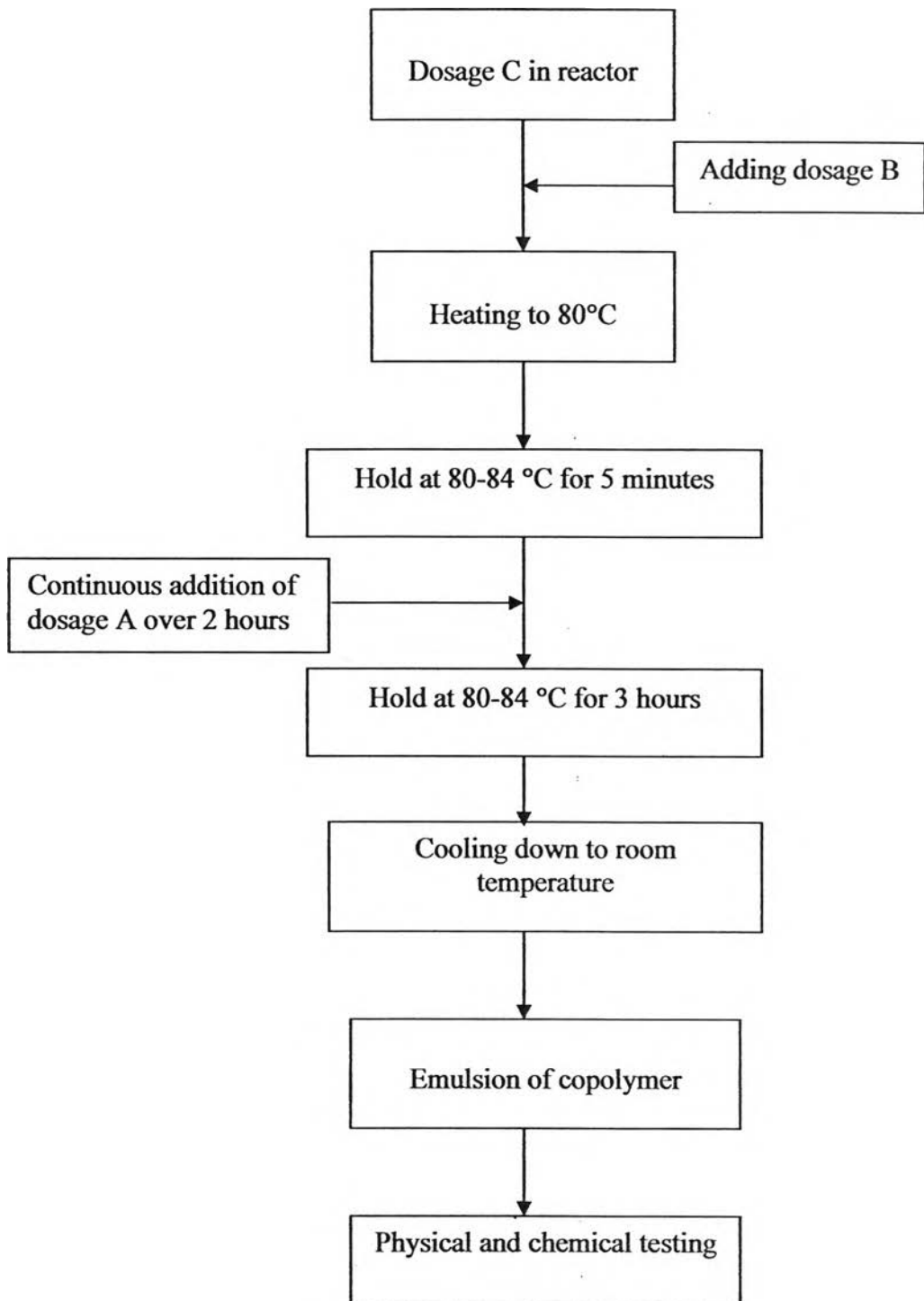
**Figure 2.1** Apparatus set up for the preparation of acrylate-methacrylic latexes from emulsion copolymerization.

