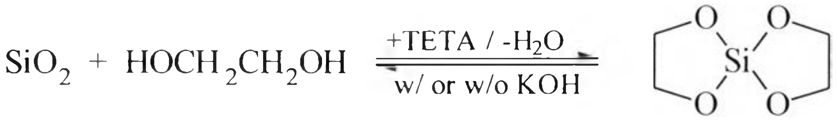
CHAPTER III
RESULTS AND DISCUSSION

3.1 Synthesis

3.1.1 Synthesis of bis(ethane-1,2-diyldioxy)silane, $Si(OCH_2CH_2O)_2$, tetra-coordinated spirosilicate

In this study, bis(ethane-1,2-diyldioxy)silane (Kemmitt and Milestone, 1995) monomer product was synthesized directly from a mixture of silicon dioxide, SiO_2, and ethylene glycol, EG, in the presence of triethylene-tetramine, TETA, as a base or catalyst and with/without potassium hydroxide, KOH, as a co-catalyst. Since water occurred during the equilibrium reaction and also hydrolyzed the product, it must be removed out from the system to push the reaction forward, as illustrated in equation (3.1).



(3.1)

In this synthesis, the reaction mixture which composed of silicon dioxide, ethylene glycol, TETA with/without KOH was started with cloudy solution. After heated to the boiling point of ethylene glycol, 200°C, under nitrogen with constant magnetically stirring, ethylene glycol and water formed as by-product were distilled off, during the reaction. The mixture was given continued heating till it turned clear, meaning that the reaction was completed.

3.1.1.1 Effect of TETA concentration on the synthesis of bis (ethane-1,2-diyldioxy)silane

At TETA concentrations of 25 and 50 mole percent equivalent to silica, the reaction took very long time to complete as compared with the reactions run with 75, 100, 125, 150, and 200% of TETA, which took place much faster. However, TETA concentrations of 150 and 200 mole percent equivalent to silica gave slightly different reaction times, suggesting that at TETA concentration higher than 150 mole % equivalent to silica, the reaction is preudo first order in base concentration, as shown in Table 3.1.

Therefore, the best TETA concentration to synthesize bis(ethanr-1,2-diyldioxy)silane was 125 mole % equivalent to silica, which was took 22 hours for the reaction solution to become clear.

Table 3.1 Effect of the TETA concentration on the reaction time.

[TETA] (mole % equivalent to SiO_2)	Reaction Time (hours)
25	72
50	40
75	28
100	24
125	22
150	21
200	20

3.1.1.2 Effect of KOH concentration on the synthesis of bis (ethane-1,2-diyldioxy)silane

According to Laine *et al*'s work, they used 100 mole percent of potassium hydroxide equivalent to silica as catalyst to synthesize pentacoordinated spirosilicate. Therefore, this work was repeated at much lower KOH concentration to specifically obtain tetracoordinated spirosilicate. The KOH concentration used was less than 10 mole percent equivalent to silica. It decreased the reaction time from 22 to 10 hours with KOH concentration less than 10 mole percent equivalent to silica without showing any penta-coordinated spirosilicates.

3.1.1.3 Effect of EG quantity on the synthesis of bis(ethane-1,2-diyldioxy)silane

At the reaction temperature of 200°C, some of ethylene glycol was distilled off with water. Ethylene glycol quantity of 5 mL gave the longest reaction time, as compared to 7.5, 15, and 20 mL. Moreover, the volumes of 15 and 20 mL gave the same reaction time. Thus, 15 mL of ethylene glycol was the best volume with enough amount of EG to react with silica although some was distilled off, as shown in Table 3.2.

Table 3.2 Effect of the EG quality on the reaction time.

EG Quantity (mL)	Reaction Time (hours)
5	32
7.5	22
15	18
20	18

3.1.1.4 Effect of reaction time on the synthesis of bis(ethane-1,2-diyldioxy)silane

3.1.1.4.1 Without potassium hydroxide (KOH)

Synthesis of bis(ethane-1,2-diyldioxy)silane was con-ducted by mixing 12.5 mmol silica, 15 mL of ethylene glycol, and 15.63 mmol TETA. The percent ceramic yield increased with decreasing reaction time {percent ceramic yield = [weight of silica from pyrolysis*100]/weight of sample before pyrolysis}, see Table 3.3. The increase in ceramic yield was caused by incompletely reacted silica. Moreover, this increase is also the result of further polymerization of spirosilicate monomer. Therefore, the optimum reaction time for bis(ethane-1,2-diyldioxy)silane synthesis was at 18 hours when fused silica was used as starting material. However, for fumed silica the reaction time was much faster, 6 hours. This is because fumed silica has higher surface area resulting in higher reactivity. The found ceramic yield 40.82 was nearly the same as the calculated value, 40.54%, where the structure belonged to the tetracoordinated spirosilicate.

Table 3.3 Effect of the reaction time on the percent ceramic yield in the absence of KOH.

Reaction Time (hours)	Percent Ceramic Yield (%)
8	87.00
10	72.47
14	59.00
18	40.82
20	45.39
24	62.50

3.1.1.4.2 With potassium hydroxide (KOH)

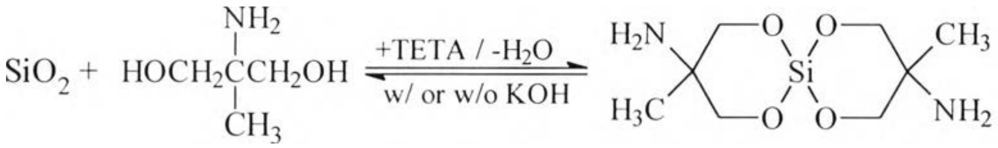
When less than 10 mole percent equivalent of KOH to silica was added, the reaction time decreased from 18 to 10 hours for fused silica and from 6 to 4 hours for fumed silica. This is because KOH is a very strong base, acting as co-catalyst, and fumed silica has higher surface area, see Table 3.4.

Table 3.4 Effect of the reaction time on the percent ceramic yield in the presence of KOH.

Reaction Time (hours)	Percent Ceramic Yield (%)
4	77.25
6	66.67
8	55.00
10	40.82
12	44.00

3.1.2 Synthesis of bis(2-amino-2-methylpropane-1,3-diyldioxy)silane, tetracoordinated spirosilicate

In this study, bis(2-amino-2-methylpropane-1,3-diyldioxy) silane(Kemmitt and Milestone, 1995) monomer product was synthesized from a mixture of silicon dioxide, SiO_2, and 2-amino-2-methyl-1,3-propanediol, C4, in the presence of TETA, as solvent and catalyst with/without co-catalyst KOH. Similarly, water occurred during the equilibrium reaction and also hydrolyzed the product, it must thus be removed out from the system to push the reaction forward, as illustrated in equation (3.2).



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3.1.2.1 Effect of reaction temperature on the synthesis of bis(2-amino-2-methylpropane-1,3-diyldioxy)silane

The ceramic yield decreased with increasing temperature, meaning that at low temperature, 140°C, under vacuum at 0.1mmHg, there is not enough energy for silica to react with 2-amino-2-methyl-1,3-propanediol, C4. However, at high temperature, 165°C, 0.1mmHg, most of the starting material and solvent, 2-amino-2-methyl-1,3-propanediol and TETA, respectively, were distilled off. Thus, the temperature of 160°C at 0.1mmHg was the most suitable condition to synthesize bis(2-amino-2-methylpropane-1,3-diyldioxy)silane, as illustrated in Table 3.5.

Table 3.5 Effect of the reaction temperature on the percent ceramic yield.

Reaction Temperature (°C), 0.1mmHg	Percent Ceramic Yield (%)
140	81.00
150	67.83
160	52.32
165	71.72

3.1.2.2 Effect of 2-amino-2-methyl-1,3-propanediol, C4, concentration on the synthesis of bis(2-amino-2-methyl propane-1,3-diyldioxy)silane

At the reaction temperature of 160°C under vacuum, 0.1mmHg, 2-amino-2-methyl-1,3-propanediol concentrations of 13.34, 20.01, and 26.68 mmol gave high ceramic yield, meaning that at C4 concentration lower than 26.68 mmol, silica was incompletely reacted, because some of 2-amino-2-methyl-1,3-propanediol was distilled off, whereas 40.02 and 53.36 mmol of C4 gave 26.88% ceramic yield, which is nearly the same as the calculated value, 25.42%, where the structure belonged to tetracoordinated species. Hence, 2-amino-2-methyl-1,3-propanediol concentration of 40.02 mmol (4.2g) at 160°C under vacuum, 0.1mmHg, was the most suitable condition to synthesize bis(2-amino-2-methylpropane-1,3-diyldioxy)silane, see Table 3.6.

Table 3.6 Effect of the C4 concentration on the percent ceramic yield.

C4 Concentration (mmol)	Percent Ceramic Yield (%)
13.34	52.32
20.01	42.97
26.68	38.44
40.02	26.88
53.36	26.88

3.1.2.3 Effect of TETA quantity on the synthesis of bis(2-amino-2-methylpropane-1,3-diyldioxy)silane

TETA amount of 0.0 and 5.0 mL gave very highly viscous solution resulting in difficulty for molecules to move and react together. However, 12.0 and 15.0 mL were too dilute causing the reaction to occur very slowly. Therefore, 10.0 mL of TETA was the best concentration to synthesize bis(2-amino-2-methylpropane-1,3-diyldioxy)silane.

3.1.2.4 Effect of KOH concentration on the synthesis of bis(2-amino-2-methylpropane-1,3-diyldioxy)silane

Again referring to Laine *et al*'s work, which used 100 mole percent of KOH equivalent to silica as catalyst to synthesize pentacoordinated spirosilicate, therefore, the KOH concentration used in this work was less than 10 mole percent equivalent to silica in order to synthesize tetracoordinated spirosilicate monomer. The result from this study showed that KOH concentration, less than 10 mole percent equivalent to silica gave only tetracoordinated spirosilicate.

3.1.2.5 Effect of reaction time on the synthesis of bis(2-amino-2-methylpropane-1,3-diyldioxy)silane

3.1.2.5.1 Without potassium hydroxide (KOH)

The synthesis study of bis(2-amino-2-methylpropane-1,3-diyldioxy)silane was conducted by mixing 6.67 mmol fumed silica and 40.02 mmol 2-amino-2-methyl-1,3-propanediol in 10 mL of TETA as catalyst and solvent. The percent ceramic yield increased with decreasing reaction time {percent ceramic yield = [weight of silica from pyrolysis*100]/weight of sample before pyrolysis}. The increase in ceramic yield was caused by incompletely reacted silica. Moreover, the longer reaction time resulted in further polymerization. Therefore, the optimum reaction time for bis(2-amino-2-methylpropane-1,3-diyldioxy)silane synthesis was at 24 hours, see Table 3.7.

