

CHATER III

RESULTS AND DISCUSSION

3.1 Synthesis

The novel copolymer synthesized from silica, catechol, hydroquinone, and 4-*t*-butylcatechol via the one step OOPS (oxide one pot synthesis) process using triethylenetetramine (TETA) and ethylene glycol (EG) as the catalyst and solvent, respectively. TETAH_4^{4+} ($\text{pK}_{\text{a}1}= 3.32$, $\text{pK}_{\text{a}2}= 6.67$, $\text{pK}_{\text{a}3}= 9.20$, $\text{pK}_{\text{a}4}= 9.92$) was the basic catalyst which forms different TETAH_n^+ counter ion species depending on the pH of solution. Catechol ($\text{pK}_{\text{a}1}= 9.46$, $\text{pK}_{\text{a}2}= 12.70$), hydroquinone ($\text{pK}_{\text{a}1}= 9.91$, $\text{pK}_{\text{a}2}= 12.04$), and 4-*tert*-butylcatechol in the ethylene glycol ($\text{pK}_{\text{a}}= 14.22$) solution, became nucleophilic species with TETAH_n^+ species as the counter ion. These nucleophilic anions attack Si-O bonds on silica particles surface to form new Si-O-C bonds. Simultaneously, byproduct water forms to drive the reaction forward.

The reaction time required to form the synthesized products depends on the structure, proportion of raw materials and conditions for the reversible reaction. The properties of this copolymer varied with the structure of products which were formed by variation of mole ratio of raw materials, amount of catalyst and reaction time. These variations were conducted to examine the properties of the synthesized copolymer.

After all starting substances were mixed together, light yellow solution was obtained, and became dark yellow solution when TETA catalyst was added. The mixture turned clear after heating for 10 minutes. The color of solution became darker yellow with increase amount of hydroquinone or TETA catalyst. After 5 h, the reaction was stopped and cooled to room temperature. Fluffy precipitate was obtained when 4-tert-butylcatechol concentration was higher (HT14, HT05). Removal of EG solvent resulted in precipitation of dark brown solutions. The precipitate was washed with methanol, and the synthesized products, pale brown powders, in general, were obtained. The color of the product became darker with increases in hydroquinone concentration. Surprisingly, it returned to be lighter in color and gave higher yield with the vacuum removal of EG solvent was increased (160° C/20 mmHg), as shown in table 3.1.

Table 3.1 Weight of the products at 5 h reaction time

sample	mole ratio <i>t</i> -butylcat.:hydroquinone	weight gain (g) ¹	weight gain (g) ²
HT05	0.0 : 0.5	4.30	5.96
HT14	0.1 : 0.4	4.14	5.04
HT23	0.2 : 0.3	3.64	4.71
HT32	0.3 : 0.2	1.54	4.57
HT41	0.4 : 0.1	3.25	4.68
HT50	0.5 : 0.0	3.70	5.92

Note 1 : vacuum distillation at 110°C/20 mmHg

2 : vacuum distillation at 160°C/20 mmHg

By considering the variation of the catalyst amount, the more TETA used in the reaction, the more weight of products obtained. Because the products dissolves only slightly in methanol, the washing step therefore used methanol solvent. The products at lower amounts of TETA do not precipitate unless solvents in the filtrate are removed. For the possible reason, at the smaller amount of TETA it may form monomer or dimer as the main product which dissolves in MeOH solvent while at the higher amount of TETA it give polymer and hexacoordinate anions which are difficult to dissolve in common solvent. Moreover, the mixture gave more SiO₂ when decreasing the amount of TETA, see Table 3.2.

Table 3.2 Weight of products at the mole ratio of hydroquinone : 4-tert-butylcatechol of 0.2 : 0.3, at 10 h reaction time at 160°C vacuum temperature

mole % TETA	weight gain (g)
10	2.77
30	2.64
50	1.60
100	3.64

3.2 Characterization

3.2.1 Variation of hydroquinone : 4-tert-butylcatechol mole ratio

When using 100 mole % TETA in of silica per 1.5 moles of catechol for 5 h, mole ratio of hydroquinone and 4-tert-butylcatechol was varied from 0.0:0.5 to 0.5:0.0 which represented in HT05, HT14, HT23, HT32, HT41, and HT50, respectively. The powder products have a specific odor, turn brown when exposed to air, and moisture. They were insoluble in a wide variety of solvents but dissolved slightly in MeOH and readily in DMSO, hot EG. Therefore, many methods for purification and characterization, e.g. chromatography, extraction,...etc. were not practical. Structural characterization and thermal properties were performed by FTIR, TGA, DSC, XRD, NMR and EI⁺-MS as discussed below.

3.2.1.1 Fourier Transform Infrared Spectroscopy (FTIR). When peak position of products were positions compared with those of the raw materials, the vibration of OH groups in the products decreased as Si-O-C bonds form in the product. The peaks in the spectrum of the products at high vacuum temperature were sharper than those of the products from at low vacuum temperature. Figure 3.1 shows the FTIR spectra obtained from the variation of hydroquinone to 4-tert-butylcatechol mole ratio at high vacuum temperature. The peak assignment are in Table 3.3.

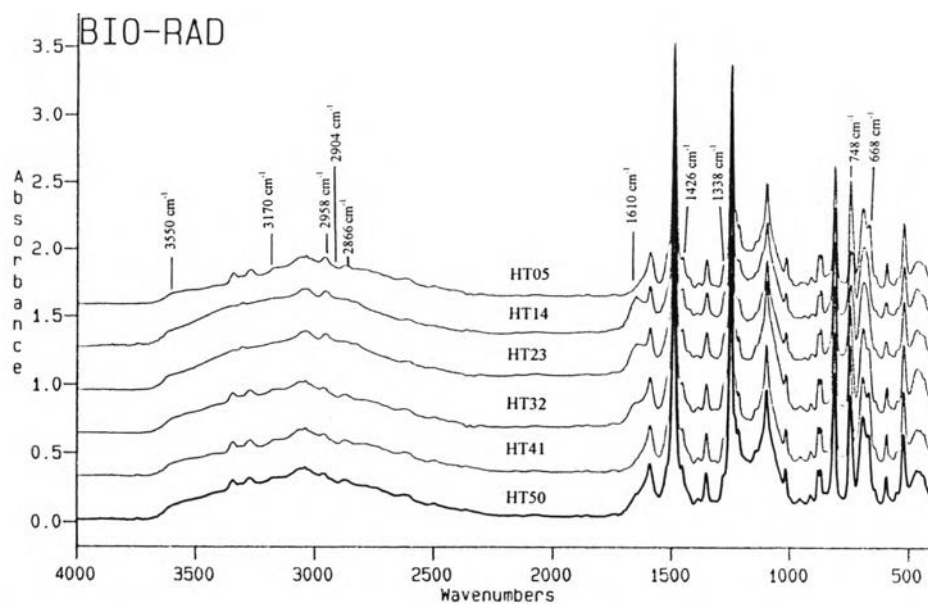


Figure 3.1 FTIR spectrum obtained from the variation of hydroquinone to 4-tert-butylcatechol mole ratio at 5 h reaction time with 100 mole % TETA.

Table 3.3 Peak assignments of the frequency vibration of functional groups in the product HT23

Part of components	Peak position (cm^{-1})	Assignment
1,2-dioxy-4-tert-butylphenyl group	2958, 2904	ν CH of CH_3 (as)
	2866	ν CH of CH_3 (s)
	1900-1700	σ CH(sum) of 1,2,4-subst.
	1628, 1524, 1601	ν C=C(skeletal)
	1426	σ CH of CH_3 (as)
	938.6, 838.6	σ CH(out of plane) of 1,2,4-
	1124, 1093	β (=CH) (in plane)

Part of components	Peak position (cm ⁻¹)	Assignment
1,4-dioxyphenyl group	3029	ν CH(aromatic)
	1900-1800	ν CH(sum) of 1,4-subst.
1,2-dioxyphenyl group	3070, 3055, 3040	ν CH(aromatic)
	1589, 1490, 1454	ν C=C(skeletal)
	1251	ν C-O
	748	σ CH of 1,2-subst.
	668	σ CH of 1,2-subst.
silicon group	1355	ν Si-O-C
	1102	ν Si-O-aryl
	1017	ν Si-O-aryl
	910	σ Si-O-aryl
TETA	3344	ν NH ₂ (free)
	3274, 3170	ν NH ₂ (associated), ν NH ₃ ⁺
	3306, 3550(broad)	ν NH, ν NH ₂ ⁺
	2937, 2816	ν CH of CH ₂ (as)
	1589	σ NH(as)
	1454	σ CH of CH ₂
	1120	ν C-N
	780	ν CH of CH ₂ (rocking)

The overall spectrum of the products were similar, except that there were slightly different peaks at 2958, 2904 and 2866 cm⁻¹, corresponding to the C-H stretching of CH₃ in the tert-butyl group, C-H deformation of the 4-tert-butyl groups at ~1426, 1338 cm⁻¹, and CH stretching of para-substituent of hydroquinone at 3029 cm⁻¹.

When 4-tert-butylcatechol component increased, the absorption of 4-tert-butyl groups was slightly increased, similarly, increasing in hydroquinone component also increased the CH stretching of para-substituent. These peaks corresponded specifically to para- and ortho-substitution on benzene ring in the products. However, the peak of ortho-substitution at 748 cm^{-1} (CH def.(out of plane)) and 668 cm^{-1} (CH def.(summation band)) were not different in all mole ratio variation of comonomers. These spectrum were different when compared with spectrum of bis(1,2-dioxyphenyl)silane which contained no comonomer, see Figure 3.2, because hydroquinone and 4-tert-butylcatechol were participated in the ladder structure of bis(1,2-dioxyphenyl)silane.

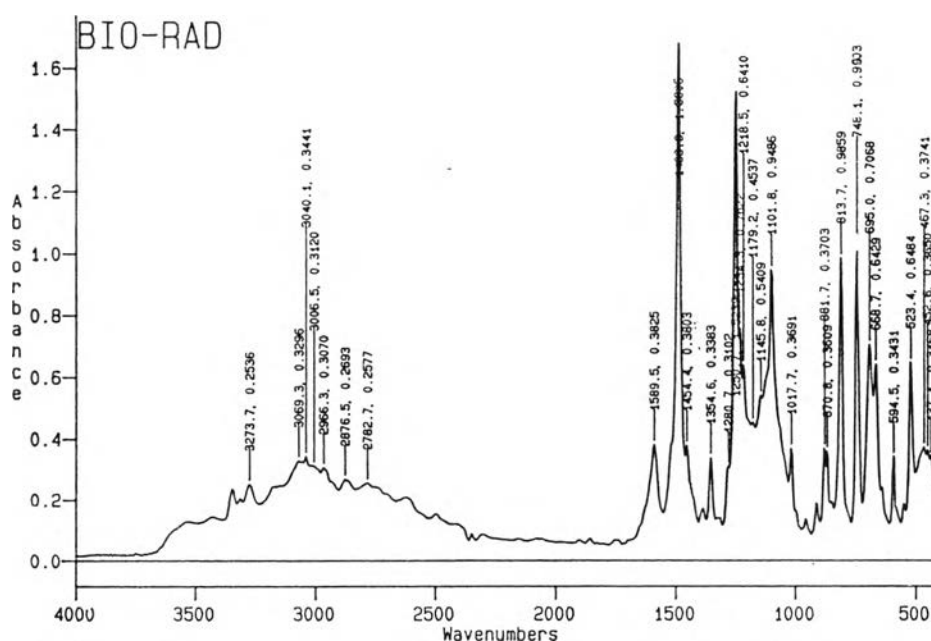


Figure 3.2 FTIR spectrum of the product ($\text{SiO}_2:\text{CAT} = 1:2$) containing no comonomer of hydroquinone and 4-tert-butylcatechol at 5 h with 100 mole % TETA.

3.2.1.2 *Thermogravimetric Analysis (TGA)*. The mass loss of a sample in a controlled atmosphere (O_2/N_2) was recorded continuously as a function of temperature. The thermogram shows the thermal decomposition curve and the thermal stability of the products during pyrolysis from ambient to $950^\circ C$ (Figure 3.3).