**Table 2.1** Formulation of acrylate-methacrylic latexes.

| Polyacrylic latexes         | Dosage A        |     |      | Dosage B        | Dosage C        |          |
|-----------------------------|-----------------|-----|------|-----------------|-----------------|----------|
|                             | (%w/w of solid) |     |      | (%w/w of solid) | (%w/w of solid) |          |
|                             | EA              | MAA | CM   | APS             | CO-436          | DI-water |
| EA21/MAA14/E0.5             | 21              | 14  | 0    | 0.2             | 0.5             | 64.3     |
| EA23/MAA14/E0.5             | 23              | 14  | 0    | 0.2             | 0.5             | 62.3     |
| EA25/MAA17/E0.5             | 25              | 17  | 0    | 0.2             | 0.5             | 57.3     |
| EA27/MAA18/E0.5             | 27              | 18  | 0    | 0.2             | 0.5             | 54.3     |
| EA29/MAA20/E0.5             | 29              | 20  | 0    | 0.2             | 0.5             | 50.3     |
| EA35/E0.5                   | 35              | 0   | 0    | 0.2             | 0.5             | 64.3     |
| EA30/MAA5/E0.5              | 30              | 5   | 0    | 0.2             | 0.5             | 64.3     |
| EA25/MAA10/E0.5             | 25              | 10  | 0    | 0.2             | 0.5             | 64.3     |
| EA21/MAA14/E0.5             | 21              | 14  | 0    | 0.2             | 0.5             | 64.3     |
| EA15/MAA20/E0.5             | 15              | 20  | 0    | 0.2             | 0.5             | 64.3     |
| EA13/MAA22/E0.5             | 13              | 22  | 0    | 0.2             | 0.5             | 64.3     |
| EA5/MAA30/E0.5              | 5               | 30  | 0    | 0.2             | 0.5             | 64.3     |
| EA21/MAA14/E0.3/C<br>M2.76  | 21              | 14  | 2.76 | 0.2             | 0.3             | 61.74    |
| EA21/MAA14/E0.4/<br>CM2.76  | 21              | 14  | 2.76 | 0.2             | 0.4             | 61.64    |
| EA21/MAA14/E0.5/<br>CM2.76  | 21              | 14  | 2.76 | 0.2             | 0.5             | 61.54    |
| EA21/MAA14/E0.75/<br>CM2.76 | 21              | 14  | 2.76 | 0.2             | 0.75            | 61.29    |
| EA21/MAA14/E1.5/<br>CM2.76  | 21              | 14  | 2.76 | 0.2             | 1.5             | 60.54    |

EA = ethyl acrylate; MAA = methacrylic acid; CM = Cross linking monomers;

APS = ammonium persulfate; CO-436 = rhodapex CO-436



**Figure 2.2** Schematic process of the emulsion polymerization

### **2.3.3 Characterization of the latex**

#### **2.3.3.1 Determination of nonvolatile content (52,53)**

The nonvolatile content was the percentage by mass of nonvolatile matter in the latex determined by evaporating the latex sample in an open atmosphere oven to dryness. The percent weight residue to the latex was calculated. The measurement of each sample was repeated for 4 times.

#### **2.3.3.2 Viscosity measurement (54)**

The viscosity of the latex was measured by Brookfield viscometer LVT. A latex sample (600 g) was filled in a 600 mL low-shaped beaker thermo stated at 25°C. A spindle (number 1) was placed into the latex holding diagonally and slightly twisted, to avoid bubble formation below the stirring disk. The measurement took place at 60 rpm. The viscosity in cP ( $\eta$ ) was calculated from the reading value (S) taken from the viscometer display according to the following equation;  $\eta = 2S$ .

#### **2.3.3.3. pH measurement (55)**

The pH of the latex was measured by pH meter (Mettler Toledo MP 220, Switzerland). A latex sample (200 g) was filled in a 250 mL beaker at room temperature. The pH meter electrode was placed into the latex. The pH meter was allowed to run until the pointer was stabilized, then the pH value was read. Measurement was carried out in duplicate; the reading should be agreed within 0.1 pH unit.

#### **2.3.3.4. Determination of minimum film forming temperature of the latex and thermochromic film (MFFT) [56]**

The suitable temperature program of MFFT instrument was selected (the MFFT of latex must stay in the temperature range of this temperature program). A latex sample was applied by using 75  $\mu\text{m}$  cube applicator from the warm end to the cold end. All latex samples should be applied within 10 minutes, and then closed with the cover. After 1 hour, the temperature where the film had coalesced over 90% of the track width was recorded as the MFFT of the latex. The measurement of the MFFT of each latex was repeated for three times.

