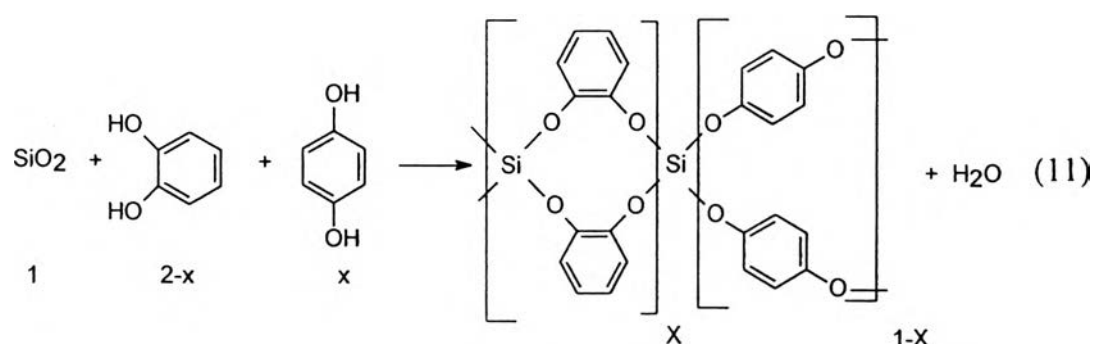


CHAPTER III RESULTS AND DISCUSSION

3.1 Synthesis

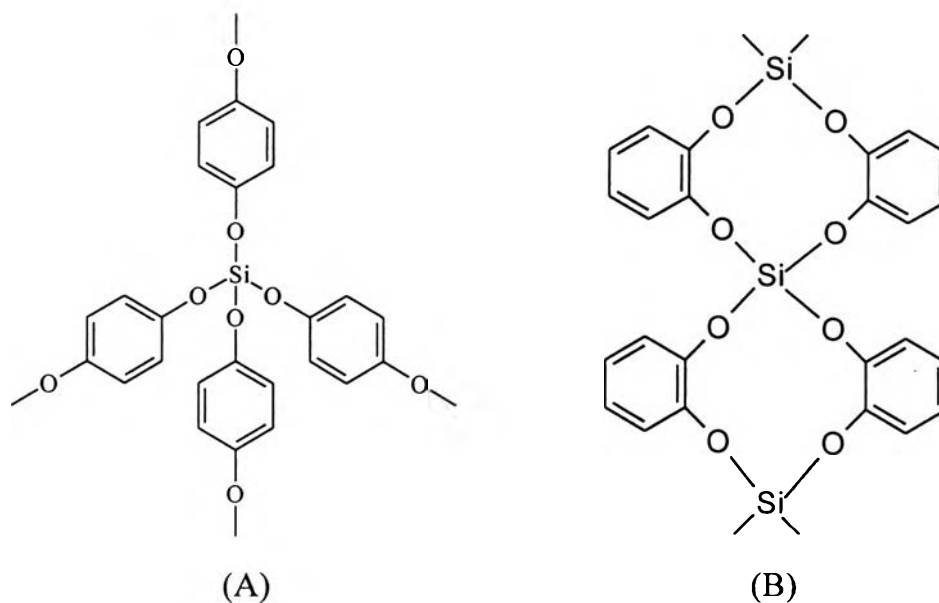
The novel copolymer derived from silica, catechol and hydroquinone can be synthesized in one step using triethylenetetramine and ethylene glycol as catalyst and solvent, respectively. Catechol and hydroquinone in the reaction solution, become strong nucleophiles species with $TETAH^+_2$ as counterion. The Si-O bond of silica is weakened by these nucleophiles and depolymerizes with form atom of new Si-O-C bonds.

The reaction requires 5 h. Since water is a by-product, it must be removed to drive the reaction forward, as illustrated in equation (11).



The properties of this copolymer depend on the conditions and composition in the reaction. These studies were conducted to examine the properties of the synthesized copolymer by varying mole ratios of the raw materials, amount of catalyst, and reaction time.

