

CHAPTER III

EXPERIMENTAL SECTION

3.1 General Material Handling

Because the products were very moisture and air sensitive, all reactions were run under inert atmosphere (N_2) with the careful exclusion of moisture and air. All solvents were dried by distillation using standard methods and were stored in bottle over molecular sieves. The glassware used for this experiment was oven dried at $120^\circ C$ prior to use.

UHP grade nitrogen; 99.99% purity was supplied from Thai Industrial Gases Public Company Limited (TIG). Aluminum hydroxide hydrate $[Al(OH)_3 \cdot xH_2O]$ was purchased from Sigma Chemical Co. Inc. (USA) and used as received. It contained 54.4% Al_2O_3 content by TGA. Ethylene glycol (EG), used as solvent, was obtained from Farmitalia CarloErba (Barcelona) and distilled under N_2 atmosphere before use. Methanol and acetonitrile were purchased from J.T. Baker Inc. (Phillipsburg, USA) and purified by standard techniques. Methanol was distilled from magnesium metal activated with iodine, while acetonitrile was distilled from calcium hydride powder. Triethanolamine (TEA) was purchased from E. Merck (Germany) and used as received. Triethylenetetramine (TETA), base catalyst, was obtained from Union Carbide Thailand Limited (Bangkok, Thailand) and purified by distillation under vacuum (10^{-2} torr) at $120^\circ C$ before use. Both TEA and TETA were purged and stored under N_2 to keep them water and air free.

All glassware was cleaned by soaking in a NaOH/*i*PrOH cleaning solution bath, followed by washing, rinsing with water and finally drying in oven at 120°C prior to use.

3.2 Instrumentation/ Characterization

3.2.1 Thermogravimetric Analysis (TGA)

Thermograms were determined using thermogravimetric analyzer from Netzsch TGA 200 to obtain the alumina content in aluminum hydroxide hydrate and decomposition profiles of products. Approximately 5-20 mg of samples were loaded in a platinum pan and heated from room temperature to 950°C with a heating rate of 10°C/min. The experiments were carried out under N₂/O₂ atmosphere with flow rate of 15 ml/min, and the balance flow set at 40 ml/min.

3.2.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were obtained on a Bio-Rad FT-45A fourier transform infrared spectrometer with 64 scans with a resolution of $\pm 4 \text{ cm}^{-1}$. Samples were ground with oven dried optical grade KBr (1:20 Sample:KBr) commercially available from Carlo Erba Reagent. The KBr was pressed hydraulically into pellet and quickly taken to the FT-IR chamber. Pure KBr pellet was used as background. The sample chamber was flushed for 10 minutes with dry N₂ to remove physisorbed CO₂ before initiating data acquisition.

3.2.3 Capillary Viscometric Instrument

(A) Ubbelohde Viscometer

Cannon-Fenske routine viscometer was used to measure the viscosity of the sample solutions at 30°C. It was supplied from Tecnico. The size was chosen to cover the suitable efflux time of each solution. The specification is shown below:

Size 100, no. 7954, K (by manufacture) = 0.0169 cSt/sec
viscosity range: 3 to 15 cSt

(B) Viscometer Thermostat and Bath

The digital thermostat model DT-2 with temperature stability $\pm 0.005^\circ\text{C}$ and effective circulation system from Heto, Denmark was used to control temperature at 30 °C.

Transparent liquid bath was modified to contain water, and covered by glassfiber and aluminum foil to maintain a constant temperature.

(C) Timing Device

A stop watch was used in this experiment to provide the time of flowing of sample solutions with a resolution of ± 0.001 second.

3.2.4 Dynamic Light Scattering

Dynamic light scattering or photon correlation spectroscopy instrument, Malvern Model series 4700 is from Malvern Instruments Ltd., was used to measure the diffusion of polymer chain. The main elements of the system 4700 are shown in figure 3.1. The system has up to eight separate units: computer (NEC 16i), (PCS 100) spectrometer, (K7032-ES) correlator, (PCS8) temperature controller/power supply, (PCS7) stepper motor controller, (RR98) pump/filter unit, laser power supply, and printer.

