CHAPTER II
EXPERIMENTAL SECTION

2.1 Materials

Since the starting materials and the products are moisture and air sensitive. all starting materials and apparatus were carried out with careful exclusion of air. Reactions were run under nitrogen atmosphere. All glassware were soaked in a base bath (NaOH/iPrOH/H_2O), washed, rinsed with water, and finally dried at $110°$-$120°C$ in the oven before use.

2.1.1 Starting Materials

Aluminum hydroxide hydrate [Al(OH)$_3$.xH_2O] was purchased from Sigma Chemical Co. Inc.(USA) and used as received. It contains 54.4% Al_2O_3 content by TGA. Triisopropanolamine (TIS) was purchased from Fluka Chemika-Biochemika (Switzerland) and used as received. Triethylene-tetramine (TETA) was obtained from Union Carbide Thailand Limited (Bangkok, Thailand) and distilled under vacuum (10^{-2} torr) at $120°C$. TETA was used as catalyst in the reaction.

2.1.2 Solvents

Methanol and acetronitrile were purchased from J.T.Baker Inc. (Phillipburg. USA) and purified by standard techniques [Vogel, (1978)]. Methanol was distilled over magnesium metal activated with iodine. Acetronitrile was distilled over calcium hydride powder. All dried solvents

were purified and stored under N_2 in glass bottles containing molecular sieves. Ethylene glycol (EG), used as solvent in the reaction, in the viscosity measurement, and dynamic light scattering, was purchased from Farmitalia Carlo Erba (Barcelona) and purified by fractional distillation at 200°C, under nitrogen atmosphere before use.

2.1.3 Gas

UHP grade nitrogen; 99.99 % purity, was purchased from Thai Industrial Gases Public Company Limited (TIG).

2.2 Instrumentation

2.2.1 Thermal Analysis

Thermogravimetric analysis (TGA) was carried out using a Netzsch Ger tebue BmbH Thermal analysis TG 200 (Germany) to establish the alumina content in aluminum hydroxide hydrate and the decomposition profiles of products. Samples (approximately 10-12 mg) were placed into an alumina crucible and heated in flowing N_2 and O_2 (10ml/min). The heating range was from room temperature to 950°C with the heating rate of 10°C/min.

2.2.2 Fourier Transform Infrared Spectrometer (FTIR)

The Bio-Rad FT-45A Fourier Transform Infrared (FTIR) spectrometer was used to obtain the functional groups of the products. The FTIR experiment was done in absorption mode with a resolution of 8 cm^{-1} and 16 numbers of scan per sample. Samples were prepared by mixing with KBr (1:20 sample : KBr) followed by hydraulically pressing into a pellet and placed in the FTIR sample chamber. The sample chamber was flushed for 10

minutes with dry N_2 to remove CO_2 before collecting the data.

2.2.3 Nuclear Magnetic Spectroscopy (NMR)

^{1}H-NMR was performed on a Brüker 200 MHz spectrometer at room temperature. The samples were pulsed at 200 MHz for proton NMR with a spin rate of 21 rpm. A relaxation delay time was 1 sec with a sweep width of 3105 Hz or about 15 rpm, using a pulse of 45 μsec. Samples were dissolved in deuterated methanol (CD_3OD) and tetramethylsilane (TMS) was used as the internal reference for chemical shift measurement.

2.2.4 Capillary Viscometer

a) Ubbelohde Viscometer

The Cannon-Fenske routine viscometer, no. 7954; capillary size 100, was used to measure the viscosity of the sample solutions at 30°C. It was supplied from Tecnico.

The viscometer has a constant K (by manufacturer) = 0.0169 Cst/sec and viscosity range 3 to 15 Cst.

b) Thermostatic Water Bath

The digital thermostat model DT-2 from Heto, Denmark was used to control the temperature at 30°C (± 0.02°C). Homemade liquid bath was used to contain water. It was modified to have a transparent window. The other sides of bath were made from stainless steel and covered by glass fiber and aluminum foil to maintain a constant temperature.

c) Timing Device

A stop watch was used to provide the flow time of the sample solutions with an accuracy of ± 0.01 second.