The copolymer powder as described in Chapter II. The samples H0-H6 can be precipitated, while the samples H7-H10 were viscously black materials after it had been removed EG solvent, and unable to precipitate. Therefore, this copolymer does not seem to form with excess hydroquinone. The reason is that hydroquinone molecule is an obstacle to form crystalline material. Silicon can bond simultaneously with both of hydroxy group of catechol molecule to form ladder-like polymers [Allcock, H.R. et al., 1972], whereas hydroquinone molecule rather form network polymer with silicon as shown in the Scheme 3.1



Scheme 3.1 Si-O bond of (A) hydroquinone, (B) catechol.

The addition of proper amount of hydroquinone amount could extend the ladder layer to give higher molecular weight. However, excess hydroquinone will obstruct the formation of ladder structure and create more network structure. Hence, the amount of hydroquinone in the reaction should play a significant role in determining copolymer properties.

At 5 h reaction times, products H0-H4 precipitate on cooling, while H5-H6 products precipitate on removal of solvent. The synthesized products are yellowish fine powder. The higher the hydroquinone concentration is, the darker color the product will be. Because hydroquinone molecule in products is oxidized so the synthesized product become dark color. The yield decreases with the increment of the amount of hydroquinone.

When the reaction time is reduced to 4 hours, the products are similar to the reactions run at 5 h. The products, H1-H4, on cooling while for H5-H6, all solvent must be removed before products precipitate. The yield also decreases as the amount of hydroquinone is increased, as shown in the Table 3.1. The yield at 4 h reaction time is higher than that at 5 h reaction time at the same ratio.

At 3 h reaction time, the H1-H6 powder precipitate out , but products H7-H9 are recovered only after all solvent is removed. The yields decrease with increasing hydroquinone content, similar to 4 h and 5 h reaction times. The result data at 3 h reaction time is also shown in the Table 3.1.

Table 3.1 Percent yield of products in each reaction time

Sample	% yield		
	3 h	4 h	5 h
H1	72.1	74.5	76.6
H2	64.2	65.1	64.3
H3	74.0	67.2	65.3
H4	84.0	69.0	68.7
H5	75.5	66.2	52.5
H6	68.3	60.1	41.9
H7	67.0	-	-
H8	65.1	-	-
H9	64.5	-	-

As can be seen from the table, sample H7-H9 can be synthesized at 3 h reaction time whereas at 4 h and 5 h reaction times, the synthesis succeed till sample 6. This is because the longer reaction times give a chance for the more hydroquinone to react, resulting in the more network structure. When the amount of hydroquinone is higher, the ladder of silicon-catechol structure content decreases. When enough hydroquinone reacts with silica, it produces a sticky substance that has a network-like structure. The ladder structure of the product still remains at short reaction time because only little hydroquinone reacts with.

The importance of catalyst concentration, TETA, was also considered in this study. In the synthesis of bis(1,2-dihydroxyphenyl), a possible intermediate in copolymer formation, the amount of TETA used for synthesized precursor was equal to 100%mol Si [Rangsitphol, J., 1995]. Higher TETA concentrations make isolation of product more difficult and possibly forms the

stable salt complex with catechol. The study of catalyst concentration variation is illustrated in Table 3.2

Table 3.2 Percent yield product H3 in each TETA variation at the reaction time and temperature of 5 h and 200 °C respectively

TETA (% molSi)	% Yields
17	58.3
33	60.2
50	61.0
67	62.5
83	62.7
100	65.3

The yield increases as the amount of TETA increases, indicating that the amount of catalyst is the auxiliary function for product increment. One explanation is that TETA forms relatively stable catechol or hydroquinone anions. Therefore the more TETA, the more anion or dianion, resulting in readily the polymerization process. However the yield of the last sample, 100% mol Si, is less than the previous one. This is because a isolation of product also depends on amount of TETA. TETA can form triethylenetetraminium tris (catecholato)silicate salt complex if the reaction contains too much TETA. The extent of TETA should be in the range 50%mol Si - 83%mol Si to obtain a better product in both quality and quantity.

To optimize the reaction, the reaction time was varied from 1 to 5 h because the reaction occurs at the surface of silica. In the synthesis of bis(1,2 dioxypyhenyl)silane synthesis, a 5 h reaction was found to be useful [Rangsitphol, J., 1995]. It was determined that the longest reaction time, 5 h,

gives the lowest product yields. The maximum yield is obtained at 3 h. All products have the same color. Table 3.3 shows all data obtained from reaction time variation.

