CHAPTER III

EXPERIMENTAL

3.1 Chemicals

3.1.1 Monomers

Isoprene ($H_2C=CHC(CH_3)=CH_2$, Aldrich, Steinheim, Germany), 99% purity, stabilized by 100 ppm of *p-tert*-butylcatechol, colorless liquid, b.p. 34°C at 760 mm Hg, m.p. −120°C, f.p. −53°C, M = 68.12 g mol^{-1}, D = 0.681 g cm^{-3}

2-(Dimethylamino)ethyl methacrylate ($H_2C=C(CH_3)CO_2CH_2CH_2N(CH_3)_2$, DMAEMA, Aldrich, Steinheim, Germany), 98% purity, stabilized by 2000 ppm of monomethyl ether hydroquinone, colorlss liquid, b.p. 182–192°C at 760 mm Hg, f.p. 70°C, M = 157.22 g mol^{-1}, D = 0.933 g cm^{-3}

2-(Dimethylamino)ethyl acrylate ($H_2C=CHCO_2CH_2CH_2N(CH_3)_2$, DMAEA, Aldrich, Steinheim, Germany), 98% purity, stabilized by 1000 ppm of monomethyl ether hydroquinone, colorlss liquid, b.p. 64°C/12 mm Hg, f.p. 58°C, M = 143.19 g mol^{-1}, D = 0.943 g cm^{-3}

2-Hydroxyethyl methacrylate ($H_2C=C(CH_3)CO_2CH_2CH_2OH$, HEMA, Siam Chemical Industry, Samutprakarn, Thailand), 97% purity, stabilized by 300 ppm of monomethyl ether hydroquinone, colorless liquid, b.p. 67°C/3.5 mm Hg, f.p. 97°C, M = 130.14 g mol^{-1}, D = 1.073 g cm^{-3}

The monomers of 2-dimethylaminoethyl methacrylate (DMAEMA), 2-dimethylaminoethyl acrylate (DMAEA), and 2-hydroxyethyl methacrylate (HEMA) were purified prior to polymerization by pouring the monomer through a column containing basic alumina. The purification was conducted for the graft copolymerization of these monomers onto natural rubber latex (NRL).

3.1.2 Initiators and Activators

Sodium persulfate ($Na_2S_2O_8$, Aldrich, Steinheim, Germany), 98+% purity, solubility in water 545 g/cm^3, M = 238.1 g mol^{-1}, D = 1.10 g cm^{-3}

Cumene hydroperoxide ($C_6H_5C(CH_3)_2OOH$, CHP, Aldrich, Steinheim, Germany), 80% purity, b.p. 100–101°C/8 mm Hg, m.p. < −25°C, f.p. 56°C, M = 152.20 g mol^{-1}, D = 1.030 g cm^{-3}

***tert*-Butyl hydroperoxide** ($(CH_3)_3COOH$, *t*-BHP, Merck, Darmstadt, Germany), 70% purity, b.p. 37°C (20 hPa), m.p. −3°C, f.p. 60°C, M = 90.12 g mol^{-1}, D = 0.901 g cm^{-3}

Potassium persulfate ($K_2S_2O_8$, Merck, Darmstadt, Germany), analytical grade, solubility in water 47 g/cm^3, m.p. 100°C, M = 270.33 g mol^{-1}, D = 2.48 g cm^{-3}

Potassium metabisulfite ($K_2S_2O_5$, Merck, Darmstadt, Germany), analytical grade, solubility in water 450 g/cm^3, m.p. 190 °C, M = 222.33 g mol^{-1}, D = 2.3 g cm^{-3}

Tetraethylenepentamine ($HN(CH_2CH_2NHCH_2CH_2NH_2)_2$, TEPA, Aldrich, Steinheim, Germany), analytical grade, b.p. 340°C, m.p. −40°C, f.p. 185°C, M = 189.31 g mol^{-1}, D = 0.998 g cm^{-3}

3.1.3 Surfactant

Sodium dodecyl sulfate ($CH_3(CH_2)_{11}O_3SNa$, SDS, Aldrich, Steinheim, Germany), 98% purity, solubility in water ~150 g/cm^3, m.p. 204–207°C, M = 288.38 g mol^{-1}, D = 1.1 g cm^{-3}

3.1.4 Other Chemicals and Reagents

Toluene (C_7H_8, Merck, Darmstadt, Germany), analytical grade

Toluene-d_8 (C_7D_8, Aldrich, Steinheim, Germany), for NMR spectroscopy

Chloroform-d_1 ($CDCl_3$, Merck, Darmstadt, Germany), for NMR spectroscopy

Deuterium oxide (D_2O, Merck, Darmstadt, Germany), for NMR spectroscopy

Ammonia solution (NH_4OH, Aldrich, Steinheim, Germany), 25%

Hydrochloric acid (HCl, Merck, Darmstadt, Germany), 37%

Sodium hydrogen carbonate ($NaHCO_3$, Merck, Darmstadt, Germany), analytical grade

1-Dodecyl mercaptan ($CH_3(CH_2)_{11}SH$, Fluka, Buchs, Switzerland), 98%

The other chemicals were used as received

3.1.5 Natural Rubber Latex

The commercial high-ammonia natural rubber latex used in this work containing a 61.9% dry rubber content (DRC) was obtained from Thai Rubber Latex Corporation Co., Ltd. (Rayong, Thailand) and was used as received. The properties of the natural rubber latex were shown in Table 3-1.

