

## CHAPTER IV

### RESULTS AND DISCUSSION

This research was to synthesize polysiloxanes from SiO<sub>2</sub> or rice husk ash and amines (triethanolamine, diethanolamine) in ethylene glycol by a following one step (condensation reaction).

Firstly, the raw material were characterised by FT-IR and <sup>13</sup>C-NMR. The FT-IR spectra of the raw materials was shown in Figure A1-A6, and the characteristics absorption are shown in the Table 4.1.

**Table 4.1** The characteristic IR group absorption of raw materials

Raw materials	Wave number (cm <sup>-1</sup> )	Functional group	Type of Vibration
SiO <sub>2</sub> from Aldrich	3442	O-H	stretching
	1100	Si-O	stretching
SiO <sub>2</sub> from Aldrich	3425	O-H	stretching
	1100	Si-O	stretching
Rice husk ash	3410	O-H	stretching
	1100	Si-O	stretching
Ethylene glycol	3390	O-H	stretching
	2956-2910	CH <sub>2</sub>	stretching
	1450-1300	CH <sub>2</sub>	bending
	1081-1032	C-O	stretching
Triethanolamine	3389	O-H	stretching
	2959-2825	CH <sub>2</sub>	stretching
	1450-1300	CH <sub>2</sub>	bending

Raw materials	Wave number ( $\text{cm}^{-1}$ )	Function group	Type of Vibration
	1147	C-N	stretching
	1081-1032	C-O	stretching
Diethanolamine	3387	O-H	stretching
	3200	N-H	stretching
	2950-2861	$\text{CH}_2$	stretching
	1450-1300	$\text{CH}_2$	bending
	1449	N-H	bending
	1126	N-H	stretching
	1050	C-O	stretching

The  $^{13}\text{C}$ -NMR spectrum of the raw materials are shown in Figures A7-A12, and characteristics chemical shifts was shown in Table 4.2.

**Table 4.2** The characteristics chemical shifts of the raw materials

Raw materials	$^1\text{H}$ -NMR	Type of Signals	$^{13}\text{C}$ -NMR	Type of Signals
Ethylene glycol $\text{HOCH}_2\text{CH}_2\text{OH}$	4.15 3.39	<u>OH</u> <u><math>\text{CH}_2</math></u>	63.5	<u><math>\text{CH}_2</math></u>
Triethanolamine $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$	5.00 3.55 2.50	<u>OH</u> <u><math>\text{CH}_2\text{OH}</math></u> <u><math>\text{CH}_2\text{N}</math></u>	59.1 56.7	<u><math>\text{CH}_2\text{OH}</math></u> <u><math>\text{CH}_2\text{N}</math></u>
Diethanolamine $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$	4.52 3.95 3.45 2.50	<u>OH</u> <u><math>\text{CH}_2\text{OH}</math></u> <u><math>\text{CH}_2\text{NH}</math></u> <u>NH</u>	60.0 51.2	<u><math>\text{CH}_2\text{OH}</math></u> <u><math>\text{CH}_2\text{NH}</math></u>

The rice husk ash was characterised by X-ray diffraction spectrometry, X-ray fluorescence spectrometry and Scanning electron microscope. In the X-ray diffraction pattern, rice husk ash showed a amorphous peak at  $21.96^\circ$ , as shown in Figure 4.1. In the X-ray fluorescence pattern, rice husk ash was shown to  $K_2O$ ,  $Na_2O$ ,  $CaO$ ,  $MgO$ ,  $Fe_2O_3$ ,  $P_2O_3$ ,  $S_2O_3$  and  $Cl$ , and has percentage of silica of 96.12, as shown in Figure 4.2, and Table 4.3. From the scanning electron micrograph, surface of rice husk ash has pores and different particle sizes, as shown in Figure 4.3. The average particle size of rice husk ash has  $13.47 \mu m$ .