Table 3.3 Typical yield of product at each reaction time

Reaction time	%Yield
1 h	65.2
2 h	64.7
3 h	74.0
4 h	67.2
5 h	65.3

The product obtained 5 h reaction time is air and moisture stable. Although it seldom dissolves in most organic solvent, it readily dissolved in hot ethylene glycol and DMSO. The structure characterization is performed as discussed below.

3.2 Characterization

3.2.1 Differential Scanning Calorimetry (DSC)

The DSC profile of sample H3 product is illustrated in Figure 3.1. The first endotherm appears at 280 °C due to partial depolymerization of the bis(1,2-dioxyphenyl)silane polymer. This can be explained by comparing with the TGA results which show some loss of polymer through depolymerization. There is also a small endothermic peak around 250 °C which can possibly be a volatilization of trace amounts of TETA, in agreement with TGA results. No

exothermic peaks are observed on cooling as the material degrades above 290 °C.

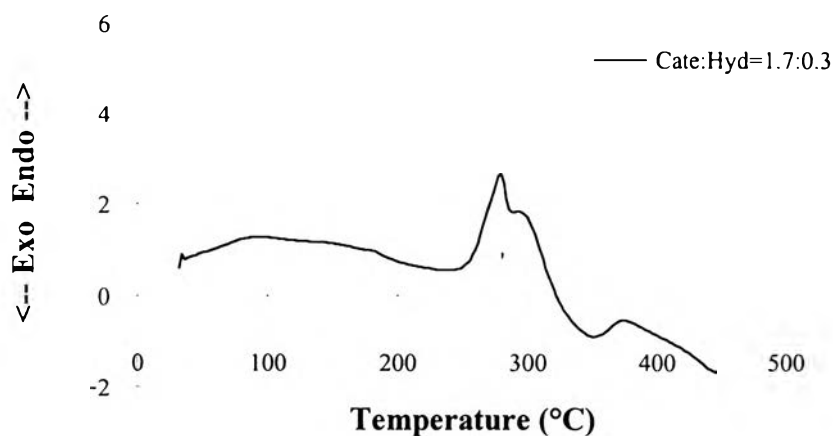


Figure 3.1 DSC profile of product H3.

From the DSC profiles in Figure 3.2, Sample H6, cate:hyd=1.4:0.6, at 5 h reaction time can be assumed not to have crystalline properties because there are broad endotherm peaks. This result coincidentally agrees with its X-ray pattern which will be discussed later.

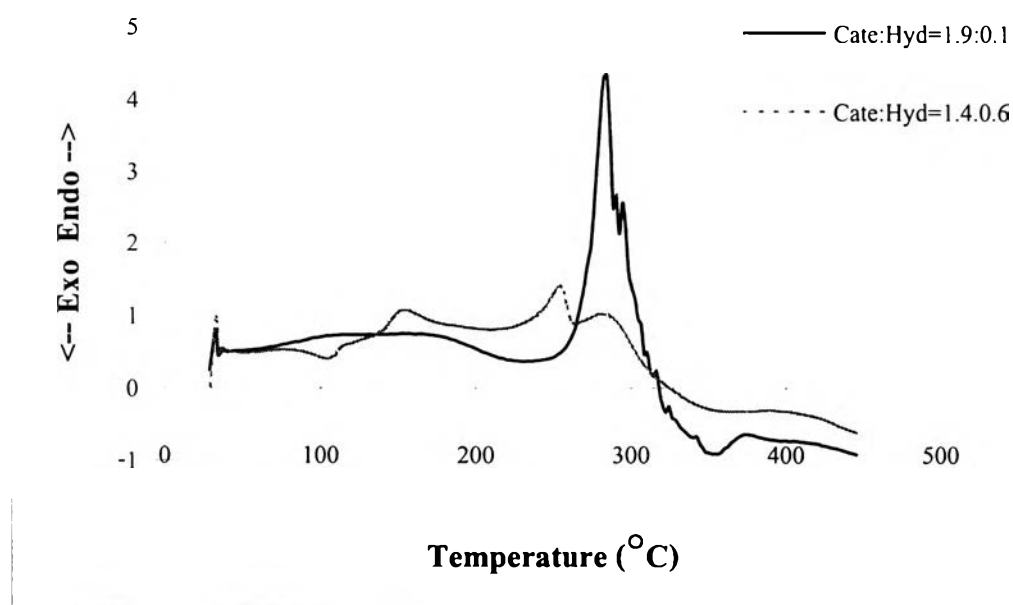


Figure 3.2 DSC profiles of samples H1 and H6 at 5 h reaction time.