Table 3-1 The properties of natural rubber latex (high ammonia grade)

Properties	Test results
Total solid content, %	61.9
Total rubber content, %	60.5
Non rubber solid, %	1.56
Ammonia content (on total weight), %	0.70
Ammonia content (on water weight), %	1.82
pH value	10.92
KOH number	0.5610
Volatile fatty acid number (VFA)	0.0194
Mechanical stability time @ 55% TSC, Sec	1,100
Specific gravity at 25°C	0.9411
CST. (cm^3)	2.4
Magnesium content (ppm)	23
Viscosity (60%TS. spindle no. 1.60 rpm) cps	64

Source: Thai Rubber Latex Corporation (Rayong, Thailand) Public Co., Ltd.

3.2 Equipment

1.	Mechanical stirrer	: Ika Werker RW20, Germany
2.	Digital thermostat bath	: Haake DC10, Germany
3.	Vacuum oven	: Hotpack 273700, U.S.A.
4.	Bottle polymerizer	: Australian locally made

5.	RC1 reaction calorimeter	: Mettler Toledo, Switzerland
6.	pH meter	: Schott CG842, Germany
7.	Face contact angle meter	: Kyowa Interface Science CA-A, Japan
8.	IR spectrometer	: Perkin-Elmer 1760x, U.S.A.
9.	NMR spectrometer	: Bruker Avance DPX400, Germany
10.	Differential scanning calorimeter	: Mettler Toledo DSC822e, Switzerland
11.	Transmission electron microscope	: Jeol JEM 1230, U.S.A.
12.	Universal testing machine	: Lloyd LR5K, U.S.A.
13.	Photon correlation spectrometer	: Brookhaven BI-9000AT, U.S.A.
14.	General laboratory glassware	

3.3 Procedures

3.3.1 Preparation of Polyisoprene Latexes

Polyisoprene latexes were prepared by conventional free radical emulsion polymerization. Isoprene was used as a monomer. Sodium persulfate ($Na_2S_2O_8$) was used as an initiator, sodium dodecyl sulfate (SDS) as a surfactant, sodium bicarbonate ($NaHCO_3$) as a buffer, and a small amount of n-dodecyl mercaptan (n-DM) was used as a chain transfer agent. The use of a chain transfer agent has been found to be essential in diene emulsion polymerizations for effective

initiation and to control the degree of branching and cross-linking (97, 98). Since DM solubility in water is very low, any residual DM in this latex would not be expected to have any effect on the polymerization of the water-soluble DMAEMA during the second-stage polymerization. The polymerization reaction of polyisoprene was carried out in two different reactors, a 500-cm^3 bottle polymerizer for determinations of suitable formulations before a large reaction was performed, and another reaction calorimeter (Mettler Toledo RC1) equipped with a 1.5-dm^3 HP 60 reactor was used for a scale-up.

The important characteristic of the latex is particle size related to the surface of the particle, which mostly are the loci for chemical reaction such as grafting. This characteristic is a function of preparation phenomena, i.e. raw materials, techniques and conditions. In the present work, a systematic study has been organized to elucidate the effect of variable parameters (surfactant, initiator, monomer concentration, and reaction temperature) on polyisoprene latex characteristics, with emphasis on size. For this purpose, practical techniques rather than theoretical aspects are considered.

3.3.1.1 Preparation of Polyisoprene Latexes in the Bottle Polymerizer

All the polymerization reactions were carried out in a 500-cm^3 reaction vessel. The bottle with crown and a bottle guard is shown in Figure 3-1. This technique and equipment are also useful for other low boiling monomers, such as butadiene and methyl acrylate, with a little pressurization of the bottle with nitrogen. A typical preparation procedure is carried out as follows. Sodium dodecyl sulfate,

sodium hydrogen carbonate, sodium persulfate, and *n*-dodecyl mercaptan, were added

to the 500-cm^3 bottle and stirred till all chemicals dissolved under N_2 bubbling for 1 h.

Figure 3-1 The 500-cm^3 reaction vessel for bottle polymerizer.

The isoprene monomer was then poured into this reaction bottle. The reaction

vessel was then sealed with a rubber seal and crimped the top lid before placing in the

temperature-controlled water bath. This bath has a rotating creel or rack within to hold

and mix the polymerization bottles. The reaction was carried out at 60–70°C with the

rotation speed about 50 rpm for 20 h to facilitate the complete conversion of monomer

to polymer. At the end of the reaction time, the reaction vessel was removed from the

water bath and allowed to cool for a few minutes. The details of the recipes are shown in Table 3-2.

