

Chapter III

Experimental

3.1 Chemicals

3.1.1 Monomers

Styrene (St) was used as monomer without further purification, supplied from Eternal Resin Co., Ltd., Bangkok, Thailand.

n-Butyl Acrylate monomer (nBA) was supplied by Eternal Resin Co., Ltd., Bangkok, Thailand. It was used as received.

3.1.2 Initiator

Benzoyl peroxide (BPO) was obtained from Merck, Hohenbrunn, Germany, with 97 % purity moistened with 25 % of water. It was used as supplied.

3.1.3 Dispersant

Poly(vinyl alcohol) (PVA GL-05) with a degree of polymerization of 500 and saponification value in a range of 86.5-89.0 was supplied from The Nippon Synthetic Chemicals Industry Inc., Osaka, Japan.

3.1.4 Crosslinking agent

Divinylbenzene (DVB) was provided by Merck, Hohenbrunn, Germany, with 65 % DVB isomer and 33 % ethylvinylbenzene measured by gas chromatography, stabilized by 0.2 of 4-tert-butylpyrocatechol.

3.1.5 Charge controlling agent

Boro bis (1,1-diphenyl-1-oxo-acetyl) Potassium salt was provided by Japan Carlit Co., Ltd., Tokyo, Japan, with a density of 1.3735 kg/m³ at 23 °C and molecular weight of 502.35.

3.1.6 Coloring agent

Black coloring agent, carbon blacks used, namely Printex 60 was from Degussa, Frankfurt, Germany, and the manufacture' s specifications is summarized in Table 3.2

3.1.7 Other chemicals

Sodium dodecyl benzenesulfonate hard type (SDS)

: Kishida chemical Co., Ltd., Tokyo, Japan

Chloroform HPLC grade (CHCl₃) : Carlo Erba, Milan, Italy

Tetrahydrofuran HPLC grade (THF) : Merck, Hohenbrunn, Germany

3.2 Glassware and Equipment

Four-necked round bottom flask

: 1000 ml, Sibata Scientific Technology Ltd., Tokyo, Japan

Reflux condensor

: Spiral type (300 mm), Sibata Scientific Technology Ltd., Tokyo,
Japan

Thermometer

Nitrogen gas inlet tube

Semicircular anchor-type blade paddle agitator

Oil bath

: OB 14, Memmert GmbH+Co.KG, Schwabach, Germany

Mechanical homogenizer

: T.K. ROBOMICS, Tokushu Kika Kogyo Co., Ltd., Osaka, Japan

Mechanical stirrer

: SCR-120, Iuchi Co., Ltd., Ibaraki, Japan

Cooling circulator

: SK 55, Haake & partner datentechnik gmbh, Offenburg, Germany

Centrifuge machine

: CR 5B2, Hitachi Koki Co., Ltd., Ibaraki, Japan

Vacuum oven

: ADP-21, Yamato Scientific Co., Ltd., Tokyo, Japan

Dessicator

Other general laboratory glassware and equipment

3.3 Apparatus

3.3.1 Scanning electron microscopy (SEM)

: Jeol, JSM-6400, Tokyo, Japan

3.3.2 Differential scanning calorimeter (DSC)

: DSC 7 Perkin Elmer, Norwalk, USA.

3.3.3 Gel permeation chromatography (GPC)

: LC-AZ AD, CTO-10AC, C-R7A plus (Shimadzu) K-806M Column
(Showa Denko Co., Ltd), Kyoto, Japan

3.3.4 Nuclear magnetic resonance (NMR)

: Jeol JNM-500 FT NMR spectrometer, Tokyo, Japan

3.3.5 Fourier transform infrared spectroscopy (FTIR)

: Perkin Elmer 1760X, Norwalk, USA.

3.3.6 Elemental analysis (EA)

: (CHNS/O Analyzer), Norwalk, USA.

3.3.7 Transmission electron microscopy (TEM)

: JEM-200CX, Tokyo, Japan

3.3.8 Rolling type of toner charger

: MS 1 Minishaker, IKA-Works, Inc., Wilmington, USA.

3.3.9 Blow-off tribo measurement unit (home made) comprising two

important units:

3.3.9.1 Electrometer : 617 programmable electrometer, KEITHLEY, Cleveland, Ohio, USA.

3.3.9.2 Vacuum cleaner : VC-Z11L 160, TOSHIBA, Tokyo, Japan

3.3.10 Printer for testing toner

: 6ex, Oki Electronics (Singapore) Pte. Limited, Singapore

3.3.11 Electronic balance

: AEX-120G Analytical balance, Shimadzu Corporation, Kyoto, Japan

3.3.12 Densitometer

: RD 915, Macbeth Corporation, Newburge, USA.