At 5 h reaction time, samples H2-H5 show broad endotherms in the range of 270°C-300°C due to volatilization and oxidative decomposition. Noticed that when on increasing hydroquinone concentration, the broader as shown in Figure 3.3. The reason is hydroquinone molecules will separate ladder structure of product. Then the crystallinity of product is reduced, therefore endothermic peak is broad at high concentration of hydroquinone.

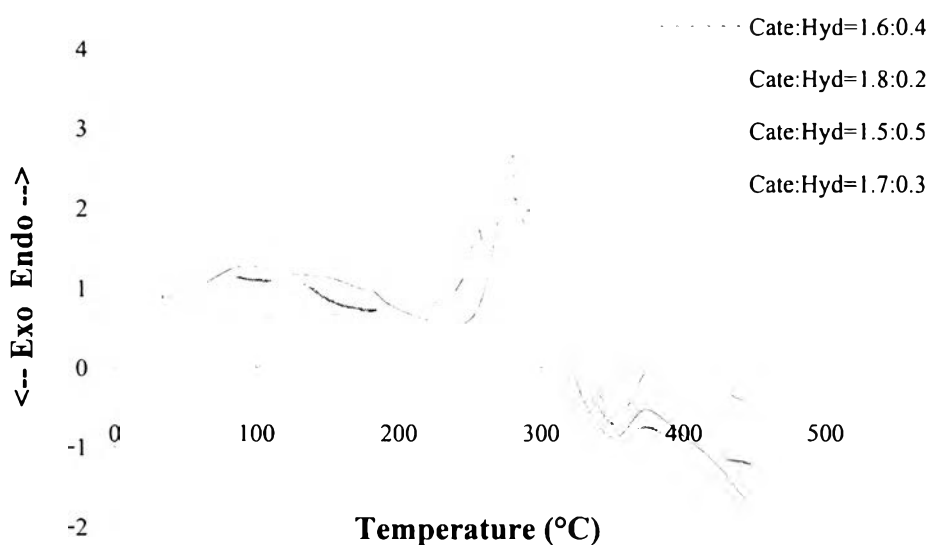


Figure 3.3 DSC profile of samples H2-H5 at 5 h reaction time.

The DSC profiles of products for each mole ratio at 3 and 4 h reaction times give the same patterns as those at 5 h reaction time. A few samples synthesized at 3 and 4 h reaction times are shown in the Figure 3.4 and 3.5, respectively.

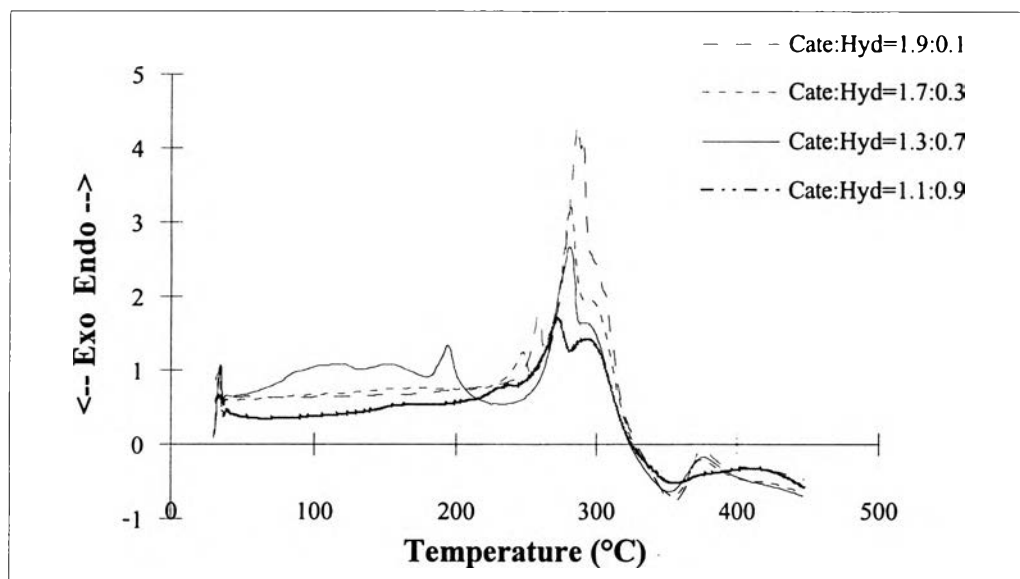


Figure 3.4 DSC profile of products H1, H3, H7, H9 at 3 h reaction time.