2.2.5 Light Scattering Instrument

The light scattering apparatus (model series 4700) is from Malvern Instruments Ltd.. The optical light source is Argon-Ion with the wavelength of 514.5 nm. The system consists of 8 units, a computer (NEC 16i), a spectrometer (PCS100), a correlator (K7032-S), a temperature controller/power supplier (PCS8), a stepper moter controller (PCS7), a pump/filter unit (RR98), a laser power supply (a-Spectra-Physics), and a printer. The DLS apparatus in this work is shown in figure 2.1

Figure 2.1 The schematic diagram of dynamic light scattering instrument (Malvern 4700).

2.2. Filtering Accessories

The 90 mm diameter of Büchner funnel with Whatmann filter paper no.5 (pore size 2.5 μm) was used to eliminate dust and large contamination in stock solutions and pure solvent, EG, before measuring with the capillary viscometer. For microfiltering, the 47 mm, diameter of Millipore sintered glass filter with a membrane filter of pore size 0.5 μm (FH type) was used to eliminate the micro-dust and impurities. Before the sample solution was filled into the light scattering cell, it was cleaned from dusts using a micro-syringe filter with a membrane filter of pore size 0.22 μm.

2.2.7 Centrifuge

The high speed refrigerated centrifuge, model PM180R from ALC International Co. Ltd., was used to clarify dust in sample solution. The centrifuge has a maximum speed of 10000 rpm.

2.3 Experiments

The experimental section is divided into three parts. The first part describes the synthetic procedure of alumatrane complexes by varying the reaction conditions, namely, the mole ratio of TIS, reaction time, reaction temperature, and TETA concentrations. The second one describes the characterization of the products by the viscosity measurement. In the last section, we focus on light scattering measurement.

2.3.1 Synthesis of Alumatrane Complexes

2.3.1.1 Variation of Al(OH)3 : TIS mole ratio   After adding 9.375g (105 mmol) of aluminum hydroxide (54.4 % Al_2O_3 content by TGA) into a 250 ml two necked round bottomed flask, the amount of

triisopropanolamine which was varied from 0-24.0168g (0-125 mmol), and 100 ml of EG were added. The reaction mixture was stirred and heated under N_2 in an oil bath controlled temperature by heater. The temperature of the oil bath was controlled at 200±1°C, while the vapor temperature in distillation system was still kept at 110±5°C under N_2 atmosphere. The water formed during the reaction was distilled off along with EG. The reaction was considered to start. Fresh EG in the same amount as the distillate was added to maintain the total reaction volume. After 3 hours of heating, the mixture was slowly cooled down to room temperature without stirring overnight, white solid of unreacted alumina precipitated out. Then the unreacted $Al(OH)_3$ was filtered off, and stirred with 50*2 ml methanol. The remaining product was separated from the methanol by evaporating the solvent in rota-evapolator at 40°C, followed by removing the ethylene glycol by vacuum distillation (10^{-2} torr) at 110±5°C until almost EG was distilled from the product. The product was purified by precipitation with dried acetronitrile, depending on the amount of the polymer mixture. The white precipitated product was then characterized by FT-IR, TGA, ^{1}H-NMR, the capillary viscometer, and dynamic light scattering instrument.

2.3.1.2 Reaction time variation   The amounts of $Al(OH)_3$ and TIS were fixed at 9.375g (105 mmol) and 9.6067g (50 mmol), respectively. The reaction times were varied from 60-240 minutes with increments of 30 minutes. The reaction temperature was controlled at 200±1°C. The procedure was followed as in 2.3.1.1, and experiments were repeated two times.

2.3.1.3 Reaction temperature variation   The experiments were carried out by fixing the amount of $Al(OH)_3$ and TIS at 9.375g (105 mmol) and 9.6067g (50 mmol), respectively. The reaction temperature was varied

from 150° to 220°C and the reaction time was set at 3 hours. The reaction temperature was controlled by a heater and an oil bath. When the temperature of oil bath reached the setting temperature, the reaction flask was set about 5 cm above the oil bath for 10 min. The reaction flask was then immersed into the oil bath at the required temperature.

