

CHAPTER II

EXPERIMENTAL SECTION

2.1. Materials

The starting materials and products are moisture and air sensitive. Therefore, all operations were carried out with careful exclusion of air. Reactions were run under nitrogen atmosphere.

UHP grade Nitrogen; 99.99% purity was obtained from Thai Industrial Gases Public Company Limited (TIG). Aluminum hydroxide hydrate $[\text{Al}(\text{OH})_3 \cdot x\text{H}_2\text{O}]$ was purchased from Aldrich Chemical Co. Inc. (USA) and used as received. It contained 57.5% Al_2O_3 content by TGA. Ethylene glycol (EG), used as solvent in the reaction, was purchased from Farmitalia Carlo Erba (Barcelona) and purified by fractional distillation at 200°C . under N_2 before use. Triisopropanolamine (TIS) was obtained 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 . Acetonitrile and methanol were purchased from J. T. Baker Inc. (Phillipburg, USA) and purified by standard techniques [VOGEL (1978)]. Acetonitrile was distilled from calcium hydride powder. Methanol was distilled from magnesium metal activated with iodine. All dried pure solvents were purified and stored under N_2 in glass bottles containing molecular sieves.

All glassware was soaked in a base bath (NaOH/iPrOH/H₂O), washed, rinsed with water, and finally dried at 110°-120°C before use.

2.2 Instrumentation

2.2.1 *Mass Spectroscopy (MS)*

Mass spectra were obtained on a 707E-Fison Instrument (VG-Autospec, Manchester, England) with a VG data system. Direct probe injection was used in the positive fast atomic bombardment (FAB⁺) mode. Cesium iodide was used as a standard for peak calibration. Samples were prepared using glycerol as a matrix. The cesium gun beam, used as the initiator, was set at 2 μ A for optimum resolution, as directed in the operating manual. The range studied was set from m/e 200 to 3000.

2.2.2 *Thermal Analysis*

Differential scanning calorimetry (DSC) experiments were carried out in flowing N₂ (15 mL/min) using a Netzsch DSC 200 (Germany). Approximately 5-20 mg sample was placed into a hermetically-sealed aluminum pan. The temperature range was set at 30 to 400°C with a ramp rate of 20°C/min. DSC studies were used to determine the glass transition temperature (T_g), the melting temperature (T_m), and/or the crystallization temperature (T_c).

Thermogravimetric analysis (TGA) was carried out using a Netzsch Gerätebau GmbH Thermal analysis TG 209 (Germany) to establish the alumina content in aluminum hydroxide hydrate and the decomposition profiles of products. Samples of approximately 5-20 mg were placed into an

aluminum pan and heated from room temperature to 950°C in N₂ or O₂ with a ramp rate of 10 °C/min.

2.2.3 Nuclear Magnetic Resonance Spectroscopy (NMR)

¹H- and ¹³C-NMR spectra were obtained using a 500 MHz JEOL (JNM-A500) spectrometer at the Scientific and Instrumental Research Equipment Center, Chulalongkorn University. Samples were dissolved in deuterated methanol (CD₃OD) and tetramethylsilane (TMS) was used as the internal reference for chemical shift measurements. ¹³C-NMR spectra were recorded at frequency of 9.066 MHz using 4000 scans, a pulse delay of 2.5 sec., a pulse width of 4.75 sec., and a sweep width of 16000 Hz. ¹H-NMR spectra were recorded at a frequency of 10 MHz using 16 scans, a pulse width of 5.5 sec., a pulse delay of 3.0 sec., and a sweep width of 16 MHz.

²⁷Al NMR were recorded on Bruker 360 MHz at the University of Michigan. Deuterated methanol was used to dissolve the samples. The spectra were obtained at frequency of 93.8 MHz, a sweep width of 27.8 kHz, 13.0 s width and using at least 1000 scans with a 0.05 sec delay between scans.

2.2.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were recorded on a Bio-Rad FT-45A Fourier transform infrared spectrometer with a resolution of ± 4 cm⁻¹. Samples were prepared by mixing with KBr (1:20 sample:KBr) and hydraulically pressing into a pellet. The sample holder was placed in the chamber which was purged with N₂ for 20 minutes to remove CO₂ before data acquisition commenced.

2.3 Synthesis of Alumatrane Complexes

Alumatrane complexes were synthesized with and without TETA.

2.3.1 *Procedure I : without TETA*

3.55 g (45.5 mmol) of aluminum hydroxide (57.5% Al_2O_3 content by TGA), 50 mL of EG, and 13.39 g (70 mmol) of trisopropanolamine were added to a 250 mL two-necked round bottomed flask. The reaction mixture was stirred and heated under N_2 in an oil bath controlled by a temperature controller. When the oil bath temperature reached 200°C , the reaction was considered to have commenced. Fresh EG in the same amount as the distillate was added to maintain the total reaction volume until the reaction mixture turned clear (about 3 hour), indicating reaction completion. After letting the reaction mixture stand without stirring overnight, white product precipitated out. After filtering, the product was stirred with dried acetonitrile overnight to remove excess TIS. The solid product was then filtered off and dried under high vacuum (10^{-2} torr) at 120°C for 5 h. Dried products were then characterized by DSC, TGA, FTIR, FAB^+ -MS and NMR.