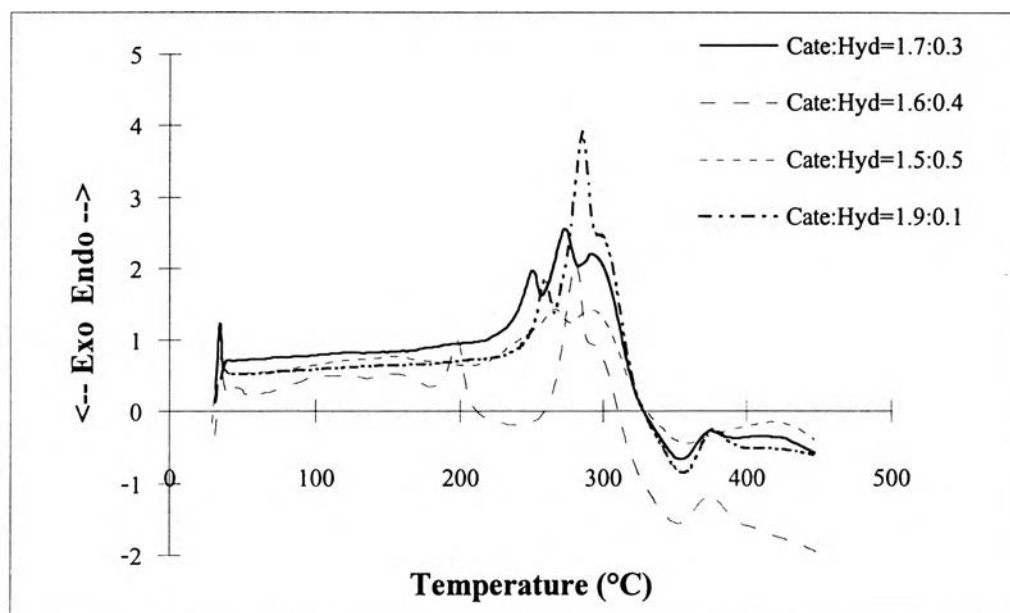


Figure 3.5 DSC profile of products H1, H3, H4, H5 at 4 h reaction time.

The DSC profiles for reactions with varying TETA concentrations are shown in Figure 3.6. The copolymer is not obtained when the catalyst, TETA, are used in equivalent of 16.67% mol Si in agreement with TGA results.

