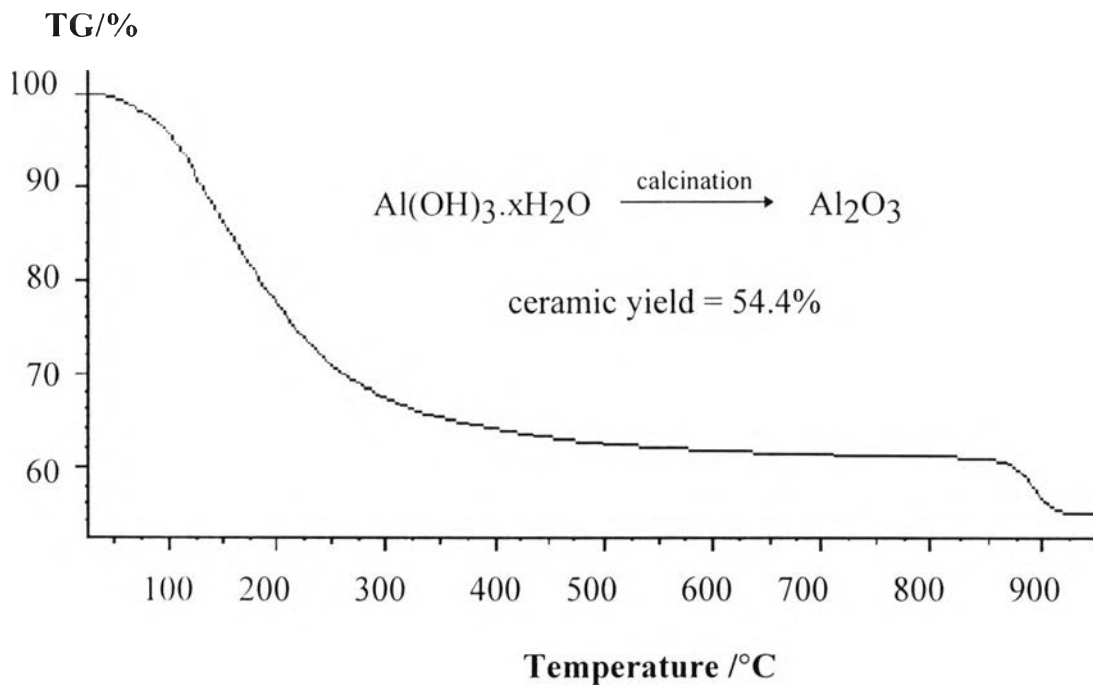# CHAPTER IV

RESULTS AND DISCUSSION

## 4.1 Synthesis

Before performing experiments, aluminum hydroxide hydrate [Al(OH)$_3$.xH$_2$O], the starting material, was calcined using TGA to obtain the exact percentage of Al$_2$O$_3$, as indicated by the % ceramic yield of Al$_2$O$_3$ content, as shown in Figure 4.1 which was 54.4%. This value was used throughout the experiments.

Figure 4.1 TGA Thermogram of Al(OH)$_3$.xH$_2$O.

After product was purified by precipitation with 2-5% methanol in acetonitrile. the yellow powder was precipitated out. The yellowish powder was completely soluble in methanol and ethylene glycol whereas most polyalkoxyalanes do not disslove in MeOH. A highly intractable polymer which was not obtained here in fact can contribute partial or complete donation of electron density from the axial N-atom to Al *[Cotton and Wilkinson, (1987)]*, depicted as monomer A. This Al-N dative bond would reduce or eliminate the potential for froming intermolecular bridges that would create an insoluble polymer.
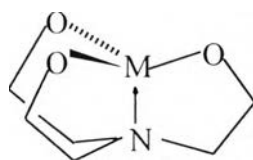
Monomer A

The products are also slightly soluble and swelled in other organic solvents. such as, methylene chloride, acetone and THF. It was hygroscopic and had a tendency to agglomerate when exposed to moisture and air *[Petchsuk et al., (1995)]*.

4.1.1 TEA Concentration Variation

Reactions were carried out by fixing the amount of aluminum hydroxide hydrate at 100 mmol reaction time and reaction temperature at 3 h and 200 °C. respectively, while the amounts of TEA were varied from 10, 20, 40, 50, 60 to 100 mmol. The relationship between the percent ceramic yield and the amount of TEA, see Figure 4.2, showed that the range of percent ceramic yield is 33.1 - 24.2 %. A higher TEA concentration shows a lower %

ceramic yield , implying a higher organic content in the product. In other words, more TEA reacts with Al(OH)₃.
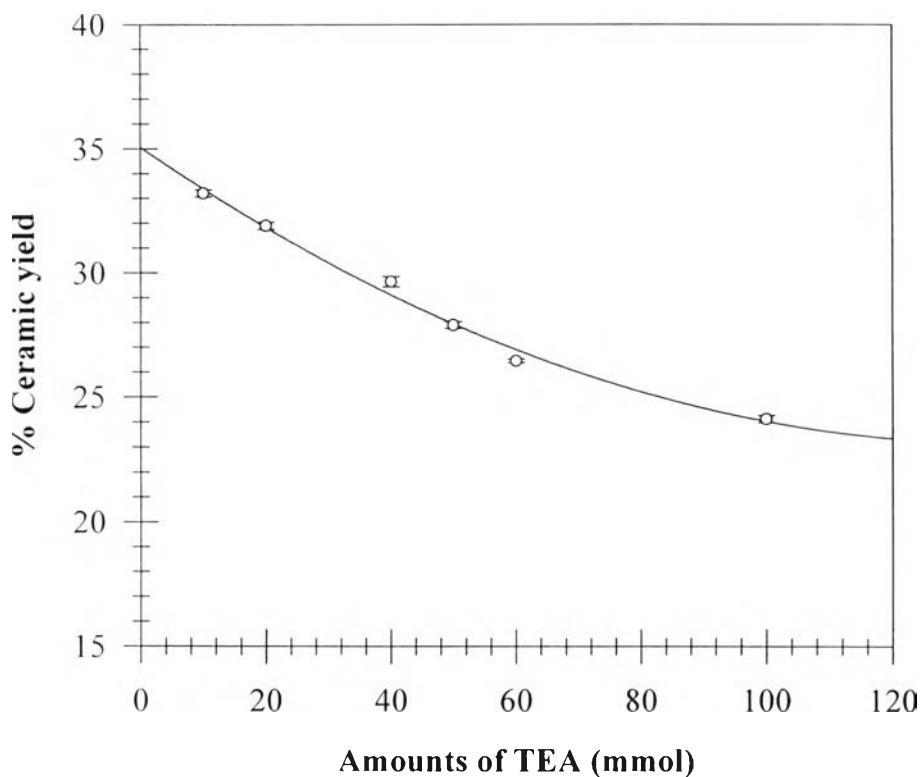
Figure 4.2 The relationship of % ceramic yield versus amounts of TEA from the reaction using Al(OH)₃:TEA = 1:x where x = 0.1, 0.2, 0.4, 0.5, 0.6 and 1 at the reaction temperature of 200 °C and the reaction time of 3 h.

4.1.2 Reaction Temperature Variation

Aluminum hydroxide and TEA concentrations were held at 100 mmol and 50 mmol, respectively. The reaction temperature was varied from 140° , 160°, 180°, 200°, and 220 °C. The reaction time was set at 3 hours. The plot of % ceramic yield versus reaction temperature is presented in Figure 4.3.

The range of percent ceramic yield is 44.2 - 26.2 %. As expected, a higher reaction temperature induceas a lower % ceramic yield, implying a higher organic content in the product. For the reaction temperature greater than 180 °C, the reaction is close to the equilibrium condition.
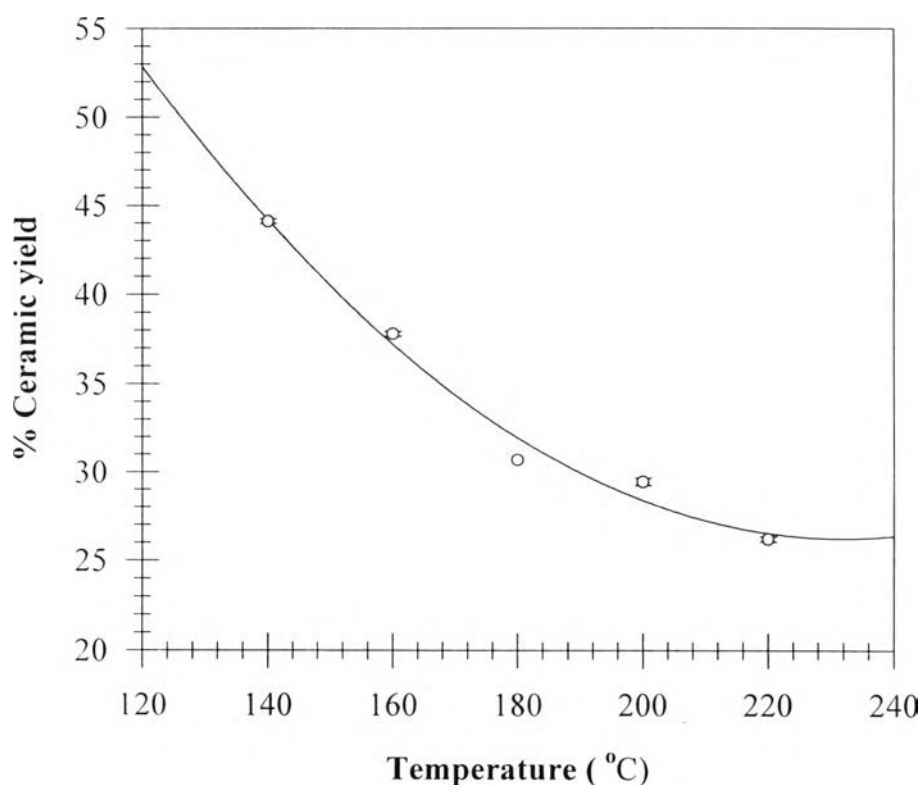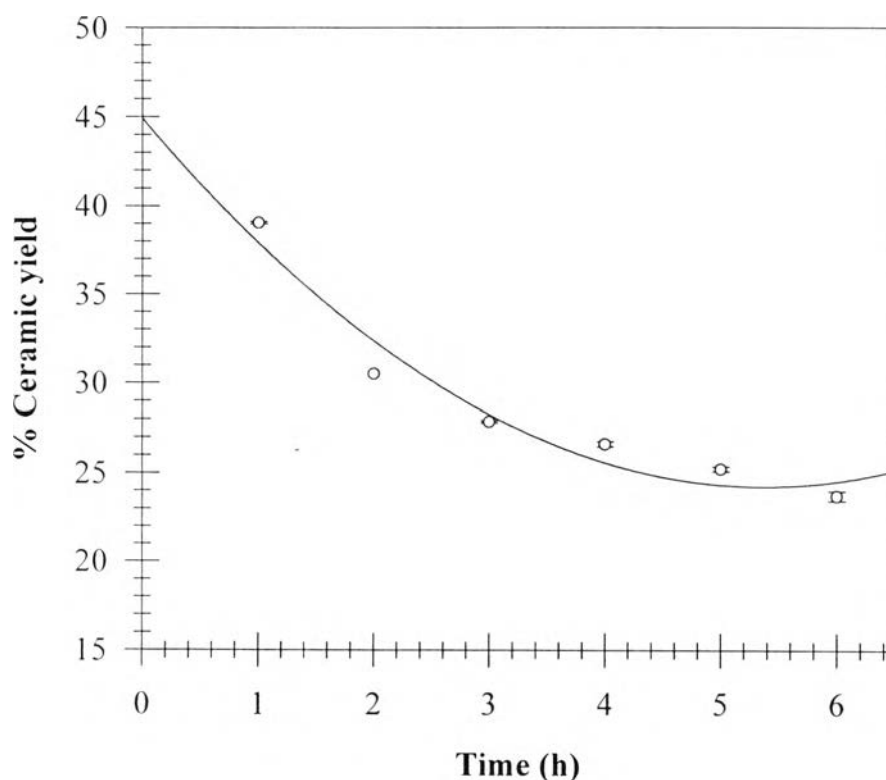