Table 3.7 Effect of the reaction time on the percent ceramic yield in the absence of KOH.

Reaction Time without KOH(hours)	Percent Ceramic Yield (%)
14	77.60
18	54.12
20	38.41
24	26.88
28	29.21
34	47.35
48	63.52

3.1.2.5.2 With potassium hydroxide (KOH)

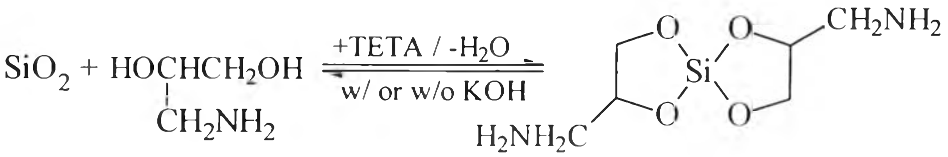
The same reason as that mentioned in the study of the reaction time without KOH was applied in this case. However, when less than 10 mole % equivalent of KOH to silica was added, the reaction time was decreased from 24 to 14 hours, owing to the strong base of KOH, acting as co-catalyst, see Table 3.8.

Table 3.8 Effect of the reaction time on the percent ceramic yield in the presence of KOH.

Reaction Time with KOH(hours)	Percent Ceramic Yield (%)
6	61.51
10	47.34
14	26.88
18	47.30

3.1.3 Synthesis of bis(3-aminopropane-1,2-diyldioxy)silane, $Si\{OCH_2CH(CH_2NH_2)O\}_2$, tetracoordinated spirosilicate

In this study, bis(3-aminopropane-1,2-diyldioxy)silane (Kemmitt and Milestone, 1995) monomer product was synthesized from a mixture of silicon dioxide, SiO_2, and 3-amino-1,2-propanediol, C3, in the presence of TETA as solvent and catalyst with/without KOH as co-catalyst. The reaction was in equilibrium, water produced during the reaction must thus be removed out from the system to push the reaction forward, as illustrated in equation (3.3).



(3.3)

3.1.3.1 Effect of reaction temperature on the synthesis of bis(3-aminopropane-1,2-diyldioxy)silane

The reaction temperature of 150°C under vacuum at 0.1mmHg gave much higher ceramic yield than theoretical ceramic yield, meaning that silica was not completely reacted due to insufficient energy for silica to react with 3-amino-1,2-propanediol. The reaction temperature of 160°C under vacuum at 0.1mmHg gave much closer ceramic yield to the calculated value, 29.13%, therefore, the temperature of 160°C at 0.1mmHg was the most proper condition to synthesize bis(3-aminopropane-1,2-diyldioxy)silane, Table3.9.

Table 3.9 Effect of the reaction temperature on the percent ceramic yield.

Reaction Temperature (°C)	Percent Ceramic Yield (%)
150	67.56
160	40.00

3.1.3.2 Effect of 3-amino-1,2-propanediol concentration on the synthesis of bis(3-aminopropane-1,2-diyldioxy)silane

Referring to the reaction temperature, 160°C under vacuum, 0.1mmHg, 3-amino-1,2-propanediol concentrations of 10 and 20 mmol gave high ceramic yield, meaning that silica was not completely reacted, because some 3-amino-1,2-propanediol was distilled off. 30 and 40 mmol C3 gave 30.45 and 30.42 %, respectively, which is nearly the same ceramic yield as the calculated value, 29.13%, where the structure was tetracoordinated species. Hence, 3-amino-1,2-propanediol concentration of 30 mmol at 160°C under vacuum, 0.1mmHg, was the most suitable condition to synthesize bis(3-aminopropane-1,2-diyldioxy)silane, see Table 3.10.

Table 3.10 Effect of the C3 concentration on the percent ceramic yield.

C3 Concentration	Percent Ceramic Yield (%)
10	68.38
20	40.00
30	30.45
40	30.42

3.1.3.3 Effect of TETA quantity on the synthesis of bis(3-aminopropane-1,2-diyldioxy)silane.

The TETA amount of 0.0 mL gave the solution with very high viscosity, resulting in difficulty for molecules to move and react together. However, 7.0 and 10.0 mL were too dilute, causing a long reaction time. 5.0 mL TETA was thus the best quantity to synthesize bis(3-aminopropane-1,2-diyldioxy)silane, see Table 3.11.

Table 3.11 Effect of the reaction time on the TETA quantity.

Reaction Time (hours)	TETA Quantity (mL)
26	0.00
14	5.00
18	7.00
20	10.00

3.1.3.4 Effect of KOH concentration on the synthesis of bis(3-aminopropane-1,2-diyldioxy)silane.

Referring to Laine *et al*'s work, using 100 mole percent of KOH equivalent to silica as catalyst to synthesize pentacoordinated spirosilicate, therefore, the KOH concentration used in this work was less than 10 mole percent equivalent to silica in order to synthesize tetracoordinated spirosilicate monomer. The result from this study showed that the reaction time was decreased from 14 to 10 hours with KOH concentration less than 10 mole percent equivalent to silica without giving any pentacoordinated spirosilicate.

3.1.3.5 Effect of reaction time on the synthesis of bis(3-amino propane-1,2-diyldioxy)silane

3.1.3.5.1 Without potassium hydroxide (KOH)

The synthesis study of bis(3-aminopropane-1,2-diyl dioxy)silane was conducted by mixing 5 mmol fumed silica and 30 mmol C3 in 5 mL of TETA as catalyst and solvent. The percent ceramic yield increased with decreasing in reaction time {percent ceramic yield = [weight of silica from pyrolysis*100]/weight of sample before pyrolysis}. The increase in ceramic yield was caused by incompletely reacted fumed silica. The percent ceramic yield also increased with increase in the reaction time, 18 and 20 hours. This increase is the result of further polymerization caused by longer reaction time. Therefore, the optimum reaction time for bis (3-aminopropane-1,2-diyldioxy)silane synthesis was at 14 hours, Table 3.12.

Table 3.12 Effect of the reaction time in the absence of KOH on the percent ceramic yield.

Reaction Time without KOH (hours)	Percent Ceramic Yield (%)
10	42.50
14	30.45
18	32.80
20	37.51

3.1.3.5.2 With potassium hydroxide (KOH)

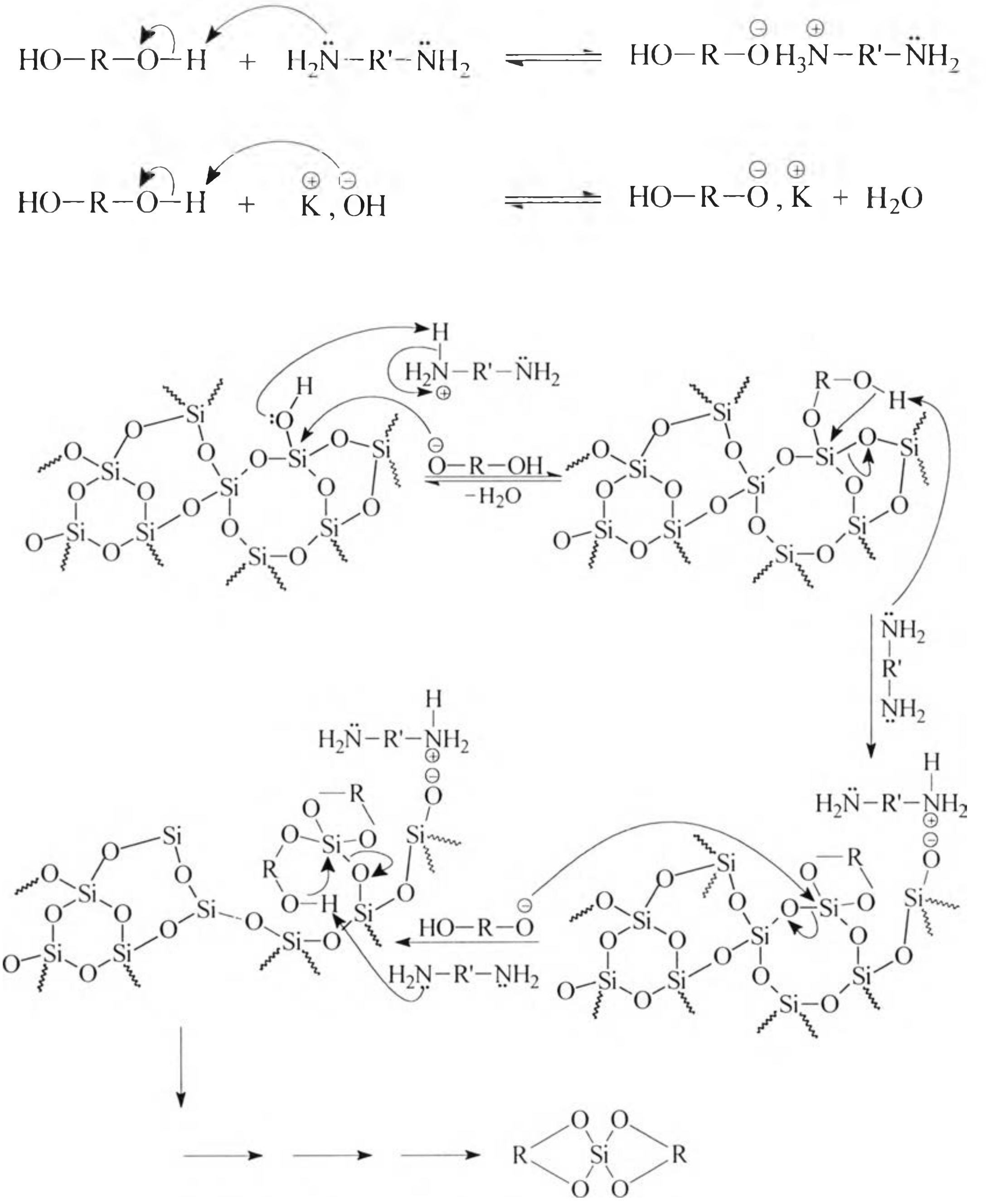
When less than 10 mole percent equivalent of KOH to silica was added, the reaction time decreased from 14 to 10 hours because of the strong base KOH, acting as co-catalyst.

As a summary of tetracoordinated spirosilicate synthesis the mechanistic model can be demonstrated in Scheme 3.1.

The mechanism to synthesize bis(ethane-1,2-diyldioxy)silane, where R: CH_2CH_2, and R': $CH_2CH_2NHCH_2CH_2NHCH_2CH_2$, was shown in Scheme 3.1. (Blohowiak *et al.* 1994, found the rate of dissolution of silica during the synthesis of pentacoordinated silicon complexes was linearly dependent on the surface area and initial base concentration).

