CHAPTER 3

EXPERIMENTAL

3.1 Materials, apparatus, and analytical instruments

3.1.1 Materials

3.1.1.1 Monomers and crosslinking monomer

2-Ethylhexyl acrylate (2-EHA)
$CH_2=CHCOOCH_2(C_2H_5)CH(CH_2)_3CH_3$ = 184.28

Methyl methacrylate (MMA)
$CH_2=C(CH_3)COOCH_3$ = 100.12

2-Ethylhexyl methacrylate (2-EHMA)
$CH_2=C(CH_3)COOCH_2(C_2H_5)CH(CH_2)_3CH_3$ = 198.31

Cyclohexylacrylate
$CH_2=CHCOOC_6H_{11}$ = 154.21

Lauryl acrylate
$CH_2=CHCOO(CH_2)_{11}CH_3$ = 240.39

Lauryl methacrylate
$CH_2=C(CH_3)COO(CH_2)_{11}CH_3$ = 254.42

Ethyleneglycol dimethacrylate (EGDMA)
$[CH_2OOC(CH_3)C=CH_2]_2$ = 198.22

All of these monomers and crosslinkers were of commercial grade (Kishida chemical Co., Ltd).

3.1.1.2 Solvents

Heptane
$CH_3(CH_2)_5CH_3$ = 100.20

Toluene
$C_6H_5CH_3$ = 92.14

All of these solvents were reagent grade and from Kishida chemical CO., Ltd.

3.1.1.3 Initiator

2,2-Azobis-2,4-dimethylvaleronitrile (ADVN); V-65
$(CN)N=NC(CN)(CH_3)CH_2CH(CH_3)CH_3$ = 164.12,
Reagent grade
Wako Pure Chemical CO., Ltd.

3.1.1.4 Inhibitor

Sodium nitrite ($NaNO_2$)
Reagent grade
Kishida Chemical Co., Ltd.

3.1.1.5 Stabilizer and emulsifier

Poly(vinyl alcohol) or PVA-217
Degree of polymerization (DP) = 1700
88.5% saponification
Kuraray Chemical Co.,.Ltd.

Sodium sulfate (SLS)
$C_{12}H_{25}NaO_4S$ = 288.38, Biochemical grade
Merck Co., Ltd.

3.1.1.6 Other chemicals

Palmitic acid methyl ester
$CH_3(CH_2)_{14}COOCH_3$ = 270.46
Tokyo Chemical Industry

Methanol
CH_3OH = 32.04
Kishida Chemical CO., Ltd.

3.1.2 Apparatus

3.1.2.1 SPG emulsification apparatus

Microporous glass membrane (SPG membrane), an annulus cylinder with a diameter 10 mm, length 20 mm, thickness 1 mm of SPG pore sizes 0.9, 5.25 and 9.0 μm
Oil tank, 20 cm^3
Emulsion storage tank, 300 cm^2
SPG stainless steel module

3.1.2.2 Polymerization setup

Three-necked glass separator flask, 500 cm^3	1 unit
Dimroth spiral condenser	1 unit
Nitrogen inlet-nozzle	1 unit
Nitrogen outlet tube	1 unit
agitator	1 unit
water bath	1 unit
thermometer	1 unit
nitrogen cylinder	1 unit