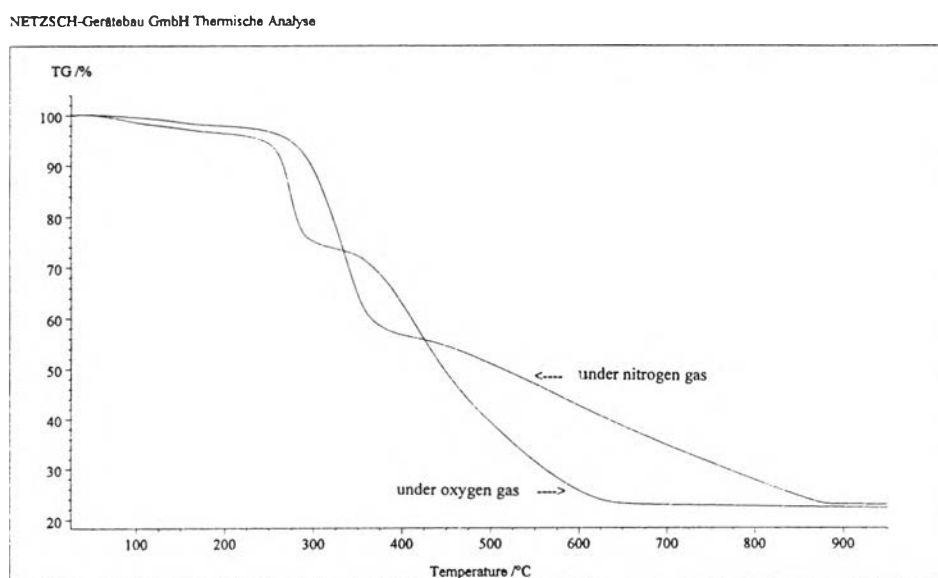


Figure 3.3 Decomposition of the products under O_2 and N_2 atmospheres.

The theoretical percent ceramic yield of polymer can be calculated when the repeating unit structure, molecular weight distribution and chemical reaction equation are known for calculation of statistic molecular weight of products. If the molecular weight of polymer is low, the weight of end chain becomes important. The % ceramic yields expected for the polymer products were lower than 24.6% of the bis(catechol)silane polymer.

The % ceramic yield indicates quantity of silica in the product. Then the product with low % ceramic yield indicates the higher organic part contented in the product. The experimental %ceramic yields were decreased and the higher the first mass loss, the more amount of 4-tert-butylcatechol contained in the products, as shown in Figures 3.4 and 3.5.

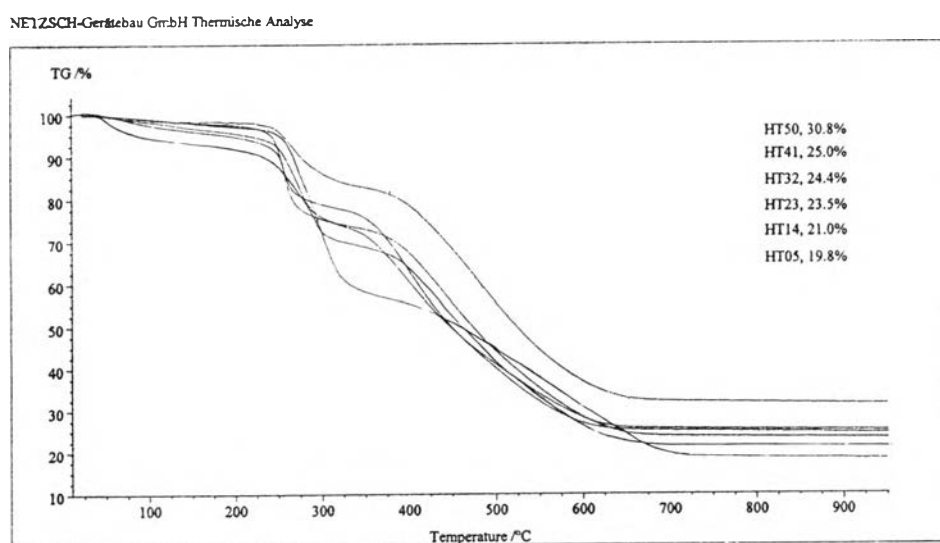


Figure 3.4 Thermograms of the products obtained by varying the mole ratio of comonomer hydroquinone and 4-tert-butylcatechol at 5 h with 100 mole % TETA.

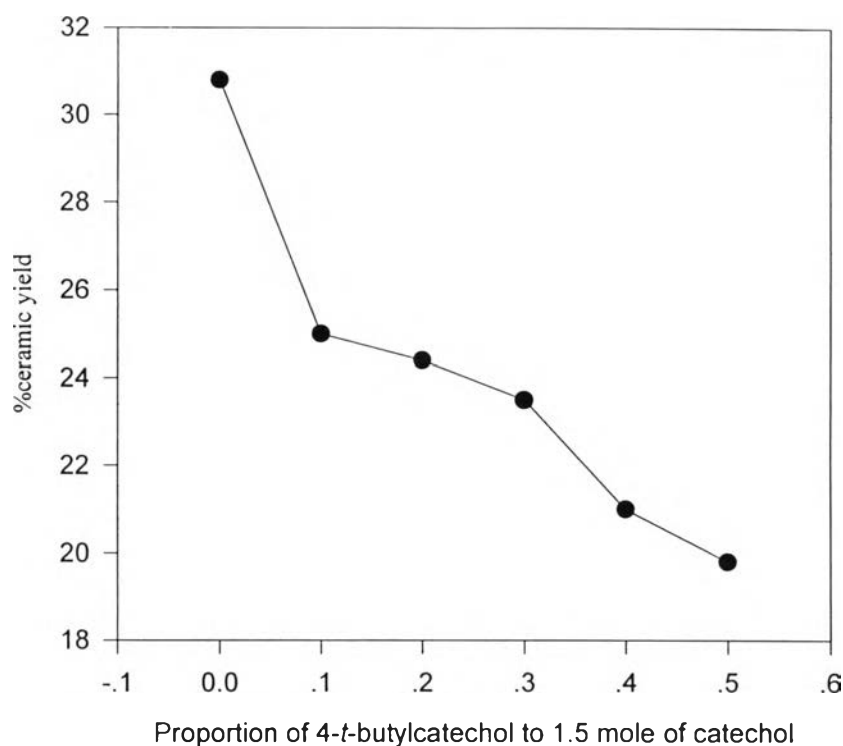


Figure 3.5 Percent ceramic yield of the products containing different amount of 4-*tert*-butylcatechol at 5 h with 100 mole % TETA.

The product obtained by using high vacuum temperature gave % ceramic yield lower than that obtained by using the low vacuum temperature. The mass loss of impurity at below 200°C was also reduced.

3.2.1.3 Differential Scanning Calorimetry (DSC). The DSC is a thermal technique in which used for measuring differential heat flow as a function of sample temperature. DSC profiles show phase transition of each mole ratio of comonomers under O₂/N₂ gas, as shown in Figure 3.6.

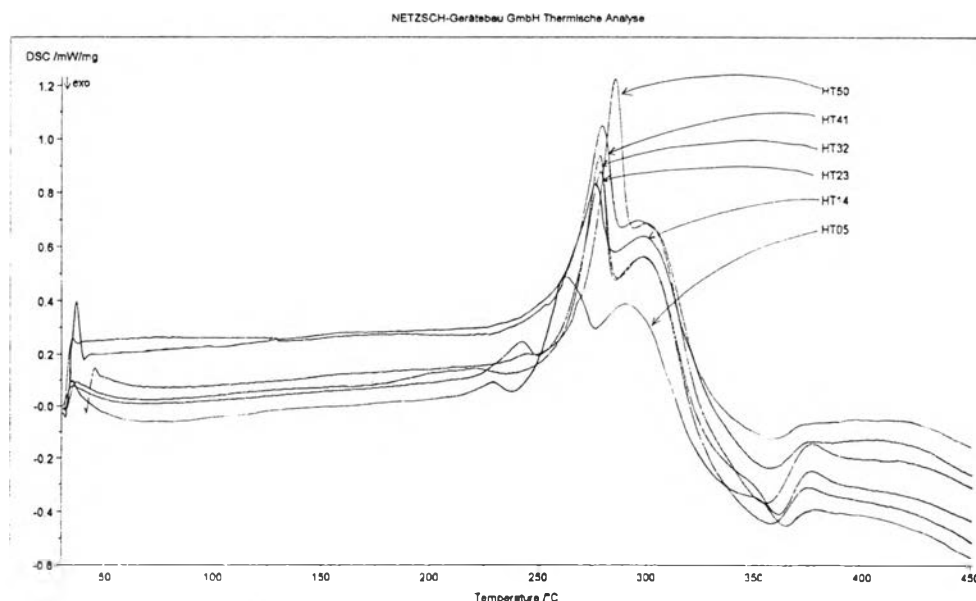


Figure 3.6 DSC profiles of the products obtained by varying the mole ratio of comonomers hydroquinone and 4-tert-butylcatechol at 5 h with 100 mole % TETA.

Generally, the products obtained showed 3 endothermic peaks on heating, but no exothermic transition appeared on cooling at all because of the degradation of the products at elevated temperature.

The first endotherm occurred in the range of 250°-285°C, the second one appeared at 285°-350°C, as well as the last one exhibited between 350°-385°C. Note that the peak was shifted to slightly lower temperature at higher amount of 4-tert-butylcatechol. The first endothermic peak was obviously smaller, broader and shifted into lower temperature as the amount of hydroquinone slightly decreased. Simultaneously, the second one was slightly higher as the amount of 4-tert-butylcatechol was increased. There was also a small endothermic peak around 230°-240°C which can possibly be a volatilization of trace amount of TETA.

3.2.1.4 *X-ray Diffraction (XRD)*. The degree crystallinity of product can be seen by XRD profile which is the method of crystallographic structure determination. The scattering from an individual atom can be represented as the scattered amplitude as a function of angle, θ , where 2θ is the angle between the direction of the amplitude which are measured and the direction of the incident radiation. Amorphous silica of raw material showed broad peak in the pattern whereas the silane copolymer of the product revealed the high crystallinity. The optimum intensity 2θ peak indicated the diffraction of elements on benzene ring at about 8.30. The other prominent peaks were 13.8, 16.6, 18.6, 20.5, 22.8, 23.5, 25.3 and 28.8. These peaks in patterns represented the main characteristics of bis(1,2-dioxyphenyl)silane that are shown in Figures 3.7 and 3.8.

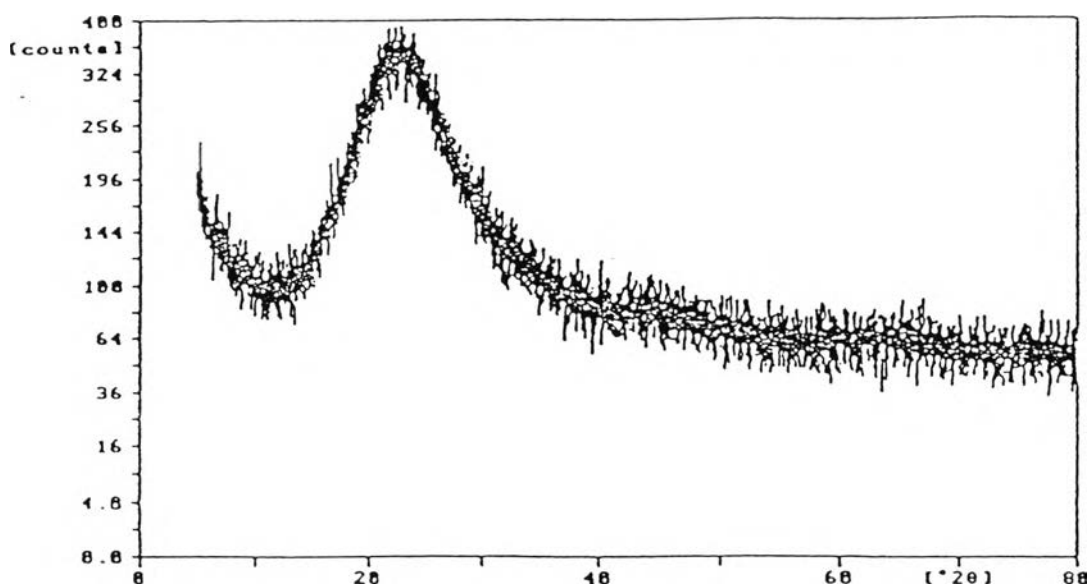


Figure 3.7-a XRD pattern of precipitated silica.