Figure 4.3 The relationship of % ceramic yield versus reaction temperature from the reaction using Al(OH)$_3$:TEA = 2:1 at the various reaction temperatures and the reaction time 3 h.

4.1.3 Reaction Time Variation

The amounts of Al(OH)$_3$ and TEA were fixed at 100 mmol and 50 mmol, respectively. The reaction time was run from 1, 2, 3, 4, 5 to 6 hours.
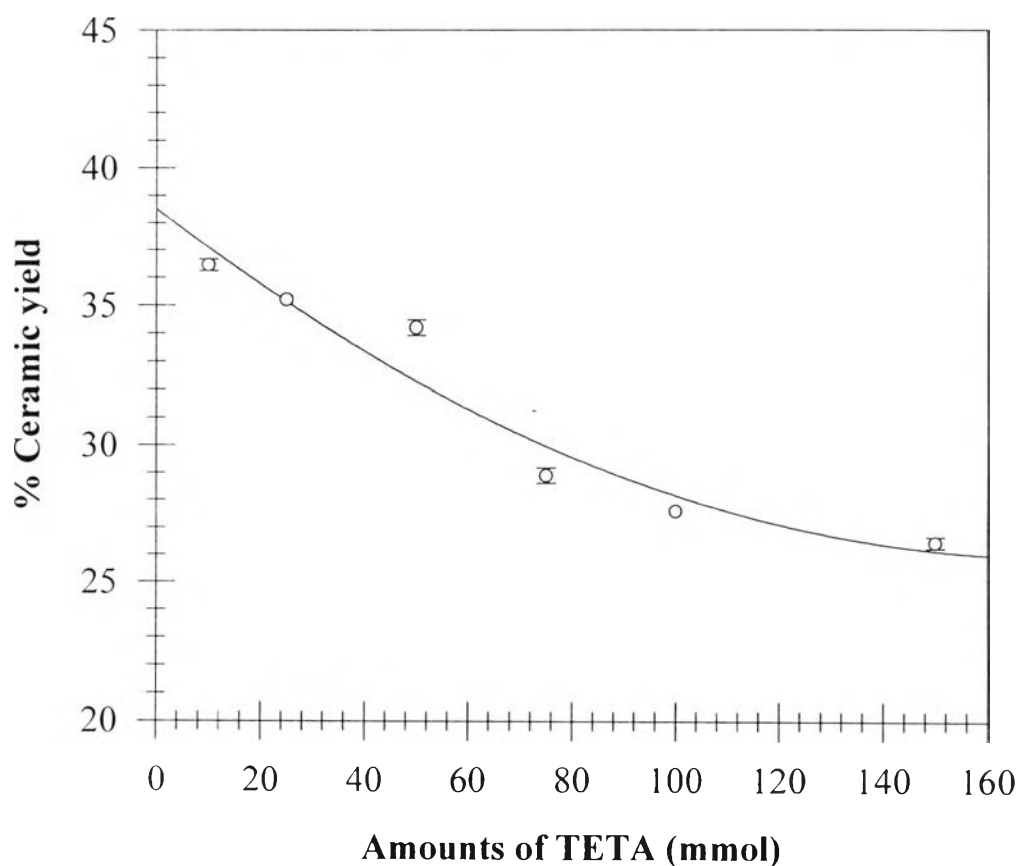
The reaction temperature was set at 200 °C. The relationship between the percent of ceramic yield against the reaction time is shown in Figure 4.4. The range of % ceramic yield is between 39.1 - 23.7 %. It shows that when the reaction time is increased, % ceramic yield decrease. At short time reaction times (1 - 2 hours), the percent ceramic yield decreases significantly, as compared with the higher reaction times.

Figure 4.4 The relationship of % ceramic yield versus reaction time from the reaction using Al(OH)$_3$:TEA = 2:1 at various reation times and the reaction temperature 200 °C.

4.1.4 TETA Concentration Variation

The reactions were run by fixing the amounts of Al(OH)$_3$ and TEA at 100 mmol and 50 mmol, respectively. The experiments were conducted by varying the amount of TETA from 10, 25, 50, 75, 100 to 150 mmol, reaction time and temperature at 3 h and 200 °C, respectively. The plot of the % ceramic yield and the amount of TETA is presented in Figure 4.5.


Figure 4.5 The relationship of % ceramic yield amounts of TETA from the reaction using Al(OH)$_3$:TEA:TETA = 10:5:x where x = 1:2.5:5:7.5:10:15 at the reaction temperature of 200 °C and the reaction time of 3 h.

The range of % ceramic yield is 36.6 - 26.6 %. The percent ceramic yield was dropped when increasing TETA concentration, suggesting that TETA catalyzed the reaction to result in more organic content in the product.

4.2 Characterization of Alumatrane Complexes

4.2.1 Thermogravimetric Analysis (TGA)

The TGA profile of precipitated product of the reaction without TETA, Figure 4.6, shows two regions of mass loss during heating. The first mass loss occured between 170 °C and 280 °C which corresponds to the oxidative decomposition of the organic ligands.

TG/%

ceramic yield = 33.1%

Temperature /°C
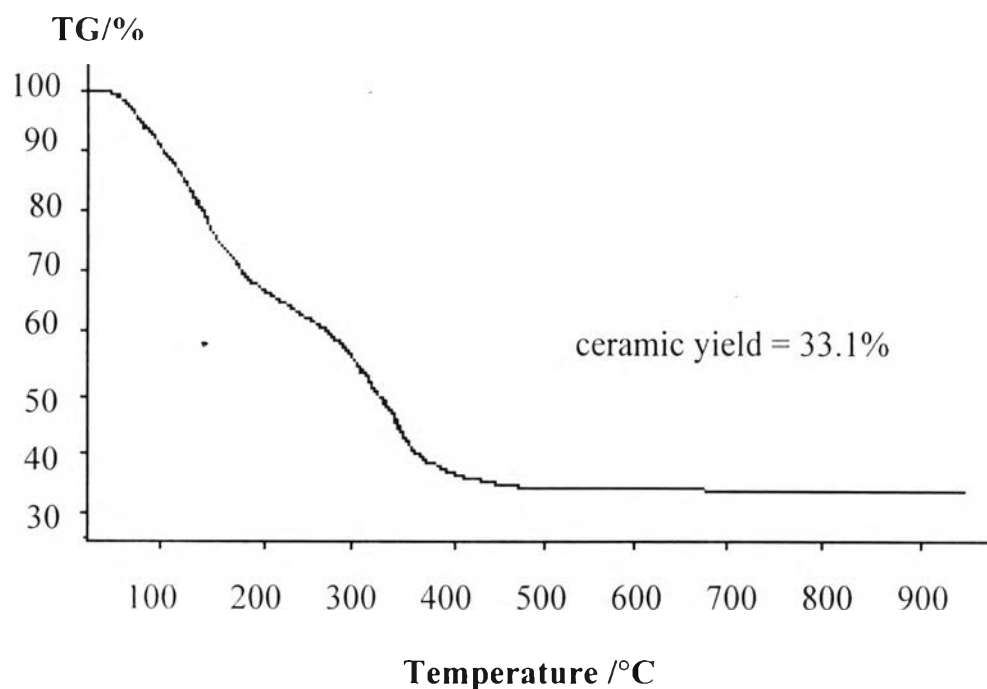
Figure 4.6 TGA Thermogram of the product from the reaction without TETA.

The second mass loss was between 280 °C and 480 °C which indicated the oxidation of residual carbon. The percent ceramic yield for this product was 33.1%.

The TGA profile of the product of the reaction with TETA showed two major mass loss at about 150 °C - 300 °C and 300 °C - 500 °C which correspond to oxidative decomposition of TETA and organic ligands, and the oxidation of residual carbon, respectively, (Figure 4.7). The percent ceramic yield of the product was 29.1%, which is lower than the product of the reaction without TETA, implying that the product of the reaction with TETA gave higher organic ligands. In other words, higher molecular weight occured in the reaction using TETA.
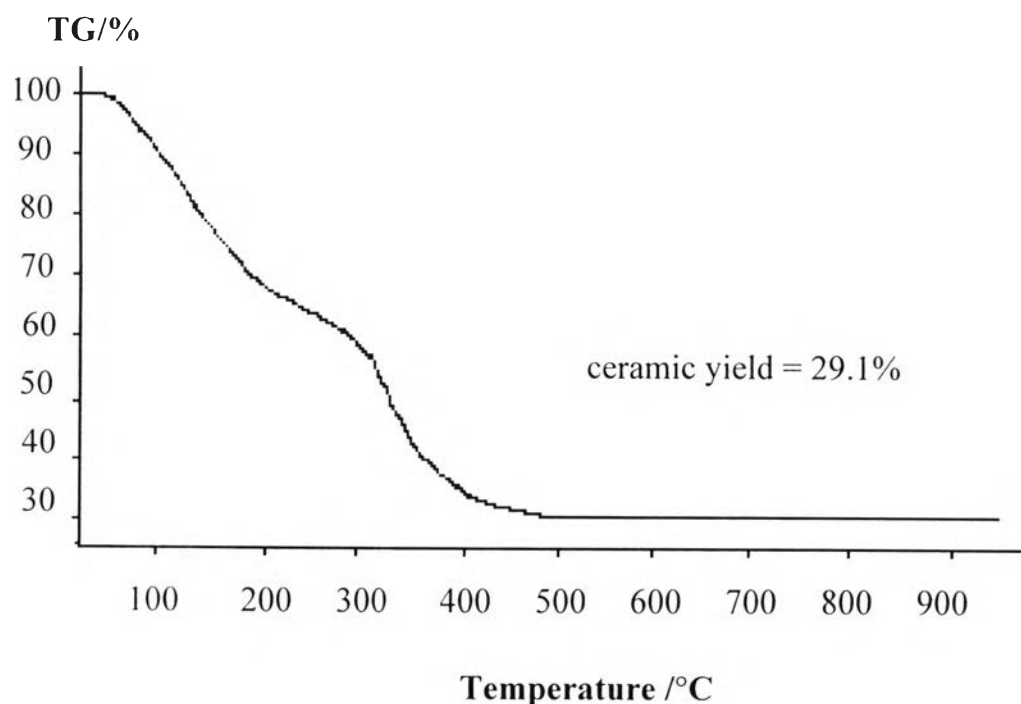
Figure 4.7 TGA Thermogram of the product from the reaction with TETA.