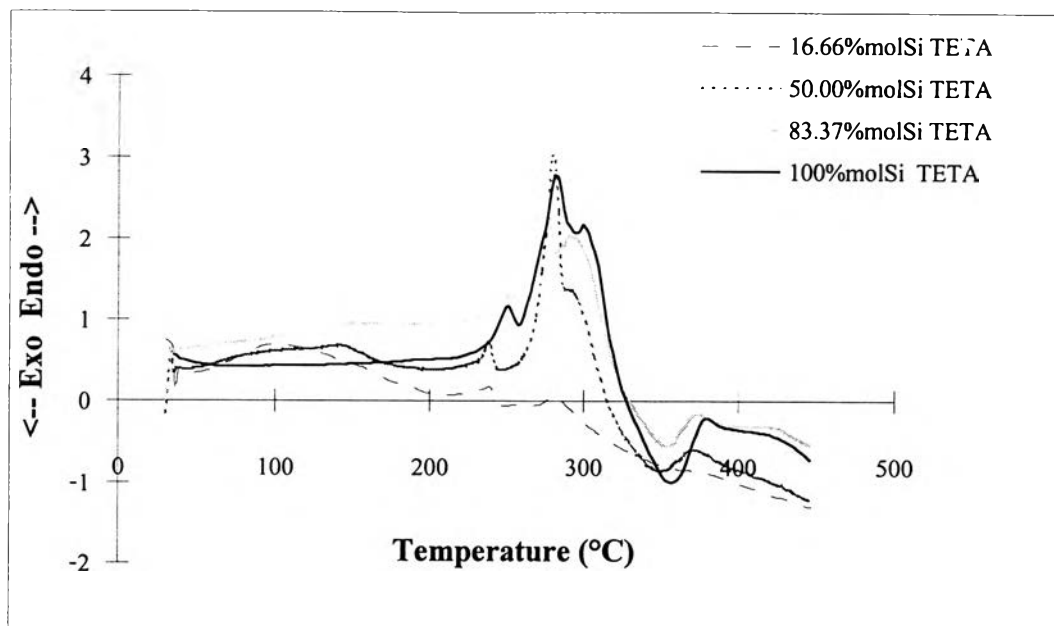


Figure 3.6 DSC profile of product H3 of TETA variation.

The effect of reaction time to product properties was studied by DSC. From DSC profiles in each reaction time, the product exhibit 2 endothermic peak as shown in Figure 3.7.

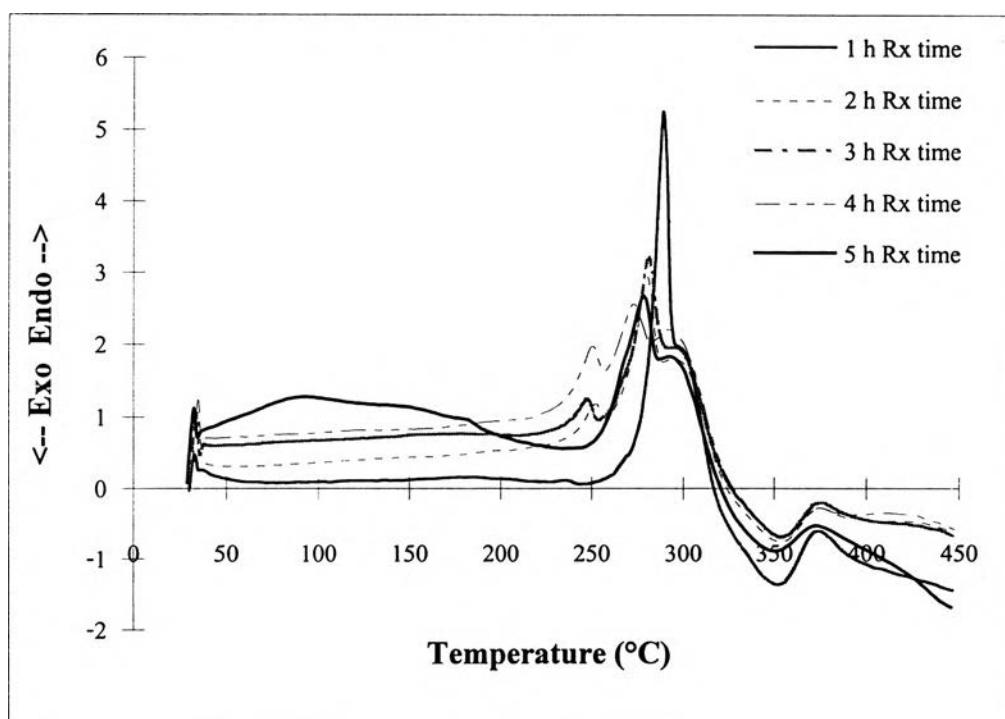


Figure 3.7 DSC profile of product H3 at each reaction time.

3.2.2 Thermogravimetric Analysis (TGA)

The pyrolysis profiles for precipitated powder show two regions of mass loss during heating under N_2 and O_2 atmosphere, see Figure 3.8. The first mass loss appears between 250-400 °C, and corresponds to oxidative decomposition of the organic ligands. The second major mass loss occurs over a wide temperature range, 400-800 °C and likely corresponds to oxidative decomposition of remaining organic residue. The percent ceramic yield is 19.1 %.

During of heating under only N_2 atm, the yellowish solid powder does not decompose completely at 950 °C as the char carbonizes. It indicates that the polymer product obtained must contain high organic ligands and therefore oxygen must be used for decomposing all organic ligands.