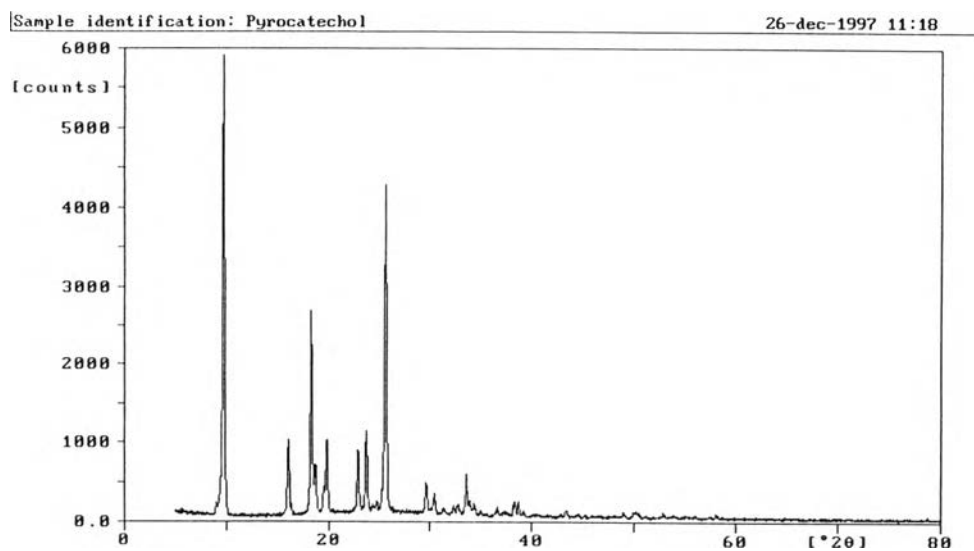


Figure 3.7-b XRD pattern of pyrocatechol raw material.

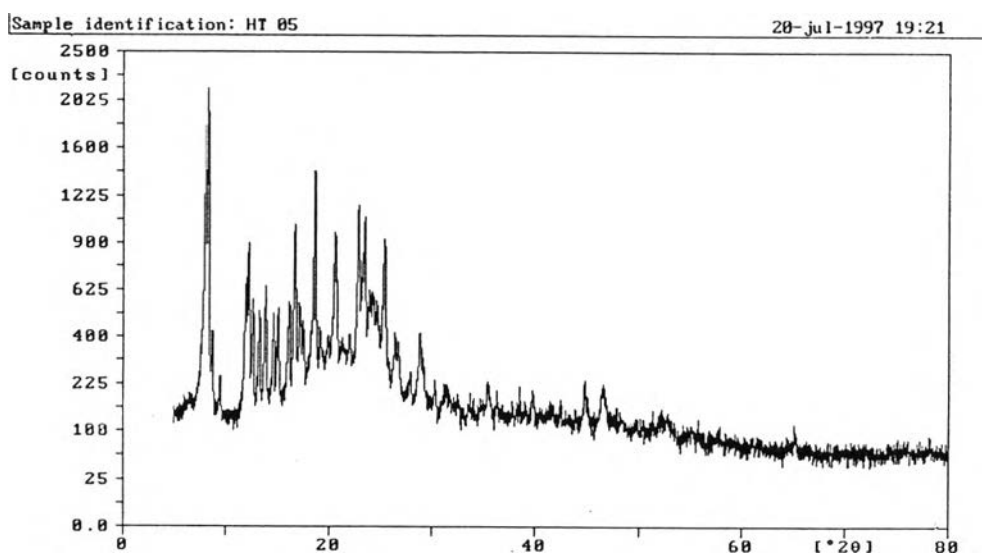


Figure 3.8-a XRD pattern of product HT05 at 5 h with 100 mole % TETA.

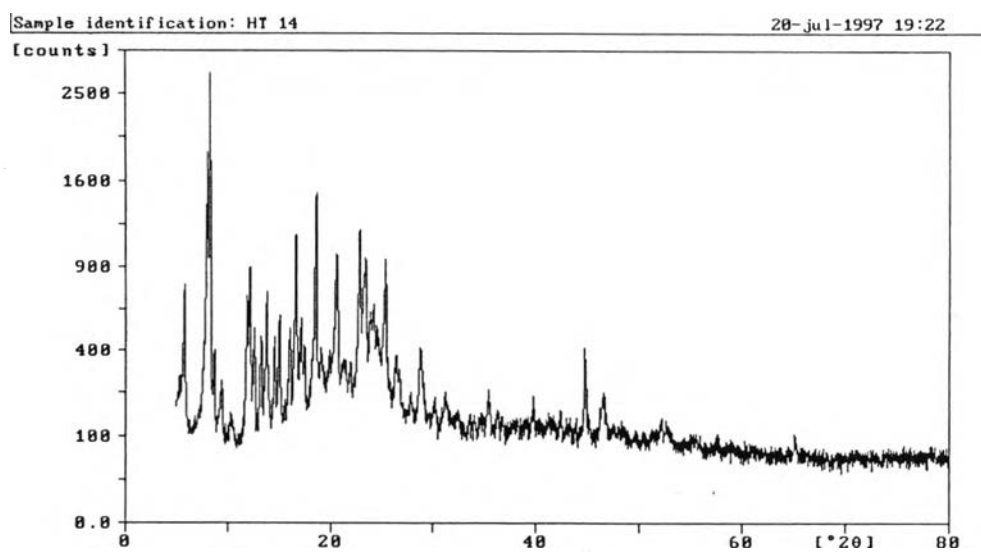


Figure 3.8-b XRD pattern of product HT14 at 5 h with 100 mole % TETA.

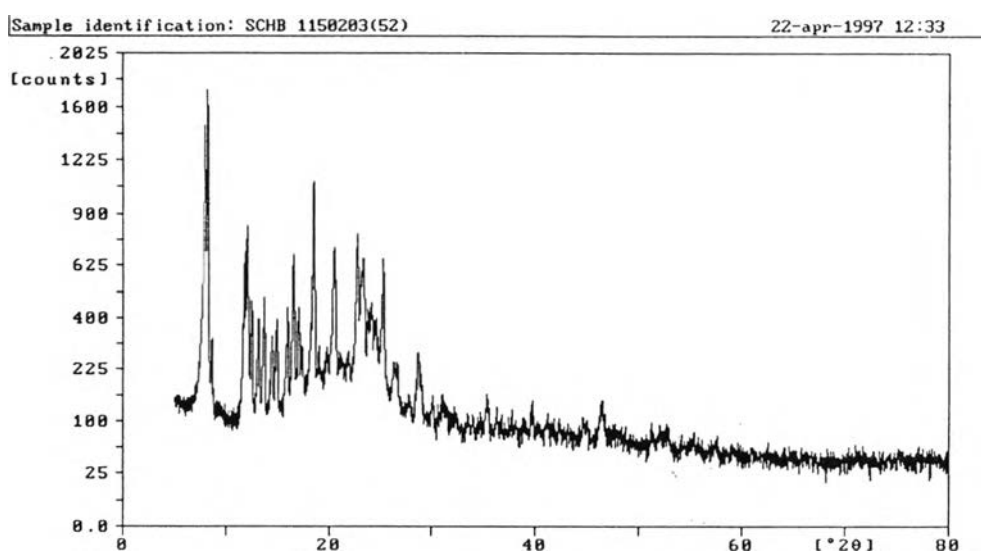


Figure 3.8-c XRD pattern of product HT23 at 5 h with 100 mole % TETA.

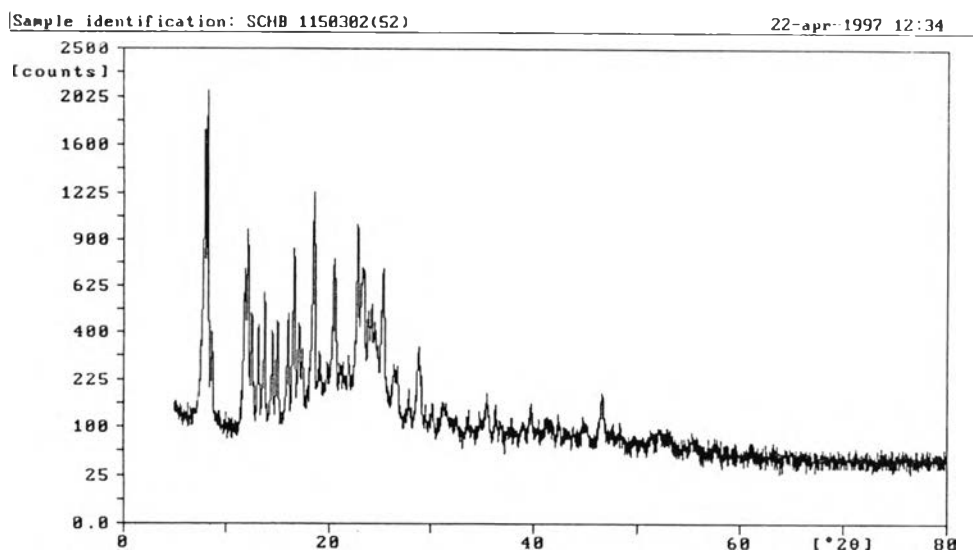


Figure 3.8-d XRD pattern of product HT32 at 5 h with 100 mole % TETA.

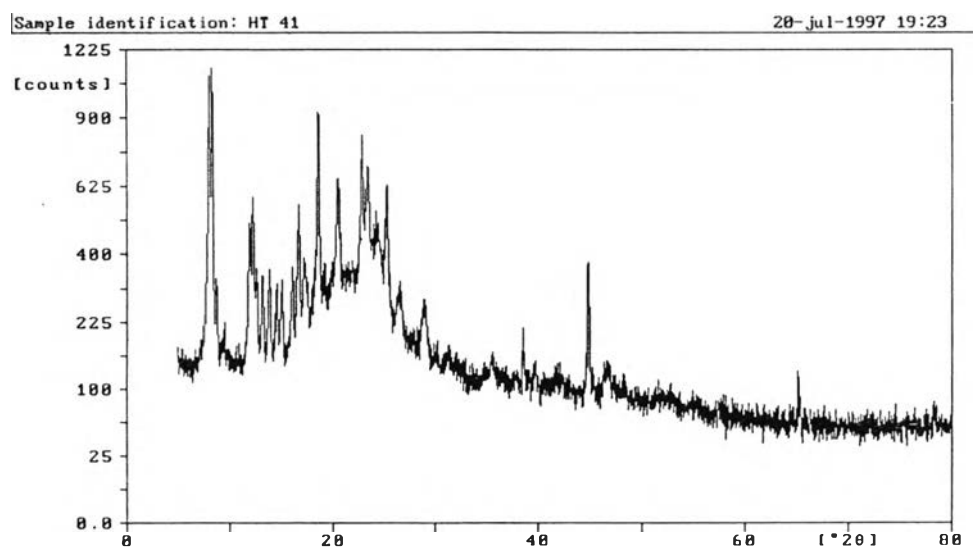


Figure 3.8-e XRD pattern of product HT41 at 5 h with 100 mole % TETA.

The XRD pattern of synthesized products obtained from mole ratio variation gave 2θ peak at 5.8 which appeared broader when the amount of hydroquinone increased, indicating more amorphous behavior.

From FTIR, TGA, DSC and XRD information, the sample at hydroquinone to 4-tert-butylcatechol mole ratio, 0.2:0.3, (HT23) was selected for further analysis for NMR, EI^+ -MS and kinetic study.

3.2.1.5 Mass spectroscopy (MS). The complex mass spectra that resulted from electron impact ionization are of importance in structural identification because its fragmentation provides the molecular weight of the molecular ion peak. The EI^+ mass spectra of sample HT23 showed the fragmentation pattern which the base peak occurs at the mass of 244 (Figure 3.9).