4.2.2 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of the precipitated product of the reaction with and without TETA are shown in Figure 4.8. Peak positions and assignments are listed in Table 4.1. From FTIR spectrum of the product of the reaction without TETA , the peak at 3100-3800 cm^{-1} corresponds to the νO-H. The multiple peak at 2700-3000 cm^{-1} indicates the -CH$_2$ and -CH$_3$ stretching from TEA which is in a component in the product. The singlet peak at 1650 cm^{-1} respresent O-H overtone and C-H bending. Another singlet peak at 1300-1520 cm^{-1} results from νC-N. A strong peak at 1000-1200 cm^{-1} corresponds to νC-O. The broad peak of high intensity at 500-850 cm^{-1} indicates νAl-O.

The FTIR spectrum of the product of reaction with TETA showed the same peaks found in the product of the reaction without TETA, Figure 4.8. The broad peak at 3000-3150 cm^{-1} results from νO-H and νN-H. The singlet peak at 1700 cm^{-1} is O-H overtone. Another singlet peak at about 1400 cm^{-1} can be assigned to νC-N and the multiple peaks at 1100-950 cm^{-1} are C-O vibrations.

Table 4.1 Peak Positions and Assignments of FTIR Spectra of Product with and without TETA

Peak Positions (cm^{-1})		Assignments
Al-TEA	TEA-Al-TETA	
3100-3800	3000-3150	νO-H and νN-H
2700-300	2700-3100	νC-H
1650	1700	O-H overtone; C-H bending
1500	1400	δC-H
1000-1200	950-1100	νC-N; O-H bending
500-850	500-800	νAl-O

Abs.
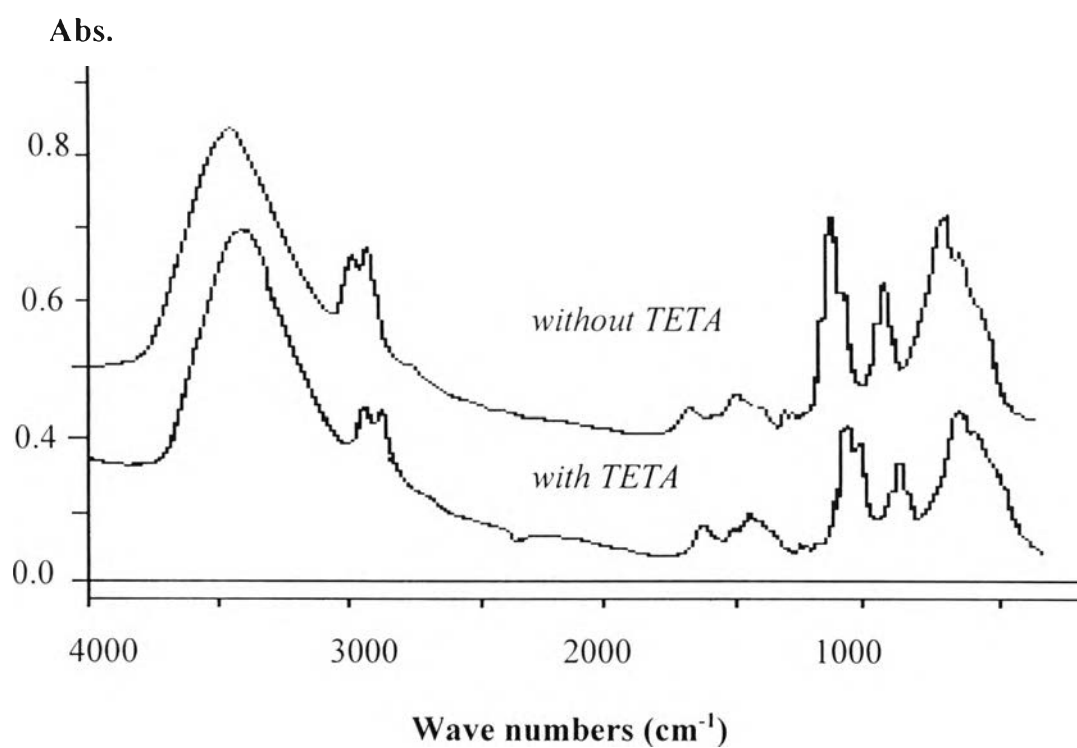
Figure 4.8 IR spectra of the products from the reaction with and without

TETA.

4.3 Viscosity Measurement

The analysis of viscosity data of alumatrane complexes solutions at various conditions was carried out in terms of reduced specific viscosity, η_{red} or η_{sp}/c; inherent viscosity, η_{inh} or $\ln\eta_r/c$; intrinsic viscosity, $[\eta]$; Huggins coefficient, k'; Kraemer coefficient, k''; and overlap concentration, C^*. Viscosity measurements were performed using Ubbelohde capillary viscometer.

4.3.1 Effect of TEA Concentration

The viscosity measurements were performed over the TEA concentration ranging from 0.3 to 3.0 g/l. Figure 4.9 shows typical results of reduced specific viscosity, η_{sp}/c, of the polymer solutions as a function of TEA concentration at different amounts of TEA, measured at 30 °C, at the reaction temperature of 200 °C and the reaction time of 3 h. It can be observed that reduced specific viscosity increases linearly with increasing TEA concentration.

Figure 4.10 is the plot of inherent viscosity of polymer solutions versus TEA concentration at 30 °C, at the reaction temperature of 200 °C and the reaction time of 3 h. The inherent viscosity of the polymer solutions increases linearly with TEA concentration.

The intrinsic viscosity, $[\eta]$, was evaluated by extrapolating η_{sp}/c and $\ln\eta_r/c$ to zero polymer concentration as expressed by the Huggins and Kraemer Equations, respectively. From Figure 4.11, shows intrinsic viscosity versus polymer concentration, measured at 30°C, of alumatrane complexes synthesized from $Al(OH)_3$:TEA = 1:x where x = 0.1, 0.2, 0.4, 0.5, 0.6 and 1 at the reaction temperature of 200 °C and the reaction time of 3 h. It can be seen
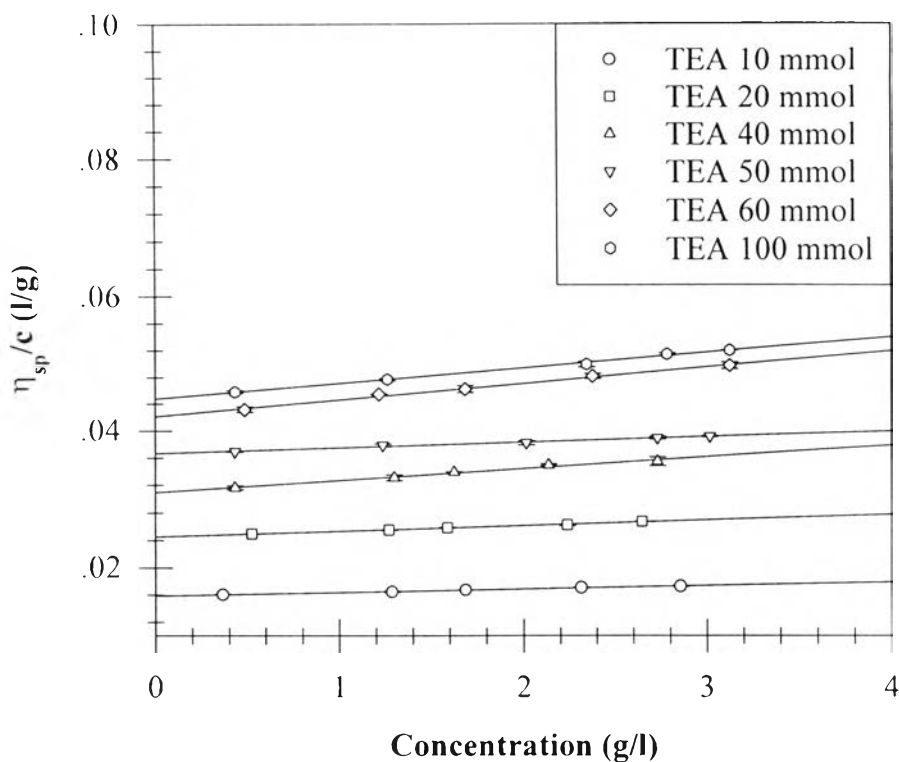
Figure 4.9 Reduced specific viscosity versus polymer concentration, measured

at 30 °C, of alumatrane complexes synthesized from $Al(OH)_3$:TEA

= 1:x where x = 0.1, 0.2, 0.4, 0.5, 0.6 and 1 at the reaction

temperature of 200 °C and the reaction time of 3 h.

that the values of intrinsic viscosity obtained via the Huggins Equation (3.5) are nearly the same as the values obtained via the Kraemer Equation (3.6).