TETA is a weak base, which has a lone pair electron. When TETA was used as catalyst and solvent, the reaction took much longer as compared to that having KOH as co-catalyst. It is simply explained that KOH is a strong base and pull proton from ethylene glycol much faster.

Similarly, the mechanism to synthesize bis(3-aminopropane-1,2-diyldioxy)silane, where R: $CH_2CH(CH_2CN_2)$ and bis(2-amino-2-methylpropane-1,3-diyldioxy)silane, where R: $CH_2(CH_3)C(NH_2)CH_2$ could be seen in **Scheme 3.1**. In these two cases, the diols containing amino group will also act as catalyst.



Scheme 3.1

3.2 Characterization

3.2.1 Synthesis of bis(ethane-1,2-diyldioxy)silane, $Si[OCH_2CH_2O]_2$, tetracoordinated spirosilicate

Bis(ethane-1,2-diyldioxy)silane was prepared according to equation 3.1, in more than 80 % overall yield directly from fused or fumed silica and ethylene glycol in the presence of TETA, as catalyst with/without KOH, as co-catalyst. The structure of glycolato spirosilicate was confirmed by FT-IR, NMR, TGA, DSC, and FAB$^+$-MS.

3.2.1.1 Fourier Transform Infrared Spectroscopy (FT-IR)

The spectra of bis(ethane-1,2-diyldioxy)silane and all starting materials, namely, silica {SiO_2} and ethylene glycol {$HOCH_2$-CH_2OH, EG} are shown in Figure 1. The FT-IR spectrum of bis(ethane-1,2-diyldioxy)silane showed broad band at 3386 cm^{-1} corresponds to the O-H stretching from water which is absorbed by the product and intermolecular hydrogen bonding (Cairn 1965), whereas 2949-2882 cm^{-1} results from the C-H stretching. The peaks at 1085, 966, and 883 cm^{-1} are assigned to Si-O-CH stretching (Launer 1978, Bieman 1989, and Robinson 1990).

3.2.1.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

3.2.1.2.1 Proton Nuclear Magnetic Resonance Spectroscopy (^1H-NMR)

The ^1H-NMR spectrum of bis(ethane-1,2-diyldioxy)silane (Figure 2) showed absorption at δ =3.27ppm with broad singlet, indicating the O-H from H_2O in DMSO and absorbed by the product, which is in agreement with FT-IR. The shape singlet peak at δ =3.38ppm results from the CH_2-O-Si (Laine, 1991, synthesized pentacoordinated gave broad singlet). The ^1H-NMR results of all starting materials, ethylene glycol, triethylenetetramine, methanol, acetonitrile, and bis(ethane-1,2-diyldioxy) silane are in Table 3.13.

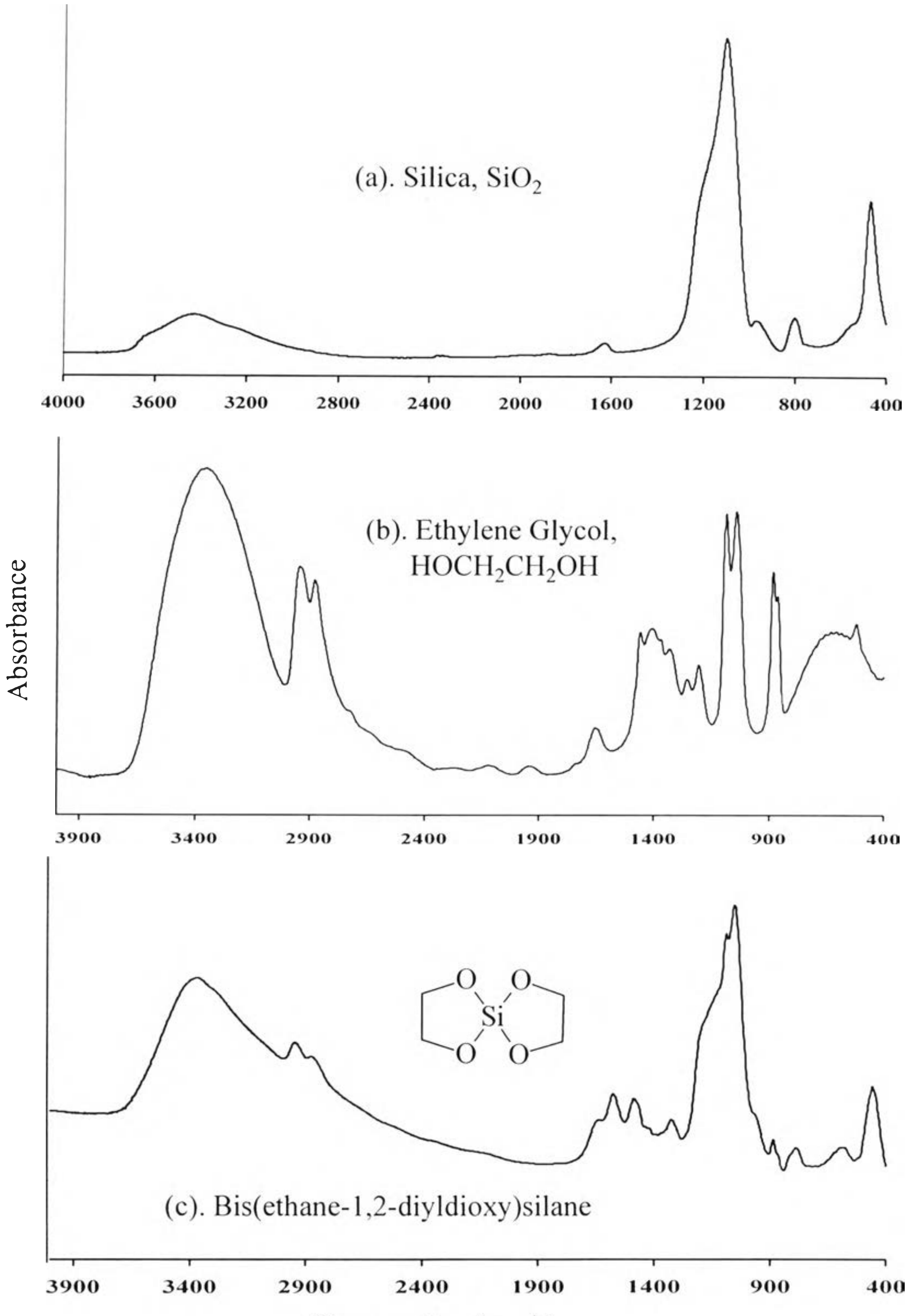


Figure 1 FT-IR of (a), (b), and (c).

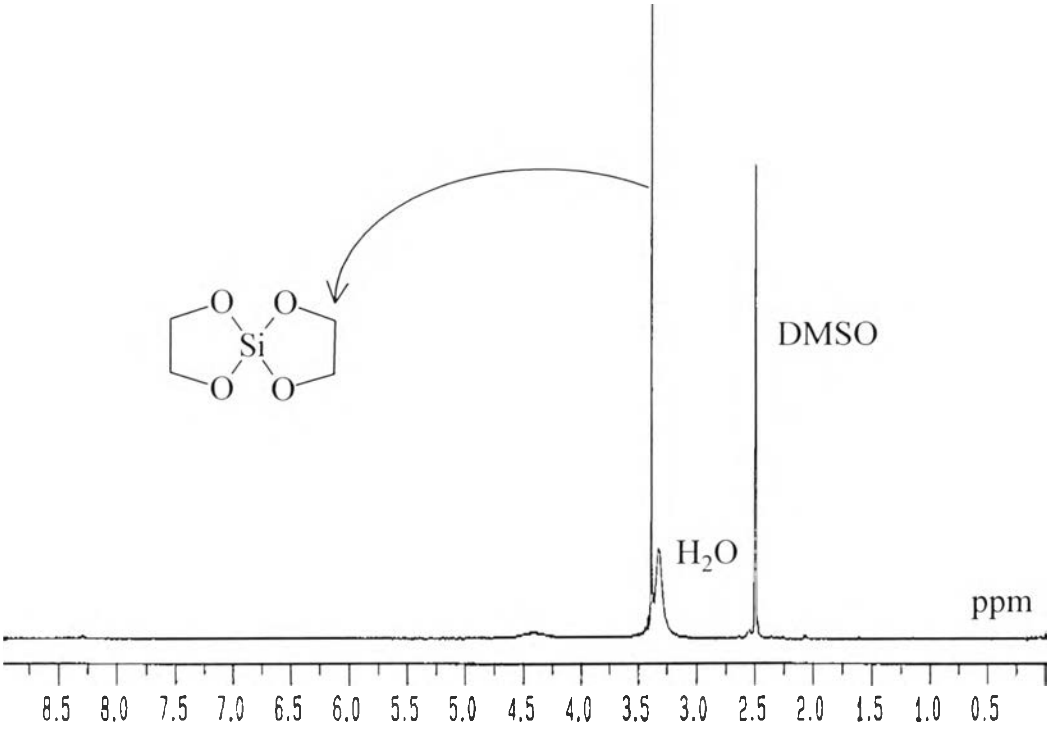


Figure 2 ^1H-NMR of bis(ethane-1,2-diyldioxy)silane.

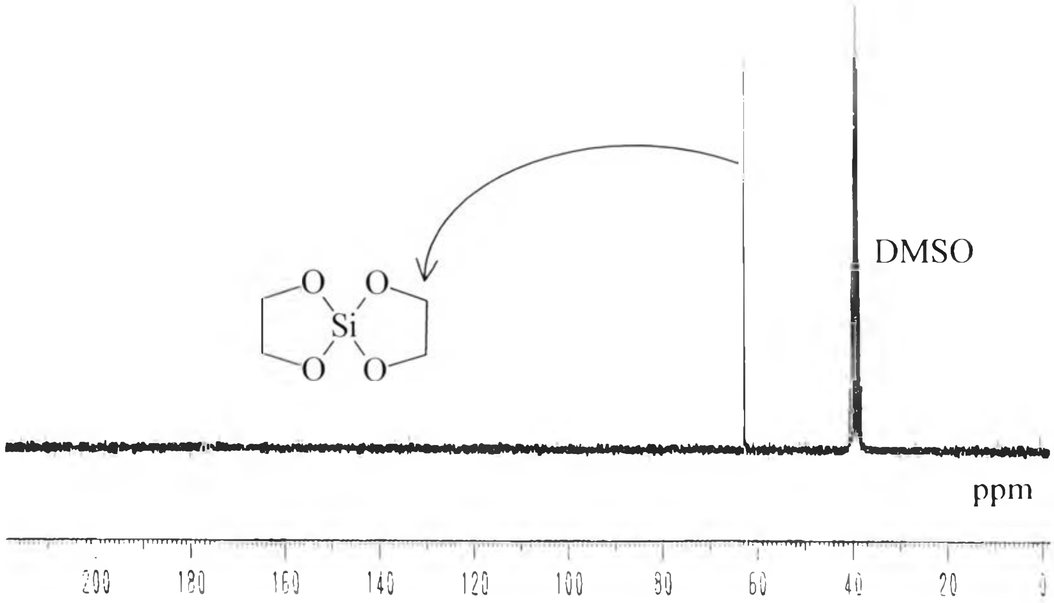


Figure 3 ^{13}C-NMR of bis(ethane-1,2-diyldioxy)silane.