3.3.13 Image analyzer

: LUZEX F, PM 10-AD, Olympus, Nireco Corp., Tokyo, Japan

3.4 Suspension Polymerization

3.4.1 Synthesis of Styrene and *n*-Butyl Acrylate Copolymer

The apparatus for the preparation of Poly(Styrene-*co*-normal butyl acrylate) was a 1000 cm³ four-necked round bottom flask equipped with a mechanical stirrer, a semicircular anchor-type blade, a reflux condenser, a thermometer and a nitrogen gas inlet tube. The oil bath was preheated to the polymerization temperature of 70°C for 30 minutes. The usual range of the monomer-to-water is 1:3 to 1:4 by weight. A mixture of styrene and normal butyl acrylate, divinylbenzene, and benzoyl peroxide used as monomer, crosslinking agents, and initiator, respectively were stirred and added into the continuous phase of an aqueous solution of poly(vinyl alcohol) as stabilizer. The resulting mixture of disperse and continuous phases was stirred by a mechanical homogenizer (T.K. ROBO MICS ; TOKUSHU KIKA KOGYO Co., Ltd.) at a constant speed of 7,000 rpm for 10 minutes. The homogeneous mixture was transferred into a four-necked glass reactor. The suspension polymerization, carried out at the temperature of the reaction mixture, was constantly maintained at 70°C, with an agitator speed of 180 rpm under slow purging of nitrogen gas for deoxygenation. The reaction was then allowed to polymerize for 8 hrs. The resulting polymer was cooled to room temperature and then was washed with deionized water to remove the residual dispersant (PVA) that adhesive at the surface of the copolymer particles. The microspheres were dispersed in water, and the dispersion was sonicated for about 5 minutes in an ultrasonic bath. The prepared polymeric microspheres were isolated from the mixture by centrifugation at a rate of 3000 rpm for 15 minutes and

the supernatant was decanted. The remaining polymer was washed with deionized water and centrifuged again by a repeatedly the above washing step for three times or more until the supernatant was clear. Then they were dried at room temperature for 24 hrs. Finally, The product was dried overnight in a vacuum oven at 30 °C for 24 hrs to remove the residual water. A flowchart for the synthesise of micron-sized polymeric toner particles by suspension polymerization is shown in Figure 3.1.

In order to investigate the effect of important parameters on suspension polymerization, a series of experiment was performed by varying the reaction variables as show in Table 3.1. The experimental conditions for these suspension polymerization are summarized in Table 3.2.