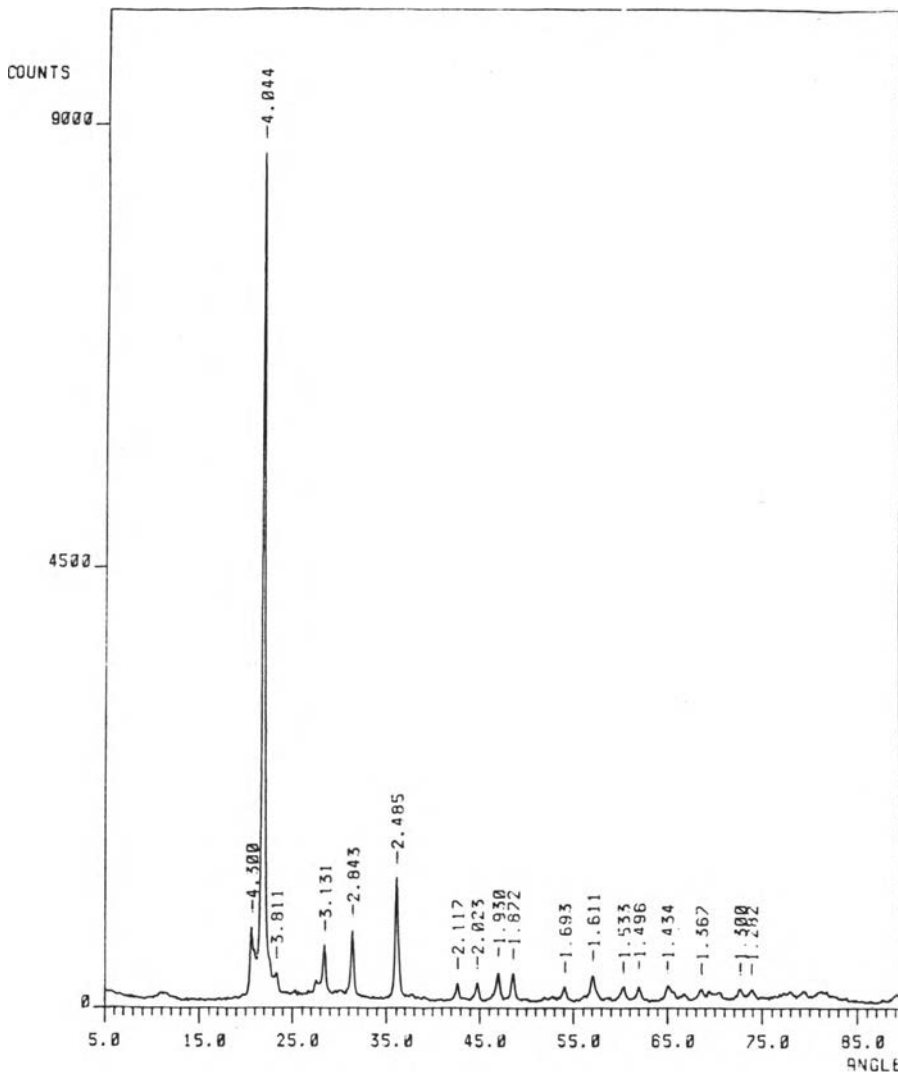
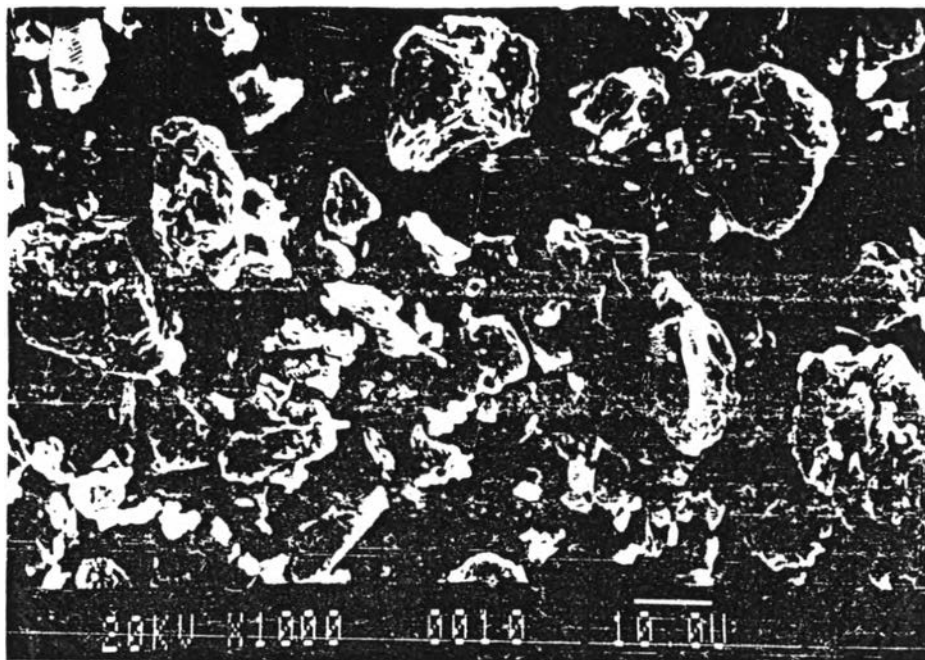