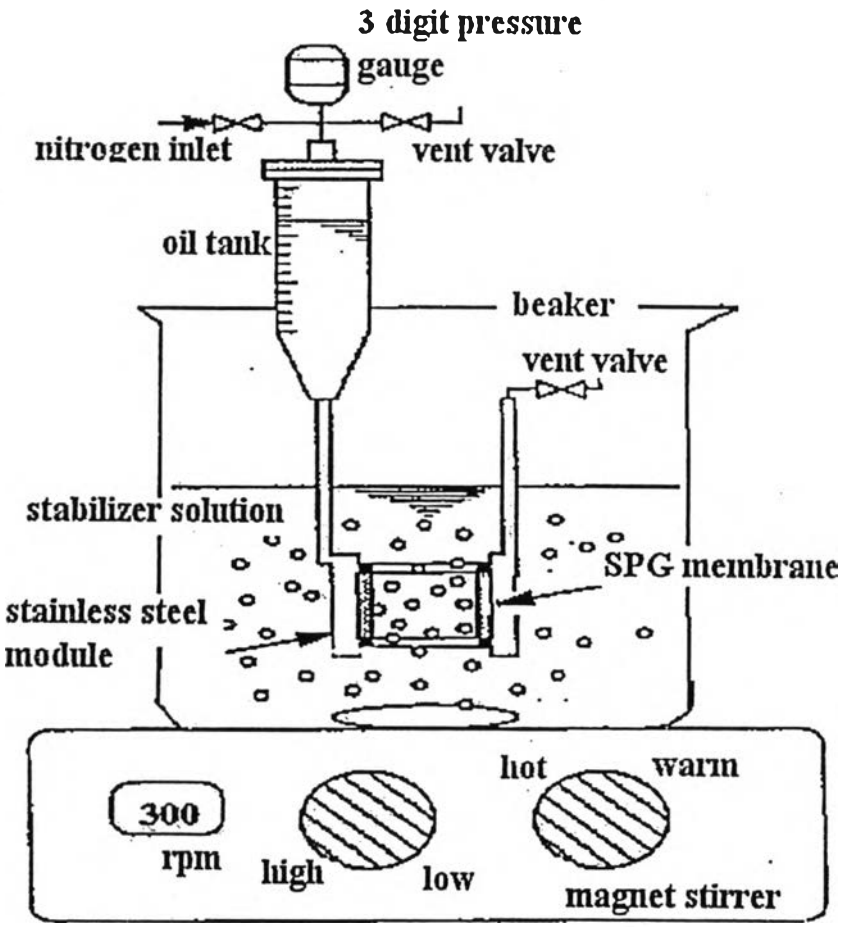
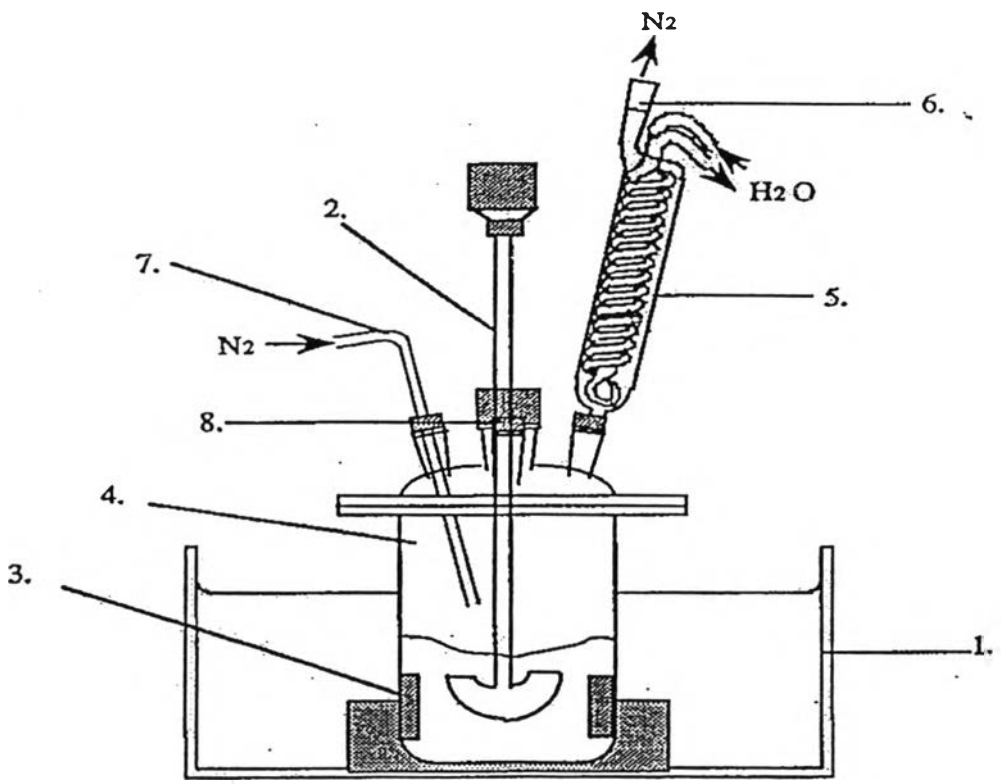


Figure 3.1 The SPG emulsification kit



1. Oil bath.
2. Agitator.
3. Baffle.
4. Reactor
5. Condenser.
6. Nitrogen outlet.
7. Nitrogen inlet
8. Rubber stopper for sampling.