Table 3-2 Recipes used in batch emulsion polymerization of isoprene in the bottle
polymerizer

Ingredient	Amount
Isoprene (mol dm^{-3})	2.82 – 3.86
Sodium persulfate (mol dm^{-3})	$8.03 \times 10^{-4} - 8.02 \times 10^{-3}$
Sodium dodecyl sulfate (mol dm^{-3})	$7.43 \times 10^{-3} - 7.08 \times 10^{-2}$
Sodium bicarbonate (mol dm^{-3})	6.88×10^{-2}
n-Dodecyl mercaptan (mol dm^{-3})	9.34×10^{-3}
Distilled-Deionized (DDI) water (g)	154.1
Reaction temperature (°C)	60, 70
Reaction time (h)	20

3.3.1.2 *Preparation of Polyisoprene Latexes in Mettler RC1 reactor*

Batch emulsion polymerizations of isoprene were carried out in a 1.5-dm^3 HP 60 reaction microcalorimeter (RC1 Mettler Toledo Metal Reactor, Switzerland) (Figure 3-2) using the recipes presented in Table 3-3. The principle of reaction microcalorimeter is shown in Appendix A.

The main features of RC1 are as follows:

- It allows chemical reactions to perform with measurements of heat **flux** under

  pressure (up to 60 bars) over a wide range of reaction temperatures (−20°C

  to 200°C).

- It allows rapid cooling and heating (the rates depend on reaction temperature,

  mass of the reactants and cooling medium), and maintains an accurate

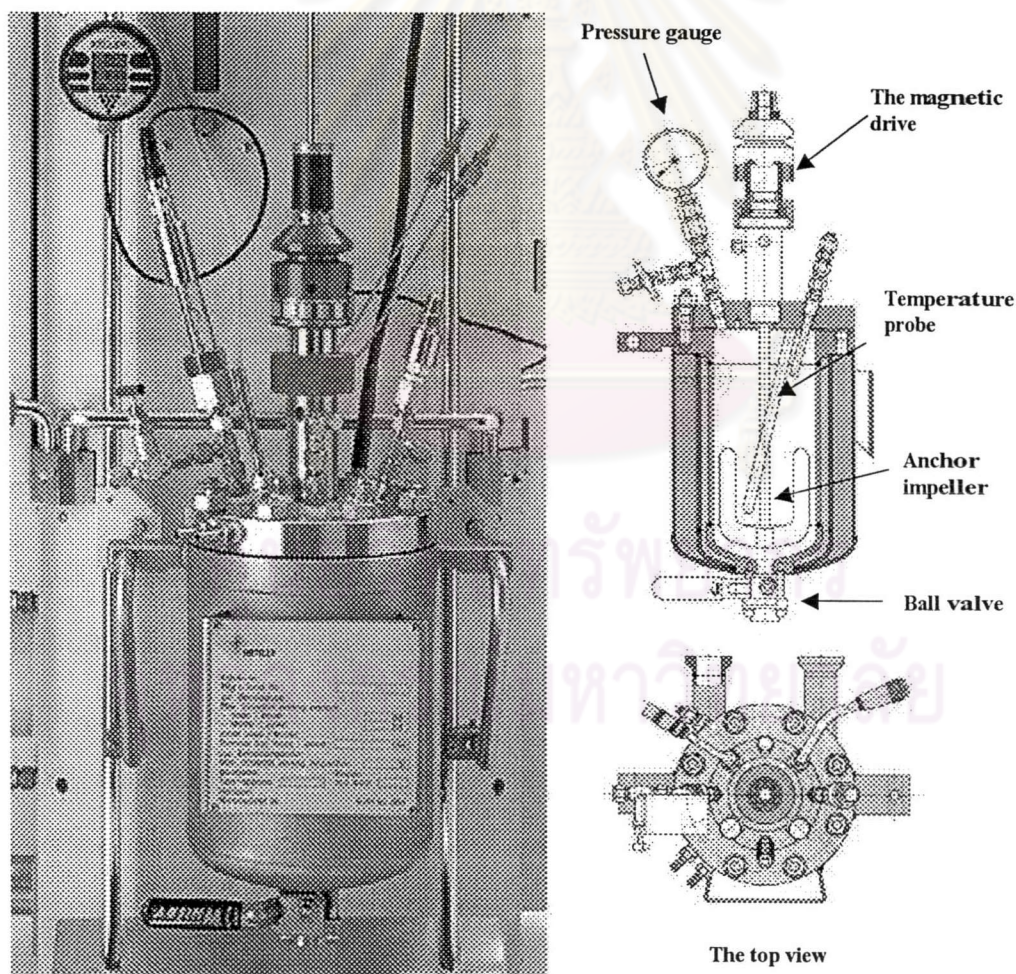 temperature control (± 0.5 K) of the reactions.

Figure 3-2 The 1.5-dm^3 HP 60 RC1 Mettler Toledo metal reactor.

- A magnetic drive, hermetically sealed, allows an operation at a high stirring speed (up to 2500 rpm) as well as the handling of highly viscous fluids.
- A ball valve installed at the bottom of the reactor allows the reaction contents to be drained after the experiment.