2.3.2 *Procedure II : with TETA*

3.55 g (45.55 mmol) of aluminum hydroxide, 13.39 g (70 mmol) of TIS and 1.46 g (10 mmol) of TETA were added into the reaction flask containing 50 mL of EG. The mixture was reacted as above. After 2 h., the reaction mixture turned clear. After letting the mixture set for overnight, the product was recovered as described above. The product was then characterized by DSC, TGA, FTIR, FAB^+ -MS and NMR.

2.4 Kinetic Studies

The optimum ratio of TIS was studied by fixing the amount of $\text{Al}(\text{OH})_3$ (57.5% Al_2O_3 content by TGA) at 22.7 mmol or 10 mmol equivalent of Al_2O_3 . The amount of TIS was varied from 0-50 mmol. The reaction time and temperature were fixed at 3 h and 200°C, respectively.

The kinetic studies were primarily conducted on the dissolution of $\text{Al}(\text{OH})_3$ as a function of changes in the reaction conditions, namely, the amount of TIS, the amount of aluminum hydroxide, reaction temperature, and time. The rate of reaction was followed by weighing the amount of unreacted $\text{Al}(\text{OH})_3$ which was converted to alumina by calcination in TGA.

The reaction temperature was controlled by a temperature controller connected to a thermocouple to detect and maintain the required system temperature. When the temperature of oil bath reached the setting temperature, the reaction flask was suspended about 5 cm above the oil bath for 10 min. The reaction flask was then immersed into the oil bath at the required temperature.

As for recovering unreacted alumina, the general procedure was as follow: After the reaction mixture was cooled, unreacted $\text{Al}(\text{OH})_3$ was filtered off, and stirred with dried methanol overnight to extract remaining product from unreacted aluminum hydroxide. The unreacted aluminum hydroxide was filtered off, washed with 2x20 mL of dried methanol, and then oven dried at 120°C for 10 h. Finally, the dried aluminum hydroxide was calcined in the TGA to obtain the alumina content. The total unreacted $\text{Al}(\text{OH})_3$ was recalculated and converted to reacted alumina.

2.4.1 Dissolution Rate as a Function of TIS Concentration

To determine the optimum TIS stoichiometry, reactions were run fixing the amount of $\text{Al}(\text{OH})_3$ (57.5% Al_2O_3 content by TGA) at 1.77 g. (22.7 mmol). The amount of added TIS was varied from 0.96-3.83 g (5-20 mmol). EG was added to make the total volume of reaction mixture 50 mL. The reaction time and temperature were set at 3 h. and 200°C , respectively. Each reaction was repeated three times. The mmol of unreacted alumina versus mmol of TIS added was then plotted (Figure 3.3).

2.4.2 Dissolution Rate as a Function of $\text{Al}(\text{OH})_3$ Concentration

The amount of TIS was fixed at 3.83 g (20 mmol) and the amount of $\text{Al}(\text{OH})_3$ was varied from 0.89-8.87 g (5-40 mmol). EG was added to make the total volume of reaction mixture 50 mL. The reaction time and temperature were set at 1 h and 200°C , respectively. Each run was repeated three times. The relationship between mmol of unreacted alumina and mmol of alumina added was plotted (Figure 3.4).

2.4.3 Determination of the Reaction Rate Constant

Amounts of $\text{Al}(\text{OH})_3$ and TIS were fixed at 1.77 g (22.7 mmol) and 0.96 g (5 mmol), respectively. The reaction time was varied from 15-120 min with increments of 15 min at 150° , 170° , 190° , and 200°C . The experiments were repeated three times. The relationship between mmol of unreacted alumina versus reaction time at each reaction temperature was then plotted (Figure 3.5).

2.4.4 Determination of the Activation Energy

After determining the reaction rate constant (k), the activation energy was calculated by plotting $\ln(k)$ versus $1/T$ (1/Kelvin) (Figure 3.6)

2.4.5 Dissolution Rate as a Function of TETA Concentration

To study the effect of [TETA] on the rate of reaction, $\text{Al}(\text{OH})_3$ and TIS quantities were fixed at 1.77 g (22.7 mmol) and 0.96 g (5 mmol), respectively. The concentration of TETA was varied from 0-4.3875 g (0-30 mmol). The reaction time and temperature were fixed at 3 h and 200°C . The relationship between mmol dissolved alumina and mmol TETA added was then plotted (Figure 3.7)

2.4.6 Dissolution Rate as a Function of Time in the Presence of TETA as a Catalyst

The effect of time on the reaction of $\text{Al}(\text{OH})_3$ and TIS with TETA as a catalyst was studied by fixing the amounts of $\text{Al}(\text{OH})_3$, TIS, and TETA at 1.77g (22.7 mmol), 0.96 g (5 mmol), and 0.18 g (1.25 mmol), respectively. The reaction temperature was fixed at 200°C and the reaction time was varied from 15-120 min. The mmoles of unreacted alumina for each run were then plotted versus time (Figure 3.8).