Figure 3.2 Suspension polymerization reactor

3.1.3 Analytical instruments

Optical microscope (OM)
Olympus DP-10

Scanning electron microscopy (SEM)
JEOL JSM-5310

Fourier-transform infrared spectroscopy (FT-IR)
Nicolet

Differential scanning calorimeter (DSC)
MAC SCIENCE 3100

Porosimeter (PROSORP VAS-3000)

3.2 Procedures

3.2.1 Purification of the monomers

All monomers of commercial grade were purified prior to use. A portion of 2-EHA, 2-EHMA or EGDMA was poured into a separating funnel containing 3% sodium carbonate solution. It was washed three times with the sodium carbonate solution, each time the aqueous phase was drained off. Then, the monomer was washed with distilled and deionized water five times. It was then dried with 4 A^{o} molecular sieve overnight. These monomers were distilled under vacuum and kept in a refrigerator prior to use.

3.2.2 Preparation of emulsion droplets

The SPG emulsification kit is shown in Figure 3.1. The glass membrane was an annulus cylinder (O.D.=10 mm., L=20 mm.) and was installed in a stainless steel cylinder, tightly ended with two O-rings. The dispersion phase, containing a mixture of the monomers, solvents, and an initiator and a water-insoluble substance, was stored in the oil storage tank. The appropriate pressure was applied to the oil storage tank depending on the pore size of the membrane and the ingredient of the dispersion phase. This phase was allowed to permeate through the microporous membrane. The droplets were stabilized by the adsorption of PVA in the continuous phase, which is an aqueous solution of a stabilizer (PVA), an emulsifier (SLS) and a water-soluble inhibitor ($NaNO_2$). The stirring rate of 300 rpm was used for preventing the creaming of the dispersion phase. After the emulsification was over, the emulsion was withdrawn from the beaker, and transferred to a reactor for polymerization.

The SPG pore sizes of 0.9, 5.25 and 9.25 μm were used for preparing these emulsion droplets.

The continuous phase is composed of water 230 cm^3, SLS $4.35x10^{-4}$ g/cm^3 in water, PVA-217 0.01 g/cm^3 in water and $NaNO_2$ $1.3x10^{-4}$ g/cm^3 in water. Dispersion phase was stored in a 20-cm^3 oil tank. The nitrogen pressure with a range of $4.6x10^{-2}$-$8.16x10^{-2}$ Kgf/cm^2 for SPG pore size 5.25 μm was applied to the system depending on the composition of dispersion phase. In case of SPG pore size 0.9 and 9.25 μm, the nitrogen pressure was applied $8.14x10^{-1}$and $2.9x10^{-2}$ Kgf/cm^2, respectively.

3.2.3 Polymerization of the emulsion droplets

A three-necked glass separator flask was employed as a reactor equipped with a semicircular anchor-type blade made of Teflon as an agitator. A nitrogen inlet nozzle and a condenser were connected to the flask. Nitrogen was purged from the top of the condenser for checking the amount of nitrogen in the system. The nitrogen inlet nozzle was immersed into the emulsion with a stirring rate of 160 rpm for 1 h, and then, it was removed from the emulsion. The suspension polymerization was carried out at 343K for 24 h under the nitrogen atmosphere.

3.2.4 Treatment of polymer particles

Before and after the polymerization, the general features of the emulsion droplets and polymer particles were observed with an optical microscope. Then, the polymer particles were removed from the serum by centrifugation at a 3000 rpm, washed with methanol and dried in a vacuum oven at room temperature.