### 2.3.3.5. Determination of particle size

The particles sizes within the latex and PPCDA vesicles solution were determined from Malvern instrument series 4700 under the following conditions: air cooled argon ion laser,  $\lambda = 488$  nm; dispersing medium = deionized water filtered by 0.21 micron membrane filter; scattering angle =  $90^\circ$ ; temperature =  $30^\circ\text{C}$ ; viscosity of dispersing medium = 0.798 cP; refractive index of dispersing medium = 1.330. The cell was filled with about 15 mL of deionized water, then a solution of diluted latex was dropped into the cell. The filled-cell was immersed in the water chamber with thermostat at  $25^\circ\text{C}$  for at least 5 minutes before starting the measurement. After 5 minutes, latex particle size was measured by the instrument. The counting number of the particles per second was around 100 – 200 counts. The measurement was repeated three times for each sample.

### 2.3.3.6. UV-vis spectroscopy

The thermochromic responses were evaluated by two mean; 1) eye observation and 2) UV-vis spectrometer. The dry films were kept at the temperature below the transition temperature in a temperature controlled chamber. The temperature was increased stepwise, typically  $5^\circ\text{C}$  for each step, and allowed to stand at each temperature for 5 min prior to each observation was made. UV-vis spectra of the thermochromic films were taken on a variable temperature UV-visible spectrometer (Cary 100 Bio). The absorption spectra were acquired after 5 min of each designated temperature had reached.

A quantitative value for the extent of blue to red color transition is given in terms of colorimetric response (%CR) defined as  $\%CR = [(PB_0 - PB_T) / PB_0] \times 100\%$  where  $PB = A_{\text{blue}} / (A_{\text{blue}} + A_{\text{red}})$ .  $A_{\text{blue}}$  is the electronic absorbance of the blue component ( $\sim 640$  nm) and  $A_{\text{red}}$  is the electronic absorbance of the red component ( $\sim 540$  nm).  $PB_0$  is the initial percent blue and  $PB_T$  is the percent blue at each tested temperature.

### 2.3.3.7. Scanning Electron Microscopy (SEM) of latex particle size

The scanning Electron Microscopy (SEM) was used to confirm the latex particle size. Latex samples for SEM were dropped on a SEM stub and tested specimens were coated with gold. The measurement was operated at 15 KV.

### **2.3.3.8. Transmission Electron Microscopy (TEM)**

TEM images were obtained using a JEOL TEM-2010 electron microscope (Japan) equipped with a CCD camera. The mixed polyacrylic latex and polydiacetylene vesicle were deposited onto carbon-coated copper grid and negatively stained with 2% uranyl acetate solution.

### **2.3.3.9. Determination of Glass transition temperature**

The glass transition temperature was measured by a differential scanning calorimeter (DSC; Mettler Toledo DSC 822 (Switzerland)). A sample of latex film of 12-13 mg was packed in aluminium crucible and was first cooled by using liquid nitrogen at -15 °C then heated to 100 °C at the rate of 40 °C/min. The temperature was cooled to -50 °C and heat again to 100 °C with scanning rate of 10 °C/min under nitrogen atmosphere. The onset temperature was recorded.

### **2.3.3.10. Measurement of film hardness**

The film hardness was tested by pencils with various hardness numbers. The scale of hardness was arranged in order as below;

6B-5B-4B-3B-2B-B-HB-F-H-2H-3H-4H-5H-6H

Softer

Harder

The pencil (Mitsubishi, Japan) was held against the film at a 40° angle and pushed away from the operator in a 6.5 mm. The hardness was recorded as pass when, no scratch of pencil on the film was observed. The number of pencil continued down if the scratch showed on the film.

### **2.3.3.11. Film appearance [56]**

A latex sample was spreaded with a 100 µm thickness casting bar (Sheen, England) over a glass slide (10 cm × 15 cm) and allowed to dry at room temperature until it formed a thin film (~ 50 µm thickness) was formed. The film was evaluated for transparency by visual observation.