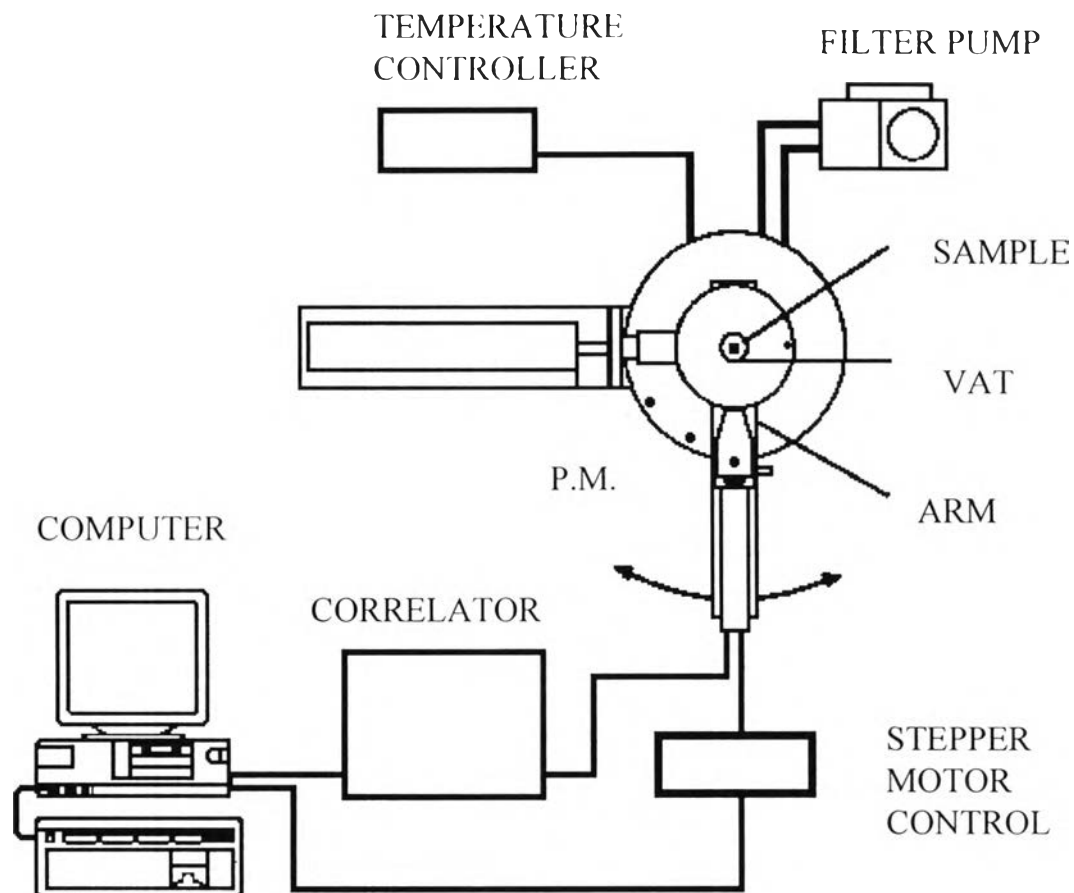


Figure 3.1 The Dynamic Light Scattering (Malvern Model 4700).

Monochromatic light emitted by the laser is focused onto the sample cell, which is held in a glass vat filled with liquid. The beam enters and leaves the vat through flat optical quality windows. The liquid filling the vat has a refractive index close to that of quartz, to reduce flare at the interfaces with the vat and sample cell. The liquid in the vat also couples the sample thermally to the temperature sensor and heating/cooling elements that keep the vat contents to within 0.1 °C of the temperature set on the temperature controller (PSC8). The sample is held in a small cell usually made of quartz.

Light scattering by the sample is collected by an optical system, so call “Pusey optical”, after its inventor, and sensed by a photomultiplier (P.M.), which is sensitive enough to count individual photons. The P.M. is mounted an arm which can be controlled by the stepper motor controller, which is connected in turn to the computer. Using this system any scattering angle between 10 and 150° can be set from computer software. The digital signal coming from the P.M. is processed by the correlator (K7032-ES) and the passed to the computer for final analysis and display.