The intrinsic viscosity, $[\eta]$, is approximately 0.009 l/g at zero amount of TEA. It increases linearly for TEA contents less than 60 mmol, then It attains value of about 0.43 l/g at the TEA content of 100 mmol, meaning that the optimal amount of TEA to synthesize the longest chain and a maximum intrinsic viscosity or hydrodynamic volume is 100 mmol. The numerical values of the intrinsic viscosity are listed in Table 4.2.
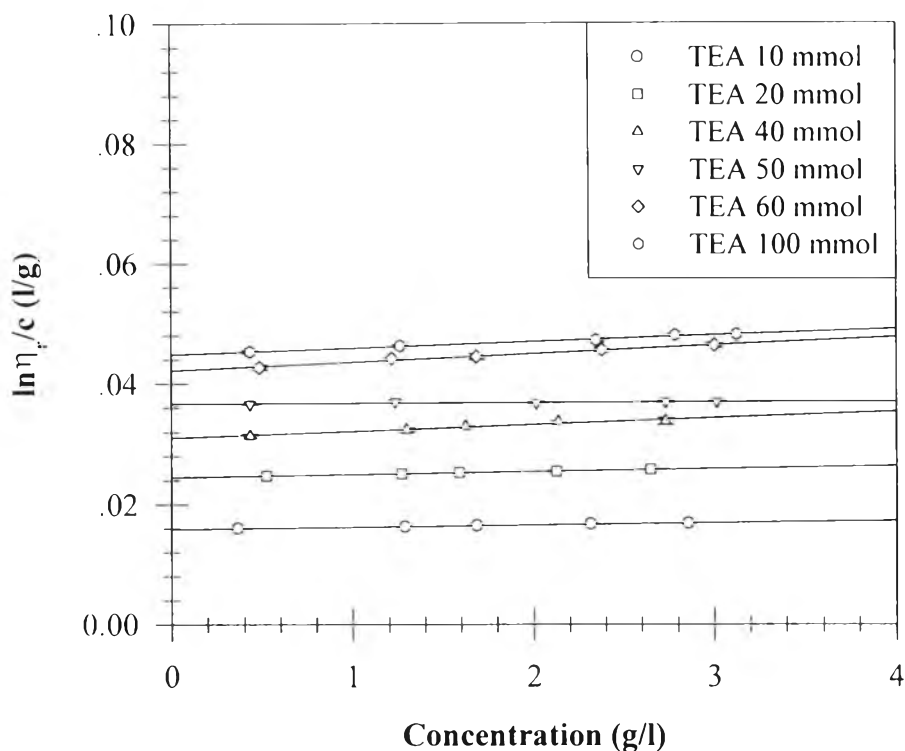
Figure 4.10 Inherent viscosity versus polymer concentration, measured at 30
°C, of alumatrane complexes synthesized from $Al(OH)_3$:TEA =
1:x where x = 0.1, 0.2, 0.4, 0.5, 0.6 and 1 at the reaction
temperature of 200 °C and the reaction time of 3 h.

The slopes of reduced viscosity and inherent viscosity versus
polymer concentration in Figures 4.9 and 4.10 give k' and k", the Huggins and
the Kraemer coefficients respectively. The determined values of k' and k" are
tabulated in Table 4.2. The Huggins coefficient is a measurement of the
quality of the solvent, ethylene glycol, to alumatrane complexes. In this regard,
the small values of k' shown in Table 4.2 indicate that ehtylene glycol is a poor
solvent for this system. Similarly, in Table 4.2, values of the Kraemer
coefficient, k", obtained for Figure 4.10 via equation 3.6 are negative in sign
and in agreement with the theoretical relation k'+k" = 0.5, further supporting
that ethylene glycol is a poor solvent for alumatrane complexes. Low values of

k' and k" for the alumatrane complex solution with TEA content of 50 mmol are possibly results of experimental error and difficulty in measuring and determining k'and k", since they were obtained as ratios of two measured quantities.
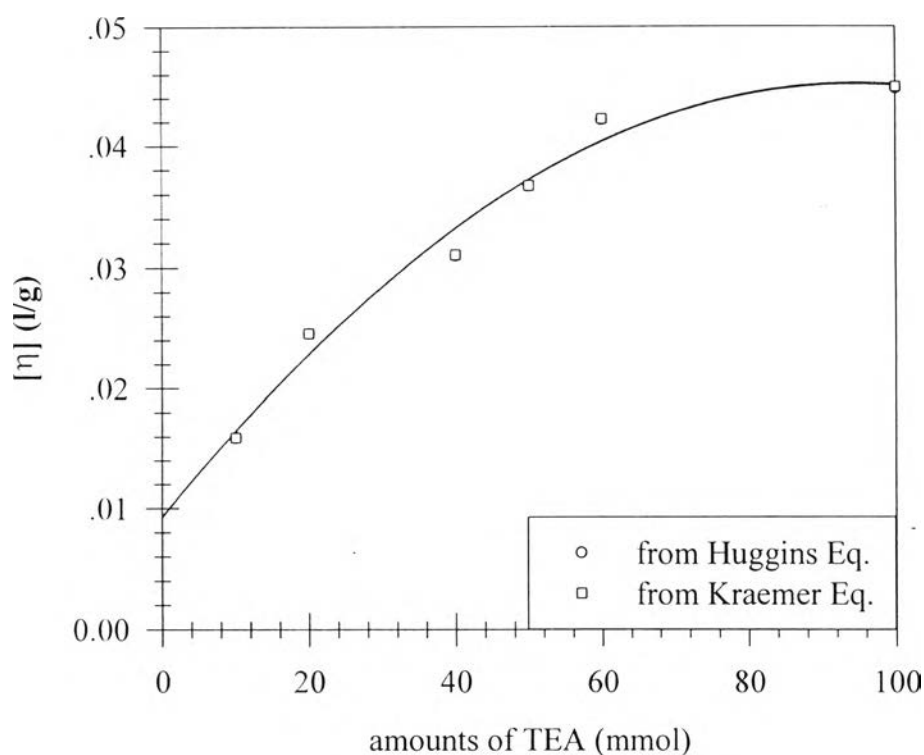
Figure 4.11 Intrinsic viscosity versus amounts of TEA, measured at 30 °C, of alumatrane complexes synthesized from $Al(OH)_3$:TEA = 1:x where x = 0.1, 0.2, 0.4, 0.5, 0.6 and 1 at the reaction temperature of 200 °C and the reaction time of 3 h.

Table 4.2 Viscometric data of polymer solutions, measured at 30 °C, that synthesized from $Al(OH)_3$:TEA = 1:x where x = 0.1, 0.2, 0.4, 0.5, 0.6 and 1 at the reaction temperature of 200 °C and the reaction time of 3 h

| TEA (mmol)	$[\eta]^*$ (l/g)	$[\eta]^{**}$ (l/g)	C^* (g/l)	k'	k''
10	0.016	0.016	63	2.0	-1.4
20	0.025	0.025	41	1.3	-0.8
40	0.032	0.031	32	1.8	-1.1
50	0.037	0.036	27	0.6	-0.2
60	0.042	0.042	24	1.4	-0.8
100	0.045	0.045	22	1.2	-0.5

* from Huggins Equation.

** from Kraemer Equation.

4.3.2 Effect of Reaction Temperature

Figures 4.12 and 4.13 show the dependence on reaction temperature of the reduced viscosity and the inherent viscosity, respectively, of alumatrane complexes in the ethylene glycol at a given reactant concentrations. The reaction temperature was varied form 140 °C to 220 °C wheaeas the reaction time was fixed at 3 h.

The polymer concentration ranged from 0.3 to 3.0 g/l. It can be observed that the reduced viscosity and inherent viscosity each increases with increase of reaction temperature. This suggests that the intrinsic viscosity must increase with increase in reaction temperature. The intercepts and slopes of these straight lines give intrinsic viscosity, $[\eta]$, and Huggins and Kraemer

coefficients, respectively. The measured and determined values are tabulated in Table 4.3.
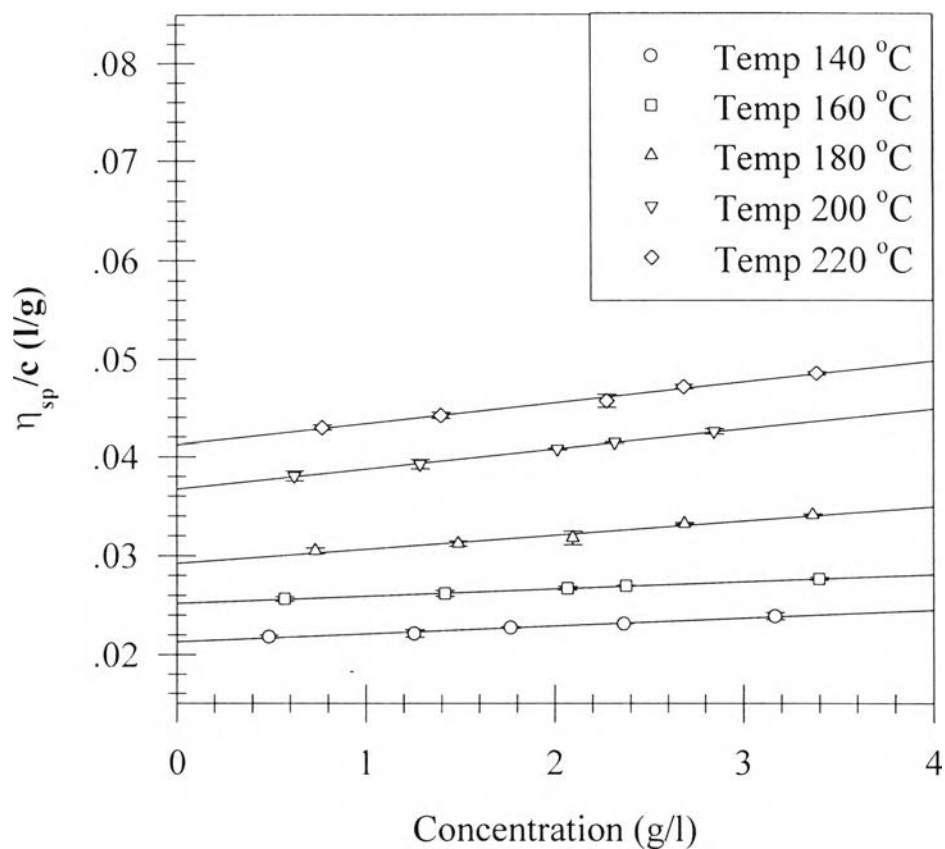
Figure 4.12 Reduced specific viscosity versus polymer concentration, measured at 30 °C, of alumatrane complexes synthesized from $Al(OH)_3$:TEA = 2:1 at the various reaction temperatures and the reaction time of 3 h.