Figure 4.1 X-ray diffraction pattern of rice husk ash





**Figure 4.3** Scanning electron micrograph of rice husk ash

### **Synthesis of Polysiloxane**

The reactions were as follows :

sample 1 :  $\text{SiO}_2$  from Aldrich Chemical Co., In., reacted with TEA and EG

sample 2 :  $\text{SiO}_2$  from PPG Siam Silica Co., reacted with TEA and EG

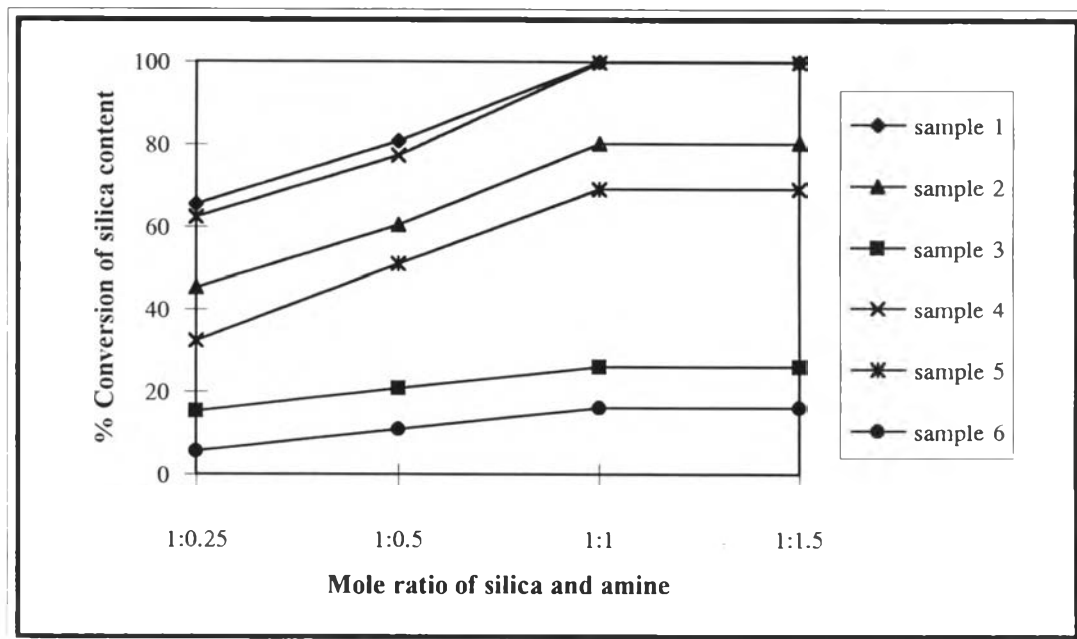
sample 3 : Rice husk ash reacted with TEA and EG

sample 4 :  $\text{SiO}_2$  from Aldrich Chemical Co., Inc., reacted with DEA and EG

sample 5 :  $\text{SiO}_2$  from PPG Siam Silica Co., reacted with DEA and EG

sample 6 : Rice husk ash reacted with DEA and EG

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**Figure 4.4** The curve of % conversion of silica content versus mole ratios of silica and amine