3.2.5 Filtering Accessories

A buschner funnel with paper filter no.5 from Whatman was used to remove the dusts and large sized contamination in prefiltering. For microfiltering, the 47 mm. diameter of Millipore sintered glass filter with a membrane filter of pore size 0.2 μm (WCN type from Milipore) was chosen to eliminate the micro-dust and impurities. Before the sample solution was filled into the light scattering cell, the sample solution was cleaned from dusts using a micro-syring filter with a membrane filter of pore size 0.22 μm .

3.2.6 Centrifuge

The high speed refrigerated centrifuge model PM180R from ALC International Co., Ltd., was used to clarification of dust. The centrifuge has a maximum speed of 10,000 rpm.

3.3 Experiments

The experimental section is separated into two parts. The first part describes the one step synthesis of alumatrane complexes directly from $\text{Al}(\text{OH})_3$ and triethanolamine by:

- variation in mol ratio of TEA and fixing mol ratio of $\text{Al}(\text{OH})_3$, reaction time, and reaction temperature,
- variation in reaction temperature and fixing mol ratio of TEA, and $\text{Al}(\text{OH})_3$, and reaction time,
- variation in reaction time and fixing mol ratio of TEA, and $\text{Al}(\text{OH})_3$, and reaction temperature,
- variation in mol ratio of TETA and fixing mol ratio of $\text{Al}(\text{OH})_3$ and TEA, reaction time, and reaction temperature.

The other describes the characterization of products by viscosity and light scattering measurements.

3.3.1 Synthesis of Alumatrane Complexes by variations of TEA concentration, reaction temperature, reaction time, and TETA concentration

3.3.1.1 Effect of TEA Concentration. The reactions were performed by fixing the amount of $\text{Al}(\text{OH})_3$ (54.4% Al_2O_3 by TGA) at 7.88 g (100 mmol). The amount of added TEA was varied from 0-17.8 g (0-100 mmol). The reaction was started by mixing TEA and $\text{Al}(\text{OH})_3$, and 100 ml of ethylene glycol into a 250 ml two-necked round bottomed flask. The solution was stirred and heated to 200°C using oil bath, under N_2 atmosphere to distill off by product, H_2O , and EG. The reaction time was measured beginning with the first drop of distillate. Fresh EG in the same amount as distilled off was added to maintain the total volume until the mixture was distilled for 3 hours.

After letting the reaction mixture stand without stirring overnight, white solid precipitated out. The precipitate was stirred with dried methanol overnight to extract remaining product from unreacted aluminum hydroxide. The unreacted aluminum hydroxide was then filtered off and washed with 2*20 ml of methanol. The remaining EG was removed by high vacuum (10^{-2} torr) distillation at 120°C for 3 hours. Product was purified by precipitation with 2-5% methanol in acetonitrile, depending on the amount of the polymer-mixture. The precipitated products were then characterized by TGA, FTIR, viscosity measurement, and light scattering measurement.

3.3.1.2 Effect of Reaction Temperature. Experiments was conducted by fixing the amounts of TEA and Al(OH)₃ at 7.46 g (50 mmol) and 7.88 g (100 mmol), respectively. The reaction temperature was varied from 140°C to 200°C. Each reaction temperature was run by fixing the reaction time at 3 hours, and followed the procedure as described in 3.3.1.1.

3.3.1.3 Effect of Reaction Time. Amounts of TEA and Al(OH)₃ were fixed at 7.46 g (50 mmol) and 7.88 g (100 mmol), respectively, while the reaction time was varied from 1-6 hours. The reaction temperature was fixed at 200°C, and the procedure was followed as described in 3.3.1.1.

3.3.1.4 Effect of TETA Concentration. The reactions were run by fixing the amounts of Al(OH)₃ and TEA at 7.88 g (100 mmol) and 7.46 g (50 mmol), respectively. The concentration of TETA was varied from 0-43.87 g (300 mmol). The reaction time and temperature were fixed at 3 hours and 200°C, respectively. The procedure was repeated as procedure described in 3.3.1.1.