Table 3-3 Recipes and conditions used in the batch emulsion polymerization of isoprene in the Mettler RC1 reactor microcalorimeter

Ingredient	Amount	
	Small seed	Large seed
Isoprene (mol dm^{-3})	2.91	2.98
Sodium persulfate (mol dm^{-3})	8.28×10^{-3}	8.44×10^{-3}
Sodium dodecyl sulfate (mol dm^{-3})	7.31×10^{-2}	7.33×10^{-4}
Sodium hydrogencarbonate (mol dm^{-3})	7.09×10^{-2}	7.24×10^{-2}
n-Dodecyl mercaptan (mol dm^{-3})	9.63×10^{-3}	9.85×10^{-3}
Distilled-Deionized (DDI) water (g)	924.7	1156
Reaction temperature ($^{\circ}$C)	60	70
Reaction time (h)	20	20
Conversion (%)	89.8	84.3
Solid content (%)	20.6	17.8
Gel Fraction (%)	47.3	60.5
Particle diameter (nm)[a]	59	137
Size polydispersity[a]	1.35	1.03

[a] Determined by dynamic light scattering (DLS).

All ingredients except isoprene monomer were dissolved in DDI water and charged into the reactor, after which the reactor was purged with nitrogen gas to remove dissolved oxygen for at least 1 h at room temperature. The specified amount of isoprene monomer was then added to the reactor and the reactor temperature ramped from room temperature to 60°C for about 10 min, the nitrogen flow was then stopped, and all valves were closed. The reaction was then allowed to proceed for 20 h with an agitation speed of 100 rpm. Unreacted isoprene monomer was removed from the resulting latex by bubbling with nitrogen gas at ambient temperature overnight followed by rotary evaporation under reduced pressure. The resulting latexes are sufficiently monodisperse that any indications of significant changes in size with pH after second-stage polymerization will be meaningful.

3.3.2 Grafting of Poly(DMAEMA) on Polyisoprene Seed Latexes

All grafting experiments were performed in the Mettler RC1 reaction microcalorimeter equipped with the 1.5-dm^3 HP 60 reactor (Figure 3-2). An anchor stirrer was used for all experiments with the impeller located 2.0 cm from the bottom. The weighed isoprene-free polyisoprene seed latex as shown in Table 3-4 was mixed with ammonia (Aldrich, 25% solution), DDI water, CHP and DMAEMA. To avoid coagulation during addition, the weighed polyisoprene latex was first mixed with ammonia solution and cooled in an ice bath. The mixture of CHP and DMAEMA was then added over 1 h, the mixture was poured into the reactor, and the headspace of the reactor flushed with nitrogen gas to remove oxygen. The reaction mixture was

Table 3-4 Conditions used in grafting reaction of poly(DMAEMA) on polyisoprene

seed latexes

Ingredient	Amount	
	Small seed	Large seed
Polyisoprene seed (g)	485.4	562.2
% Solid contents of seed	20.6	17.8
Seed particle diameter (nm)	59	137
Mass of seed polymer (g)	100	100
DMAEMA monomer (g)	63.33	63.33
Cumene hydroperoxide (g)	1.727	1.727
TEPA (g)[a]	1.084	1.084
25% NH_3 (g)	46.67	46.67
Distilled-deionized (DDI) water (g)	467	467
Particle number density N_p (dm^{-3})	2.4×10^{17}	0.20×10^{17}
Reaction time (h)	20	20
Reaction temperature (°C)	15	15
TEPA feeding time (h)	0.5, 1, 2, 4 and 6	1
Total particle surface area (nm^2 dm^{-3})	1.1×10^{22}	0.47×10^{22}

Reactions were carried out with an agitation speed of 100 rpm.

[a] Diluted to 54.2 g with distilled H_2O.

agitated at 100 rpm under nitrogen atmosphere for 1 h to allow the partitioning of CHP into the seed particles before the injection of TEPA solution. The TEPA solution was delivered in water to give a final concentration of 5.3×10^{-3} M in a

continuous feed at 25°C using an RD10 dosing controller over a period of 0.5, 1.0, 2.0, 4.0 or 6.0 h. The reactor was controlled in the isothermal mode for all the experiments and was maintained at 15°C for 20 h. A low temperature was chosen because this should minimize gel formation (99) without severely slowing down the reaction (the propagation rate coefficient of DMAEMA at 15°C is probably similar to that of methyl methacrylate, which is $2.4 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ at that temperature (100)). All ingredients were used without purification. It is reasonable to adopt the assumption commonly made in this field that the redox initiator rapidly removes all inhibitors and hence that any inhibitor effects will be only present at the earliest stages of the reaction process.

3.3.3 Grafting of Hydrophilic Monomers on Natural Rubber Latexes

The graft copolymers of 3 hydrophilic vinyl polymers, poly(DMAEMA), poly(DMAEA), and poly(HEMA), onto the natural rubber latex were prepared from the high ammonia natural rubber (HANR) latex by emulsion graft copolymerization.