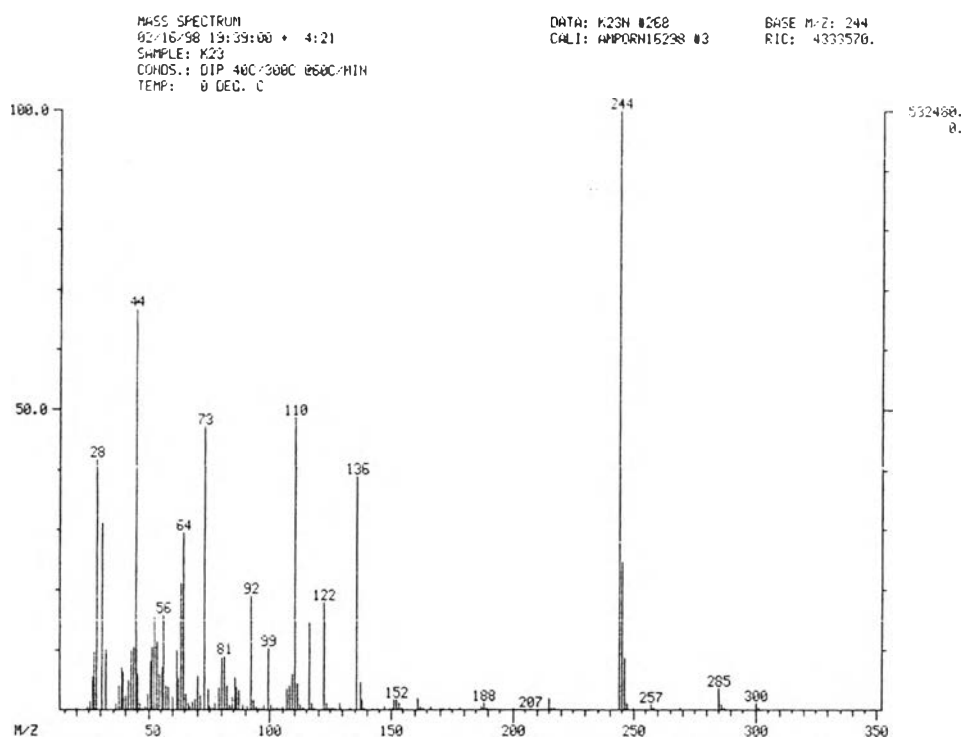
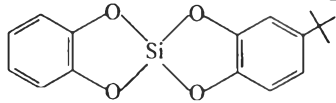
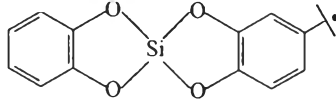
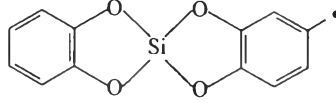
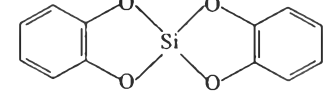


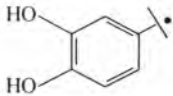
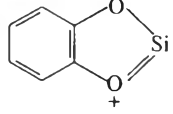
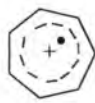
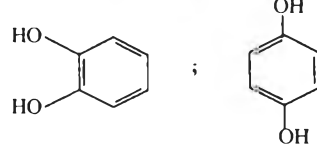

Figure 3.9 EI^+ mass spectra of sample HT23 at 5 h with 100 mole % TETA.

The molecular ion peaks for the oligomers and polymers were not observed because they were broken into repeating unit ion by the ionization with high electron energy (70 eV). The mass peaks at 244 m/z of bis(1,2-dioxyphenyl)silane radical cation and at 300 of (1,2-dioxyphenyl-1',2'-dioxy-4'-tert-butylphenyl)silane radical cation are proposed as fragments of the random copolymer product. The fragments of m/z 285 and m/z 151, were derived from the loss of a methyl groups from those of m/z 300 and 166 respectively.

Apparently, TETA fragmentation is seen at m/z 142 in which only trace amounts still remains in the product, as indicated by NMR spectrum. There were also the ion peak of free catechol (m/z =110) from unreacted sublime catechol, some decomposition of organic ligand from tri(catecholato)silicate and fragment of mass peak 244 m/z. The suggested fragment structure of the products is shown in Table 3.4.

Table 3.4 Proposed structures of the product fragments HT23

m/z	Intensity	Species
300	1.0	
285	3.6	
257	0.9	
244	100.0	

m/z	Intensity	Species
151 (152+H ⁺)	1.7	
136	38.9	
123 (122+H ⁺)	17.8	
110	48.6	
99	10.3	C ₇ H ₁₅ ⁺
73	47.0	C ₄ H ₉ O ⁺
64	20.8	
44	66.6	CH ₂ =CH(OH) ⁺ , C ₂ H ₆ N ⁺ , CO ₂ ⁺ , C ₃ H ₈ ⁺
30	31.3	CH ₂ =NH ₂ ⁺
28	41.3	C ₂ H ₄ ⁺ , CO ⁺ , N ₂ ⁺

3.2.1.6 Nuclear Magnetic Resonance Spectroscopy (NMR). The NMR spectra of a synthesized compound at the mole ratio HT23 were investigated using DMSO-d₆ as a solvent. DMSO-d₆ is a common polar-aprotic solvent capable of dissolving organic compounds and having ability to solvate ion of many salt. Effect of different solvents on ¹H-NMR spectrum causes the deshielding effect by hydrogen bonding between compound with

solvent by attracting around nuclei and shifting to downfield. The chemical shifts can thus be compared with referenced compound at the same type of solvent. ^1H - and ^{13}C -NMR spectra of compounds are always recorded relative to TMS as the reference and set as zero. The chemical shift (δ) of nuclei can then be correlated with molecular structure in various molecular environments.

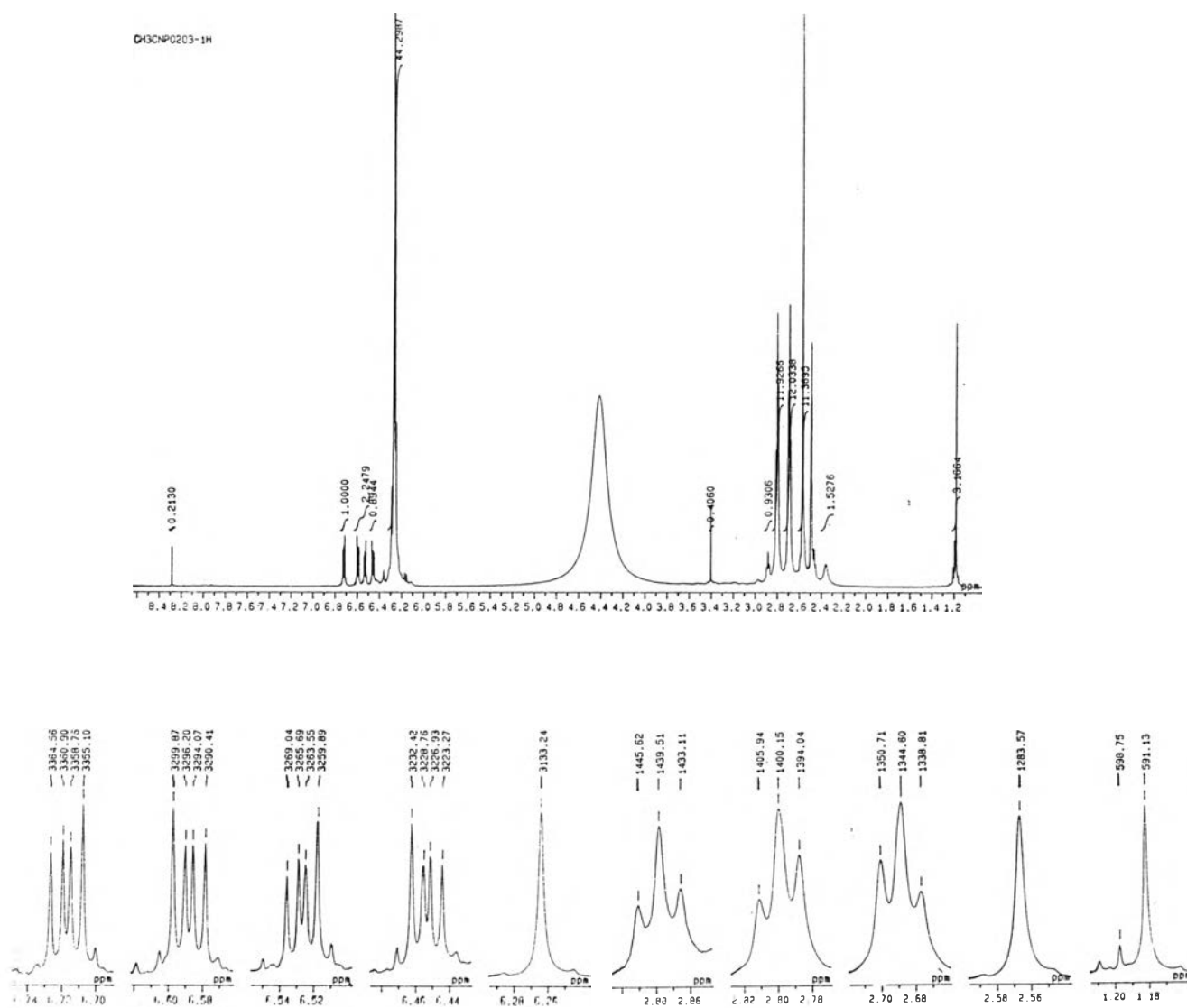


Figure 3.10 ^1H -NMR spectrum of the product HT23 at 5 h with 100 mole % TETA.

The $^1\text{H-NMR}$ spectrum of product HT23 is shown in Figure 3.10, the multiplet peaks at 6.27 ppm represented the proton on benzene ring of bis(1,2-dioxyphenyl)silane polymer which shifted to upfield from the proton on benzene ring of catechol at 6.7 ppm because electronegativities of silicon atom is lower than H, C, N or O. Unoccupied d-orbital of silicon atom offers free space for lone pair electrons from oxygen atom to reside and reduces the deshield effect on the four proton around the outer side of benzene ring. As a result, aromatic ring current from the interaction of π electron with the applied magnetic field is thus decreased.

The same rational is applied to the protons on aromatic ring of 1,2-dioxy-4-tert-butylphenyl proton. Three protons at 6.55, 6.4 and 6.2 ppm showed a little relative intensity as the intensity of proton in tert-butyl group at 1.2 ppm. The proton of hydroquinone comonomer showed a small singlet peak at 6.6 ppm. The other two symmetrical multiplet peaks at 6.7-6.6 ppm and 6.5-6.4 ppm were from the protons on benzene ring of 1,2-dioxyphenyl group of tris(1,2-dioxyphenyl)silane which were couple with protons of free catechol molecule. The TETA left in the product displayed the coupling protons at 8.3 ppm (singlet, RNH_3^+ , RNH_2^+), 2.7-2.8 ppm (double triplet of CH_2 in TETA), 2.6 ppm (triplet of NH_2), 1.2 ppm (singlet of RNH_3^+ , RNH_2^+) which formed amine salts, 2.9 and 2.5 ppm (triplet of proton in derivative of TETA).

The peaks at 2.5 ppm (septet) and 3.4 ppm were from the protons in the solvent, DMSO-d_6 , corresponding to the methyl groups in the molecule, and water absorbed in the solvent. The last broad peak at 4.7 ppm was the proton exchange of water.

$^{13}\text{C-NMR}$ spectrum of the sample HT23 is shown in Figure 3.11.