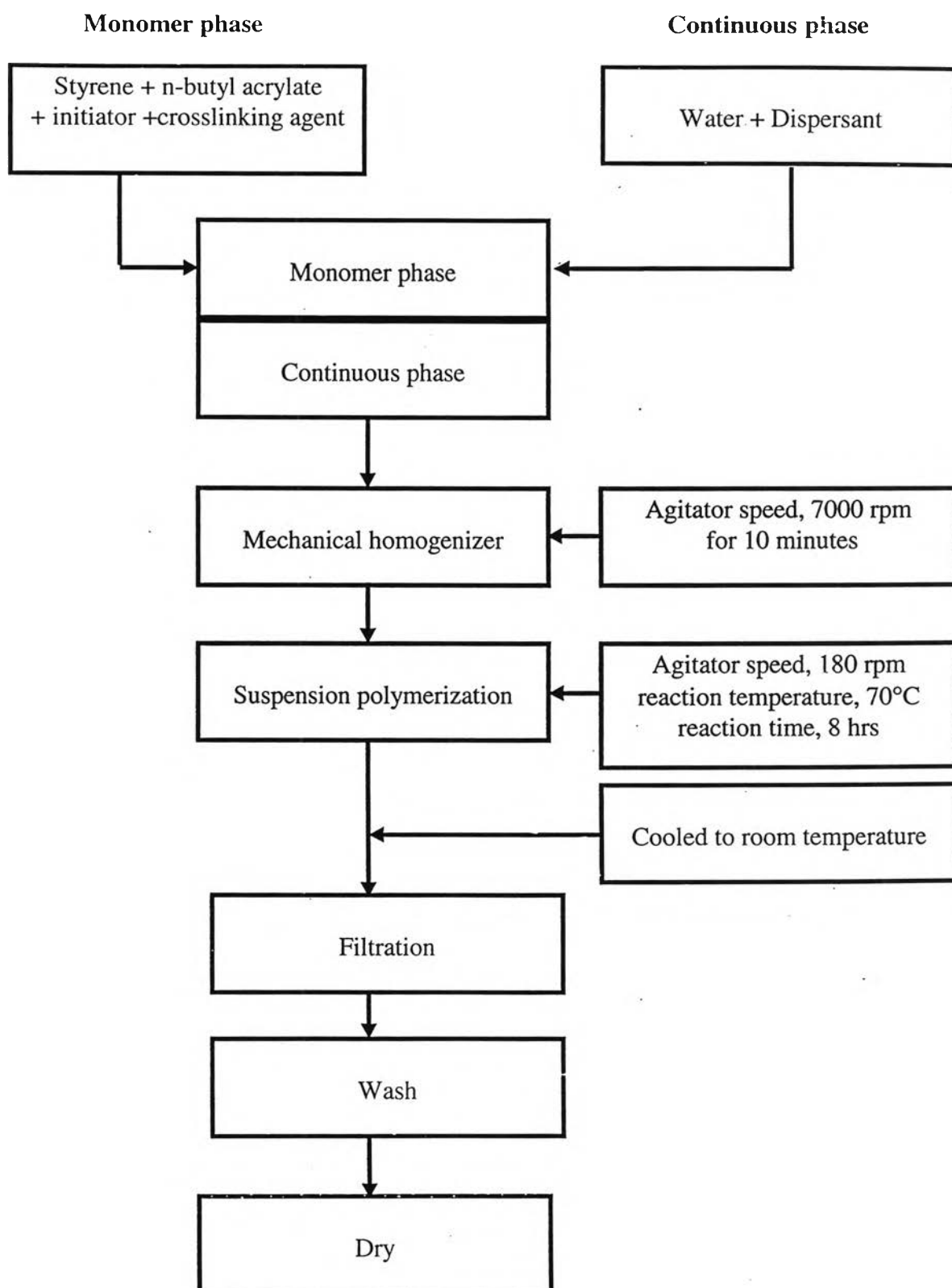


Figure 3.1 Flowchart for synthesise of the micron-sized polymeric toner particles by suspension polymerization

Table 3.1 The reaction parameters investigated in suspension polymerization

Parameter	Standard recipe	Variable condition
Initiator concentration (wt %)	1	0.2, 0.6, 1, 1.4, 2
Dispersant concentration (wt %)	5	1, 3, 5
Momomer ratio (mol %)	80:20	80:20, 85:15, 90:10
Reaction temperature (°C)	70	70, 75, 80, 85
Reaction time (hrs)	8	6, 8, 10,12
Agitation rate (rpm)	180	140,180, 240, 300
Mechanical homogenizing speed (rpm)	7000	7000, 8000, 9000, 10000,12000
Crosslinking agent concentration (wt %)	6	1, 3, 6, 8

3.4.2 Determination of the conversion

Suspension copolymerization of styrene and n-butyl acrylate was repeated by stopping the reactions at the following times : 6, 8, 10 and 12 hours, respectively. The polymeric beads were isolated from the reaction mixture and determined gravimetrically. The conversion is then calculated as below.

$$\% \text{ Conversion} = \frac{\text{weight of the copolymer}}{\text{weight of the initial monomers}} \times 100 \quad (1)$$

3.4.3 Preparation of Micron-Sized Polymerized Toner by Suspension Polymerization

The above experiments will give an appropriate experimental condition for the preparation of polymerized toners by the suspension polymerization method.

To produce an electrophotographic toner, these suspension polymerizations were carried out essentially were the similar technique as in Section 3.4.1 by following the standard recipe shown in Table 1. The charge control agent and carbon black, which is used as a colorant are dispersed in the aqueous phase by shearing it at a high speed of 3,000 rpm for 3 minutes using the mechanical homogenizer (T.K. ROBO MICS ; TOKUSHU KIKI KOGYO CO., Ltd.) and then the whole pigments were added to the mixture of dispersed phase. The resulting mixture was stirred by a mechanical homogenizer again at a constant speed of 7,000 rpm for 10 minutes. The homogeneous mixture was transferred into a four-necked glass reactor. The reaction

was then allowed to polymerize for 8 hrs. Then the effects of carbon black on various physical properties of polymerized toner were investigated.

3.4.3.1 The effect of carbon black

Suspension polymerization of polymerized toner was carried out by including the carbon black contents of 1, 3, 5, and 7 % by weight of monomer. The physical properties of carbon black used is presented in Table 3.2

Table 3.2 Properties of carbon blacks

Carbon black	Particle size (nm)	PH	Surface area ($\text{m}^2 \text{g}^{-1}$)
Printex 60	21	10	115

A flowchart for the preparation of micron-sized polymerized toner by suspension polymerization is shown in Figure 3.2

3.4.3.2 The effect of charge control agent

Suspension polymerization of polymerized toner was carried out by including the charge control agent concentrations of 1, 2, and 4 % by weight of monomer.