3.2.1.2.2 Carbon Nuclear Magnetic Resonance Spectroscopy (^{13}C-NMR)

The ^{13}C-NMR results of all starting materials and solvents are also shown in Table 3.13. The ^{13}C-NMR spectrum showed only single absorption at δ =62.75ppm corresponding to the CH_2-O-Si, Figure 3 (Laine 1991 synthesized pentacoordinated gave two peaks of the ^{13}C-NMR).

3.2.1.2.3 Silicon Nuclear Magnetic Resonance Spectroscopy (^{29}Si-NMR)

The ^{29}Si-NMR spectrum, see Figure 4, showed only one peak at δ = -104ppm, see Table 3.13, which is consistent with those previously reported for aliphatic, pentacoordinated spirosilicates showing the monomeric pentacoordinated species (Kemmitt and Milestone 1995). However, in this case the ^{29}Si-NMR was conducted using the reaction solution. There is therefore a partial bonding between the product and TETA in the solution, as indicated by Frye's group.

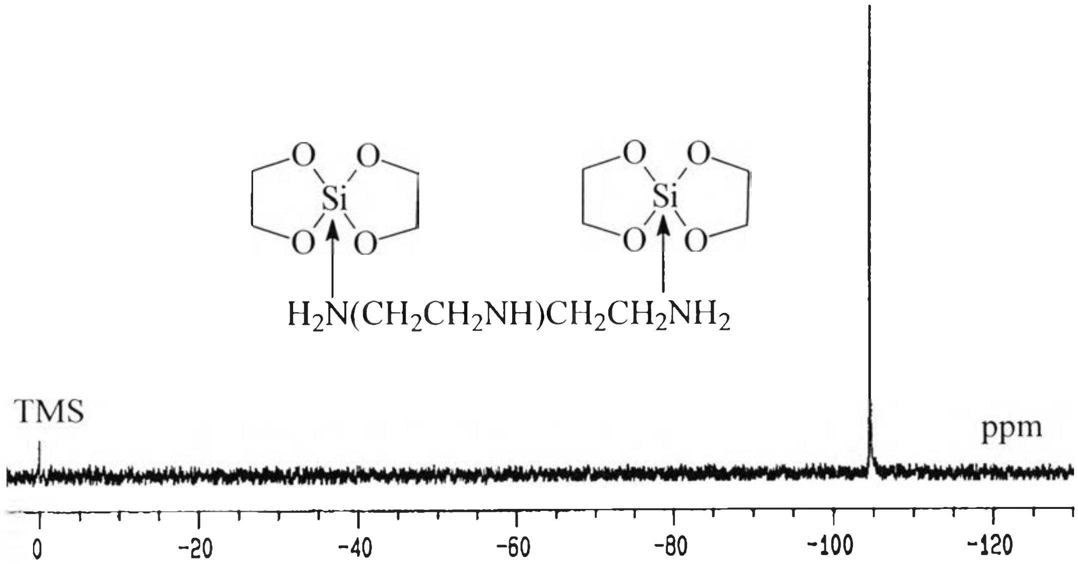
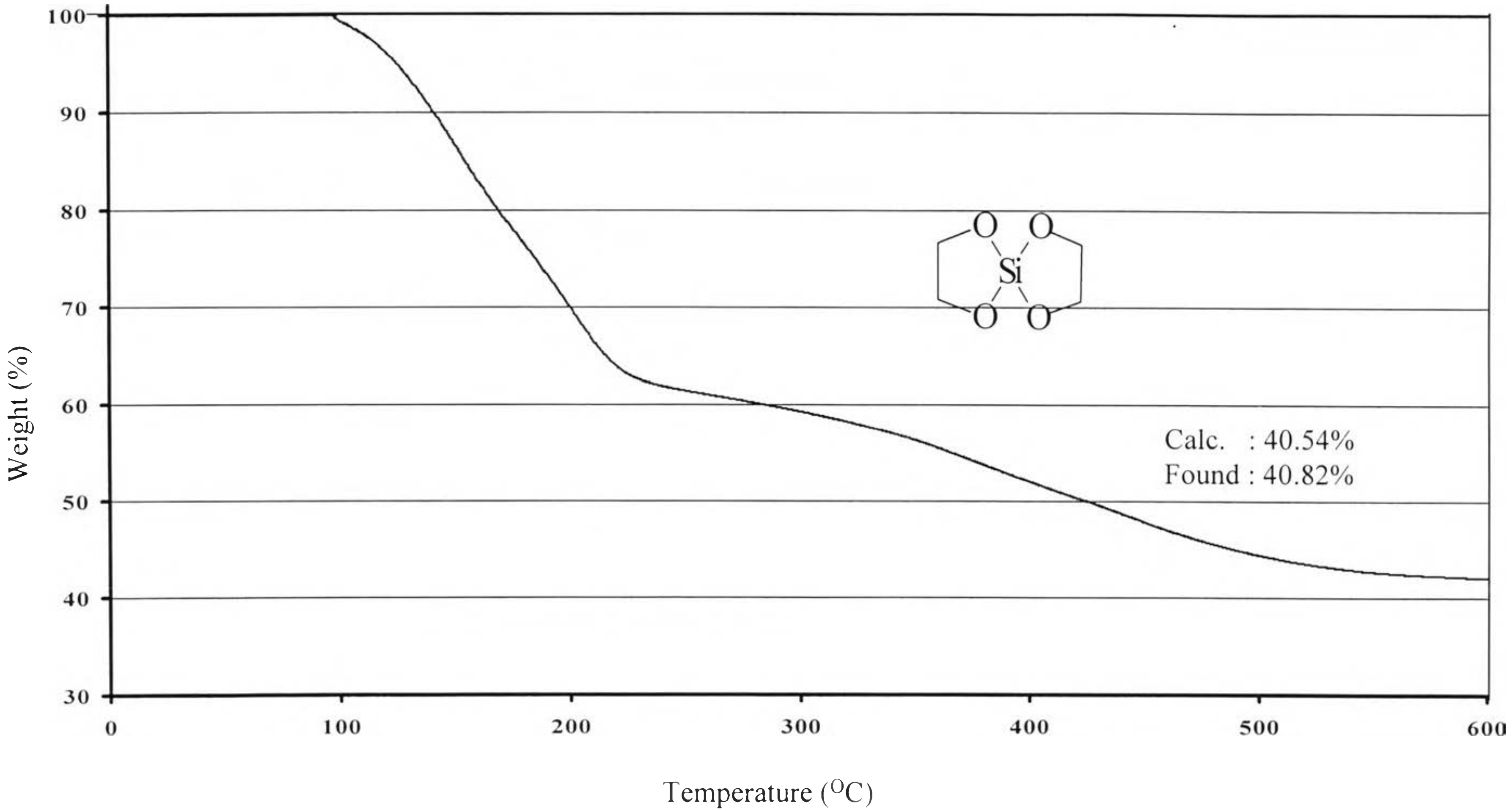


Figure 4 ^{1}H-NMR of bis(ethane-1,2-diyldioxy)silane.



Calc. : 40.54%
Found : 40.82%

Figure 5 TGA of bis(ethane-1,2-diyldioxy)silane.

Table 3.13 Summary of ^{1}H-NMR, ^{13}C-NMR, and ^{29}Si-NMR results of starting materials, solvents, and bis(ethane-1,2-diyldioxy) silane.

Sample	^{1}H-NMR(ppm)	^{13}C-NMR(ppm)	^{29}Si-NMR(ppm)
Triethylene-tetramine	1.25(s) 2.50(t) 2.75(t)	39.2, 40.3 42.0, 46.3 46.9	
Methanol	3.34 and 4.11	49.00	
Acetonitrile	2.00	1.3 and 117.7	
Ethylene Glycol	3.62(s) and 4.23(s)	63.4	
Bis(ethane-1,2-diyldioxy)silane	3.27(broad, s) and 3.38(s)	62.75	-104

3.2.1.3 Thermogravimetric Analysis (TGA)

The result from TGA, as indicated in Figure 5, gave 40.82% ceramic yield which was nearly the same as the calculated value, 40.54%, where the structure was tetracoordinated species.

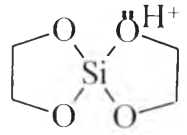
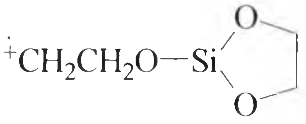
3.2.1.4 Differential Scanning Calorimetry (DSC)

Bis(ethane-1,2-diyldioxy)silane showed two endothermic peaks with different temperatures. The first one occurring at lower temperature can be defined as the melting point of the compound.

3.2.1.5 Positive Fast Atomic Bombardment Mass Spectroscopy (FAB$^+$-MS)

Mass spectral analysis suggests that there is only one bis(ethane-1,2-diyldioxy)silane monomer (m/e 149). However, the molecular weight of this monomer was hardly shown, due to the high energy used in the FAB$^+$MS mode. Therefore, the stability of molecular structure will not be stable giving the base peak at m/e = 57. The fragmentation of the product is shown in Table 3.14.

Table.3.14 The proposed structure and fragmentation of product.

m/e	Intensities	Proposed Structure
149	7.00	
132	31.57	
72	9.11	$^{\cdot+}\mathrm{CH_2CH_2O{-}Si}$
58	100	$^{\cdot+}\mathrm{CH_2O{-}Si}$
44	80.94	$^{\cdot+}\mathrm{O{-}Si}$

3.2.2 Synthesis of bis(2-amino-2-methylpropane-1,3-diyldioxy) silane, *$Si[OCH_2(CH_3)C(NH_2)CH_2O]_2$*, tetracoordinated spirosilicate

Bis(2-amino-2-methylpropane-1,3-diyldioxy)silane was prepared according to equation 3.2 in more than 80% overall yield directly from fumed silica and 2-amino-2-methyl-1,3-propanediol in the presence of TETA used as both catalyst and solvent. The structure of bis(2-amino-2-methylpropane-1,3-diyldioxy)silane was also determined by the following techniques.