All grafting experiments were carried out using a 500-cm^3 round bottom reactor. Table 3-5 shows the graft copolymerization recipes. The HANR latex (83.4 g, DRC 61.9%) was placed in and mixed with 100 cm^3 ammonia solution, $K_2S_2O_8$ (t-BHP or CHP, 0.1–1 phr) and DMAEMA (DMAEA or HEMA, 5–20 phr), respectively. The reaction mixture was agitated for 1 h to allow the partitioning of $K_2S_2O_8$ (t-BHP or CHP) into the seed particles and the dissolved oxygen present in the ingredients was removed by purging nitrogen gas for at least 1 h through the mixture before the injection of $K_2S_2O_5$ or TEPA solution (0.1–1 phr). The TEPA

solution was adjusted to 10%w/w and then added in the reactor for 1 h to initiate polymerization. The polymerization reaction was performed at a stirring speed of 100 rpm at the desired temperature (15–30°C) for 24 h. At the completion of the reaction, an aliquot of the resulting latex was cast in a glass tray and then dried to a constant weight in a vacuum oven at 40°C. The procedures of preparation of graft natural rubber and the characterization are summarized in Figure 3-3.

Table 3-5 Experimental conditions for graft copolymerization of DMAEMA and DMAEA monomers onto natural rubber latex

Ingredients	DMAEMA	DMAEA	HEMA
NR (61.9% DRC, g)	83.4	83.4	83.4
2.5% NH_3 solution (g)	100	100	100
$K_2S_2O_8/K_2S_2O_5$ (1:1, phr)	0.5	-	-
t-BHP/TEPA (1:1, phr)	0.5	-	-
CHP/TEPA (1:1, phr)	0.1, 0.25, 0.5, 1.0	0.1, 0.25, 0.5, 1.0	0.5
Monomer concentration (phr)	5, 10, 15, 20	5, 10, 15, 20	5, 10
SDS concentration (phr)	-	-	5
Reaction temperature (°C)	15, 20, 25, 30	15, 20, 25, 30	25
Reaction Time (h)	24	24	24

The reaction was carried out with an agitation speed of 100 rpm.

Because poly(DMAEMA) and poly(DMAEA) exhibit a lower critical solution temperature (LCST, i.e., chain collapse) at about 40°C in water (101), all syntheses and measurements were performed at 25°C or below.

NRL + 2.5% NH₃ solution

- Stirrer speed 100 rpm in
  N₂ atmosphere at ~10°C for 1 h
- Add CHP + Monomer slowly

Parameter studies for
- Effect of types of redox initiator
  (CHP/TEPA, *t*-BHP/TEPA, K₂S₂O₈/K₂S₂O₅)

Add in the reactor

- Stirrer speed 100 rpm in
  N₂ atmosphere at ~15-30°C for 24 h
- Add TEPA solution

Parameters study for
- Effect of monomer types and concentration
  (DMAEMA, DMAEA, HEMA)
- Effect of initiator concentration
- Effect of reaction temperature