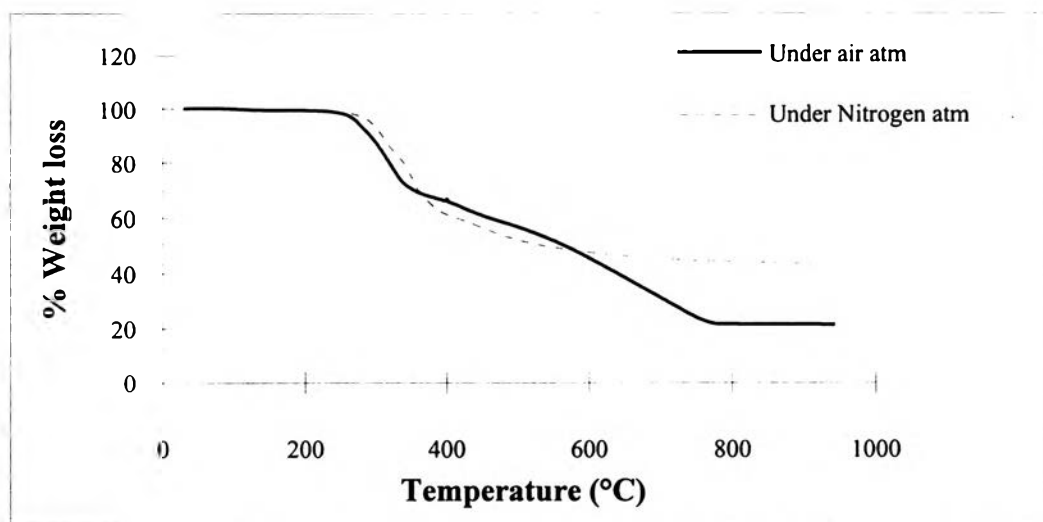


Figure 3.8 TGA profile of synthesized products under N_2 and O_2 atm.

The tendency of %ceramic yield increases with the increment of hydroquinone as shown in Figure 3.9. The silica in the product will be amorphous. The %ceramic yield indicates quantity of silica of product. Thus the product which has high % ceramic yield rarely show crystalline behavior.

For example, sample H6 at 5 h reaction time has 40 % ceramic yield. It shows a broad XRD powder pattern different from other products due to amorphous character. All of synthesized products contain amount of Si atom in range of 17% to 25% by observation from %ceramic yield.

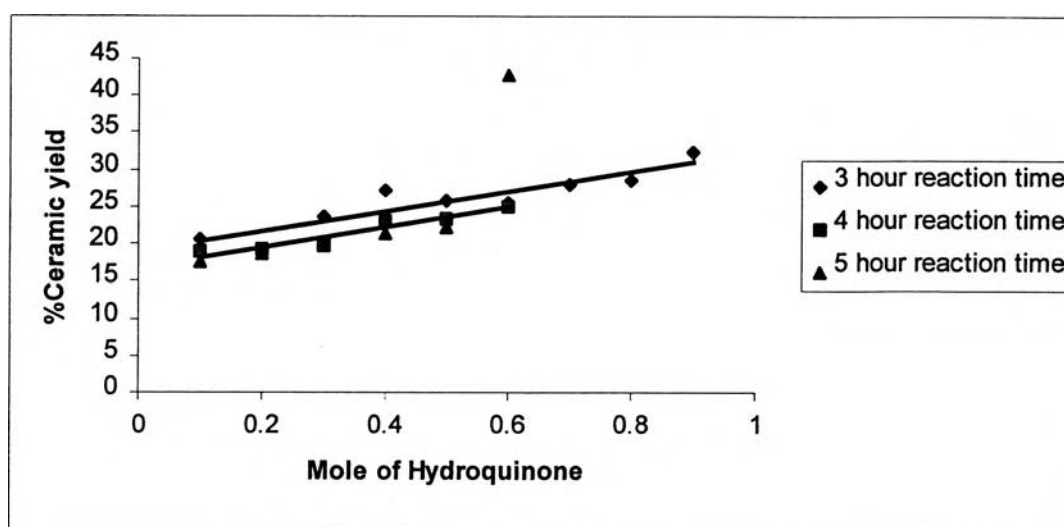


Figure 3.9 Relationship of percent ceramic yield at each mole ratio at 3h, 4 h, and 5 h reaction time in air.