Figure 4.14 shows the intrinsic viscosity as functions of reaction temperature and the reaction time of 3 h. It can be seen that the intrinsic viscosity increases monotonically with reaction temperature, at least in the range of reaction temperature studied. This suggests that the molecular weight

of the product is higher for higher reaction temperatures. Both k′ and k″ values obtained indicate that ethylene glycol is a poor solvent for the alumatrane complexes obtained at the reaction temperatures between 140 °C to 220 °C, and the reaction time of 3 h.
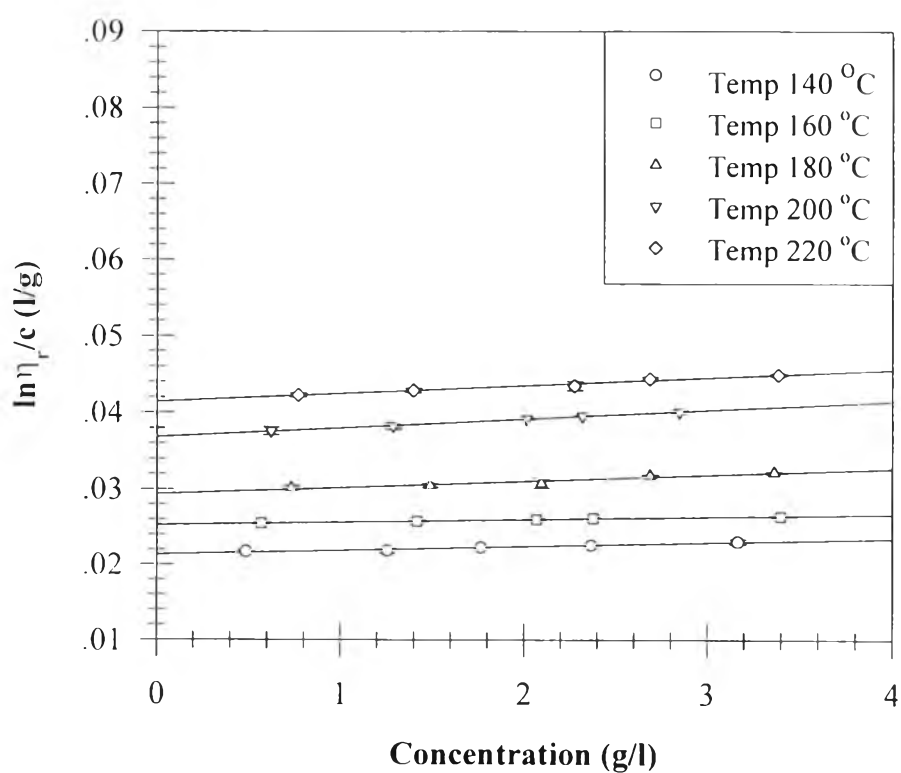
Figure 4.13 Inherent viscosity versus polymer concentration, measured at 30 °C. of alumatrane complexes synthesized from $Al(OH)_3$:TEA = 2:1 at the various reaction temperatures and the reaction time of 3 h.

There are , however, disadvantages in using a high reaction temperature, because the reaction goes faster and distills off more by-products, ethylene glycol and water, at the high reaction temperature. Also, for the high reaction temperature, the reaction is difficult to control and undesirable decomposition of product occurs.
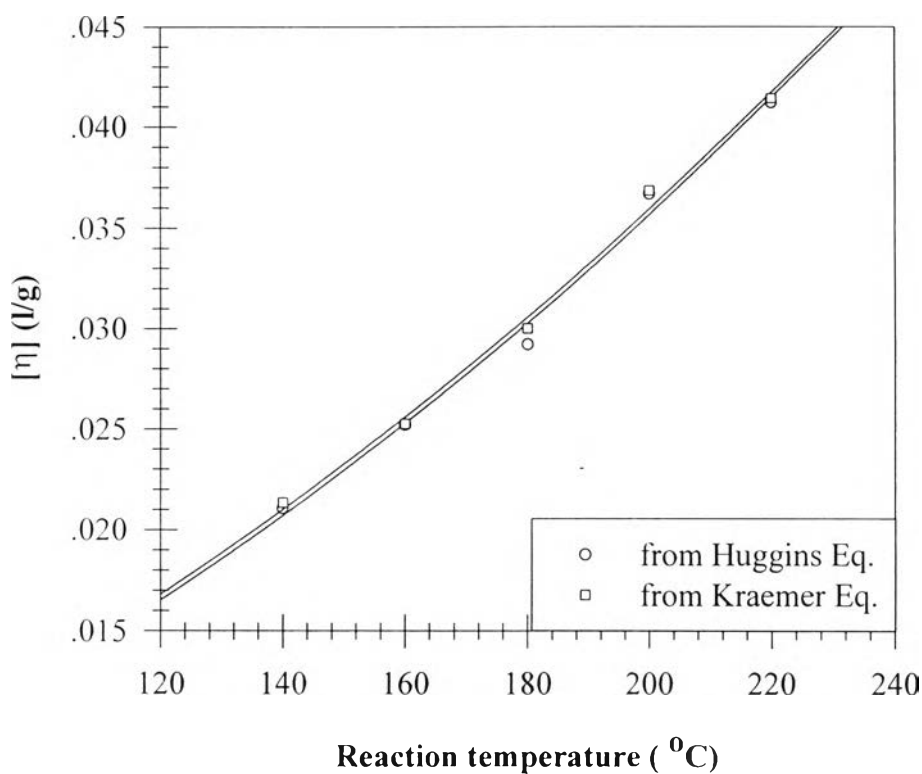
Figure 4.14 Intrinsic viscosity versus reaction temperature, measured at 30 °C, of alumatrane complexes synthesized from Al(OH)₃:TEA

$= 2:1$ at the reaction time of 3 h.

Table 4.3 Viscometric data of polymer solutions, measured at 30°C, that synthesized from Al(OH)$_3$:TEA = 2:1 at various reaction temperatures and at the reaction time of 3 h

Temperature (°C)	[η]* (l/g)	[η]** (l/g)	C* (g/l)	k′	k″
140	0.021	0.021	47	1.8	-1.1
160	0.025	0.025	40	1.1	-0.6
180	0.029	0.030	34	2.0	-0.7
200	0.037	0.037	27	1.5	-0.9
220	0.041	0.041	24	1.3	-0.6

* from Huggins Equation.

** from Kraemer Equation.

4.3.3 Effect of Reaction Time

The reaction times of 1 to 5 h were chosen for synthesizing the alumatrane complexes of Al(OH)$_3$:TEA of 2:1, at the reaction temperature of 200 °C. The intrinsic viscosity and the inherent viscosity versus polymer concentration, for the alumatrane complex solutions at 30 °C, in terms of reaction time are shown in Figures 4.15 and 4.16, respectively. Both viscometric functions vary linearly with polymer concentration, for all the reaction times studied. The [η], that calculated from Huggins and Kraemer Equations. k′, and k″ were determined and are tabulated in Table 4.4.
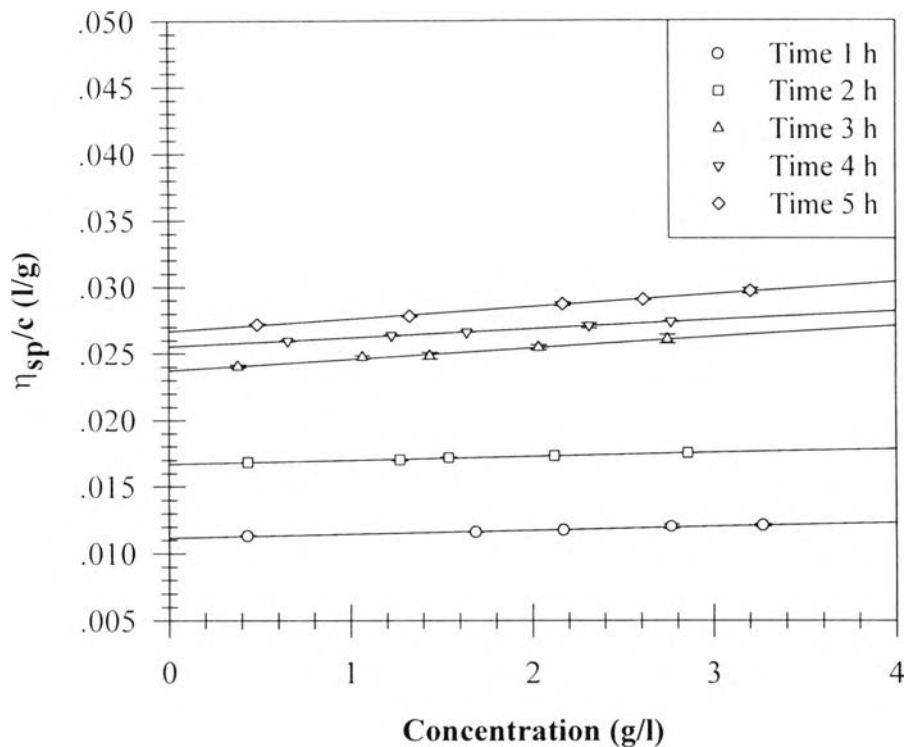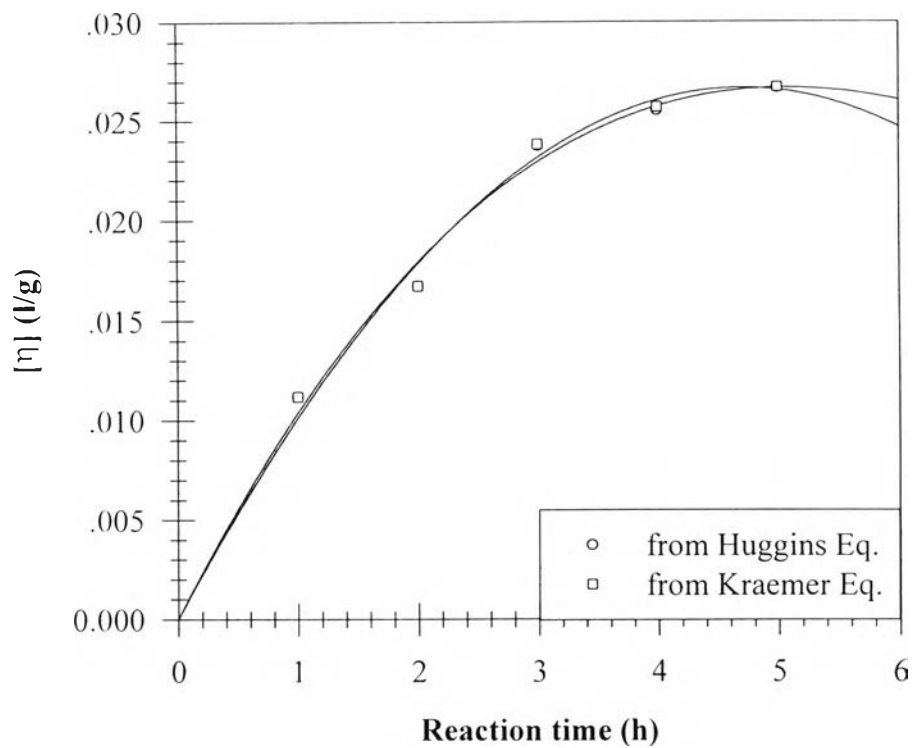
Figure 4.15 Reduced specific viscosity versus polymer concentration, measured at 30 °C, of alumatrane complexes synthesized from Al(OH)₃:TEA = 2:1 at various reaction times and at the reaction temperature of 200°C.