2.3.1.4 Variation of TETA concentration   The reaction of aluminum hydroxide and TIS in the presence of catalytic amounts of TETA was quite effective. The synthesis procedure was the same as described in 2.3.1.1, except that the added mmol of TETA was varied from 0-150 mmol with the increment of 50 mmol. The experiments were performed by fixing the amount of $Al(OH)_3$ and TIS at 9.375g (105 mmol) and 9.6067g (50 mmol), respectively. The reaction time and temperature were fixed at 3 hours, and 200°C.

2.3.2   Viscosity Measurement

The method widely used for the determination of polymer molecular weights is based on solution viscosity measurements [D.Campbell and J.R.White, (1989)]. It is reasonable to presume that the viscosity of a polymer solution would be dependent both on concentration and on the average molecular size of the sample and hence the molecular weight.

(a) Measurement of solution viscosity

The viscosities of dilute polymer solutions most commonly are measured using capillary viscometer. The feature of the viscometer is that a measuring bulb, with upper and lower etched marks, is attached directly above the capillary tube. The solution is either drawn or forced into the measuring

bulb from a reservoir bulb attached to the bottom of the capillary tube, and the time required for it to flow back between the two etched marks is recorded.

For Cannon-Fenske routine, U-tube viscometer, the pressure head-giving rise to flow depends upon the volume of solution contained in the viscometer, and so it is essential that this volume is exactly the same for each measurement. This normally is achieved after temperature equilibration by carefully adjusting the liquid level to an etched mark just above the reservoir bulb.

Before use, it is essential to ensure that the viscometer is thoroughly clean and that the solvent and solutions are freed from dust by filtration, otherwise incorrect and erratic flow times can be anticipated. The viscometer is placed in a thermostatic water bath with temperature control of $\pm0.01°C$ or better because viscosity generally change rapidly with temperature. After allowing sufficient time for temperature equilibration of the solution, several measurements of flow time are made and should be reproducible to $\pm0.1\%$ when measured visually using a stopwatch.

Under conditions of steady laminar Newtonian flow, the volume V of liquid which flows in time t through a capillary of length l and radius r is related to both the pressure difference P across the capillary and the viscosity η of the liquid by *Poiseuille's equation*

$$V = \pi r^4 Pt / 8\eta l \qquad (2.1)$$

The radial velocity profile corresponding to this equation is parabolic with maximum velocity along the axis of the capillary tube and zero velocity at the wall. During the measurement of flow time, P continuously decreases and normally is given by

$$P = <h> \rho \, \mathbf{g}$$

where $<h>$ is the average pressure head, ρ is the density of the liquid and $\mathbf{g}$ is the acceleration due to gravity. Thus Poiseuillie's equation can be rearranged to give

$$\eta = \pi r^4 <h> \rho \, \mathbf{g} t / 8Vl \qquad (2.2)$$

which has the form

$$\eta = A \rho t \qquad (2.3)$$

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

In certain conditions, absolute measurements of viscosity are not required in dilute solution viscometry since it is only necessary to determine the viscosity of a polymer solution relative to that of the pure solvent. Application of equation (2.3) leads to the following relation for the relative viscosity

$$\eta_r = \eta / \eta_o = \rho t / \rho_o t_o \equiv t / t_o \qquad (2.4)$$

where η_o is the viscosity of the pure solvent, t_o is solvent flow time and ρ_o is the solvent density.

For infinitely dilute solutions the value of η_r approaches unity,

and it is useful to define the specific viscosity η_{sp} as

$$\eta_{sp} = \eta_r - 1 = (t - t_o) / t_o \qquad (2.5)$$

The specific viscosity is a measure 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, $[\eta]$

$$[\eta] = (\eta_{sp}/c)_c \longrightarrow 0 \qquad (2.6)$$

In practice, Huggins equation

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \qquad (2.7)$$

is most commonly employed. From Eq.2.7 a plot of η_{sp}/c versus c will be linear with $[\eta]$ as the intercept. The term k' is derived from the slope of the plot and is commonly referred to as the " Huggins viscosity constant." Actually, k' is not a constant, the value of k' depending on a variety of conditions. The parameter k' has a value of 0.4-0.8 for general good solvent and above 0.8 for theta solvent.