3.2.2.1 Fourier Transform Infrared Spectroscopy (FT-IR)

The spectra of bis(2-amino-2methylpropane-1,3-diyldioxy)silane and all starting materials, namely, silica {SiO_2} and 2-amino-2-methyl-1,3-propanediol {$HOCH_2(CH_3)C(NH_2)CH_2OH$, C4} are shown in Figure 6. The FT-IR spectrum of of bis(2-amino-2-methylpropane-1,3-diyldioxy)silane showed broad band at 3406 cm^{-1} indicating the O-H stretching, from water which is absorbed by the product, N-H stretching in the molecule, and intermolecular hydrogen bonding (Cairn 1965), whereas 2953-2868 cm^{-1} corresponds to the C-H stretching. The peaks at 1082, 962, and 883 cm^{-1} are assigned to Si-O-CH stretching.

3.2.2.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

3.2.2.2.1 *Proton Nuclear Magnetic Resonance Spectroscopy (^1H-NMR)*

The ^1H-NMR spectrum of bis(2-amino-2-methyl-propane-1,3-diyldioxy)silane, see Figure 7, showed a singlet at the chemical shift δ =0.83ppm corresponding to 6H of CH_3. The singlet at δ=3.13ppm indicates the CH_2-O-Si, and broad singlet at δ =3.35ppm results from the OH of H_2O in DMSO and absorbed by the product, which is in good agreement with FT-IR. The ^1H-NMR results of all starting materials, methanol, acetonitrile, triethylenetetramine, 2-amino-2-methyl-1,3-propane diol, and bis(2-amino-2-methyl propane-1,3-diyldioxy)silane are shown in Table 3.15.

3.2.2.2.2 Carbon Nuclear Magnetic Resonance Spectroscopy (^{13}C-NMR)

The ^{13}C-NMR spectrum of bis(2-amino-2-methyl-propane-1,2-diyldioxy)silane, see Figure 8, showed chemical shift at δ =21.99ppm referring to the -CH_3, whereas the peak at δ =53.47ppm corresponds to the tertiary carbon (C) and at δ =67.08ppm results from the CH_2-O-Si, which is in agreement with both FT-IR and ^1H-NMR. The ^{13}C-

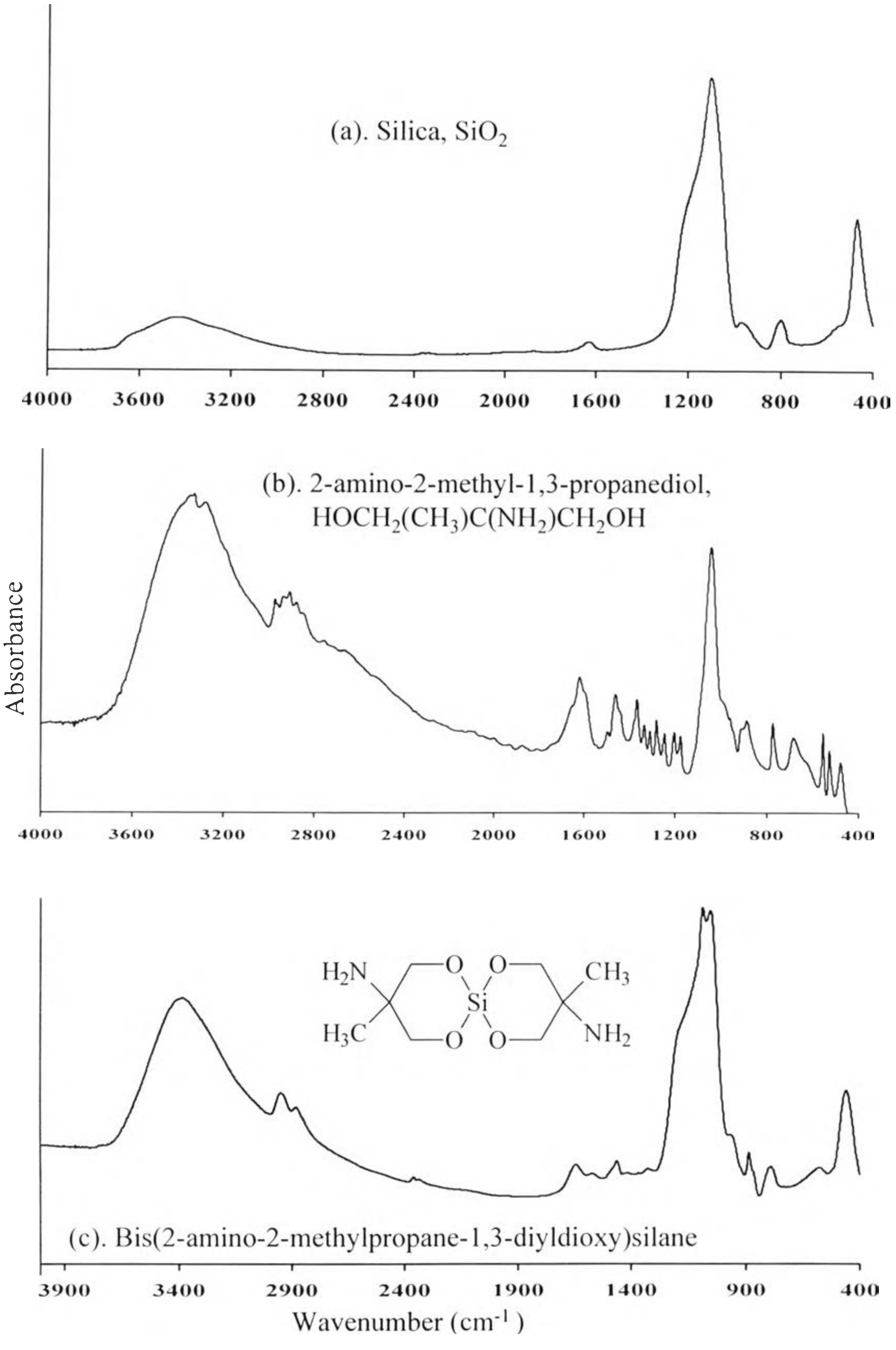


Figure 6 FT-IR of (a), (b), and (c) .

NMR results of methanol, acetonitrile, triethylenetetramine, 2-amino-2-methyl-1,3-propanediol, and bis(2-amino-2methylpropane-1,3-diyldioxy) silane are also shown in Table 3.15.

3.2.2.2.3 Silicon Nuclear Magnetic Resonance Spectroscopy (^{29}Si-NMR)

The ^{29}Si-NMR spectrum of bis(2-amino-2methylpropane-1,2-diyldioxy)silane showed only one absorption peak at δ = -77ppm, as illustrated in Figure 10 and Table 3.15, which is consistent with those previously reported for aliphatic, tetracoordinated spirosilicates (Kemmitt and Milestone 1995), although the ^{29}Si-NMR was conducted using the reaction solution, six-membering of spirosilicate is steric hindrance.

Table 3.15 Summary of ^{1}H-NMR, ^{13}C-NMR, and ^{29}Si-NMR results of starting materials, solvents, and bis(2-amino-2-methyl-propane-1,3-diyldioxy)silane.

Sample	^{1}H-NMR(ppm)	^{13}C-NMR(ppm)	^{29}Si-NMR(ppm)
Triethylenetetramine	1.25(s) 2.50(t) 2.75(t)	39.2, 40.3 42.0, 46.3 46.9	
Methanol	3.34 and 4.11	49.00	
Acetonitrile	2.00	1.3 and 117.7	
2-amino-2-methyl-1,3-propanediol	1.04, 3.49, and 4.78	21.52, 54.71, and 68.26	
Bis(2-amino-2-methylpropane-1,3-diyldioxy)silane	0.83(s), 3.13(s), and 3.35(broad, s)	21.99, 53.47, and 67.08	-77

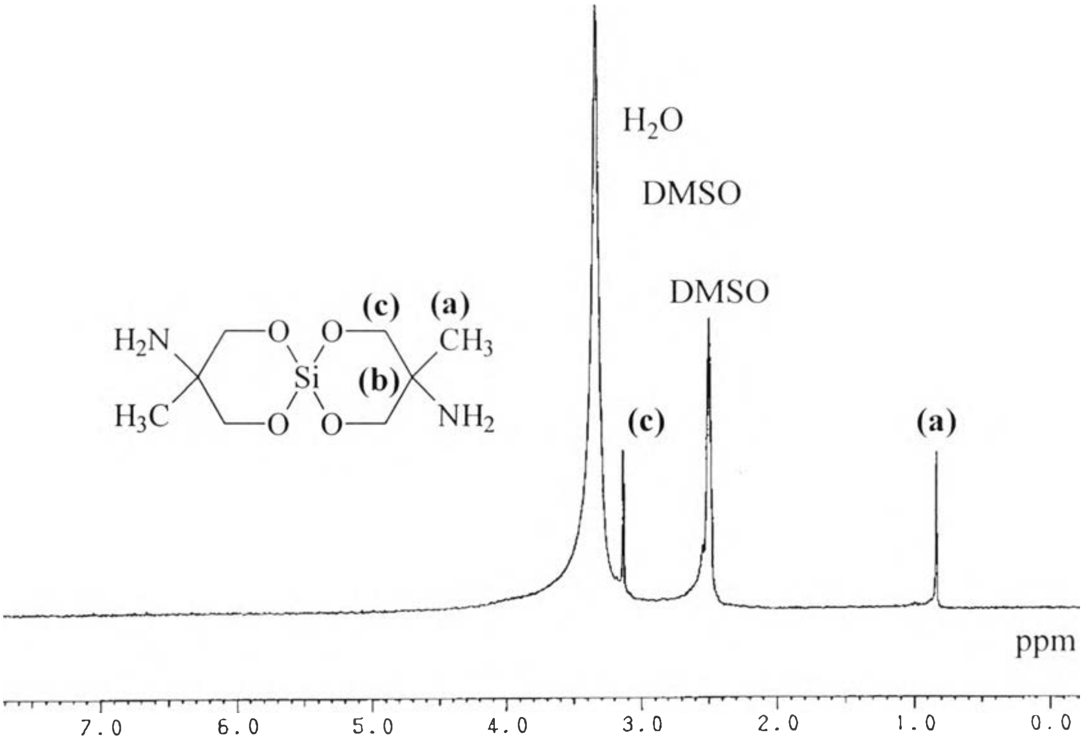


Figure 7 ^{1}H-NMR of bis(2-amino-2-methylpropane-1,3-diyldioxy)silane.