Figure 4.17 shows [η] calculated from Huggins and Kraemer Equations as functions of reaction time; they increase from 0.011 l/g to the asymptotic value of 0.027 l/g when the reaction time was varied from 1 to 5 h. After 5 h, the intrinsic viscosity approaches a constant value, implying that the reaction has gone to completion and an optimum high molecular weight product is obtained. Both k' and k" values shown in Table 4.4 indicate that with increase of reaction time the polymer product is more poorly solvated by the ethylene glycol.
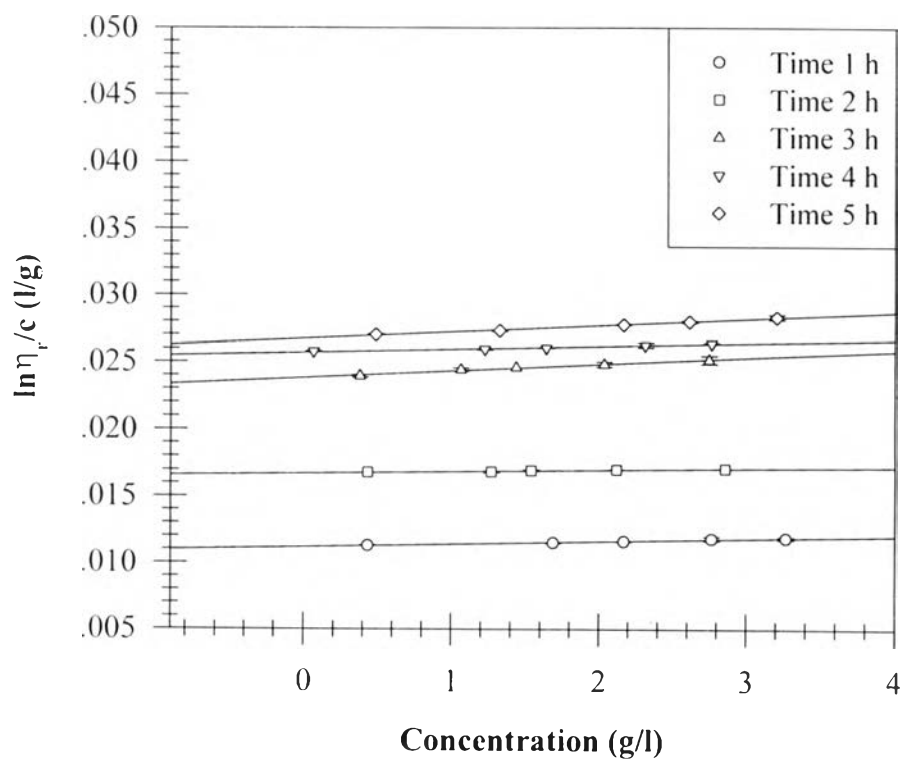
Figure 4.16 Inherent viscosity versus polymer concentration, measured at 30

°C, of alumatrane complexes synthesized from Al(OH)$_3$:TEA

= 2:1 at various reaction times and at the reaction temperature

of 200°C.

Figure 4.17 Intrinsic viscosity versus reaction time, measured at 30

°C, of alumatrane complexes synthesized from Al(OH)$_3$:TEA

= 2:1 at the reaction temperature of 200 °C.

Table 4.4 Viscometric data of polymer solutions, measured at 30°C, that synthesized from Al(OH)$_3$:TEA = 2:1 at various reaction time and the reaction temperature 200°C

| Reaction time (h)	$[\eta]^*$ (l/g)	$[\eta]^{**}$ (l/g)	C^* (g/l)	k'	k''
1	0.011	0.011	90	2.3	-1.7
2	0.017	0.017	60	1.0	-0.5
3	0.024	0.024	42	1.5	-0.9
4	0.026	0.026	39	1.0	-0.4
5	0.027	0.027	38	1.3	-0.7

* from Huggins Equation.

** from Kraemer Equation.

4.3.4 Effect of TETA Content

Figures 4.18 and 4.19 show reduced and inherent viscosities versus polymer concentration as functions of amount of TETA which was used as the catalysis. The alumatrane complexes were synthesized using Al(OH)$_3$:TEA equal to 2:1, the reaction time of 3 h, and the reaction temperature of 200 °C. Both graphs show the same trend as found for the other conditions discussed previously. The concentration range of 0.4-3.0 g/l was used in these measurements. [η] was calculated from Huggins and Kraemer Equations. k' and k" were determined as functions of TETA contents and are tabulated in Table 4.5.
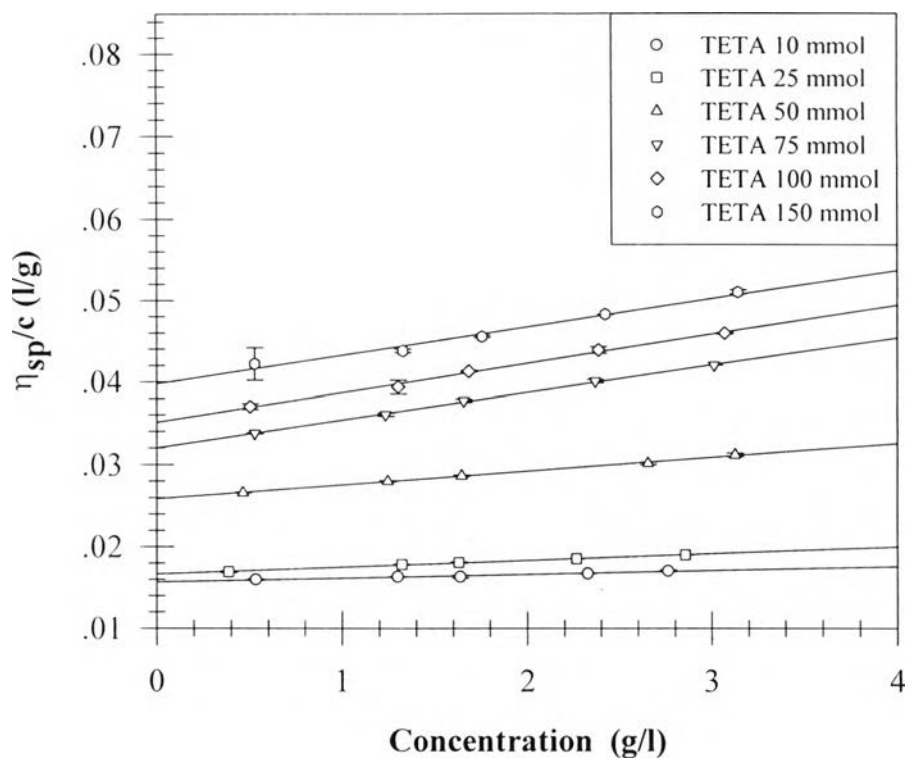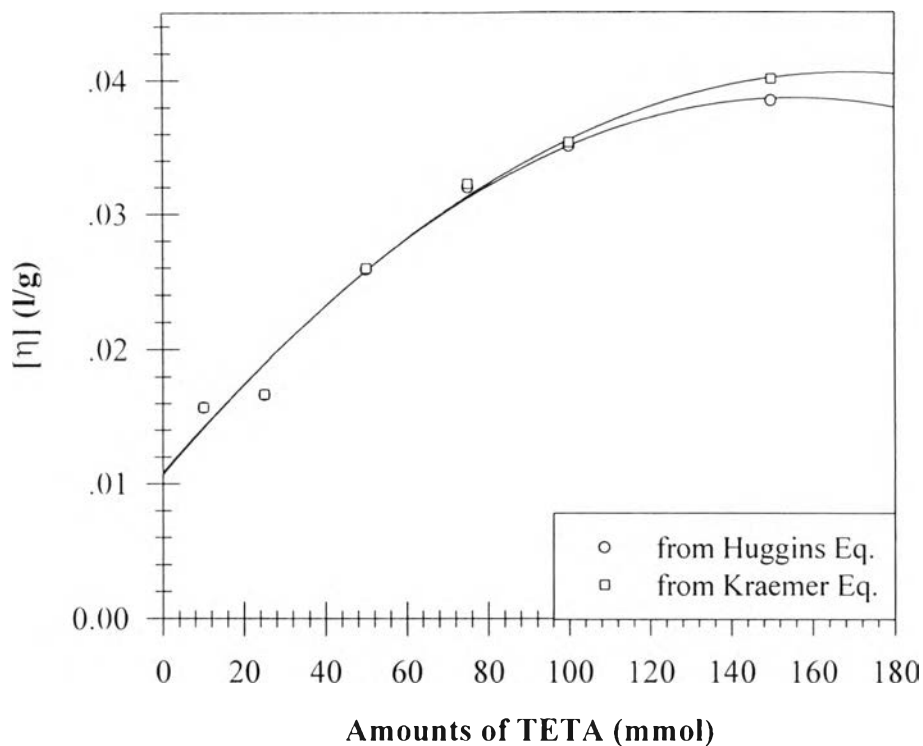
Figure 4.18 Reduced specific viscosity versus polymer concentration,

measured at 30 °C, of alumatrane complexes synthesized from

Al(OH)₃:TEA:TETA = 10:5:x where x = 1:2.5:5:7.5:10:15

at the reaction time of 3 h, and the reaction temperature of 200 °C.
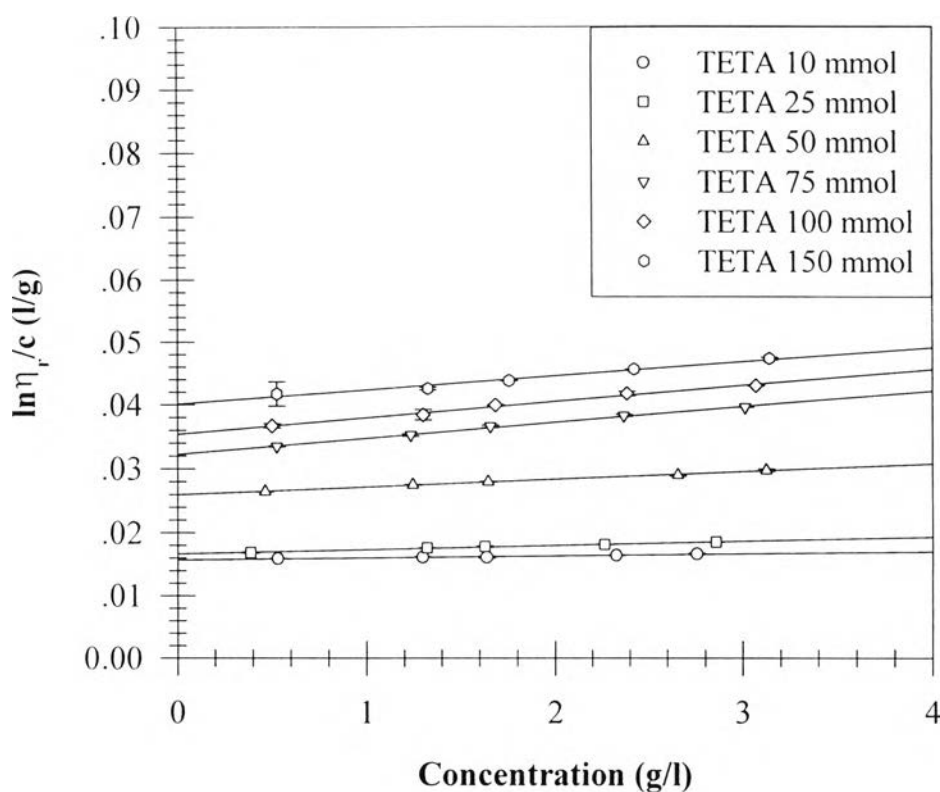
Figure 4.19 Inherent viscosity versus polymer concentration, measured at 30
°C, of alumatrane complexes synthesized from
$Al(OH)_3$:TEA:TETA = 10:5:x where x = 1:2.5:5:7.5:10:15
at the reaction time of 3 h, and the reaction temperature of 200 °C.