3.3.2 Viscosity Measurement

Solution viscosity is basically a measure of the size or extension in space of polymer molecules. It is empirically related to molecular weight for linear polymers, the simplicity of the measurement and the usefulness of the

viscosity-molecular weight correlation are so great that viscosity measurement constitutes an extremely valuable tool for the molecular characterization of polymers.

(A) Measurement of solution viscosity

Measurements of solution viscosity are usually made by comparing the efflux time, t , required for a specified volume of polymer solution to flow through a capillary tube with the corresponding efflux time, t_0 , of the solvent.

The viscosity of a liquid flowing through a capillary is given by *Poiseuille's equation* [G.B. Howard and W.M. Jimmy, (1991)]

$$t = 8V\eta l / \rho g h r^4 \pi, \quad (3.1)$$

which can be simplified to

$$\eta = A t \rho. \quad (3.2)$$

A is a constant for a particular viscometer. Poiseuille's equation does not take into account the energy dissipated in imparting kinetic energy to the liquid, but it is satisfactory for most viscometers provided that the flow times exceed about 180s

In macromolecular chemistry, the relative viscosity η_r is often measured. The relative viscosity is the ratio of the viscosity of solution to that of the solvent

$$\eta_r = \eta / \eta_0 = \rho t / \rho_0 t_0 \cong t / t_0, \quad (3.3)$$

where η_0 is the viscosity of the pure solvent, t_0 is solvent flow time and ρ_0 is the solvent density.

The specific viscosity η_{sp} is obtained from the relative viscosity by subtracting one unit from η_r

$$\eta_{sp} = \eta_r - 1 = (t - t_0) / t_0. \quad (3.4)$$

The specific viscosity is a measurement of the increase in viscosity brought about by the addition of polymer. The ratio η_{sp}/c is a measure of the specific capacity of the polymer to increase the relative viscosity and, in the limit of infinite dilution, is known as the intrinsic viscosity, $[\eta]$,

$$\text{Huggins Equation} \quad \eta_{sp}/c = [\eta] + k'[\eta]^2c, \quad (3.5)$$

$$\text{Kraemer Equation} \quad \ln \eta_r/c = [\eta] + k''[\eta]^2c. \quad (3.6)$$

Where k' is referred to as the “Huggins Coefficient”. For polymer in good solvents, k' often has a value of about 1/3, while values of 0.5-1 are typically found in poor solvent quality. k'' is known as the Kraemer coefficient. For polymers in good solvents, k'' is negative in sign and smaller in magnitude than k' and $k' - k'' = 0.5$. The preferred procedure is to plot both equations and to take the mutual intercept as $[\eta]$ as shown in Figure 3.2.

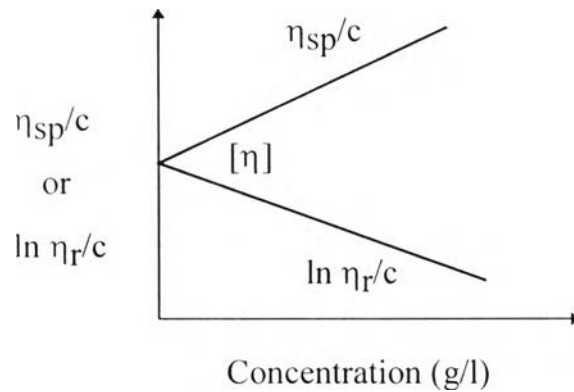


Figure 3.2 Typical plot of η_{sp}/c and $\ln \eta_r/c$ versus c . The mutual intercept is $[\eta]$.

The kinematic viscosity, ν , is obtained from the measured efflux time, t , multiple with the calibration constant, k , of each viscometer

$$\nu = kt, \quad (3.7)$$

where k = the calibration constant (centistokes/second),

t = the efflux time (second).

The basis for relating $[\eta]$ to the structure of a dissolved polymer was laid by Einstein [D.campbell and J.R. White (1989)] Who showed for spherical particles that the solution, η_s by

$$\eta = \eta_0 (1 + 2.5\phi), \quad (3.8)$$

where φ is the volume fraction. The result holds for a dispersion of non-hydrodynamically interacting particles. The volume fraction is given by

$$\varphi = (C/M)N_A V_h, \quad (3.9)$$

where V_h is the hydrodynamic volume, and rearranging, we obtain

$$\eta_{sp}/C = 2.5N_A V_h / M, \quad (3.10)$$

where $\eta_{sp} = (\eta / \eta_0 - 1) = \eta_r - 1$ is the specific viscosity and η_r is the relative viscosity.