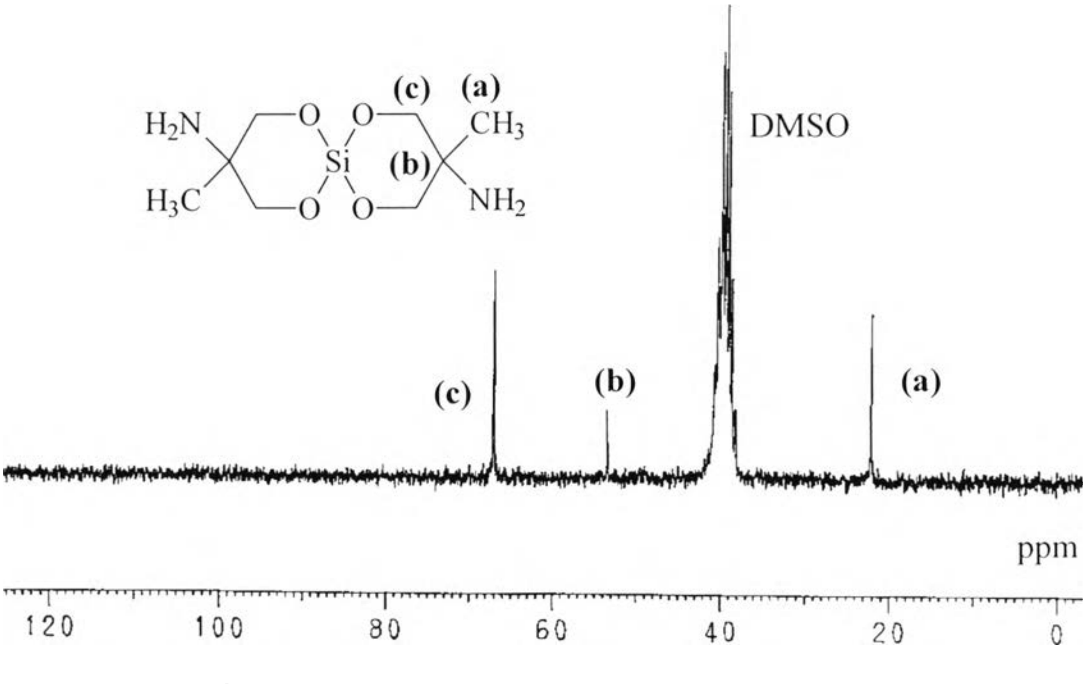


Figure 8 ^{13}C-NMR of bis(2-amino-2-methylpropane-1,3-diyldioxy)silane.

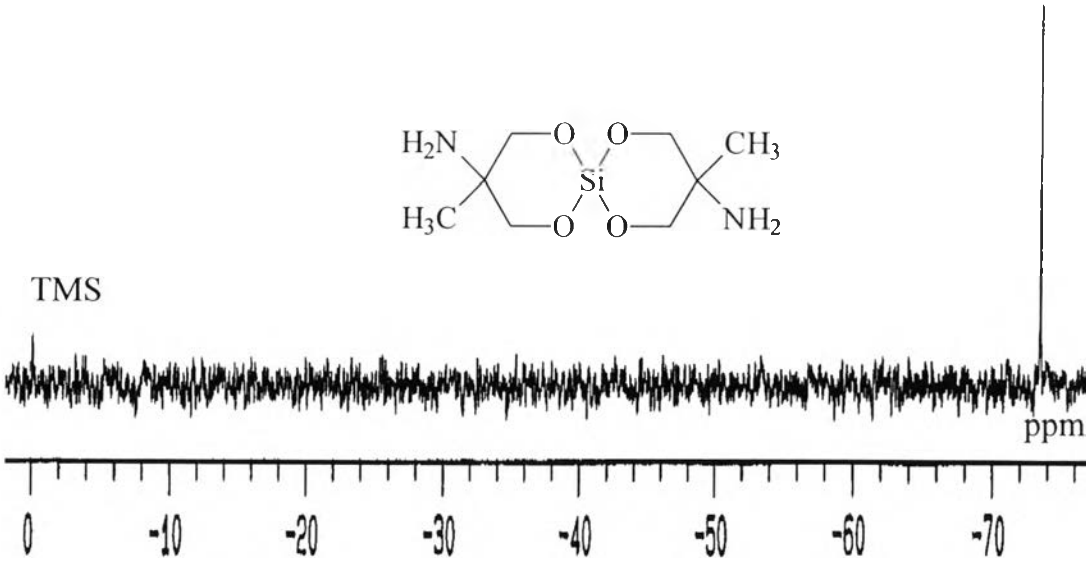


Figure 9 ^{29}Si-NMR of bis(2-amino-2-methylpropane-1,3-diyldioxy)silane.

3.2.2.3 Thermogravimetric Analysis (TGA)

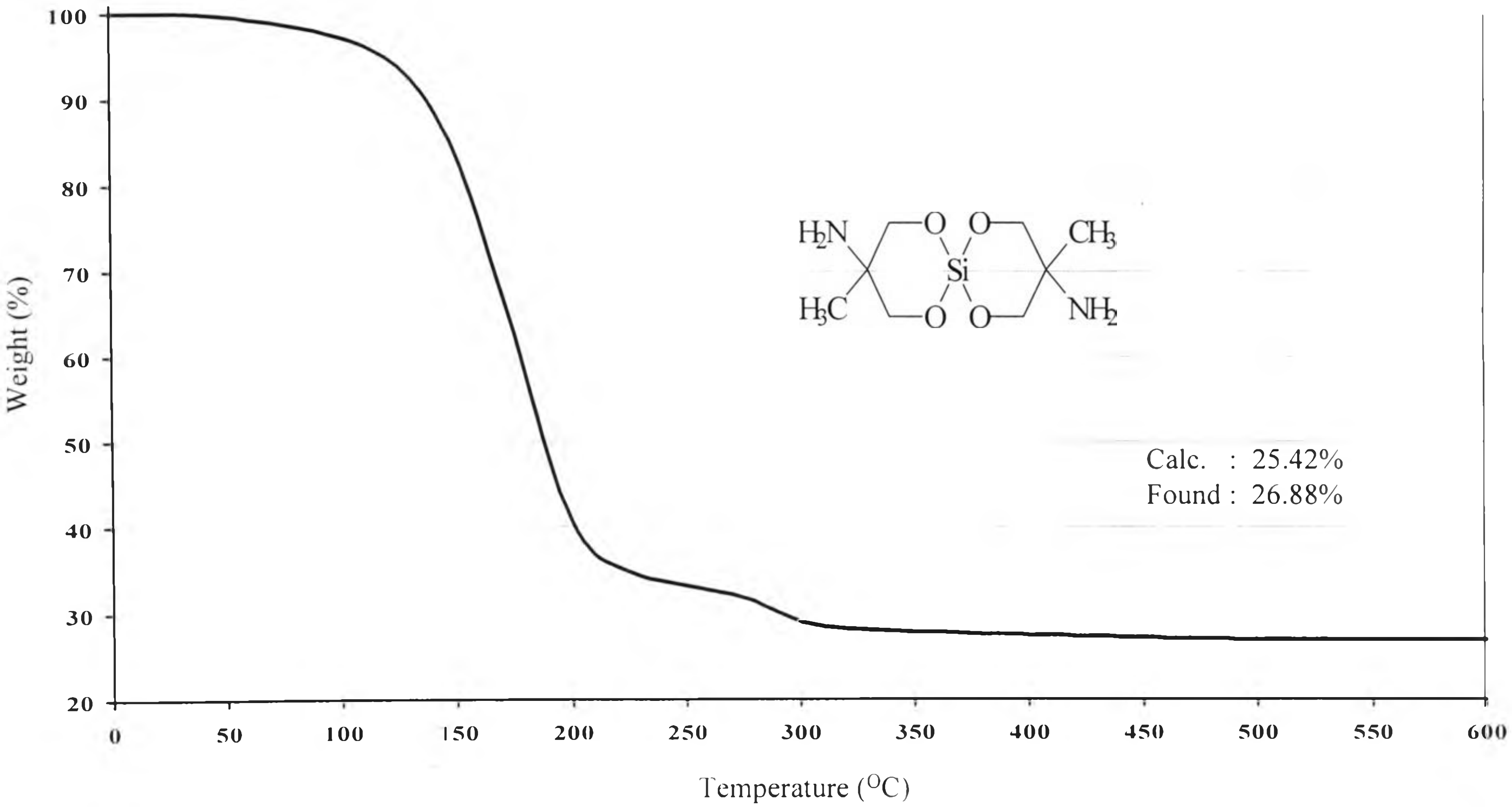
The result from TGA, as indicated in Figure 10, gave 26.88% ceramic yield which was nearly the same as the calculated value, 25.42%, where the structure was tetracoordinated species.

3.2.2.4 Differential Scanning Calorimetry (DSC)

Bis(2-amino-2-methylpropane-1,3-diyldioxy)silane showed two endothermic peaks with different temperatures. The first one occurring at lower temperature can be defined as the melting point of the compound.

3.2.2.4 Positive Fast Atomic Bombardment Mass Spectroscopy (FAB$^+$-MS)

The spectrum showed that the expected product, bis(2-amino-2-methylpropane-1,3-diyldioxy)silane monomer (m/e 232) was obtained. Again, with high energy used in the FAB$^+$-MS model, the

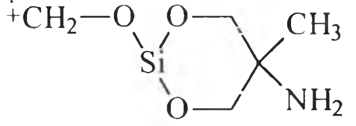
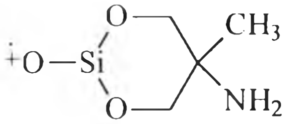
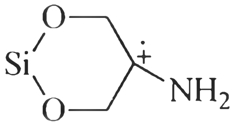
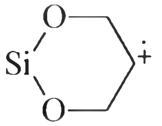


Calc. : 25.42%
Found : 26.88%

Figure 10 TGA of bis(2-amino-2-methylpropane-1,3-diyldioxy)silane.

molecular peak of this monomer was hardly shown due to the instability of the molecular structure at that high temperature. The fragmentation of the product is shown in Table 3.16.

Table.3.16 The proposed structure and fragmentation of product.

m/e	Intensities	Proposed Structure
161	0.78	
147	1.2	
116	13	
100	28	
88	16	$^{\dot{+}}CH_2O{-}Si{-}OCH_2^{\dot{+}}$
74	46	$^{\dot{+}}CH_2O{-}Si{-}O$
58	54	$^{\dot{+}}CH_2O{-}Si$
44	100	$^{\dot{+}}O{-}Si$

3.2.3 Synthesis of bis(3-aminopropane-1,2-diyldioxy)silane, $Si[OCH_2CH(CH_2NH_2)O]_2$, tetra-coordinated spirosilicate

Bis(3-aminopropane-1,2-diyldioxy)silane was prepared according to equation 3.3 in more than 70% overall yield directly from fumed silica and 3-amino-1,2-propanediol in the presence of TETA used as both catalyst and solvent. The structure of bis(3-aminopropane-1,2-diyldioxy) silane was also identified by the following techniques.