Figure 4.20 shows the intrinsic viscosity versus TETA content for the
alumatrane complexes synthesized. The intrinsic viscosity increases initially
form 0.016 l/g to the asymptotic value of about 0.038 l/g when TETA content
was varied from 10 mmol to 150 mmol.

Figure 4.20 Intrinsic viscosity versus amounts of TETA, measured at 30

°C, of alumatrane complexes synthesized from

Al(OH)$_3$:TEA:TETA = 10:5:x where x = 1:2.5:5:7.5:10:15

at the reaction time of 3 h, and the reaction temperature of 200 °C.

In Table 4.5, k′ and k″ provide a measurement of the quality of solvent in this system. It can be seen ethylene glycol is a poor solvent for this system; k′ is large than 1 and k″ is negative in sign with charge in the concentration of TETA. These is no systematic dependence of k′ and k″ on TETA.

Table 4.5 Viscometric data of polymer solutions, measured at 30 °C,

synthesized from $Al(OH)_3$:TEA:TETA = 2:1:x where

x = 1:2.5:5:7.5:10:15, at various TETA contents at the reaction time

of 3 h and the reaction temperature of 200 °C

TETA (mmol)	$[\eta]^*$ (l/g)	$[\eta]^{**}$ (l/g)	C^* (g/l)	k'	k''
10	0.016	0.016	63.7	1.88	-1.29
25	0.017	0.017	60.0	2.99	-2.33
50	0.026	0.026	38.6	2.47	-1.75
75	0.032	0.032	31.1	3.27	-2.38
100	0.035	0.035	28.4	2.91	-2.04
150	0.038	0.039	25.4	2.69	-1.71

* from Huggins Equation.

** from Kraemer Equation.

4.4 Light Scattering Measurement

In this part, physical properties of alumatrane complexes for different TETA contents were investigated by light scattering technique.

In dynamic light scattering experiment, real-time fluctuations in the scattered light intensity were recorded by a specialized multichannel analyzer. The physical properties of alumatrane complexes can be investigated by the measured value of the translational diffusion coefficient, D, and the hydrodynamic radius, R_h. The value of the diffusion coefficient depends on the concentration of the polymer solution whereas the hydrodynamic radius is determined by extrapolation of D to zero

concentration and hence describes the behavior of a single polymer chain in this system.

The concentration dependence of the diffusion coefficient is given by the following equation:

$$D = D_o (1 + k_D C), \tag{4.1}$$

where, $$k_D = 2A_2M - k_f - V_2, \tag{4.2}$$

A_2 is the second virail coefficient, M is the molecular weight, k_f is the concentration dependence of the frictional coefficient and V_2 is the partial specific volume *[Wyn Brown, 1993]*.

The hydrodynamic radius, R_h, is calculated from D_o using the Stokes-Einstein equation:

$$D_o = k_B T / 6\Pi\eta R_h \tag{4.3}$$

where η is solvent viscosity, T is temperature (°K) and k_B is Boltzmanns constant.

To avoid the problem of large particles, the measurements was carried out by measuring D_{app} at various q^2 as shown in Figure 4.21. D_{app} increases linearly as q^2 increases, suggesting alumatrane polydispersity and contributions from the internal mode of motion. From the intercept of this line, $q^2 = 0$, the center of mass diffusion, D_{cm}, was obtained.
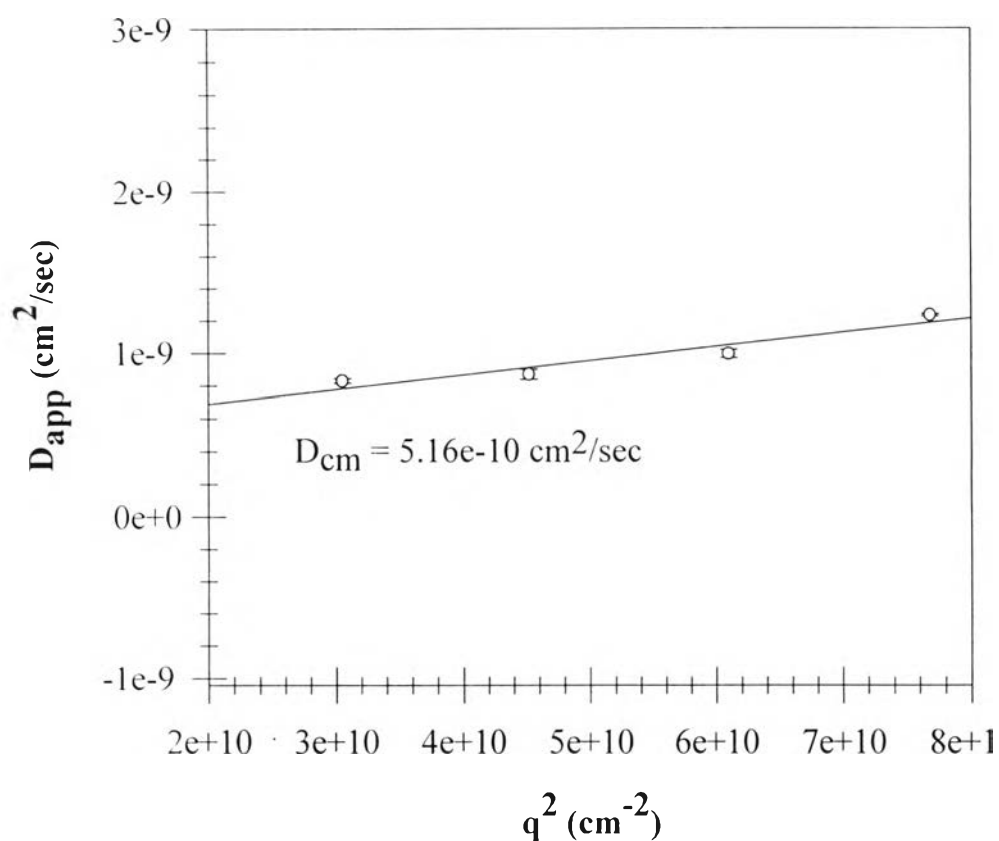
Figure 4.21 Angle-dependendence of the apparent diffusion coefficient of the alumatrane complex versus q^2 at the concentration of 1.634 g/l measured at 30 °C using $Al(OH)_3$:TEA:TETA = 10:5:7.5, the reaction time of 3 h , and the reaction temperature of 200 °C.

From Figure 4.21, we found that the center of mass diffusion coefficient, D_{cm}, of the alumatrane complexe, at the concentration of 1.634 g/l using $Al(OH)_3$:TEA:TETA = 10:5:7.5, the reaction time of 3 h , and the reaction temperature of 200 °C is 5.16 e-10 cm^2/sec.

D_{cm} was measured at various polymer concentrations and plotted in Figure 4.22. D_0 was obtained from the intercept of the linear dependence between D_{cm} and polymer concentration. D_0 was determined to be 8.92e-10 cm^2/s, for the alumatrane complexe of $Al(OH)_3$:TEA:TETA equal to 10:5:7.5, at the reaction time of 3 h, and the reaction temperature of 200 °C. D_{cm} decreases linearly as polymer concentration increases. The apparent negative slope of D_{cm} versus concentration suggests that the parameter k_D is negative. confirming the the viscometric result that ethylene glycol is a poor solvent. K_D values are tabulated in Table 4.6.

Table 4.6 Parameter K_D from the reaction using $Al(OH)_3$:TEA:TETA
= 10:5:x where x = 1:2.5:5:7.5:10:15, the reaction time of
3 h, and the reaction temperature of 200 °C

TETA (mmol)	K_D
10	-2.24e-10
25	-1.27e-10
75	-1.40e-9
100	-1.07e-10
150	-2.25e-10
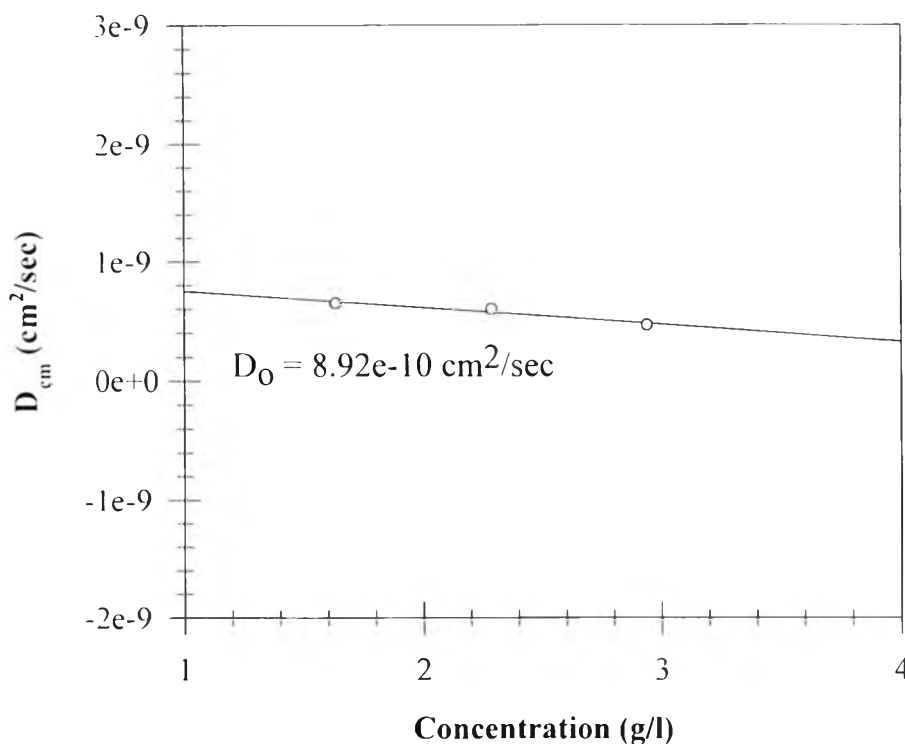
Figure 4.22 Center of mass diffusion coefficients of the alumatrane

complexes versus polymer concentration, measured at 30 °C,

using $Al(OH)_3$:TEA:TETA = 10:5:7.5, reaction time of 3 h ,

and reaction temperature of 200 °C.