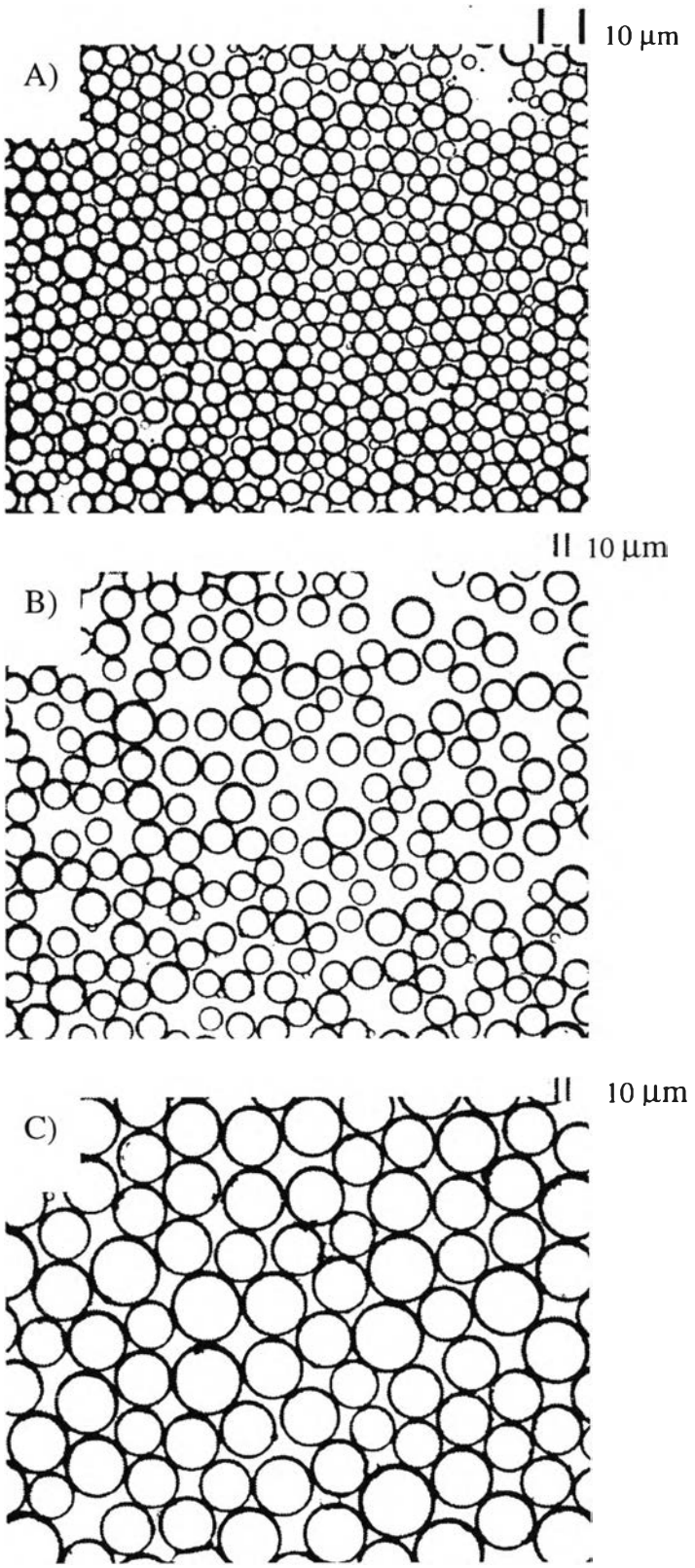


Figure 3.3 Photographs of emulsion droplets taken by an optical microscope with various SPG pore sizes: a) 0.9 μm, b) 5.25 μm, c) 9.25μm.