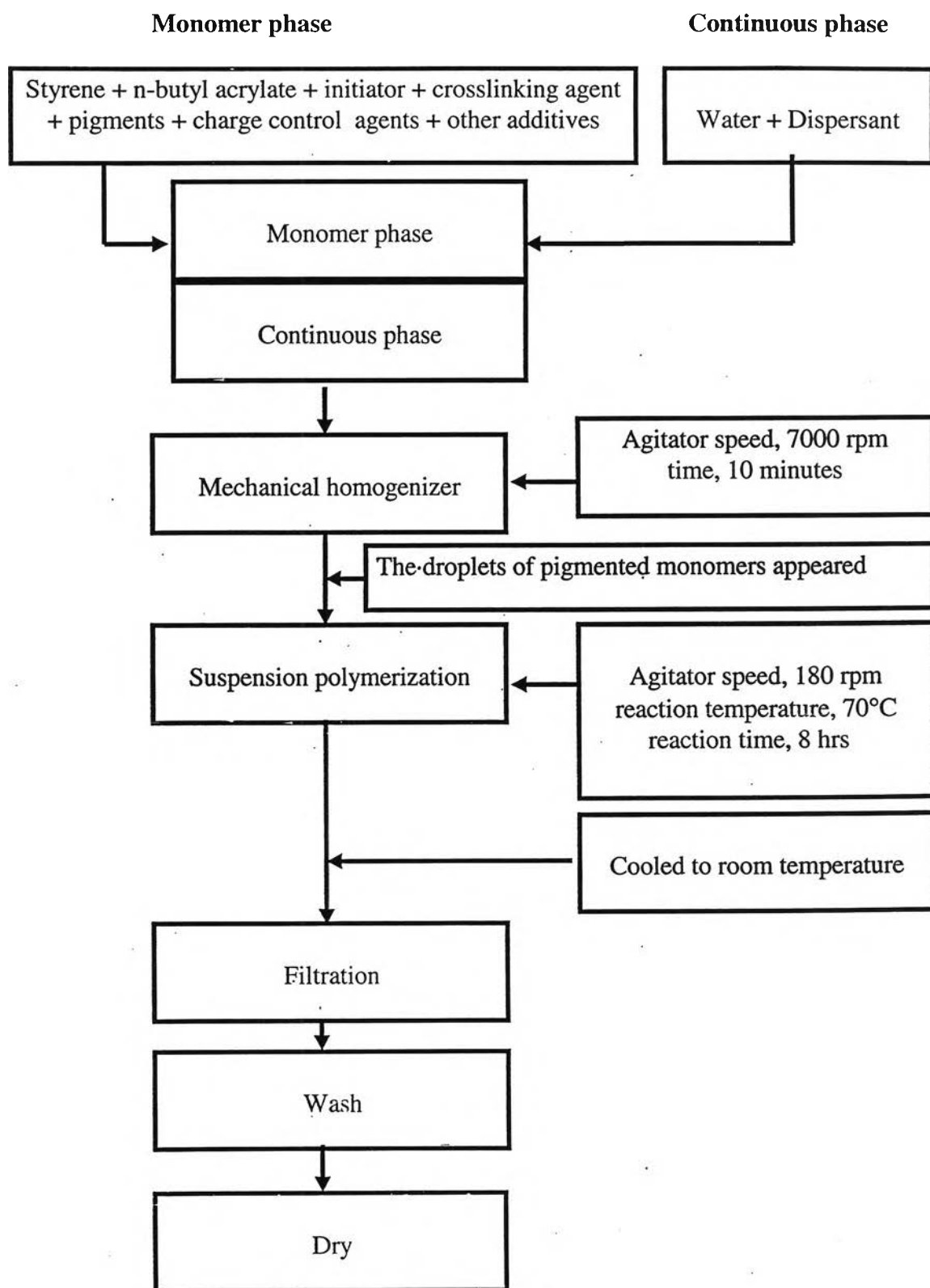


Figure 3.2 Flowchart for the preparation of micron-sized polymerized toners by suspension polymerization