Graft copolymerization reaction

Film casting

Conversion (%), Gel content

Extraction
- Toluene
- Acidified water

Grafting efficiency

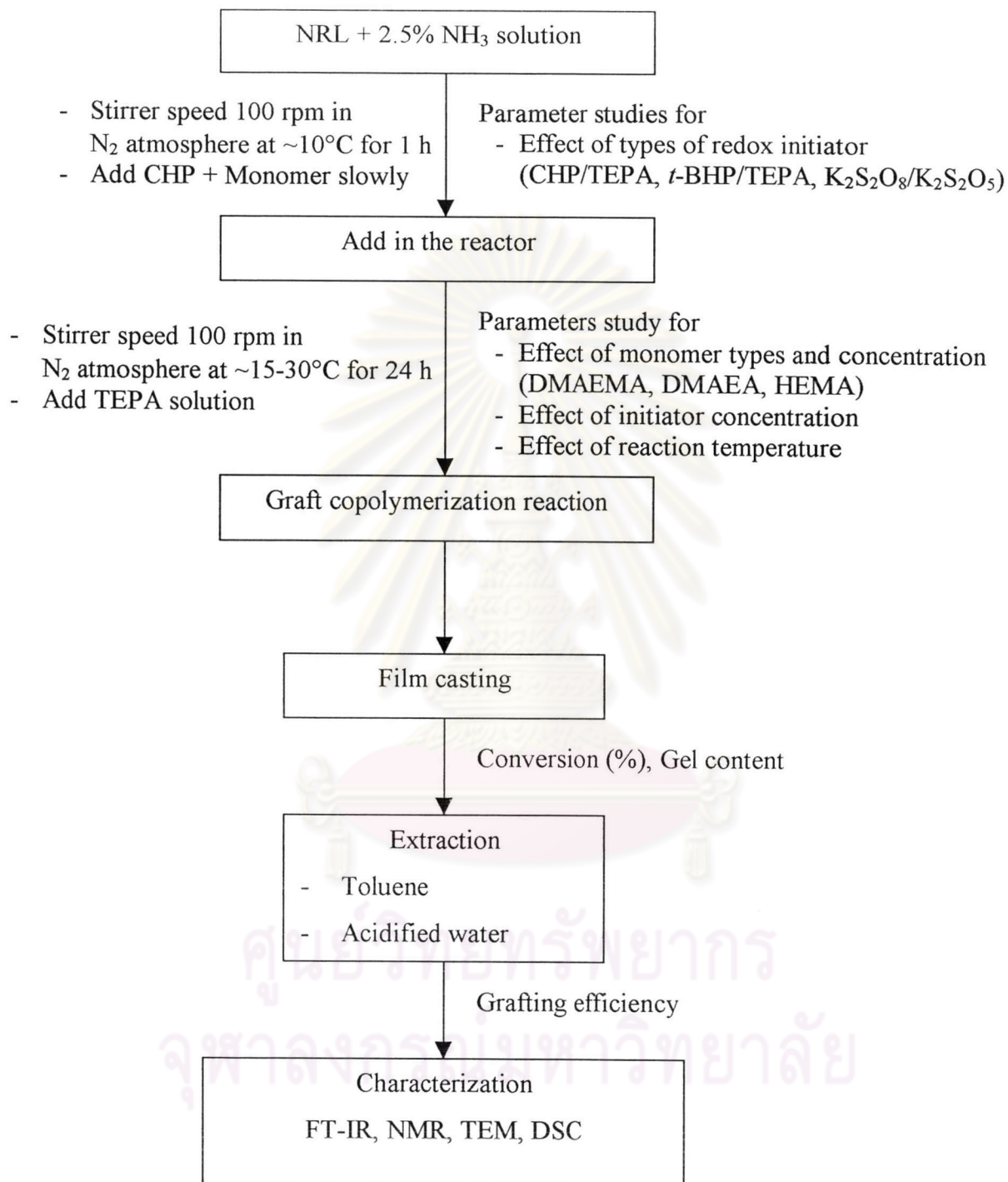Characterization
FT-IR, NMR, TEM, DSC

Figure 3-3 The overall schematic experimental process.

In this work, the effects of redox initiation systems, cumene hydroperoxide (CHP) /tetraethylenepentamine (TEPA), *tert*-butyl hydroperoxide (*t*-BHP)/TEPA, potassium persulfate ($K_2S_2O_8$)/potassium metabisulfite ($K_2S_2O_5$) on the grafting properties were also studied.

3.4   Characterization

3.4.1   Determination of Polymerization Kinetics

The RC1 reaction calorimeter provides values of heat of reaction as a function of time, determined once every 2 s. The use of calorimetry for monitoring of polymerization kinetics has been extensively described elsewhere (102-107).

The rate of polymerization is calculated directly from the heat of reaction data using:

$$R_p = -\frac{d[M]}{dt} = \frac{Q_r}{\Delta H_p V_{aq}}$$
(3-1)

where Q_r is the rate of heat generation in the reaction, R_p is the reaction rate, [M] is the total number of moles of monomer per unit volume of the reactor (equal to the monomer concentration, corrected for the ratio of volume of continuous phase to total volume, if all monomer molecules are located uniformly in the continuous phase), V_{aq} is the total volume of the aqueous phase, and ΔH_p is the molar enthalpy of

polymerization. There are no reliable experimental values for ΔH_p of DMAEMA, so the value for methyl methacrylate (MMA) polymerization in bulk (5.6×10^4 J mol^{-1}) was applied to allow semi-quantitative interpretation of the data; reported values for methacrylate monomers all lie within a few kJ mol^{-1} (108). It was not possible to determine ΔH_p experimentally in this work due to difficulties in accurately determining final conversion by gravimetry, probably arising from the tacky nature of the polyisoprene seed and presence of some amounts of both poly(DMAEMA) and DMAEMA monomer in the interior of the particles.

The monomer concentration at any reaction time t ($[M]_t$) is obtained by integration of the heat flow/time curves $Q_r(t)$ using:

$$[M]_t = [M]_0 - \frac{\int_0^t Q_r(t)\,dt}{\Delta H_p V_{aq}} \qquad (3\text{-}2)$$

where $[M]_0$ is the initial monomer concentration.

3.4.2 Determination of Solid Content and Conversion

The solid content and conversion of monomers were determined by gravimetry. Latex samples (about 2 g, W_2) were weighed to 4 significant figures in an aluminium pan (W_1) and dried in air at 60°C until a constant weight (W_3) was achieved. The solid content and the conversion were calculated from the weight loss of the samples from the following equations:

$$\text{Solid content (\%)} \quad = \quad \frac{W_3 - W_1}{W_2 - W_1} \times 100 \tag{3-3}$$

$$\text{Conversion (\%)} \quad = \quad \frac{\text{weight of polymerized monomer}}{\text{weight of total monomers}} \times 100 \tag{3-4}$$

3.4.3 Determination of Grafting Parameters

The free NR and free homopolymers, poly(DMAEMA) and poly (DMAEA), were removed by Soxhlet extraction. Toluene and acidified water were used for extracting the free rubber and free polymers for 24 h, respectively, and the grafted natural rubbers samples were then dried in vacuum at 40°C until constant weight. The weight difference between the initial sample and the extracted samples is the measure of the grafting properties, grafting efficiency (GE), the percentage of homopolymer, and the percentage of free NR, which were calculated using the following relationships:

$$\text{Grafting efficiency (\%)} \quad = \quad \frac{\text{weight of monomers grafted}}{\text{weight of monomers polymerized}} \times 100 \tag{3-5}$$

$$\text{Homopolymer (\%)} \quad = \quad \frac{(M_o \times C) - (M_1 - M_2)}{M_o} \times 100 \tag{3-6}$$

$$\text{Free NR (\%)} \quad = \quad \frac{M_3 - M_4}{M_5} \times 100 \tag{3-7}$$

where M_o is the mass of monomer (g), C is the conversion of monomer (%), M_1 is the total mass of dry rubber and polymer after extraction and drying (g), M_2 is the mass of dry rubber in the sample, M_3 is the mass of sample after separation of the monomer, homopolymer (g), M_4 is the mass of residue after extraction and drying (g), and M_5 is the total mass of all solids of NR latex and the monomer (g).