From Equation (3.10) we need to extrapolate to zero concentration to correct for hydrodynamic interactions between particles

$$\lim_{c=0} (\eta_{sp} / C) = [\eta] = 2.5N_A V_h / M. \quad (3.11)$$

The quantity on the left hand side of Equation (3.11) is called intrinsic viscosity, and clearly it is dependent only on particle structure. For compact spheres of density ρ , $[\eta]$ is small

$$[\eta] = 2.5 / \rho. \quad (3.12)$$

For polymer molecules which expand and entrap solvent molecules, the hydrodynamic volume is very large and generally a strong function of molecular weight.

$$V_h \sim M^a, \quad (3.13)$$

V_h is the equivalent hydrodynamic sphere. For flexible molecules, the *Flory-fox equation* relates $[\eta]$ to the radius of gyration

$$[\eta] = \phi \langle R_g^2 \rangle^{3/2} / M. \quad (3.14)$$

Where $\phi = 10/3 [R_h / \langle R_g^2 \rangle^{1/2}]^3 / M$ is a phenomenological constant. Originally, it was anticipated that ϕ might be a universal constant. Subsequently, it has emerged that ϕ decreases slightly with chain expansion [*D. Campbell and J.R. White (1989)*].

(B) Sample preparation

To prepare the stock solution of polymer, alumatrane complexes were weighed out by 4-digit weight balances and then dissolved in the ethylene glycol. The solutions were gently agitated by using a magnetic stirrer for at least 3 days for complete dissolution and allowed to settle overnight to get an equilibrium condition.

The stock solutions were then filtered through the paper filter no.5 from Whatman to remove dust particles. The stock solution was diluted by ethylene glycol.

(C) Conditions

The measurement temperature was fixed at 30 °C which was controlled by a thermostat. It's necessary to filter the solution through the paper filter no.5 from Whatman before putting into the viscometer because dusty particles can affect the flow time. The solutions were allowed in water bath for 15-20 minutes to achieve the thermal equilibrium before the measurement.

3.3.3 Dynamic Light Scattering Measurement

Dynamic Light Scattering or photon correlation spectroscopy (PCS) measurement is one of the most popular methods for determining molecular physical properties, such as the diffusion coefficient and the hydrodynamic radius [*Barth, (1991)*].

Dynamic Light Scattering is related to the frequency distribution of the light scattered from thermally excited density fluctuations due to polymer molecules. The scattering particles in a sample of interest are usually in a relatively narrow size range. Particles move with similar velocities, although in the random direction. Because of their similar motions, the scatter light from the particles is said to be correlated in time [*D. Campbell and J.R. White (1989)*].

$$g(\tau) = \lim_{t_0} (1/T) \int_{t_0}^{t_0+T} A(t)B(t-\tau) dt, \quad (3.15)$$

where τ is a delay time, t_0 the starting time and T the averaging time. If B is a delayed form of A , then the relation is called "autocorrelation".

In the homodyne mode, the intensity autocorrelation function is obtained, and its normalized form is defined by

$$g_2(\tau) = \langle I_S(0)I_S(\tau) \rangle / \langle I_S \rangle^2. \quad (3.16)$$

The intensity autocorrelation function is related to the normalized electric field autocorrelation function [$g_1(\tau)$],

$$g_1(\tau) = \langle E_S(0)E_S^*(\tau) \rangle / \langle I_S \rangle, \quad (3.17)$$

through the Siegert relation,

$$g_2(\tau) = A[1 + B(g_1(\tau))^2], \quad (3.18)$$

where the constant A measures the baseline and B measures the degree of coherence achieved in a particular optical arrangement.