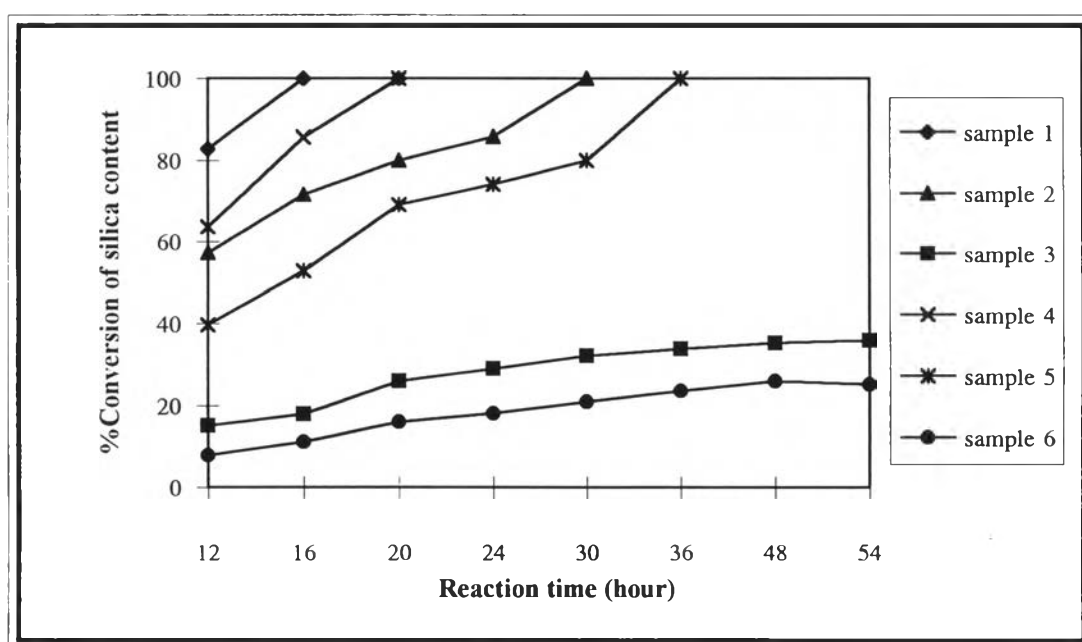
### 3. The effect of reaction time

The effect of reaction time is shown in the table 4.4 and figure 4.5. The reaction temperature was fixed at 200°C and the mole ratio of silica and amine was 1:1. The % conversion of silica increased with increasing reaction time. It can be concluded that the appropriate reaction times for sample 1-6 are 16, 30, 48, 20, 36, and 48 hours, respectively.

The reaction with triethanolamine was faster than the reaction of diethanolamine. It was also found that reaction time was decreased with decreasing the particle size of silica. This is expected as smaller particles have a large surface area/mass ratio.

**Table 4.5** The % conversion of silica or rice husk ash was synthesized with various reaction time.

Reaction time	% Conversion of silica content					
	sample 1	sample 2	sample 3	sample 4	sample 5	sample 6
12	82.76	57.13	15.15	63.59	39.63	7.85
16	100	71.71	17.94	85.73	52.78	11.13
18	100	80.06	26.01	100	69.08	16.08
24	-	85.87	29.04	-	74.21	18.12
30	-	100	32.13	-	80.05	20.87
36	-	-	33.85	-	100	23.62
48	-	-	35.31	-	-	25.38
54	-	-	35.96	-	-	25.12