3.4.4 Determination of Particle Size and Polydispersity Index

Photon correlation spectroscopy (PCS) was used to measure mean diffusion coefficient of the particles in the dispersion. The corresponding mean hydrodynamic diameter was calculated from the diffusion coefficient measurement, which, in the high dilution with negligible particle-particle interaction, is calculated by using the Stokes-Einstein equation (109):

$$D \; = \; \frac{k_B T}{3\pi\eta D_H} \tag{3-8}$$

where D is the diffusion coefficient of the latex particle, η the viscosity of the medium, k_B the Boltzmann constant, and T the absolute temperature of the dispersion. The diameter D_H measured in this manner is usually known as the hydrodynamic diameter.

The PCS measurements were carried out using a Brookhaven model BI9000AT 72-channel digital correlator (Brookhaven Instruments Corp., Holtsvile, NY). The correlator was used with an argon ion laser. The reference PCS measuring conditions

were at the temperature of 25°C, a scattering angle of 90°, and a wavelength of 632.6 nm. The software provided by Brookhaven Instruments was modified to continually adjust the sample time between measurements to obtain an optimal auto-correlation function in a continuous data acquisition mode. The method of cumulants was used for data analysis.

The polydispersity index (*PDI*) was determined as follows (26):

$$\bar{D}_n = \frac{\sum\limits_{i=0}^{n} n_i d_i}{\sum\limits_{i=0}^{n} n_i} \tag{3-9}$$

$$\bar{D}_w = \frac{\sum\limits_{i=0}^{n} n_i d_i^4}{\sum\limits_{i=0}^{n} n_i d_i^3} \tag{3-10}$$

$$PDI = \frac{\bar{D}_w}{\bar{D}_n} \tag{3-11}$$

where, $\bar{D}_n$ is number average diameter, $\bar{D}_w$ is weight average diameter; n_i is the number of particles of diameter d_i.

3.4.5 ^{1}H-NMR Measurement

After the double extraction of the grafted copolymer, 10–15 mg of dried samples of toluene and water extractions were dissolved in 650 µl of CDCl$_3$ or D$_2$O. ^{1}H-NMR spectra were recorded with Bruker Avance 400-MHz instrument.

3.4.6 FT-IR Measurement

After the double extraction of the grafted natural rubber, functional groups of the grafted natural rubber were determined by Fourier Transform Infrared Spectrophotometer (Perkin Elmer model 1760X, U.S.A). The grafted natural rubber samples were dissolved in toluene and cast on the KBr cell for IR investigation.

3.4.7 Stability of Modified Latex at Low pH

A few drops of the grafted natural rubber latex were placed into a 5 cm^3 of 6% HCl solution for testing the stability of the modified latex at low pH. The stability of the latexes was observed visually and compared to the unmodified natural rubber latex.

3.4.8 Determination of Gel Content

The gel contents were obtained by dissolving the dried polymer (0.05 g) in an excess of toluene (15 g) for one week, after which the solid fraction was collected by filtration and weighed to give an estimated amount of the gel fraction.

The low-impact method is thought to avoid disrupting the polymer matrix and generating disperse particles of microgel (110).

3.4.9 Water Absorption of Modified Film

Modified films with known weights were immersed in deionized water for 48 h at ambient temperature (25°C). After 48 h of immersion, the swollen films were removed and blotted dry between two pieces of filter paper before weighing. The water absorbed, S was calculated as:

$$S \; = \; \frac{(W_1 - W_o)}{W_o} \times 100 \qquad (3\text{-}12)$$

where W_o is the initial weight of the sample, and W_1, the weight of the sample after immersion in water.

3.4.10 Contact Angle Measurement

After the modified rubber latex films were washed with hot water for 1 h and followed by water several times and then dried in vacuum at 40°C for 24 h, the hydrophilicity of the rubber latex film was assessed by the contact angle of a drop of water placed on the film surface. A microsyringe was used to dispense accurately 1 μl of water and the contact angle was measured at 25°C under a microscope at different time intervals, measurements should be made with several drops in order to obtain an average value.

3.4.11 Transmission Electron Microscopy

Particle morphology of the grafted NR is vital in this work. The transmission electron microscopic (TEM) technique is given below for reproducible results.