The correlation function $g_1(\tau)$ is a simple exponentially decaying as function of τ for a monodisperse solution system:

$$g_1(\tau) = \exp(-\Gamma\tau) \quad (3.19)$$

Γ is the decay constant which can be expressed by

$$\Gamma = 1/T_q = Dq^2, \quad (3.20)$$

where T_q = the relaxation time which is obtained from the experiment data of $g_1(\tau)$,

q = the scattering wave vector = $(4\pi n/\lambda) \sin(\theta/2)$,

D = diffusion defined in the limit of scattering vector q as D equal to $(\Gamma/q^2)_{q \rightarrow 0}$,

n = the index of refraction of the fluid,

λ = the wavelength of incident light, and

θ = the angle of observation.

R_h is evaluated from the diffusion coefficient at infinite dilution, D_0 ,

$$R_h = k_B T / 6\pi\eta_s D_0. \quad (3.21)$$

In viscosity measurement and dynamic light scattering measurements and analysis, concentration regime can be divided in 2 regimes; the dilute and semidilute regimes.

In the dilute regime, the individual polymer coils remain separated in the solution. Presumably the hydrodynamic interaction is minimal. If the polymer concentration is above (C^*), the coils start to overlap; the regime is called the “semidilute” concentration regime. For high molecular weight polymers, C^* can be determined from [*Brown, (1993)*],

$$C^* = 3M/4\pi N_A R_g^3 \cong M/ N_A R_g^3 \cong [\eta]^{-1}, \quad (3.22)$$

where M is the molecular weight, N_A is the Avogadro constant, R_g is the radius of gyration, and $[\eta]$ is the intrinsic viscosity.

Actually, the polymer may have more than one component or process in the system mixtures of particles or polymers of different size, polydispersity combination of various diffusion processes, and internal modes of polymers. So the cumulant method is often employed to fit a polynomial. Cumulant refers to the full measured correlation function being represented by a theoretically infinite series, each term representing a statical moment of successive by high order. The cumulant expansion can be expressed by,

$$\ln g_1(\tau) = -K_1\tau + (1/2)! (K_2)\tau^2 + \dots, \quad (3.23)$$

$$K_1(q) = \Sigma w_i \Gamma_i = \bar{\Gamma}, \quad (3.24)$$

where w_i is the weight fraction of particles characterized by the relaxation rate $[\Gamma_i = D_i/q^2]$. The first cumulant (K_1) represents the mean relaxation rate ($\bar{\Gamma}$).

However, most deviations from the single exponential behavior are mainly due to interactions. Therefore the first few cumulants are sufficient for measurement. The first cumulant may be used to define an “apparent coefficient”, D_{app} .

$$D_{app} = K_1/q^2 \quad (3.25)$$

For a polydisperse system, the analysis can proceed via the method of cumulants.

$$g_1(\tau) = A \exp(-\bar{\Gamma}\tau + (1/2!)(\mu_2/\bar{\Gamma})(-\bar{\Gamma}\tau)^2 - (1/3!)(\mu_3/\bar{\Gamma})(-\bar{\Gamma}\tau)^3 + \dots), \quad (3.26)$$

$$\ln g_1(\tau) = -\bar{\Gamma}\tau + (1/2!)(\mu_2/\bar{\Gamma})(-\bar{\Gamma}\tau)^2 - (1/3!)(\mu_3/\bar{\Gamma})(-\bar{\Gamma}\tau)^3 + \dots, \quad (3.27)$$

where

$$\bar{\Gamma} = \int_0^\alpha Q(\Gamma)d\Gamma = \langle D \rangle/q^2, \quad (3.28)$$

$$\mu_n = \int (\Gamma - \bar{\Gamma})^n Q(\Gamma)d\Gamma, \quad (3.29)$$

τ is the correlation time delay, $g(\tau)$ is the normalized correlation function, and $Q(\Gamma)$ is the distribution of Γ values.

In the present measurement and the data analysis, the following conditions were chosen. (1) the second order (first cumulant) fit of monomodal mode which means the second term of the equation and (2) a suitable sample time.

$$\log [(g_2(\tau)/B) - 1] = a + b\tau + c\tau^2 + \dots \quad (3.30)$$

Different polymer solutions having different suitable sample time values were chosen from measurement of relaxation time against sample time. A point where relaxation time was independent of the sample time was used for each polymer sample solution.