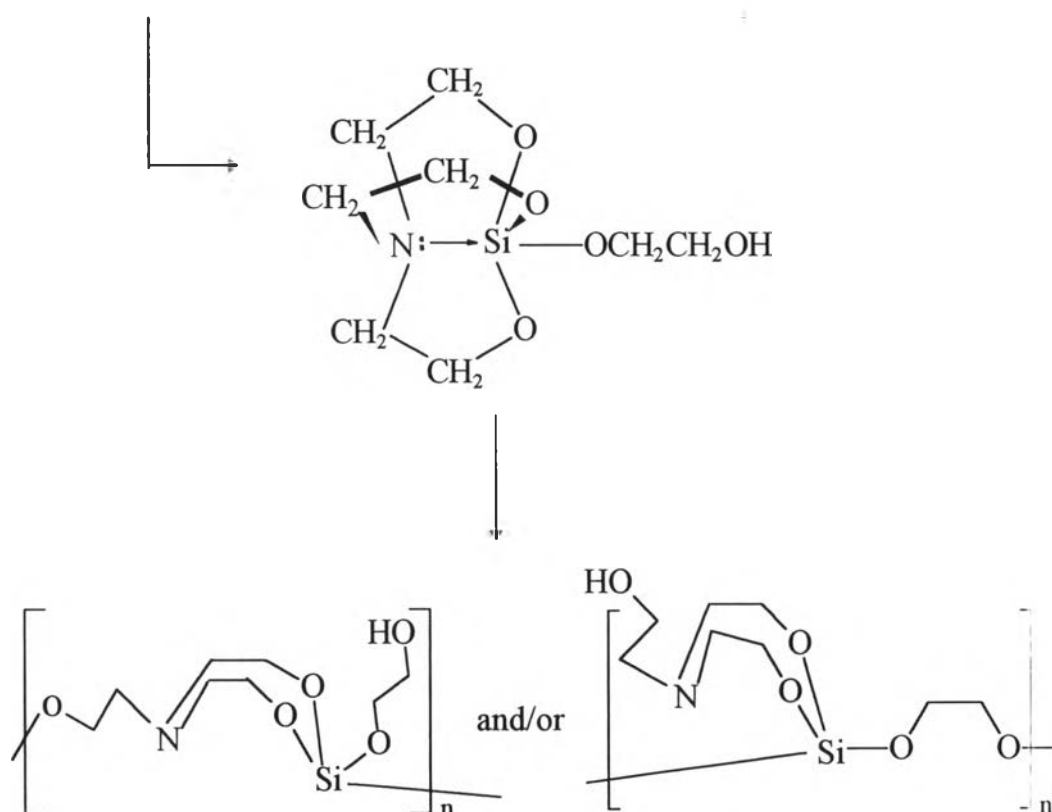


**Figure 4.5** The curve of % conversion of silica or rice husk ash was synthesized with various reaction time.

#### 4. Characterization of products

The products were characterised by FT-IR Spectrometer,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ ,  $^{29}\text{Si-NMR}$  Spectrometer, Elemental Analysis, X-ray Fluorescence Spectrometer and Thermal properties.

##### 4.1 Synthesized products by using TEA



The FT-IR spectra of the samples 1-3 under optimum condition are shown in Figures A13-A15, and the characteristic absorptions are shown in the Table 4.6. They show the same peaks which indicate the presence of strong OH stretching at  $3365\text{ cm}^{-1}$ . The peak at  $2990\text{-}2850\text{ cm}^{-1}$  corresponds



to the CH<sub>2</sub> stretching, whereas the peak at 1460-1350 cm<sup>-1</sup> corresponds to the CH<sub>2</sub> bending. The peak at 1277 cm<sup>-1</sup> is the C-N stretching. The presence of strong Si-O stretching is 1090 cm<sup>-1</sup> and the strong peak at 1050 cm<sup>-1</sup> corresponds to the C-O stretching. The peak at 577 cm<sup>-1</sup> is the Si ← N dative bond of the structure of silatrane.

**Table 4.5** The characteristic IR group absorption of samples 1-3.

Samples	Wave number (cm <sup>-1</sup> )	Functional group	Type of Vibration
1-3	3365	O-H	stretching
	2990-2850	CH <sub>2</sub>	stretching
	1460-1350	CH <sub>2</sub>	bending
	1277	C-N	stretching
	1090	Si-O	stretching
	1050	C-O	stretching
	577	Si←N	stretching

The <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and <sup>29</sup>Si-NMR spectrums were consistent with the structure of products. It was concluded that the samples 1-3 had the same structure and the silatrane complexes in the molecular structure.

The products from samples 1-3 were dissolved in deuterated dimethyl sulfoxide (d<sub>6</sub>-DMSO). The <sup>1</sup>H-NMR spectra (Figures A16-A18) showed signals of N-CH<sub>2</sub> at 2.8-2.9 ppm and N-CH<sub>2</sub>CH<sub>2</sub> at 3.6-3.7 ppm in the silatrane structure. The signals of O-CH<sub>2</sub> at 3.4-3.5 ppm, CH<sub>2</sub>OH 4.2-4.3 ppm, and CH<sub>2</sub>OH at 4.55 ppm [17].

The results from  $^{13}\text{C}$ -NMR spectrums in the Figures A19-A21, indicated the silatrane structure due to signals at 50.0 ppm ( $\text{NCH}_2$ ), and 57.1 ( $\text{CH}_2\text{O}$ ), 59.2-60.2 ( $\text{CH}_2\text{O}$ ) and 62.7-72.1 ( $\text{CH}_2\text{OH}$ ) ppm [22]. And other signals cannot be elucidated but indicate the presence of substantial impurities.

The  $^{29}\text{Si}$ -NMR spectra of samples 1-3 showed one peak at -96 ppm which corresponds to a pentacoordinate Si [22, 23] as shown in figures A22-A24, as only one Si peak was observed, the impurities apparent in the  $^{13}\text{C}$  spectra must be non-silicon compounds .

The characterization by the Elemental Analysis and X-ray Fulorescence Spectrometry, are shown in Table 4.7.