3.2.3.1 Fourier Transform Infrared Spectroscopy (FT-IR)

The spectra of bis(3-aminopropane-1,2-diyldioxy)silane and all starting materials, namely, silica {SiO_2} and 3-amino-1,2-propanediol {$HOCH_2CH(CH_2NH_2)OH$} are shown in Figure 11. The FT-IR spectrum of bis(3-amino propane-1,2-diyldioxy)silane showed broad band at 3397 cm^{-1} referring to the O-H stretching, which is water absorbed by the product, N-H stretching in the molecule and intermolecular hydrogen bonding (Cairn1965), whereas the 2955-2889 cm^{-1} peak shows the C-H stretching. The bands at 1090, 966, and 872 cm^{-1} correspond to the Si-O-CH stretching.

3.2.3.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

3.2.3.2.1 Proton Nuclear Magnetic Resonance Spectroscopy (^1H-NMR)

The ^1H-NMR spectrum of bis(3-aminopropane-1,2-diyldioxy)silane showed one singlet absorption at δ =2.05ppm indicating the NH_2; δ =2.45ppm multiple results from 4H of the CH_2-N; δ =3.29ppm multiplet shows 4H of the CH_2-O-Si; 2H of CH-O-Si unfortunately is overlapped with the H_2O peak; and δ =3.35ppm broad singlet is belong to water in DMSO and absorbed by the product, which is in good agreement with FT-IR, as indicated in Figure 12. The ^1H-NMR results of all materials: methanol, acetonitrile, triethylenetetramine, 3-amino-1,2-propanediol and bis(2-amino-2-methyl propane-1,2-diyldioxy)silane are shown in Table 3.17.

3.2.3.2.2 Carbon Nuclear Magnetic Resonance Spectroscopy (^{13}C-NMR)

The ^{13}C-NMR spectrum of bis(3-aminopropane-1,2-diyldioxy)silane showed chemical shift at δ =44.9ppm referring to the CH_2-N, δ =64.02ppm peak results from CH_2-O-Si, and the peak at δ =72.68ppm is assigned to CH-O-Si, which is in agreement with both FT-IR and ^1H-NMR, as indicated in Figure13. The ^{13}C-NMR results of methanol, acetonitrile,

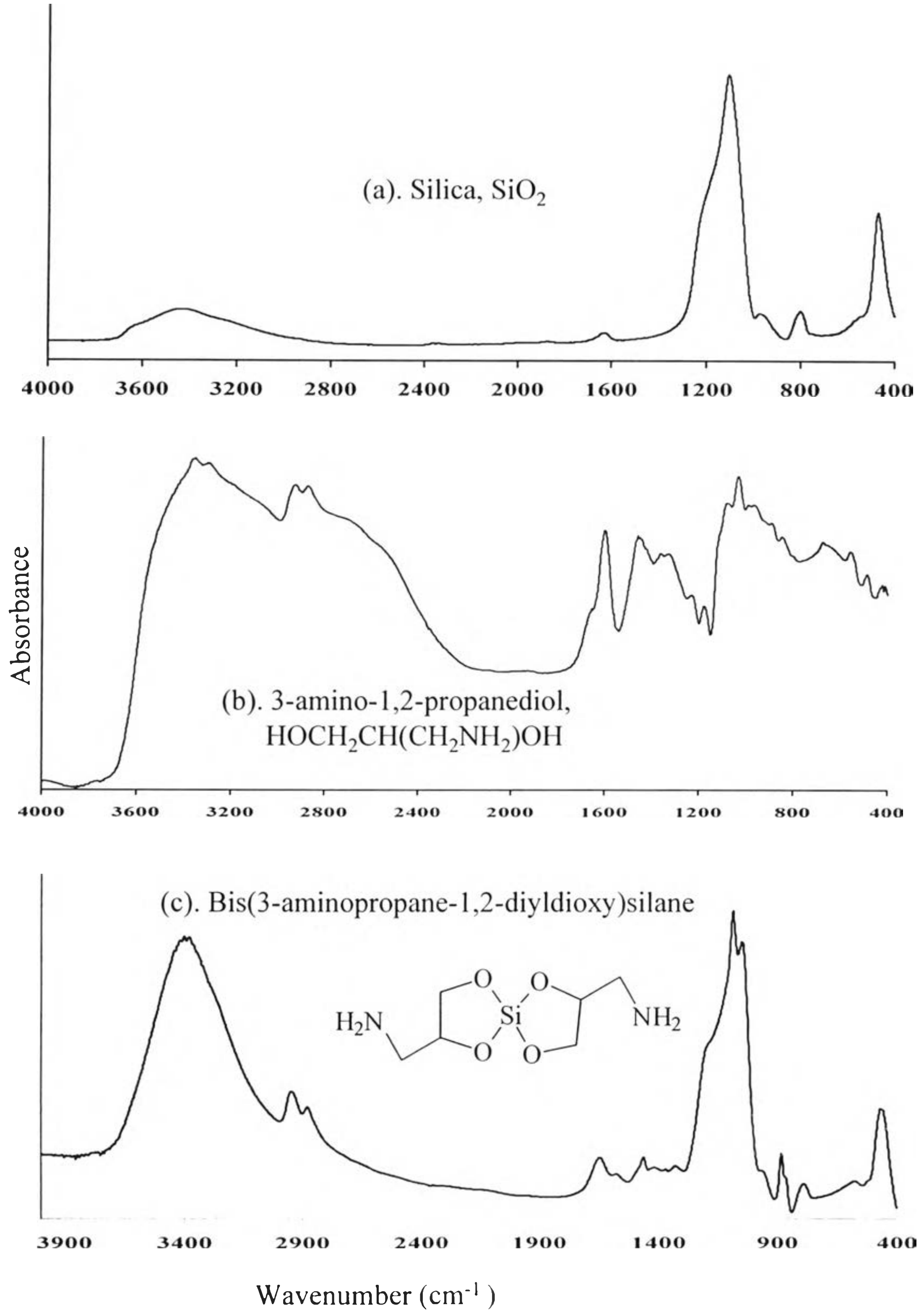


Figure 11 FT-IR of (a), (b), and (c).

triethylenetetramine, 3-amino-1,2-propanediol, and bis(3-aminopropane-1,2-diyldioxy)silane are summarized in Table 3.17.

3.2.3.2.3 Silicon Nuclear Magnetic Resonance Spectroscopy (^{29}Si-NMR)

The ^{29}Si-NMR spectrum of bis(3-aminopropane-1,2-diyl dioxy)silane showed only one absorption peak at $\delta = -103$ppm, as indicated in Figure 14 and Table 3.17, which is again consistent with those previously reported for aliphatic, pentacoordinated spirosilicates (Kemmitt and Milestone 1995). As rationalized previously, we run the ^{29}Si-NMR from the reaction solution, there is a partial bonding between the product and TETA, as suggested by Frye's group.

Table 3.17 Summary of ^{1}H-NMR, ^{13}C-NMR, and ^{29}Si-NMR results of starting materials, solvents, and bis(3-aminopropane-1,2-diyldioxy)silane.

Sample	^{1}H-NMR(ppm)	^{13}C-NMR(ppm)	^{29}Si-NMR(ppm)
Triethylene-tetramine	1.25(s) 2.50(t) 2.75(t)	39.2, 40.3 42.0, 46.3 46.9	
Methanol	3.34 and 4.11	49.00	
Acetonitrile	2.00	1.3 and 117.7	
3-amino-1,2-propanediol	2.80, 2.95, 3.77, and 4.78	45.53, 65.53, and 74.29	
Bis(3-amino propane-1,2-diyldioxy)silane	2.05(s), 2.45(m), 2.61(m), and 3.29(broad, s)	44.90, 64.02, and 72.68	-103

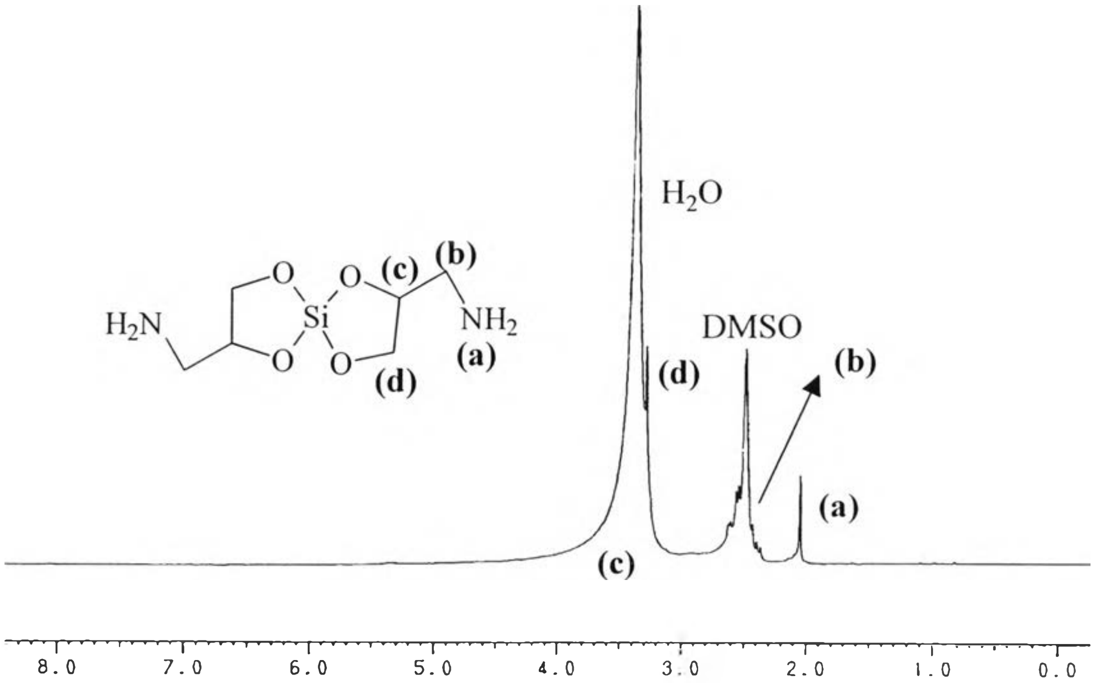


Figure 12 ^{1}H-NMR of bis(3-aminopropane-1,2-diyldioxy)silane.