3.5 Triboelectrification measurements

3.5.1 Measurement of charging properties of the rotating roller mechanism

A shaker (IKA: MS 1 Mini-shaker) was used for mixing the polymerized toner and carrier. The shaker rotates a mixing cell with an eccentric radius of 2.5 mm. The rotation speed was set at 1000 rpm. The toner concentration is 3 wt%, the mixing cell used is a glass bottle (inside diameter 24 mm). The q/m measurements were carried out in an approximately 0.12 gram sample, which result was taken from the developer at 30, 60, 90, 120, 240, 360, 720 seconds. The toner charge is measured by a blow-off method. The mixture of toner and carrier is thinly layered on the metal mesh #500 (500 apertures/inch) which is locked in a cylindrical Faraday cage. Using a vacuum cleaner to suction the carrier from the back of the mesh. The toner is removed from the carrier and forced to exit the cage. The carrier is retained in the cage by the screen. The mass lost and the resultant charge on the Faraday cage are measured, and thus the average charge-to-mass ratio (q/m) of the mixture is measured.

3.6 Evaluation of print quality

3.6.1 Printing experiment

The resulting polymerized toner from the section 3.4.3 was poured into a developing unit of the OKI 400 micro line CL Printer. One type of plain paper sheets and the appropriate toner condition were printed with a test form, which was produced by the fifth version Aldus Pagemaker program. Ten plain paper sheets were printed by the same toner. Each sheet consisted of "A to Z" characters, different percent halftones of 20, 40, 60, and 100, and the lines with a size of 0.5 points. The print-outs were measured for solid density and background density. The densities were measured by a reflection densitometer, which was calibrated with black and white tiles; and the background density was measured by a null density mode of the reflection densitometer, which was calibrated to be zero on the same type of paper surface.

3.7 Characterization

3.7.1 Particle Characterization

Particle diameters and particle size distribution of the copolymer particles were measured using a scanning electron microscopy (SEM). The particles from a diluted aqueous dispersion were deposited onto a glass cover-slip glued to an aluminium stud. They were dried under vacuum, and sputter coated with 15 nm gold at the intensity of 15.0 kV under various magnifications.

The number average diameter (d_n) and weight average diameter (d_w) of the polymer particles were determined by measuring 50-100 particles (N) on the electron micrograph to calculate their diameters from the following equations.

$$\bar{d}_n = \frac{\sum_{i=1}^N d_i}{N} \quad (2)$$

$$\bar{d}_w = \frac{\sum_{i=1}^N d_i^4}{\sum_{i=1}^N d_i^3} \quad (3)$$

The polydispersity index (PDI), the coefficient of variation (CV), and the standard deviation (σ), are defined as:

$$PDI = \frac{\bar{d}_w}{\bar{d}_n} \quad (4)$$

$$CV = \frac{\left[\frac{\sum_{i=1}^N (d_i - \bar{d}_n)^2}{N - 1} \right]^{\frac{1}{2}}}{\bar{d}_n} \times 100 \quad (5)$$

$$\sigma = \frac{CV \cdot \bar{D}_n}{100} \quad (6)$$

3.7.2 Determination of Average Molecular Weights and Molecular Weight Distribution of Styrene and n-Butyl Acrylate Copolymer

The average molecular weights and molecular weight distribution (MWD) of the copolymer were measured by using a Gel Permeation Chromatography (GPC) (LC-10AD, CTO-10AC, C-R7A plus (Shimadzu) with an ultraviolet-visible detector, and a pair of Showa Denko columns (Shodex GPC K-806 M; 300 mm × 8 mm I.D. ; packing with styrene-divinylbenzene gels having the number of theoretical plates of 17,000). The HPLC grade chloroform was used as an eluent at a flow rate of 1.0 cm³ min⁻¹ and the working temperature at 25 °C.

The calibration curve of the molecular weight versus elution volume was prepared using standard polystyrenes (Shodex standard S-66.0 with molecular weights of 560,000, 156,000, 66,000, 2,950, respectively), and was used for determination of \bar{M}_n and \bar{M}_w of the polymers. Polystyrene standards of 0.05 % each in chloroform (HPLC grade) were prepared and the injection volume, 70 μ l of each standard was injected. For each samples, 0.05 % solution of dried polymer sample was prepared in chloroform (HPLC grade), then filtered, 70 μ l of the filtered polymer solution was then injected into the GPC for analysis.

3.7.3 Determination of the Thermal Property

Thermal behavior of the copolymer was measured by differential scanning calorimeter (DSC) to obtain the glass transition temperature (T_g). The sample with 10-20 mg was put in an aluminium pan and sealed with a cover lid. The measurements were carried out over a temperature range of 0 to 150 °C with a heating rate of 20°C min⁻¹ under nitrogen atmosphere.