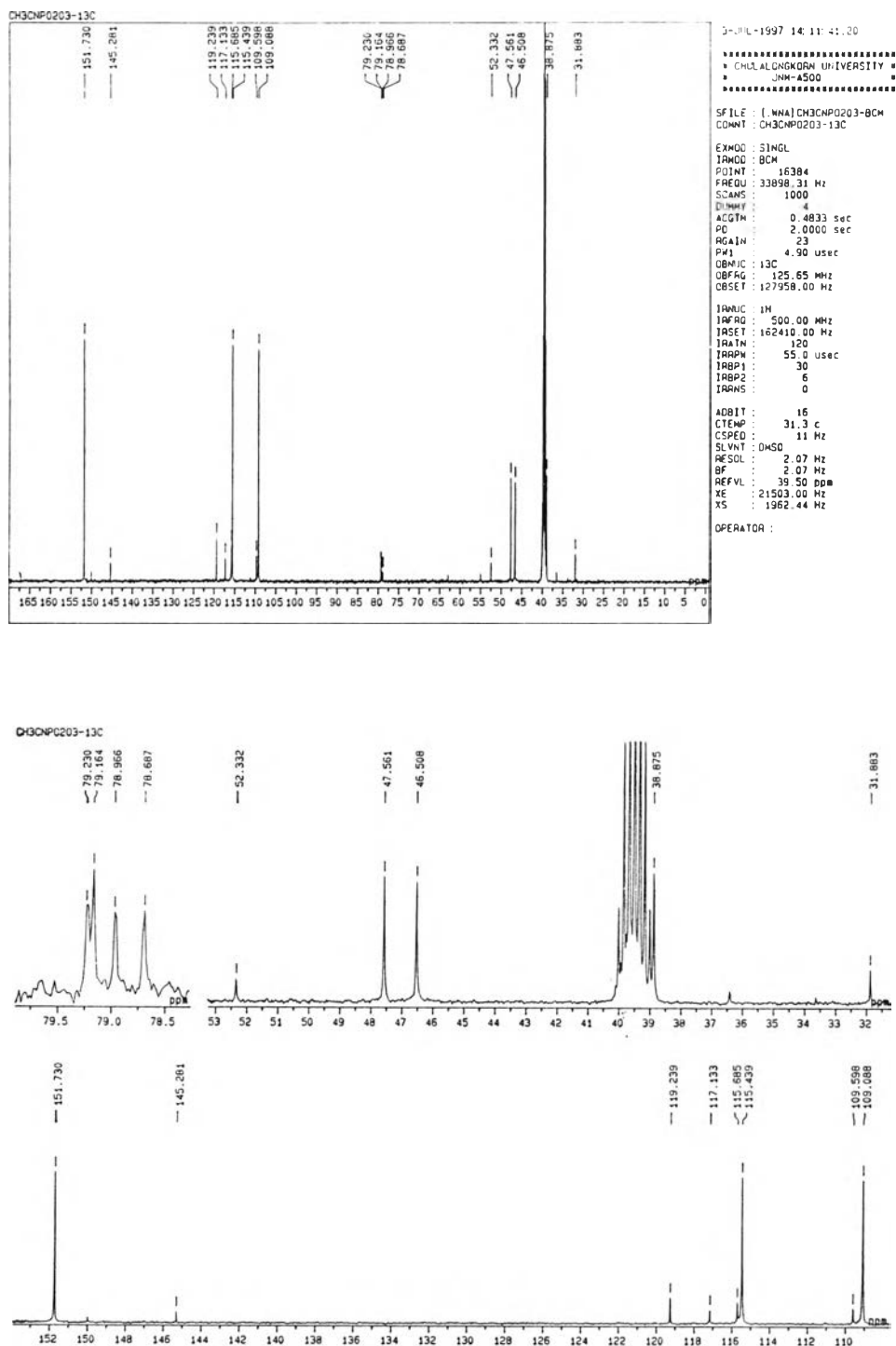
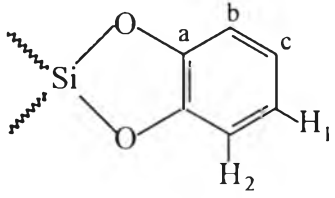
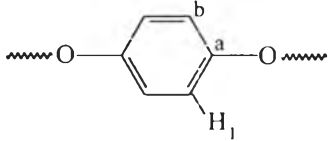


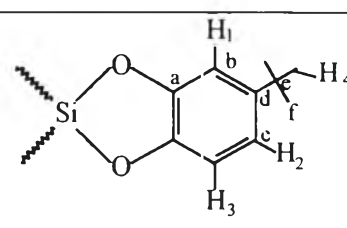
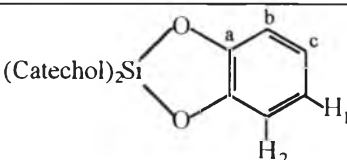
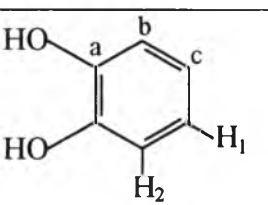
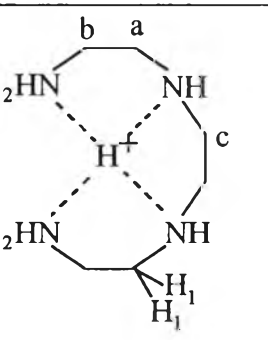
Figure 3.11 ^{13}C -NMR spectrum of the product HT23 at 5 h with 100 mole % TETA.

The peaks at 151.7, 115.4 and 120.0 ppm resulted from carbon atoms on the benzene ring of bis(1,2-dioxyphenyl)silane polymer. The appearance of a little peaks at 150.0 ppm was due to the carbon atom on benzene ring connecting to tert-butyl groups. The peaks at 31.9 ppm (CH₃) and 36.4 ppm (4°-carbon) were representing the carbons in 4-tert-butyl groups. The carbon peak of 1,4-dioxyphenyl group cannot be found in this spectrum. It might be because there was little amount of hydroquinone in the product.

The peaks of free catechol were also seen at 145.3, 119.2, and 115.7 ppm by Allcock (1972), while the appearance of the peaks at 117.1 and 109.6 ppm were due to the carbon atoms of 1,2-dioxyphenyl group in tris(1,2-dioxyphenyl)silane. Effect of having TETA in the products are shown by the peak at 38.9 ppm (C-NH), 47.6 ppm (C-NH₂⁺), 46.5 ppm (C-NH₃⁺), and their derivative forms occurred at 55.0, 52.3, and 36.4 ppm. The septet peaks at 39.7 ppm were from the CH₃ of the solvent, DMSO-d₆. All results are presented in Table 3.5.

Table 3.5 ¹H- and ¹³C-NMR chemical shifts of the product at hydroquinone to 4-tert-butylcatechol mole ratio is 0.2:0.3 (HT23)

Assigned Structure	¹ H-NMR(ppm)	¹³ C-NMR(ppm)
	multiplet, 6.3	151.7(a) 115.4(c) 109.1(b)
	singlet(decoupled), 6.62(H ₁)	(invisible) δ of C a > δ of C b

Assigned Structure	¹ H-NMR(ppm)	¹³ C-NMR(ppm)
	doublet, 6.4(H ₃) doublet, 6.4(H ₂) single, 6.2(H ₁) triplet, 1.2(H ₄), J=5.8	151.7(a) 115.4(c) 109.1(b) 150.0(d) 36.4(e), 31.9(f)
	double quartet of doublet, 6.7(H ₁), J=64.7, 5.8, 3.7, 0.31 double quartet of doublet, 6.5(H ₂), J=36.6, 5.8, 3.7, 0.31	151.7(a) 117.1(c) 109.6(b)
	multiplet, 6.7	145.3(a) 119.2(c) 115.4(b)
	triplet, 1.2(NH ₂ ⁺), J=10.1 triplet, 2.6(NH ₂), J=10.1 double triplet, 2.7(CH ₂), J=55.2, 5.8, 0.31 singlet, 8.3(NH ₃ ⁺ , NH ₂ ⁺)	47.6(a) 46.5(b) 38.9(c)

3.2.2. Variation of TETA concentration on the reaction

The amount of catalyst, TETA, also influenced in the product properties as indicated in FTIR, TGA, and $^1\text{H-NMR}$. The products at 10, 30, and 50 mole % TETA that came from precipitation of filtrate by removing the methanol solvent. They gave the same pattern in FTIR spectra and TGA thermogram, as shown in Figures 3.12 and 3.13.

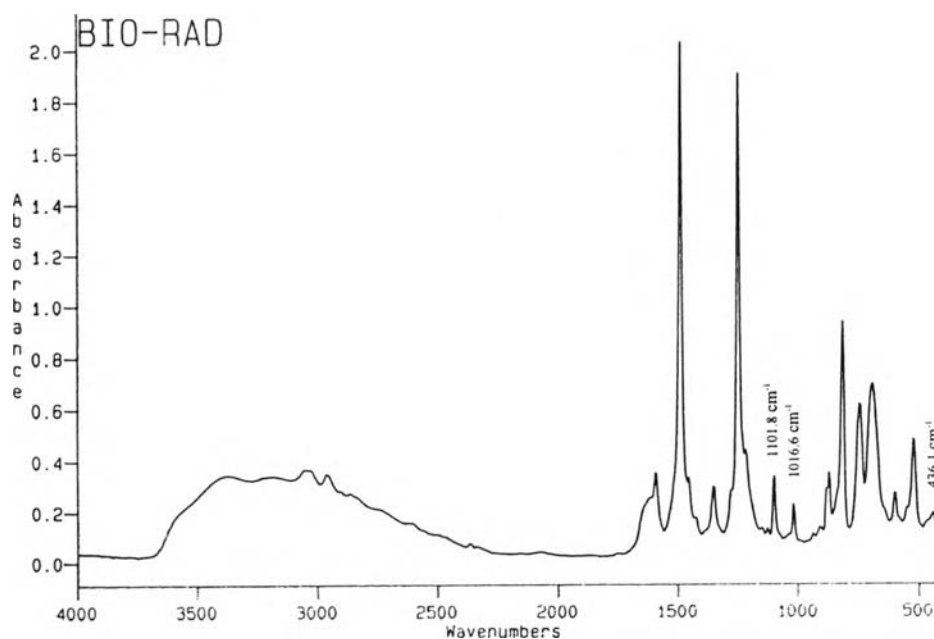


Figure 3.12 FTIR spectrum of the product HT23 at 10 mole % TETA for 10 h reaction time.

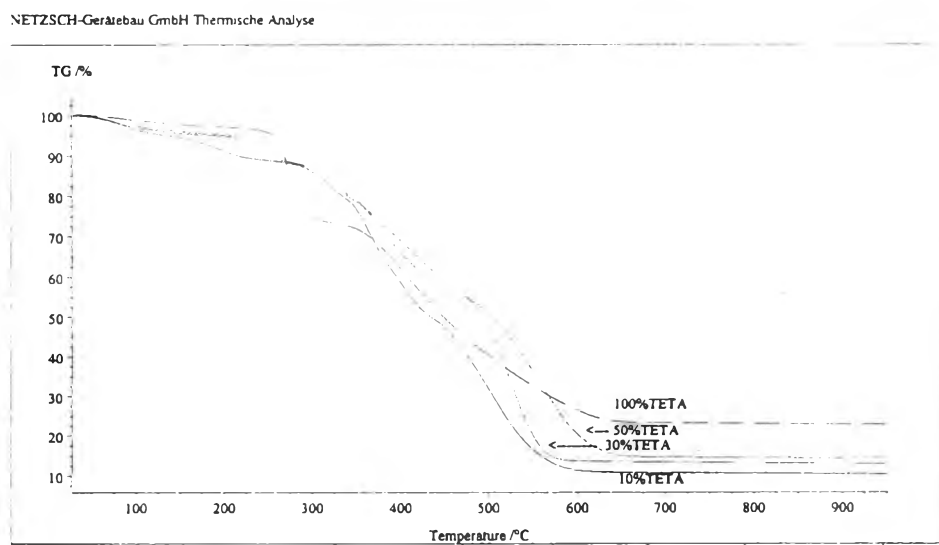


Figure 3.13 Thermogram of the product HT23 by varying the amount of TETA at 10 h reaction time.

FTIR spectra, surprisingly, gave small the absorption peaks of Si-O-C stretching at 1100.6 and 1018 cm^{-1} and bending of Si-O at 473 cm^{-1} . However, when we considered FTIR spectrum and % ceramic yield of residue products obtained after filtration, it showed mainly silica, as shown in Figures 3.14 and 3.15. The more mole % TETA, the less silica left in the products.

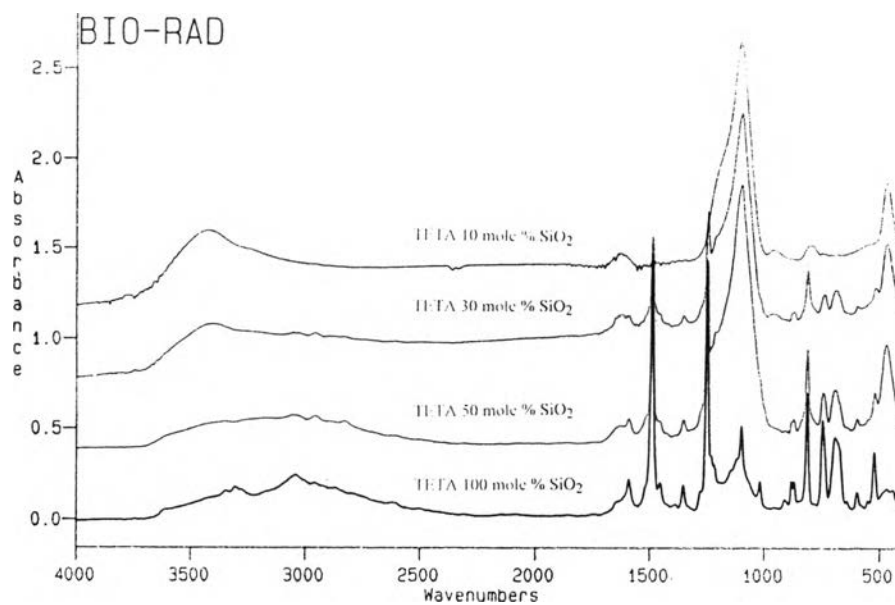


Figure 3.14 FTIR spectrum of the residue products HT23 by varying the amount of TETA at 10 h reaction time.