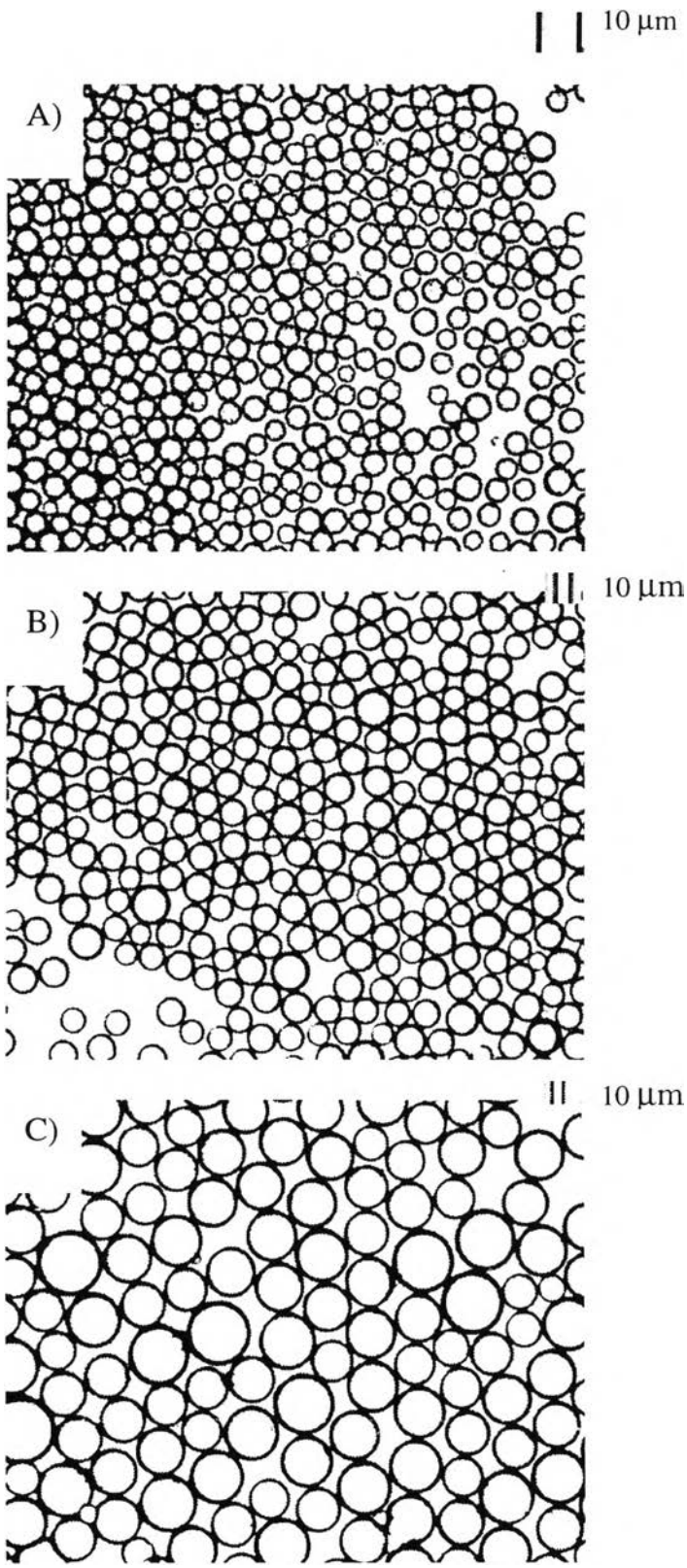


Figure 3.4 Photographs of polymer particles taken by an optical microscope with various SPG pore sizes: a) 0.9 µm, b) 5.25 µm, c) 9.25µm.

3.3 Characterization

3.3.1 Percent conversion of monomer

Gravimetric method was used to determine percent conversion of the monomer. After polymerization, 5 cm^3 of the weighed polymer latex was collected in a 20-cm^3 weighing bottle, 5 drops of HCl was dropped into the solution and stirred, then one drop of potassium aluminium sulfate saturated solution was dropped and stirred. Finally, 10-15 cm^3 of methyl alcohol was added and stirred again until the polymer particles were completely precipitated. The polymer particles were separated by the centrifugation at 3000 rpm. The polymers were dried in the vacuum oven at room temperature and the weight was weighed.

3.3.2 Determination of swelling degree

One gram of the dry polymer particles was immersed in toluene or heptane in a closed container for one night (24 h) and the swollen polymer was weighed and the swelling degree was calculated as follows [38]:

$$\text{Swelling degree} = \frac{\text{swollen weight}}{\text{original weight}} \tag{3.1}$$

3.3.3 Determination of average diameters of the particles

An optical microscope equipped (Olympus DP-10) with a camera was used to observe the average diameter of emulsion droplets. The average diameters of 200 droplets were measured from the photographs. Polymer particle was observed by SEM to measure average diameter.

The average droplet size (d_e) and particle diameter (d_p), standard deviation (σ) and a coefficient of variation (CV) were calculated by the following equations [39].

$$d_n = \frac{\sum n_i d_i}{\sum n_i} \tag{3.2}$$

where d_n is the number average of the particles, n_i is the number of particles of a diameter d_i.

$$\sigma^2 = \frac{\sum n_i [d_i - d_n]^2}{(\sum n_i) - 1} \quad (3.3)$$

$$CV = (\sigma / d_n)\, 100 \quad (3.4)$$

3.3.4 Determination of the general feature of polymer particles

General feature of the polymer particles was observed with scanning electron microscopy (SEM, JEOL, JSM 5300). A sample was prepared by placing the purified polymer powder on a brass stub, which was mounted with a double-faced conducting carbon tape. In case of a liquid sample, the sample was diluted with water and dropped on an aluminum tape and kept in a dessicator until it is dried. Then, it was coated with a thin layer of gold under vacuum before viewing in SEM.

3.3.5 Determination of Tg of the polymer

Glass transition temperature of the polymer was observed using a differential scanning calorimeter (DSC, MAC SCIENCE 3100). The sample weighing 5-8 mg was placed in an aluminium pan and was sealed and put on the sensor at room temperature along with an empty pan as a reference. The sample was heated at a heating rate of 10°C per minute while recording its changes according to the thermal transition.

3.3.6 Determination of the copolymer composition

Fourier-Transform infrared spectroscopy (FT-IR, Nicolet) was used to characterize the functional groups of the copolymer with the KBr pellet

method. The carbonyl bands of MMA and acrylate comonomers appear to be overlapped at 1730-1740 cm^{-1}.

3.3.7 Determination of the polymer porosity

The porosimeter (PROSORP VAS-3000) was used to measure the porosity, the pore size distribution, and the specific surface area of the resulting polymer.