In the dilute solution, in the limit of $qR_h \ll 1$, the polymer coil size is much smaller than the probing wavelength, the polymer chain is seen as a dot. Here the measured diffusion coefficient refers to the center of mass diffusion. When $qR_h \gg 1$, the polymer coil size is larger than the probing wavelength, the motion of individual monomers is seen. The diffusion coefficient measured is resulting from internal motion of the polymer chain. In the intermediate regime, $qR_h \approx 1$, it can be expected that both diffusive characters can be observed. Thus by increasing q, one moves smoothly from probing the center of mass diffusion to probing the internal dynamics *[Goddard, (1993)]*.
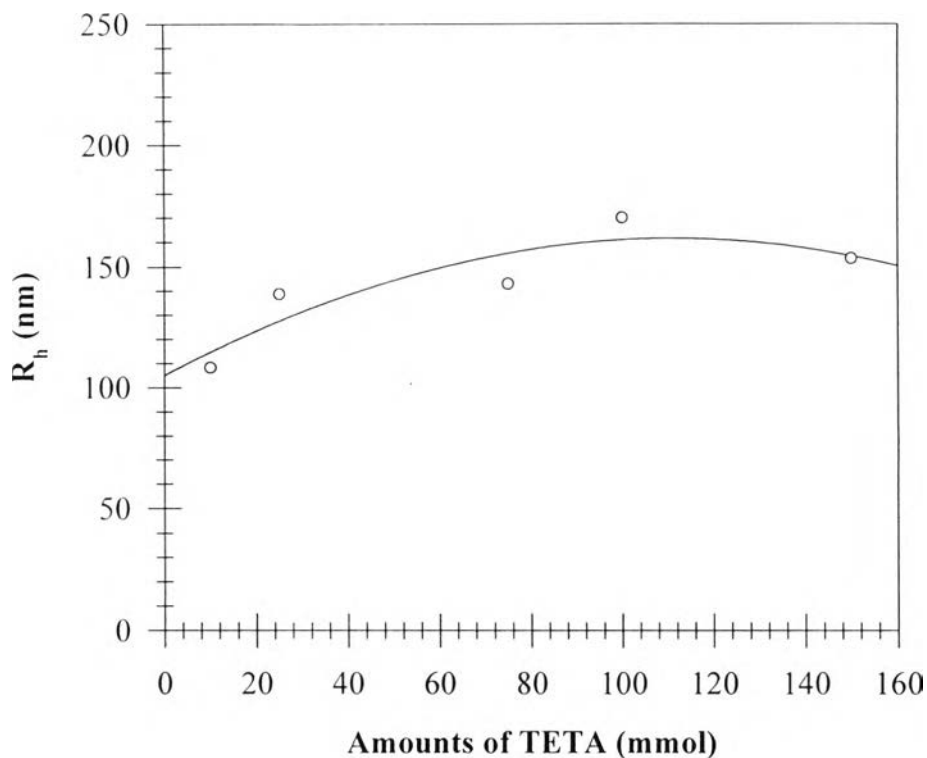
Figure 4.23 Hydrodynamic radius of the alumatrane complexes versus
amounts of TETA, measured at 30 °C, using
$Al(OH)_3$:TEA:TETA = 2:1:1.5, the reaction time of 3 h ,
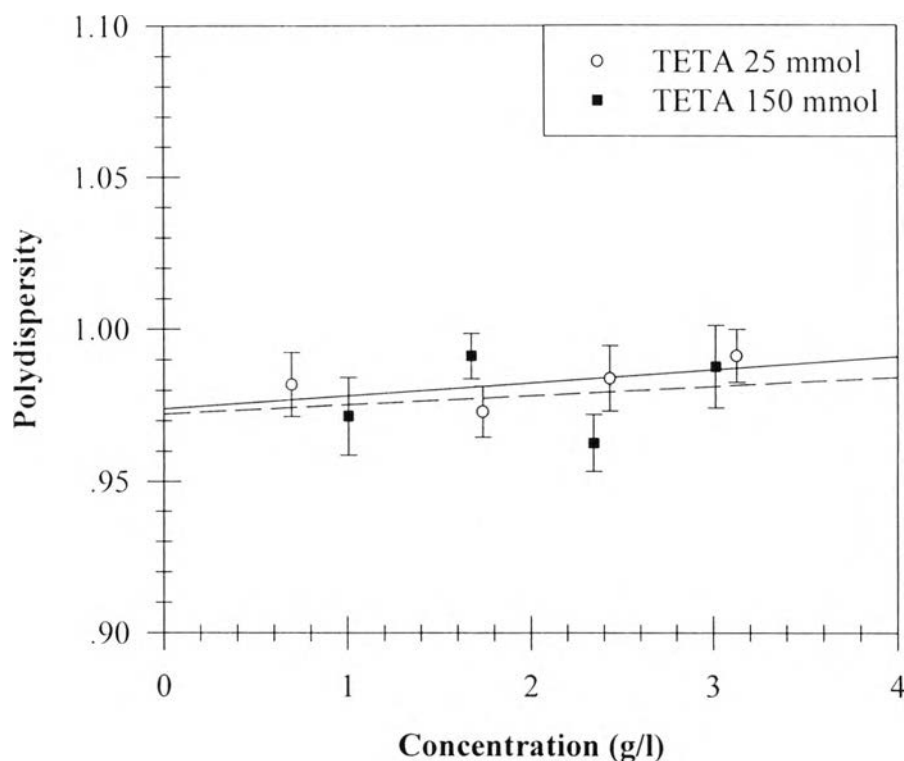and the reaction temperature of 200 °C.

The diffusion coefficient of infinite dilution was used to calculate the hydrodynamic radius according to equation 4.3 and the value of R_h of 108 to 170 nm at 30 °C was obtained. Figure 4.23 shows the dependence of the hydrodynamic radius on the amount of catalyst, TETA. It can be concluded that polymer size slightly increases with TETA content.
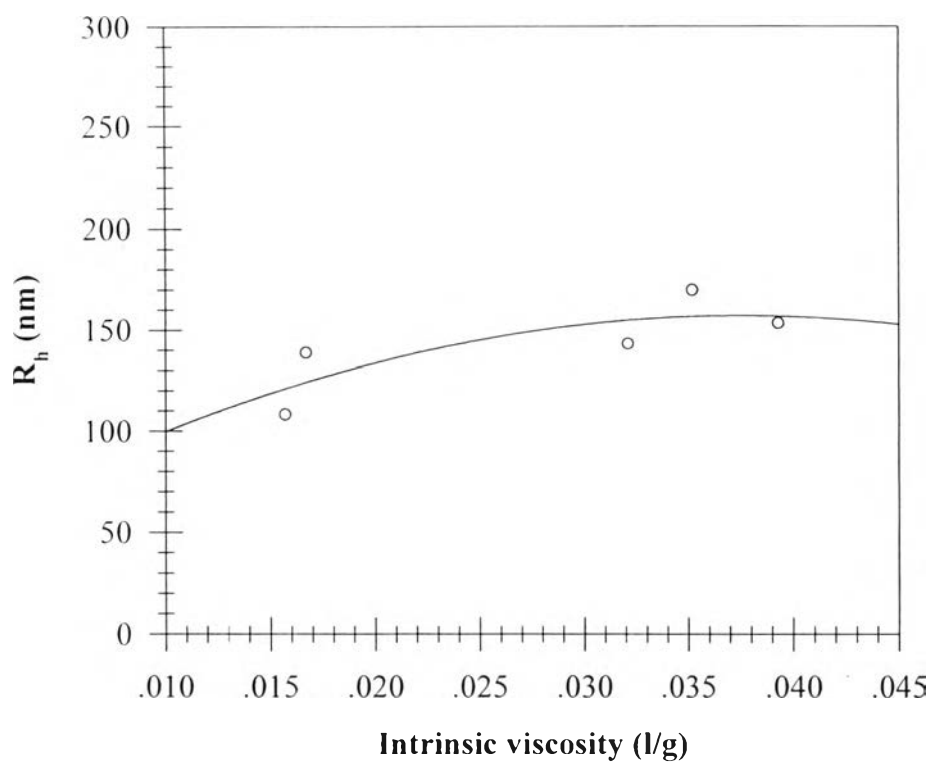
Figure 4.24 Hydrodynamic radius versus intrinsic viscosity of alumatrane
complexes measured at 30 °C using Al(OH)$_3$:TEA:TETA
= 2:1:1.5, the reaction time of 3 h , and the reaction temperature
of 200 °C.

Figure 4.24 shows the linear relationship between the hydrodynamic
radius and intrinsic viscosity of the alumatrane complexes synthesized by
using TETA content between 10 mmol and 150 mmol. This data suggests
that, by using TETA as the catalyst, alumatrane complex size can be varied as
much as 50%, as confirmed by both viscometric and light scattering
measurements.

Figure 4.25 Polydispersity of relaxation time of alumatrane complexes versus
polymer concentration measured at 30 °C in the reaction of
$Al(OH)_3$:TEA:TETA = 2:1:0.5 and $Al(OH)_3$:TEA:TETA
= 2:1:1.5 , reaction time 3 h , reaction temperature 200 °C and
q = 60°.

Figure 4.25 shows that the polydispersity of relaxation time measured
and polymer concentration, for the alumatrane complexes using TETA
contents of 25 and 150 mmol. The ratios of $Al(OH)_3$:TEA:TETA were
2:1:0.5 and 2:1:1.5, the reaction time was 3 h, and the reaction temperature
was 200 °C. The experiment was performed at a fixed angle scattering 60°
and polymer concentration was varied. It can be seen that there are only some

small   differencnces in polydispersity of relaxation time between the alumatrane complexes using TETA contents of 25 and 150 mmol. The value of polydispersity ~ 1.0 means that the normalized second cummulant ~ 1.0 which means that the varance is distribution of D_{cm} values is ~ 100%, i.e. the alumatrane complexe polymer are highly polydisperse.