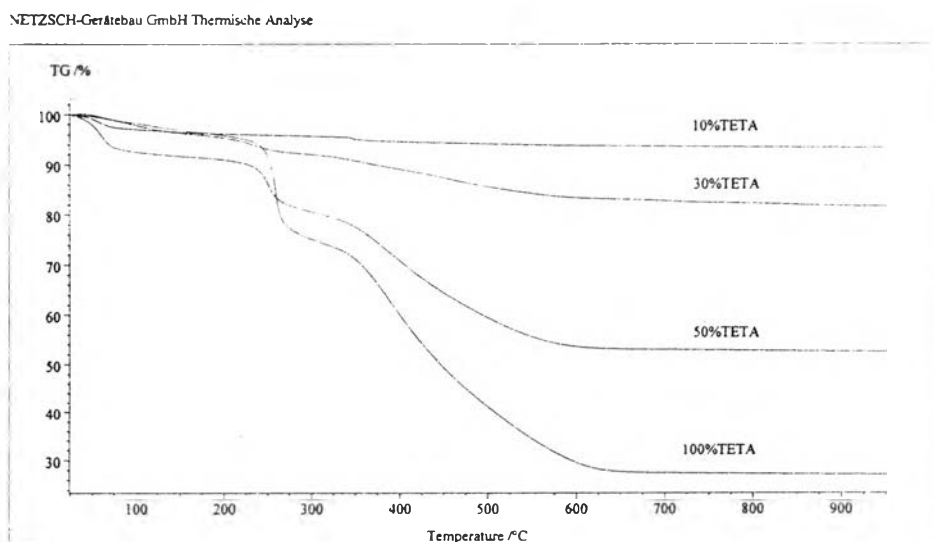


Figure 3.15 Thermogram of the residue products HT23 by varying the amount of TETA at 10 h reaction time.

For TGA thermograms of products, the percents ceramic yield of products obtained at 10, 30, and 50 % TETA were nearly the same (~11.2%), as shown in Figure 3.13. For the product obtained at 100 mole % TETA, the reaction that took longer reaction time gave the lower yield than that at 5 h reaction time.

The product at 10 mole % TETA that gives ¹H-NMR spectra, as shown in Figure 3.16.

The $^1\text{H-NMR}$ spectra of samples at 10 mole % TETA were the same as those of products at 100 mole % TETA, except that spectra of 10 mole % TETA gave higher intensity of protons in hydroquinone and tert-butyl group than the other one. The peaks for methanol and acetonitrile still remained in the product including low amounts of TETA. However, the reaction that used small amounts of TETA gave the lower product yield. The reason is that the reaction was incomplete, especially, a lot of unreacted starting material, silica, still remained. Therefore, this condition was chosen to study kinetics.

For kinetic study, the unreacted SiO_2 was removed from the reaction mixture for quantitative determination. The liquid phase was collected for structural analysis followed by removing EG under vacuum at $160^\circ\text{C}/20\text{mmHg}$ and washing with methanol under N_2 atmosphere. The FTIR and TGA were used to characterize the products as a function of time and temperature, as shown in Figures 3.17 and 3.18, respectively.

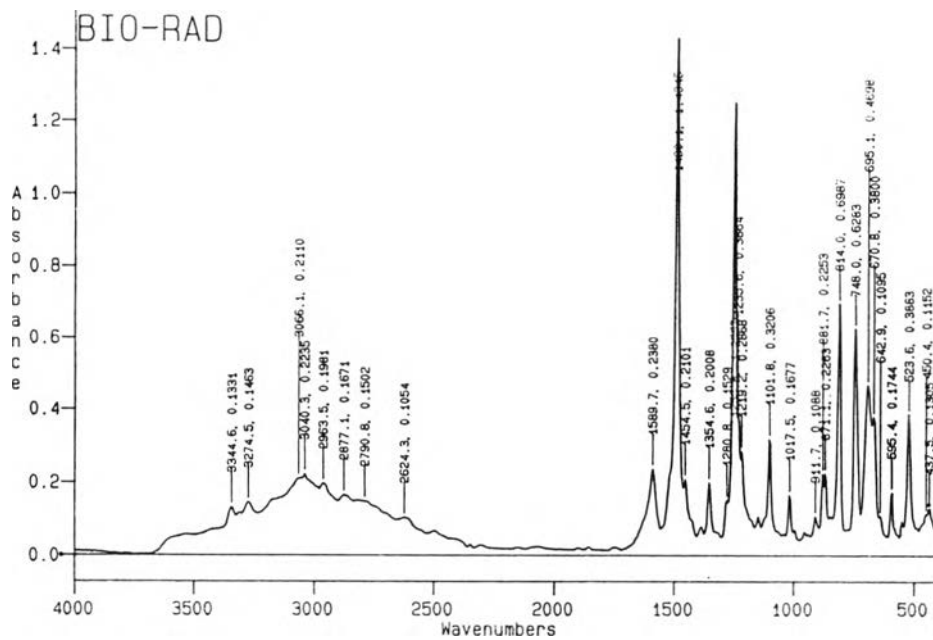


Figure 3.17 FTIR spectrum of the product precipitated from the liquid phase.

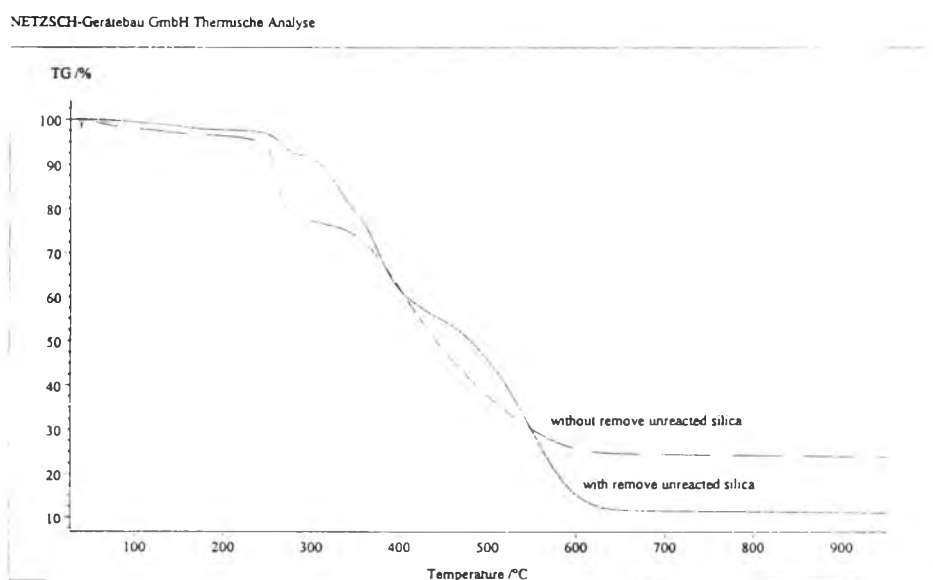


Figure 3.18 Thermogram of the product precipitated from the liquid phase.

Figures 3.19 and 3.20 show the comparison of FTIR and TGA of the product precipitated from the liquid phase obtained from using 15 or 30 min and 2 h reaction time.

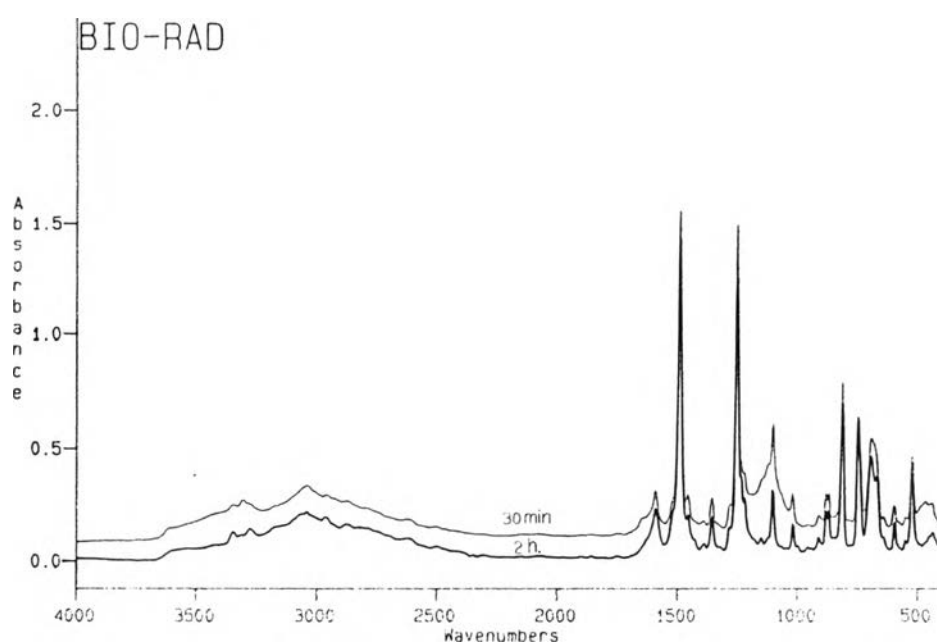


Figure 3.19 Comparison of FTIR spectra between the product precipitated from the liquid phase at 200°C for 30 min and that for 2 h with 100 mole % TETA.

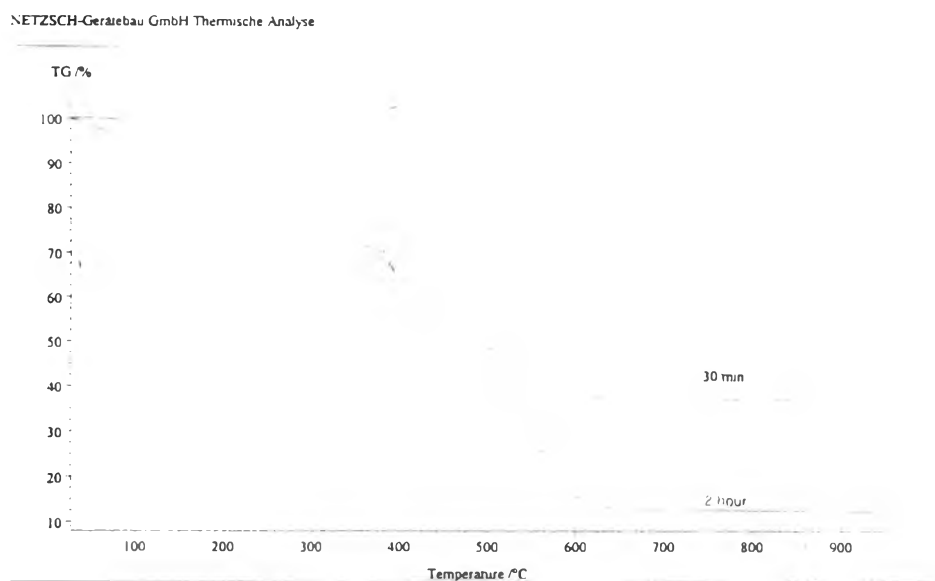


Figure 3.20 Comparison of thermogram between the product precipitated from the liquid phase at 200°C for 30 min and that for 2 h with 100 mole % TETA.

The reaction using 100 % TETA gives good yields of product. It provides the fastest reaction although it needs a sufficient time to polymerize in the process.

The EI⁺-MS and NMR of the liquid phase are give in Figures 3.21 and 3.22, respectively.