**Table 4.7** The samples 1-3 characterized by Elemental Analysis and X-ray Fluorescence

Samples	% C <sup>a</sup>	% H <sup>a</sup>	% N <sup>a</sup>	% Si <sup>b</sup>	% O <sup>c</sup>
1	40.06	6.80	5.01	11.45	36.68
2	39.92	6.79	4.99	1.43	36.47
3	39.98	6.76	4.97	11.50	36.79

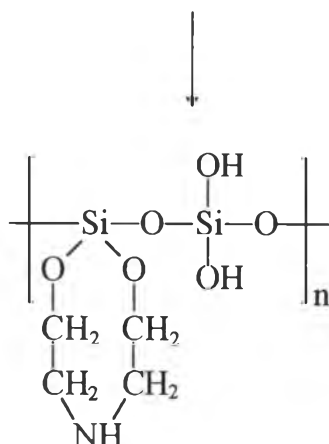
<sup>a</sup> characterized by Elemental Analyser

<sup>b</sup> characterized by X-ray Fluorescence

<sup>c</sup> % O = 100- (% C + % H + % N + % Si)

The elemental and x-ray fluorescence composition of the expected structure can be calculated as % C 40.85, % H 7.23, % N 5.96, % Si 11.92 and % O 34.04 according to analysis.

#### 4.2 Synthesis products by using DEA



The samples 4-6 were not soluble in organic solvents so that they were characterized by FT-IR, <sup>13</sup>C-Solid State NMR Spectroscopy, Elemental Analysis and X-ray Fluorescence Spectroscopy.

The FT-IR spectra (Figure A28-A30) showed the similar peaks. The strong peaks at 3397 cm<sup>-1</sup> indicated the presence of OH stretching. The peaks at 2950-2843 cm<sup>-1</sup> correspond to the CH<sub>2</sub> stretching, whereas the peak at 1450-1380 cm<sup>-1</sup> result from CH<sub>2</sub> bending. The peak at 3200 cm<sup>-1</sup> corresponds to the N-H stretching and the peak at 1466 cm<sup>-1</sup> refers to the N-H bending. The C-N stretching vibration is at 1230 cm<sup>-1</sup>. The Si-O stretching is at 1080 cm<sup>-1</sup> and the strong peak at 1050 cm<sup>-1</sup> is due to the C-O stretching (Table 4.8).

**Table 4.8** The characteristic IR group absorption of samples 4-6

Samples	Wave number (cm <sup>-1</sup> )	Functional group	Type of Vibration
4-6	3397	O-H	stretching
	3200	N-H	stretching
	2950-2843	CH <sub>2</sub>	stretching
	1466	N-H	bending
	1450-1380	CH <sub>2</sub>	bending
	1230	C-N	stretching
	1080	Si-O	stretching
	1050	C-O	stretching

The <sup>13</sup>C-Solid State NMR spectra are shown in Figures A31-A33. The spectra shows signals of the aliphatic C between chemical shifts 56-76 ppm but the exact structure could not be elucidated, nor could it be determined whether one or more species were present.

The percentage of C, H, N and Si were determined (Table 4.9) by Elemental Analysis and X-ray Fluorescence Spectroscopy, respectively.

**Table 4.9** The samples 4-6 characterized by Elemental Analysis and X-ray Fluorescence.

Samples	% C <sup>a</sup>	% H <sup>a</sup>	% N <sup>a</sup>	% Si <sup>b</sup>	% O <sup>c</sup>
4	20.79	5.63	5.10	24.42	44.06
5	20.70	5.70	5.11	24.49	44.00
6	20.75	5.62	5.11	24.40	44.12

<sup>a</sup> characterized by Elemental Analyser

<sup>b</sup> characterized by X-ray Fluorescence

<sup>c</sup> % O = 100 - (% C + % H + % N + % Si)

The elemental and x-ray fluorescence composition of the expected structure can be calculated as % C 21.33, % H 4.89, % N 6.22, % Si 24.89 and % O 42.67 according to analysis.

#### Thermal properties of the products

The white solid powder of samples 1-3, synthesized using triethanolamine, showed similar regions of mass loss in the thermogravimetric thermogram, as shown in Figures A25-A27.

The first small mass loss occurred between 240°C which corresponds to the loss of traces of residual ethylene glycol and triethanolamine. The second major mass loss occurred at the thermal decomposition temperature (Td) of the product in 390°C. The percent final ceramic yields of these products were approximately 24.

For the white solid powder of samples 4-6, synthesized using diethanolamine, showed similar mass losses of products, as shown in Figures A34-A36.

The first small mass loss between 200°C corresponds to the loss of traces of residual ethylene glycol and diethanolamine. The final mass loss from 350°C corresponds to organic ligand decomposition. The percent final ceramic yield of these products were approximately 50.

The determination of particle size by Mastersizer S, before and after reaction of rice husk ash, showed that the particle size after reaction was smaller than before reaction. The particle size after reactions which using triethanolamine and diethanolamine under optimum condition, were 10.83  $\mu\text{m}$  and 11.12  $\mu\text{m}$ , respectively.