Kraemer proposed an alternate expression for evaluating $[\eta]$, that is,

$$\ln \eta_r /c = [\eta] + k''[\eta]^2 c \qquad (2.8)$$

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 typical plot of η_{sp}/c and $\ln \eta_r /c$ versus c, the mutual intercept is $[\eta]$ as shown in Figure 2.2.
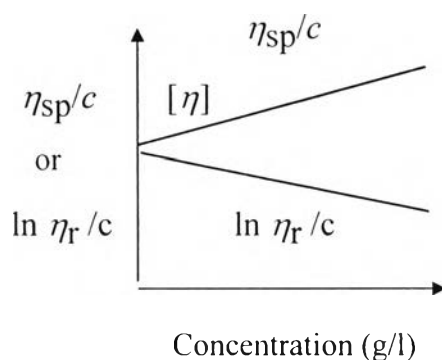

Figure 2.2 The typical plot of η_{sp}/c and $\ln \eta_r /c$ versus concentration.

For spherical particles, true hydrodynamic radius, R_h, and hydrodynamic volume, V_h, can be calculated from $[\eta]$ by using the expression

$$[\eta] = 2.5 N_A V_H/M = 10 N_A \pi R_H^3/3M. \tag{2.9}$$

where N_A is Avogrado's number and M is molecular weight of polymer.

The overlap concentration, c^* can give us approximately the critical concentration between dilute and semidilute regimes which can be defined by

$$c^* = [\eta]^{-1}. \tag{2.10}$$

The highest molecular weight has the lowest c^* that implies it forms an entangled polymer network more easily than the lower molecular weight.

(b) Sample preparation

Preparation of alumatrane complex stock solution

A weighed amount of product was placed in a 100.0 ml volumetric flask. The polymers were allowed to dissolve in distilled ethylene glycol. The solution was magnetically stirred at room temperature for at least 3 days for complete dissolution and allowed to settle overnight to get an equilibrium condition. Then the stock solutions were filtered through Whatman paper filter no.5 to eliminate large dust particles. The stock solutions were stored at room temperature. The alumatrane concentration is expressed in gram per liter.

Preparation of alumatrane solutions

A certain amount of alumatrane stock solutions were diluted with filtered ethylene glycol to the concentration of 1,2,3,4,5 g/l. The dilutions were magnetically stirred at room temperature for 1 day before measurement.

(C) Conditions

The measurement temperature was set at 30°C and controlled by a thermostat. The solutions were immersed in water bath for 15 minutes to reach equilibrium before each measurement. The solution was then drawn up the capillary tube by suction using a hand aspirator until it was above the upper etched mark. The time for a constant volume of the solution to flow between the two etched marks was determined using a stopwatch.

2.3.3 Dynamic Light Scattering Measurement

Dynamic light scattering (also called quasi-elastic light scattering and photon correlation spectroscopy) is concerned with the time behavior of the scattered intensity obtained from a suspension of particles. This approach contrasts with traditional light-scattering techniques that measure the average scattered intensity. Submicrometer-sized particles in suspension exhibit significant random motion because of collision with the molecules of the surrounding liquid medium (Brownian motion). As a result, when a colloidal dispersion is illuminated by light source, the phases of each of the scattered waves (arriving at a detector at a fixed angle) fluctuate randomly in time because of the fluctuations in the positions of the particles that scatter the waves. Because these waves mutually interfere, the net intensity of the scattered light fluctuates randomly in time around a mean value. The DLS technique makes use of the fact that the time dependence of the intensity fluctuations (calculated from the autocorrelation function of the scattered intensity) can be related to the translational diffusion coefficient of the particles, which in turn is related to the particle size through the Stokes-Einstein equation.