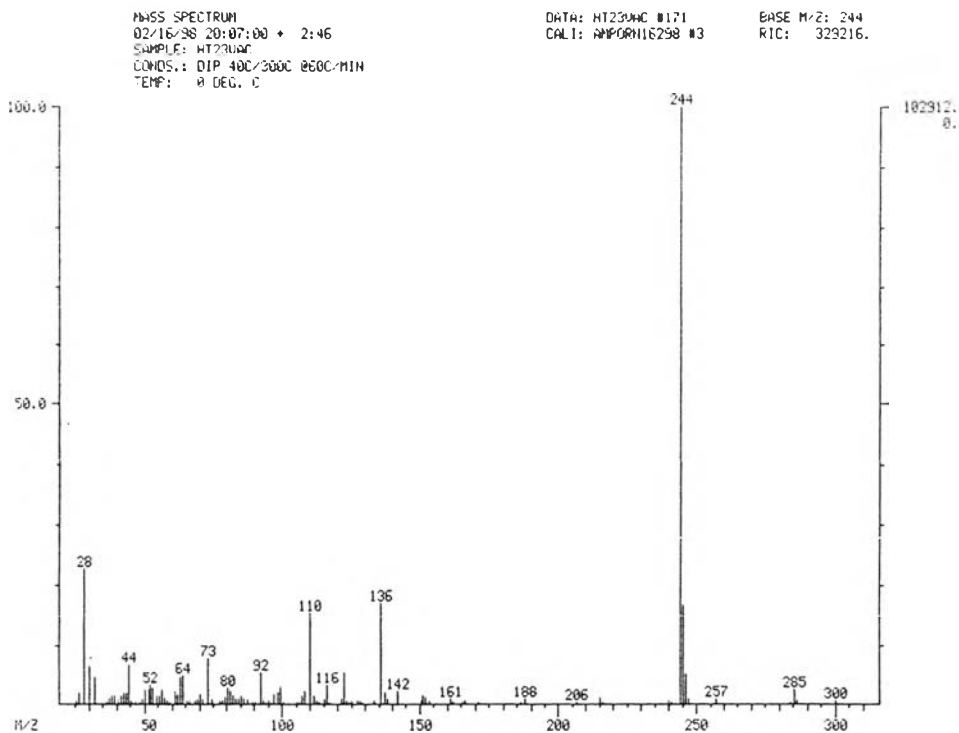


Figure 3.21 EI⁺ mass spectrum of the product precipitated from the liquid phase at 200°C for 2 h with 100 mole % TETA.

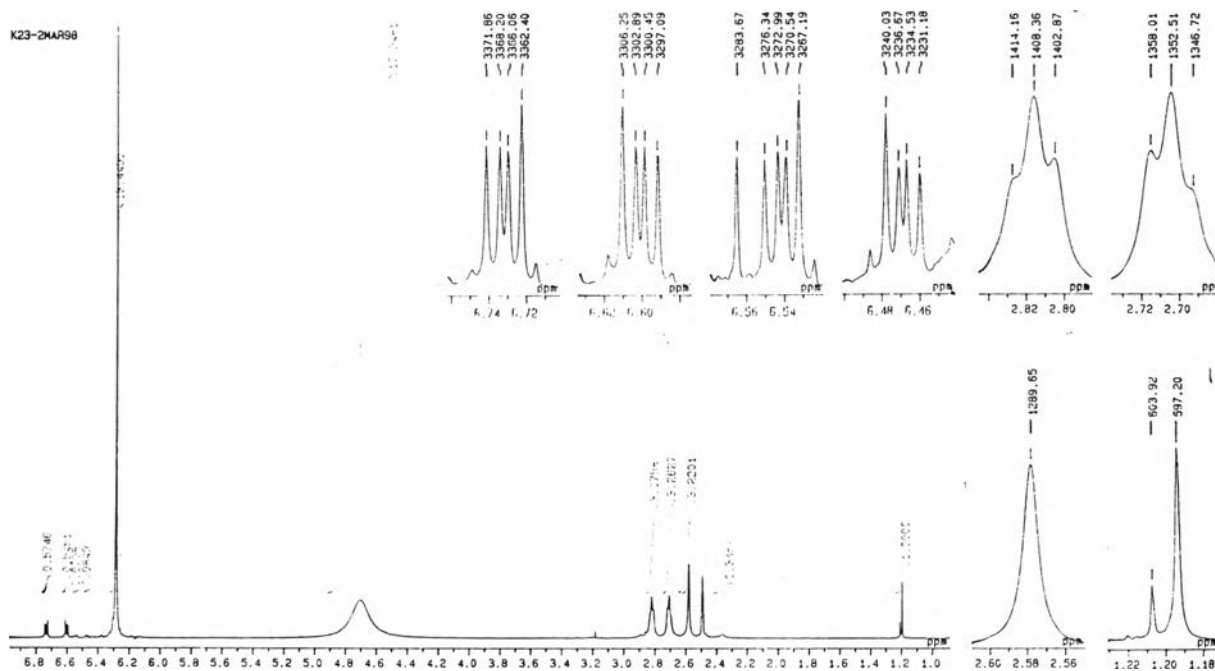


Figure 3.22-a ¹H-NMR spectrum of the product precipitated from the liquid phase at 200°C for 2 h with 100 mole % TETA.

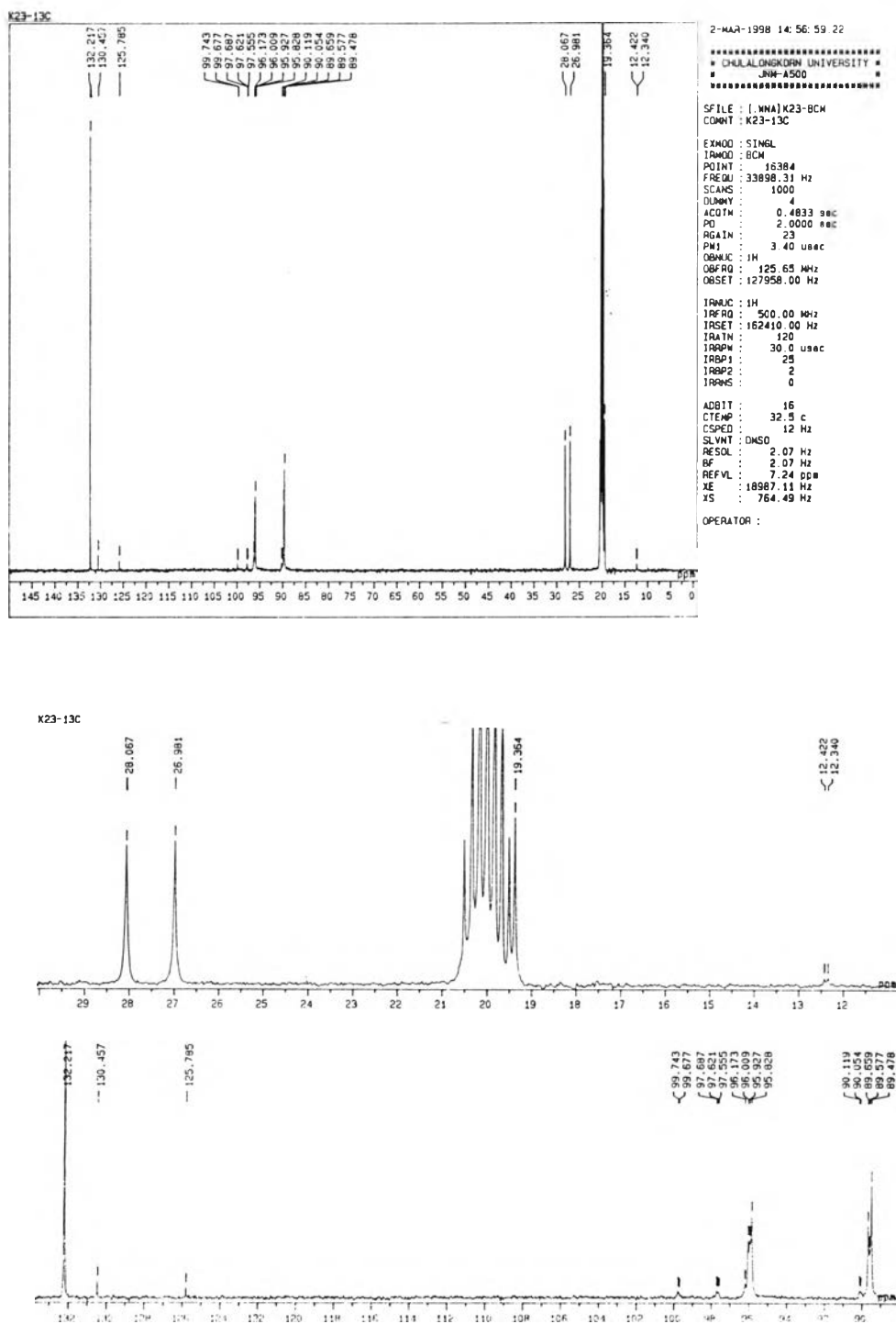


Figure 3.22-b ^{13}C -NMR spectrum of the product precipitated from the liquid phase at 200°C for 2 h with 100 mole % TETA.

For the TGA thermogram, the first mass loss occurring below 280° C, resulted from decomposition of TETA whereas the mass loss between 280° C-320°C represented to catechol, hydroquinone and 4-tert-butylcatechol left in the product. The mass loss between 320°-430°C corresponded to the decomposition of organic ligand and the last mass loss between 430°-650°C corresponded to the remaining organic residue in the product (Figure 3.23).

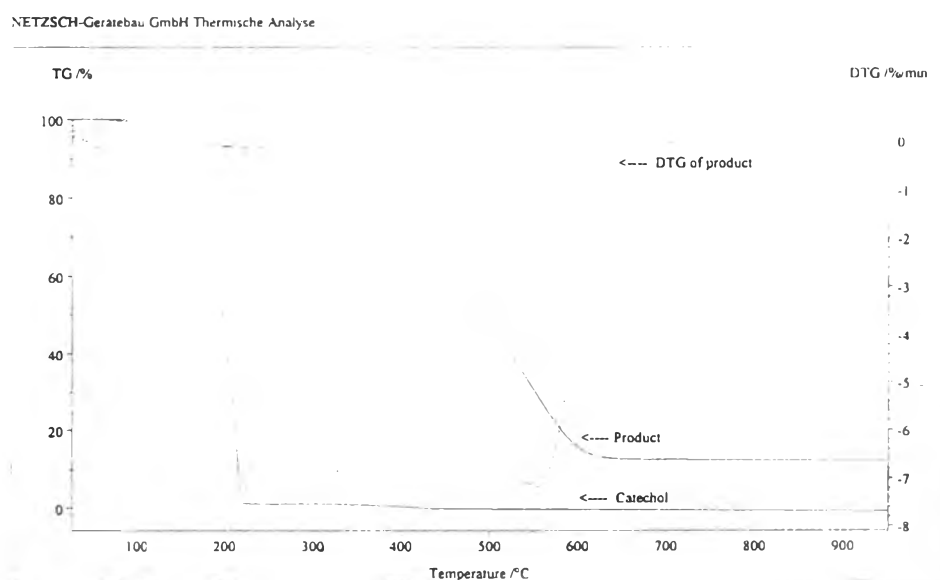


Figure 3.23 Thermograms of the product precipitated from the liquid phase at 200°C for 2 h with 100 mole % TETA as compared to that of pyrocatechol raw material.

The XRD profile showed that the product obtained from precipitation of the liquid phase gave more crystalline behavior which is possibly belong to ammonium salt of tri(catecholato)silicate, as shown in Figure 3.24.

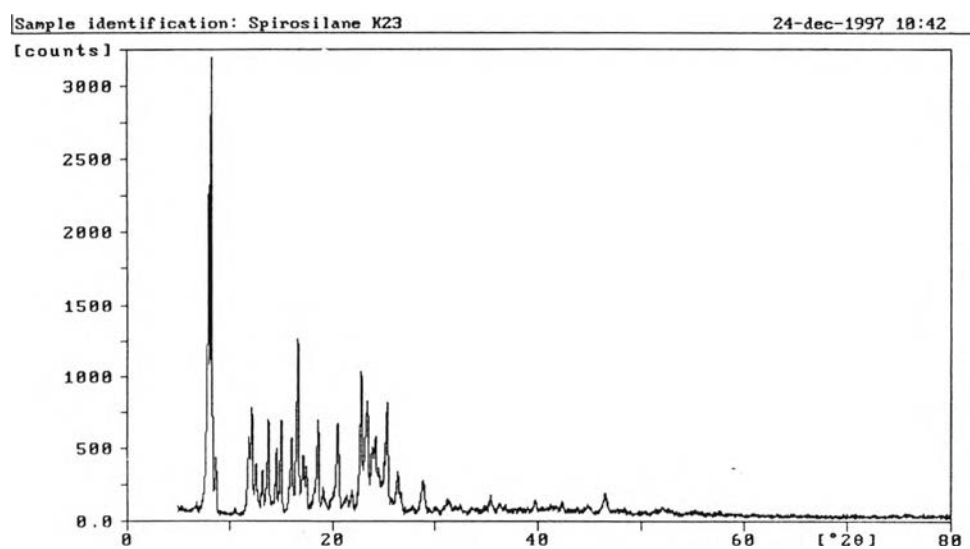


Figure 3.24 XRD spectrum the product precipitated from the liquid phase at 200°C for 2 h with 100 mole % TETA.