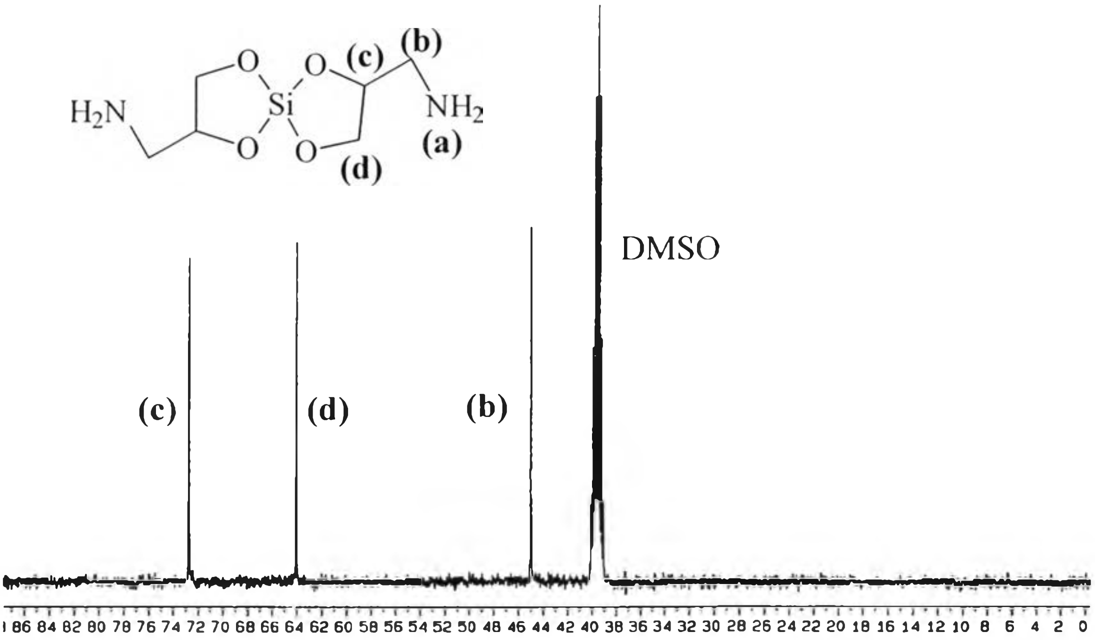


Figure 13 ^{13}C-NMR of bis(3-aminopropane-1,2-diyldioxy)silane.

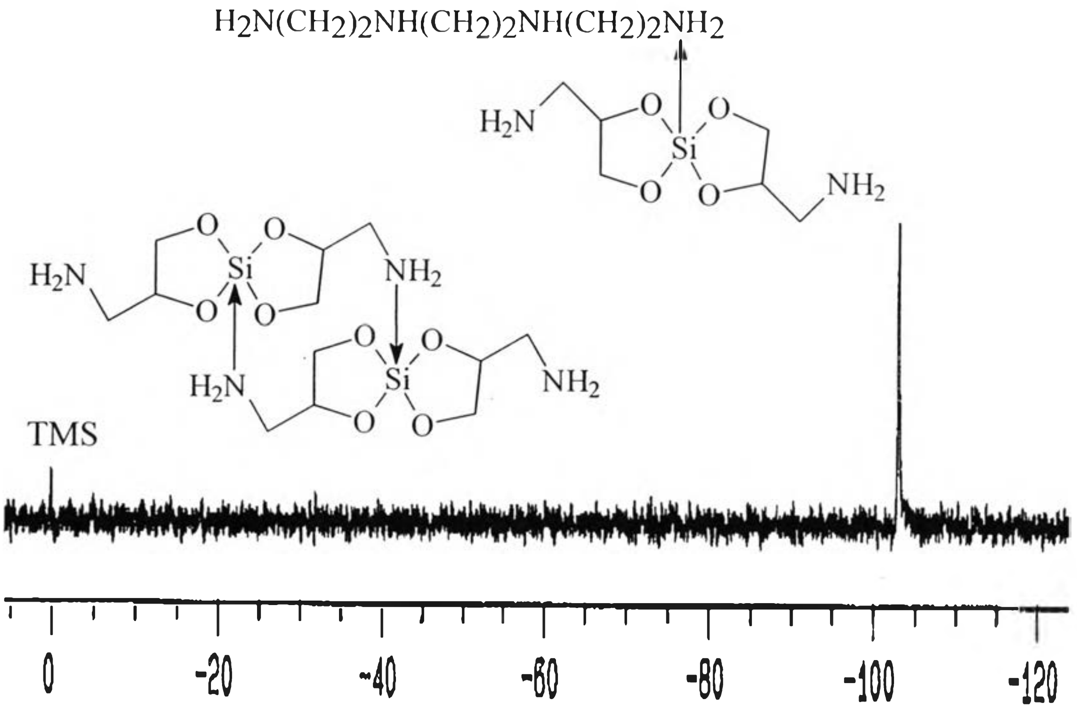


Figure 14 ^{29}Si-NMR of bis(3-aminopropane-1,2-diyldioxy)silane.

3.2.3.3 Thermogravimetric Analysis (TGA)

The result of bis(3-aminopropane-1,2-diyldioxy)silane from TGA, as indicated in Figure 15, gave 30.45% ceramic yield, which is nearly the same as the calculated value, 29.13%, where the structure was tetra-coordinated species.

3.2.3.4Differential Scanning Calorimetry (DSC)

Bis(3-aminopropane-1,2-diyldioxy)silane showed two endo-thermic peaks with different temperatures. The first one occurring at lower temperature can be defined as the melting point of the compound.

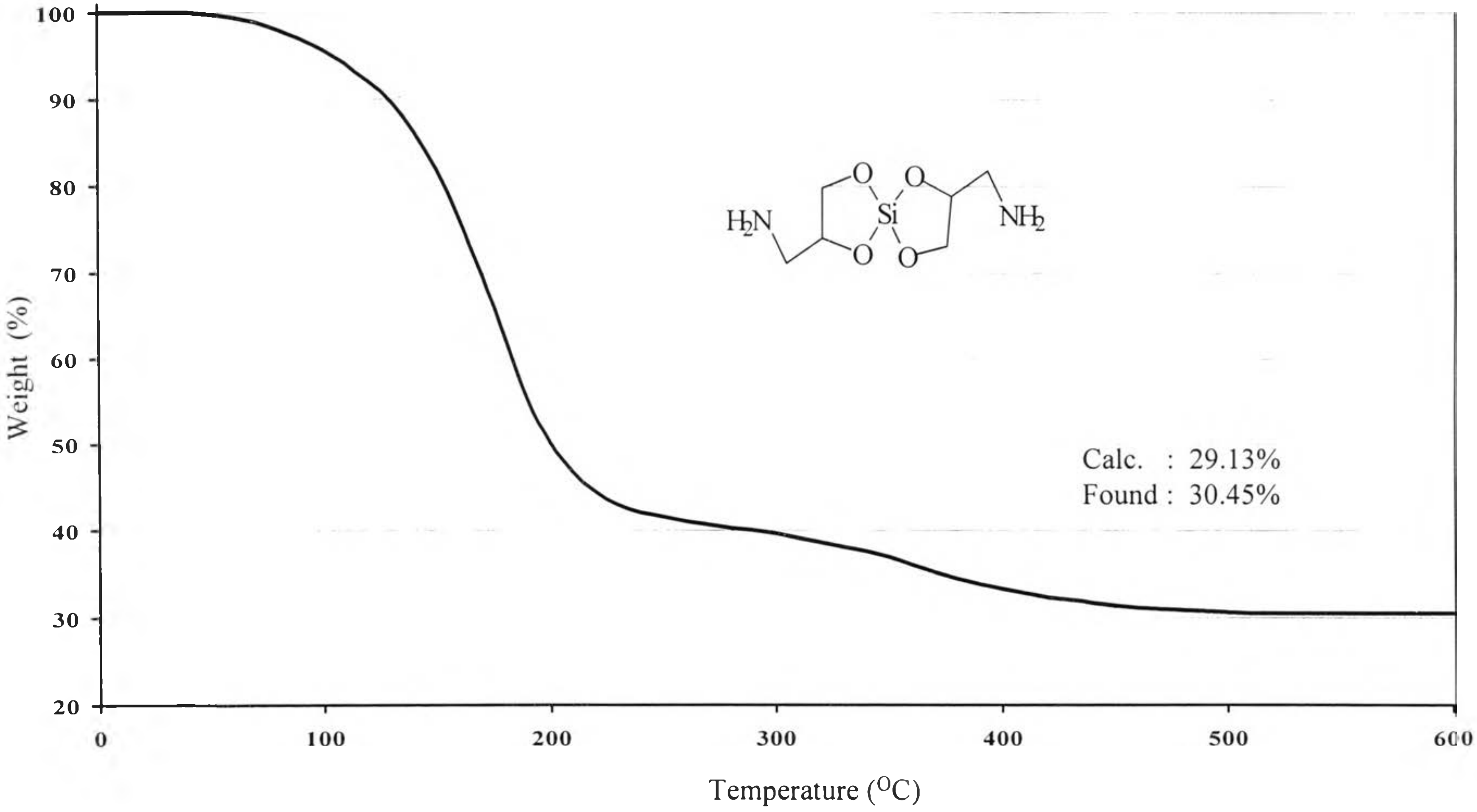
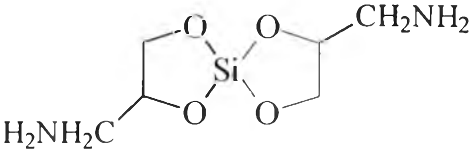
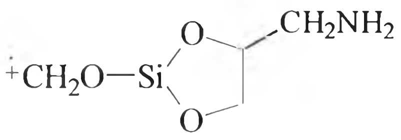
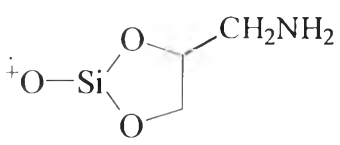


Figure 15 TGA of bis(3-aminopropane-1,2-diyldioxy)silane .

3.2.3.5 Positive Fast Atomic Bombardment Mass Spectroscopy (FAB^{+}-MS)

Mass spectrum resulted in bis(3-aminopropanee-1,2-diyldioxy)silane monomer product (m/e 206), however, the molecular peak of this monomer was hardly seen, due to the high energy FAB^{+}MS mode used. Thus, molecular structure is not being stable at this condition. The fragmentation of the product is shown in Table 3.18.

Table.3.18 The proposed structure and fragmentation of product.

m/e	Intensities	Proposed Structure
206	0.77	
147	17.62	
133	100	
58	4.94	$^{\cdot+}CH_2O{-}Si$
44	42.28	$^{\cdot+}O{-}Si$