(a) Data Analysis

The autocorrelation function $G^{(2)}(t')$ of the scattered light intensity is given by:

$$G^{(2)}(t') = <I(t)I(t+t')>$$

(2.11)

where I(t) is the intensity at time t, and t' is a time delay. The $<\,>$ symbol indicates a running sum of products taken at different times, t. For $t' \longrightarrow \infty$, $G^{(2)}(\infty) = <I(t)>^2$, which is the square of the average scattered intensity, equal to the

base line of the autocorrelation function. The normalized first order autocorrelation function, $g^{(1)}(t')$, can be calculated from the measured function:

$$G^{(2)}(t') = B(\ 1 + \beta|\ g^{(1)}(t')|^2)$$ (2.12)

where B is the base line and β $(0 < \beta < 1)$ is an instrument-related constant.

For system of uniform particle size, $g^{(1)}(t')$ is a simple exponentially decaying function of t':

$$g^{(1)}(t') = \exp(\ -\ \Gamma t')$$ (2.13)

The decay constant Γ is related to the translational diffusion coefficient D_t by:

$$\Gamma = D_t q^2$$ (2.14)

where q is the scattering wave vector, which depends on the wavelength (in vacuum) of the light source (λ_0), the solvent refractive index (n), and the angle of detection, θ:

$$q = 4\pi n \sin(\theta/2) \lambda_0$$ (2.15)

For random diffusion of noninteraction particles, the single-particle diffusion coefficient (D_t) is obtained from equation 2.13-2.15. The mutual diffusion coefficient determined at a finite concentration is characterized by concentration, k_D;

$$D_t = D_o (1 + k_D c_P + \ldots.),$$ (2.16)

where D_o is the mutual diffusion coefficient at infinite dilution and D_t is the value at concentration c. The parameter $k_D > 0$ for general good solvent and $k_D < 0$ for poor solvent. The hydrodynamic radius R_H is obtained from D_t via the Stokes-Einstein equation:

$$R_H = \frac{k_B T}{6\pi\eta D_o} \qquad (2.17)$$

where k_B is the Boltzmann constant, T is the temperature (kelvins), and η is the shear viscosity of the liquid medium.

In the dilute solution, the translational diffusion coefficient, D_t, refers to the center of mass diffusion in the limit of $qR_H \ll 1$, and the case of $qR_H \gg 1$. D is the diffusion coefficient resulting from the internal motions of the polymer chain. In semidilute solutions ($c > c^*$), the correlation length, ξ, of entangled coiled is obtained instead of hydrodynamic radius, RH. In this regime, two modes of motion exist. One is the fast diffusion mode (D_f) which corresponds to the concentration fluctuation and the other of the multichains in solution.

For a polydisperse suspension, $g^{(1)}(t)$ is a weighed sum of exponentially decaying functions, each of which corresponds to different particle diameter D_i with decay constant Γ_i.

$$g^{(1)}(t) = \int_0^\infty G(\Gamma) \exp(-\Gamma t')\, d\Gamma \qquad (2.18)$$

$G(\Gamma)$ is the normalized distribution of the decay constants of the scatters in the suspension. In this approach, $\ln g^{(1)}(t')$ is fitted

$$\ln g^{(1)}(t) = -\bar{\Gamma}t' + (1/2!)\mu_2 t'^2 - (1/3!)\mu_3 t'^3 \qquad (2.19)$$

where $\overline{\Gamma}$ is the mean value of the decay distribution, and μ_m is the m th central moment of $G(\Gamma)$, defined as:

$$\mu_m = \int_0^\infty G(\Gamma)(\Gamma - \overline{\Gamma})^m \, d\Gamma \qquad (2.20)$$

The second moment, μ_2, related to the variance by $\sigma = \mu_2 / \Gamma^2$, represents the deviation of the relaxation rates with respect to the width of the distribution [Wyn Brown, (1993)].

(b) Sample preparation

The stock solutions and the dilutions prepared in the same way as in viscosity measurement were then filtered through the Millipore filter 0.45 μm for removal of dust particles, and through micro-syringe filter with a membrane filter of pore size 0.22 μm.

(c) Conditions

The measurement temperature was fixed at 30°C by a thermostat and the angle was varied from 45-105 degrees. The polymer solutions were carefully prepared to minimize the dust. The solutions were filtered through 0.45 μm membrane filters prior to inserting into the scattering cell. Before running the experiment, the scattering cell was left in the light scattering unit for at least 20-25 minutes to achieve the thermal equilibrium.