From all results, it shows that the product precipitated from the liquid phase was mainly tri(catecholato)silicate.

3.3 Kinetic study

The silica raw material and unreacted silica were weighed at room temperature after its has dried in furnace at 1000°C for 30 minutes. The impurities in silica (e.g. humidity, organic residues) were lost to determine the actual unreacted silica. The ceramic yield of silica was measured as silicon dioxide (SiO₂) using TGA. The variation of the %ceramic yield of SiO₂ before and after furnace dried depends on the proportion of impurity contained.

3.3.1 Variation of reaction time

The reaction time was varied from 0.5, 1.0, 1.5, to 2.0 h for two differently initial concentration of SiO₂ while the other concentrations, amount of catalyst and solvent were fixed, as discussed in section 2.3.2., at fixed reaction temperature (210°C). The initial rates of SiO₂ dissolution were measured to determine the reaction order with respect to SiO₂ by the initial method. The initial rate of the higher SiO₂ concentration was higher than that of the lower one, see Figure 3.25. The reaction occurs at the surface of silica, therefore, the higher the dissolution of silica took the longer reaction time. However, the rate of dissolution was slowly retarded because the active site groups, silanol groups, on the surface area of silica decreased.

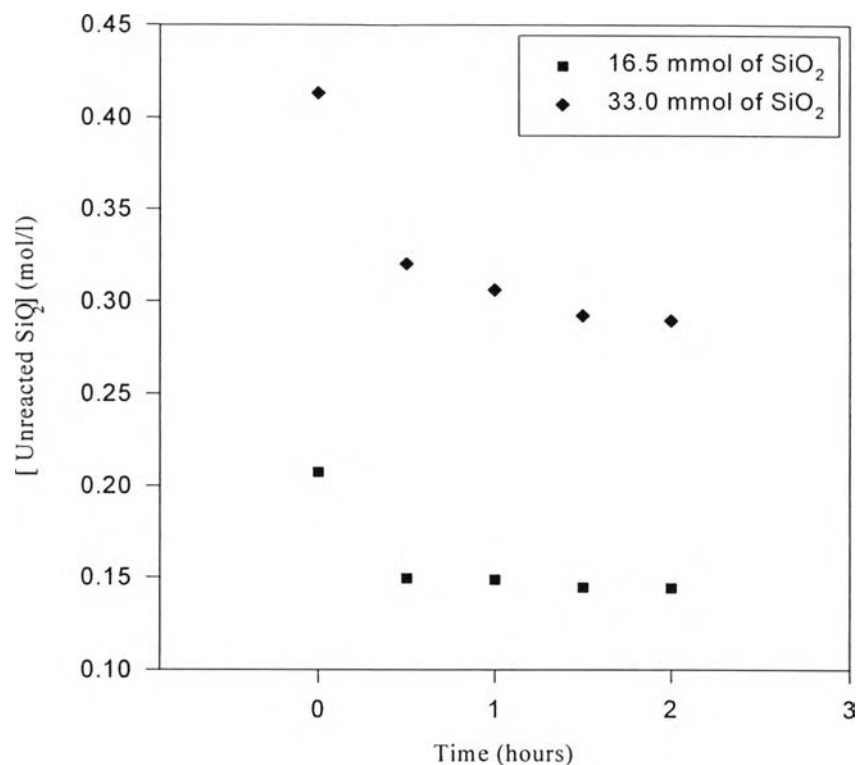


Figure 3.25 Relationship between [unreacted SiO₂] versus time at the reaction temperature 200°C.

The initial rate was obtained from the slope which passed through [unreacted SiO₂] at time equal to zero. Thus, the rate of reaction is

$$-d[\text{SiO}_2]/dt = r = \text{rate}$$

After integration, we can get

$$[\text{SiO}_2]_t = [\text{SiO}_2]_0 - r t$$

The order of SiO₂ (α) was determined by

$$\alpha = \ln[r_{0,1}, r_{0,2}] / \ln\{[\text{SiO}_2]_{0,1} / [\text{SiO}_2]_{0,2}\}$$

As a result see Table 3.2, The order is equal to 1.06. That is, the rate of SiO₂ dissolved was the first order function.

3.3.2 Variation of reaction temperature

The effect of temperature on the rate of reaction was studied. The initial rates ($r_0 = -d[\text{SiO}_2]_0/dt$) and the J ($J = k [\text{Cat}]^\beta [\text{Hydro}]^\gamma [\text{tert-Butcat}]^\lambda [\text{TETA}]^\eta$) constants were increasing as the temperature increased, whereas the orders with respect to SiO_2 (α) were decreasing. Thus the activation energy is positive, as presented in Figure 3.26 and Table 3.6. The average order (α) is equal to 1.05, as the first order with respect to SiO_2 .

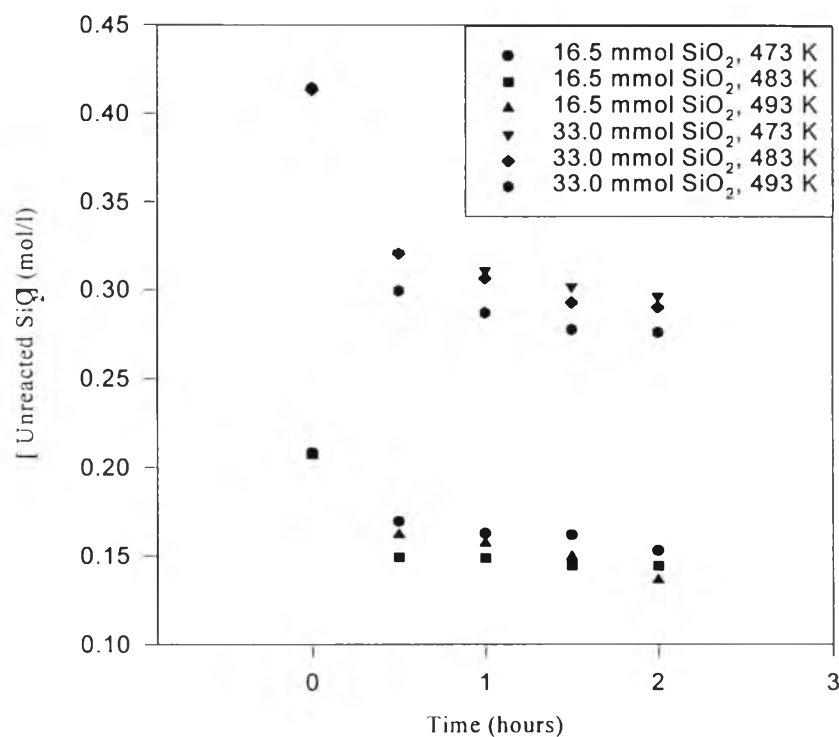


Figure 3.26 Relationship between [unreacted SiO_2] versus time at the reaction temperatures of 473 K, 483 K and 493 K.

Table 3.6 Data of kinetic study

T(K)	473		483		493	
ratio of SiO ₂	0.5	1.0	0.5	1.0	0.5	1.0
r ₀ (mol l ⁻¹ hr ⁻¹)	0.0236	0.0263	0.0309	0.0515	0.0545	0.0603
α	1.12921		1.06125		0.095886	
ln J	-1.97352		-1.96890		-1.96648	

The $k(T)$ data of reactions in solution fit the Arrhenius equation ;
 $k = A \exp(-E_a/RT)$. The Arrhenius activation energy, which is a characteristics of the reaction, can be determined from the plot of $\ln J$ versus $1/T$ where $J = k [\text{Cat}]^\beta [\text{Hydro}]^\gamma [\text{tert-Butcat}]^\lambda [\text{TETA}]^\eta$ to give a straight line with slope equal to $-E_a/R$, as presented in figure 3.2.3. The certain minimum energy required to break the appropriate bonds and allow new compounds to be formed was calculated in J/mol or cal/mol.

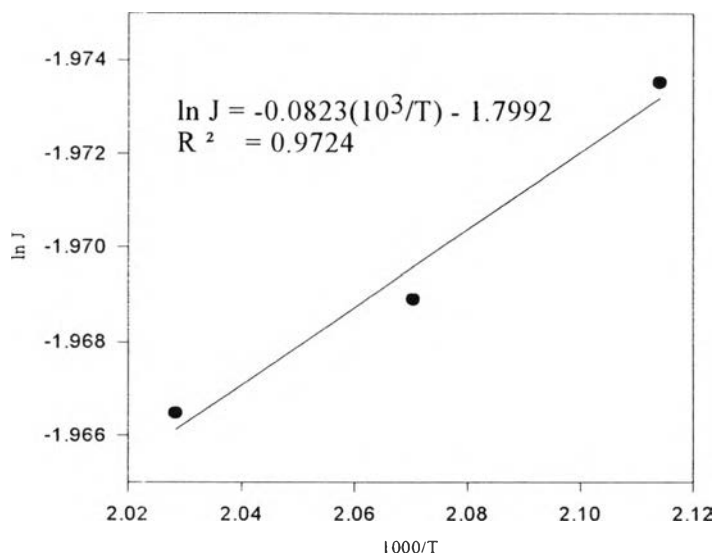
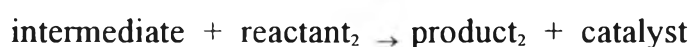


Figure 3.27 Relationship between $\ln J$ versus $1/T$

$$\begin{aligned} \text{the slope} &= E_a/R ; E_a = 0.0823 \cdot 10^3 \cdot 8.314 = 684.2422 \text{ J/mol} \\ &= 0.0823 \cdot 10^3 \cdot 1.987 = 163.5301 \text{ cal/mol} \end{aligned}$$

As a result, the activation energy was 160 cal/mol (680 J/mol).

In most cases, the catalyzed mechanism has a lower activation energy than that of the uncatalyzed mechanism and provides an alternate mechanism that is faster than the mechanism of the reaction without the catalyst. A simple scheme for a catalyzed reaction is



where reactant_1 = catechol, hydroquinone, 4-tert-butylcatechol

reactant_2 = SiO_2

catalyst = triethylenetetramine (TETA)

intermediate = $(\text{reactant}_1 \text{ anion})^- \text{TETAH}^+$

The rate law of a catalyzed reaction frequently has the following form

$$r = k_0 [A]^\alpha \dots [L]^\lambda + k_{\text{cat}} [A]^\alpha \dots [L]^\lambda [\text{cat.}]^\gamma$$

where k_0 is the rate constant in the absence of catalyst at $[\text{cat.}] = 0$.

k_{cat} is the rate constant in the presence of catalyst

If the lowering of E_a is substantial, the first term in the rate law is negligible, as compared with the second term, unless $[\text{cat.}]$ is extremely small. For this study TETA, 100% mole of SiO_2 , was used in high amounts, the rate law for the calculation of E_a and the order of the reaction can be assumed of the form in second term and use the initial method for the calculation.

The equilibrium constant (K°) for the overall reaction is determined by $\Delta G^\circ = -RT \ln K^\circ$ and is therefore independent of the reaction mechanism. A catalyst cannot alter the equilibrium constant of the reaction, meaning that a catalyst for a forward reaction must be a catalyst for the reverse reaction. A TETA catalyst present in the same phase of EG solvent, reactants and products will change the activity coefficients (γ_i) or others e.g. equilibrium mole fractions of reactants and products which the mole fractions equilibrium constant (K°) is

$$K^\circ = \prod_i (a_i, \text{eq})^{\nu_i}, a_i = \gamma_i x_i,$$

From the results, it showed that $E_a < RT$. When $E_a \gg RT$, the temperature dependence of E_a and A is usually too small to be detected by the rather inaccurate kinetic data available, unless a wide temperature range is studied.