Depositing latices on grids. Grids were prepared for TEM as follows. Grids were initially coated with a thin film of Formvarw [poly(vinyl formal)] or Pioloforme [poly(vinyl butyral)]. A specified amount of the latex was diluted with distilled water. This dilution should be sufficient to produce a film coverage on the TEM grid to be less than a monolayer of particles. A small piece of the diluted was dropped onto the grid and dried overnight at room temperature. In some cases, a vapor stain (such as osmium tetroxide) was also applied, to enhance phase contrast of the phases.
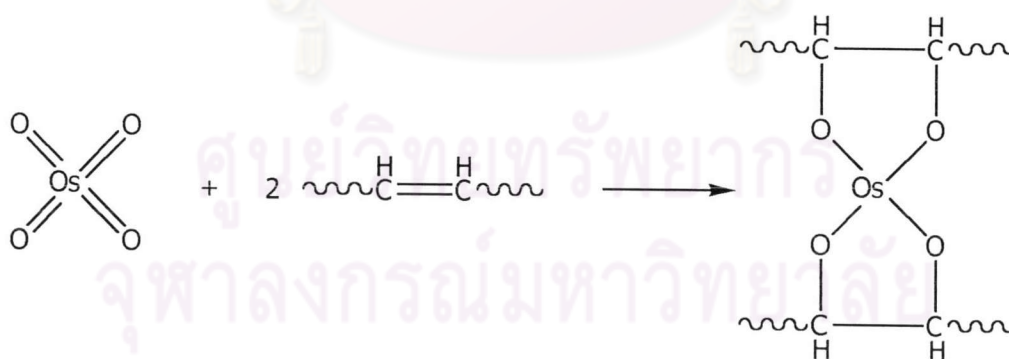
Figure 3-4 Demonstration of crosslinking reaction of polymer chains and OsO_4 (111).

Osmium tetroxide staining. OsO_4 strongly reacts with double bonds on NR chains. It reacts with unsaturated carbon-carbon bonds as shown in Figure 3-4. Vapour staining was found to be the most effective method of using this material. A

2% OsO_4 solution was first prepared by dissolving osmium tetroxide in distilled water. This solution could be stored in a freezer for a number of weeks before a reduction in staining power was noted. This was easily checked by exposing a small piece of natural rubber glove to the vapour, and noting the time taken for black staining to be visible. A few drops of this solution was placed on a small piece of cotton in a glass chamber as shown in Figure 3-5. The TEM grids as substrate for the polymer to be stained were placed on the mesh for overnight for effective staining, and they were then dried at ambient temperature. Transmission electron micrographs were taken on a JEOL model JEM-1230 at 100 kV.
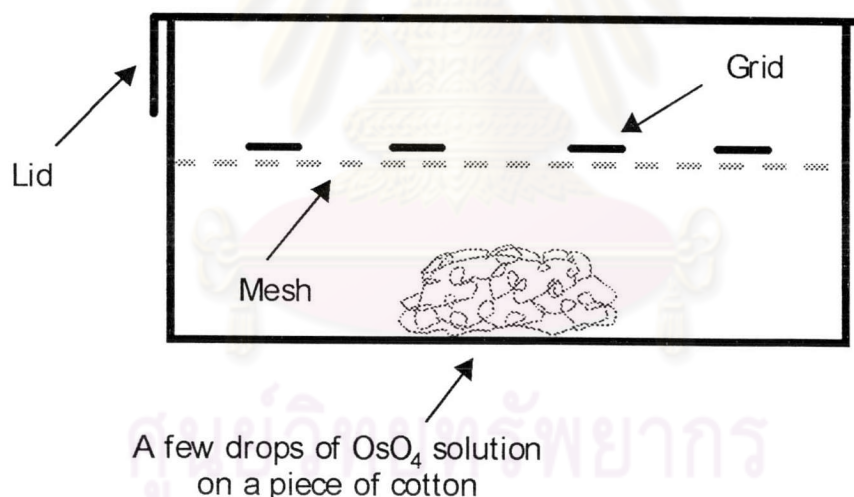
Figure 3-5 Illustration of a chamber used for vapor staining in the
preparation of TEM sample.

Phosphotungsnic acid negative staining. Phosphotungsnic acid (PTA) acts as a negative stain. One drop of latex was placed in 1 cm^{-3} of 1 % by weight PTA in water solution. After 10 min a drop of this solution was placed on a grid and allowed to dry.

The stain would deposit on the support film covering the grid as the diluted latex sample dried.

3.4.12 Thermal Properties of Graft Natural Rubber

Thermal behavior of the grafted natural samples was examined by a differential scanning calorimeter (Mettler Toledo DSC822e) to obtain glass transition temperatures. The sample weighing, 10–12 mg was put in the aluminum pan and sealed with another aluminum pan. The measurements were carried out over a temperature range of -100 to $50°C$ with a heating rate of $20°C$ min^{-1}, under the nitrogen atmosphere.

3.4.13 Tensile Strength Measurement

The tensile test was carried out to evaluate the change in mechanical properties of the samples obtained at various stages during the course of the reaction. Dumbbells were cut from the modified NR latex film and the tensile strength (T_s) as well as the elongation at break (E_b) were determined in accordance with ASTM D412-C. This was done using a Lloyd model LR 5K universal testing machine at a crosshead speed of 500 mm min^{-1}. The dumbbell pieces were conditioned at $25°C$ overnight prior to tensile measurements.