When insufficient of TETA is used, the product obtained consists mainly of silica so the % ceramic yield is unusually high, like 16.67% molSi of TETA as shown on Figure 3.10 % ceramic yield will be decreased when the amount of TETA increased.

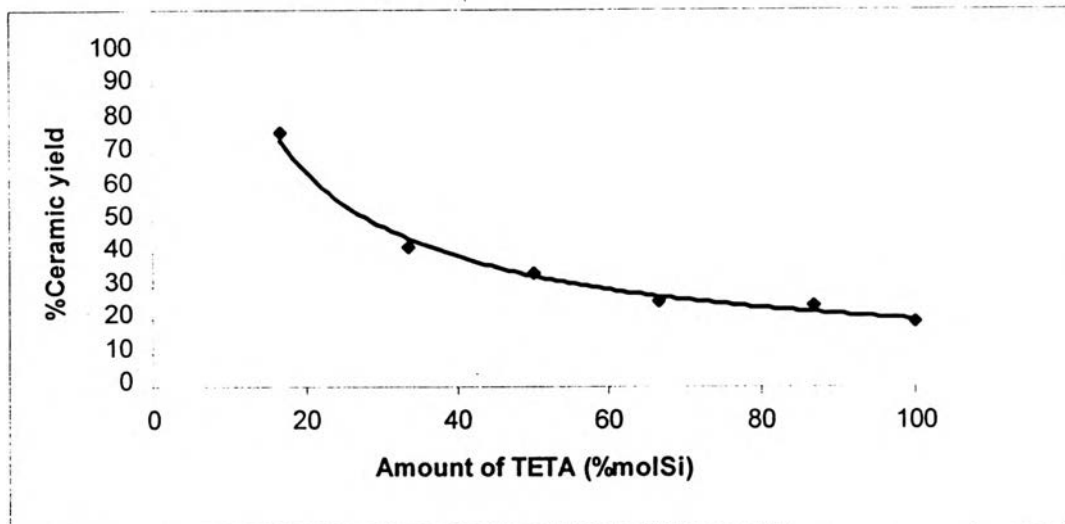


Figure 3.10 Percent ceramic yield at each amount of TETA.

3.2.3 X-ray Diffraction

The XRD pattern of amorphous silica is shown in Figure 3.11 for comparison with the synthesized product, H3, in Figure 3.12. Obviously, the several sharp peaks of synthesized compound indicate it is crystalline. The highest intensity 2θ peak is at 8.5. The primary 2θ peaks are at 7.3, 9.1, 12.0, 16.7, 18.6, 20.4, 23.1, and 25.3 respectively.

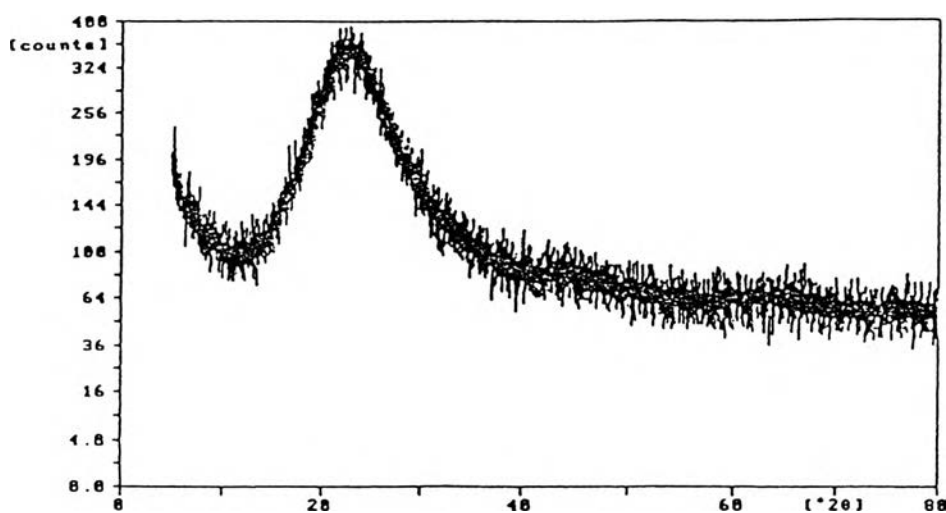


Figure 3.11 XRD pattern of starting material silica.

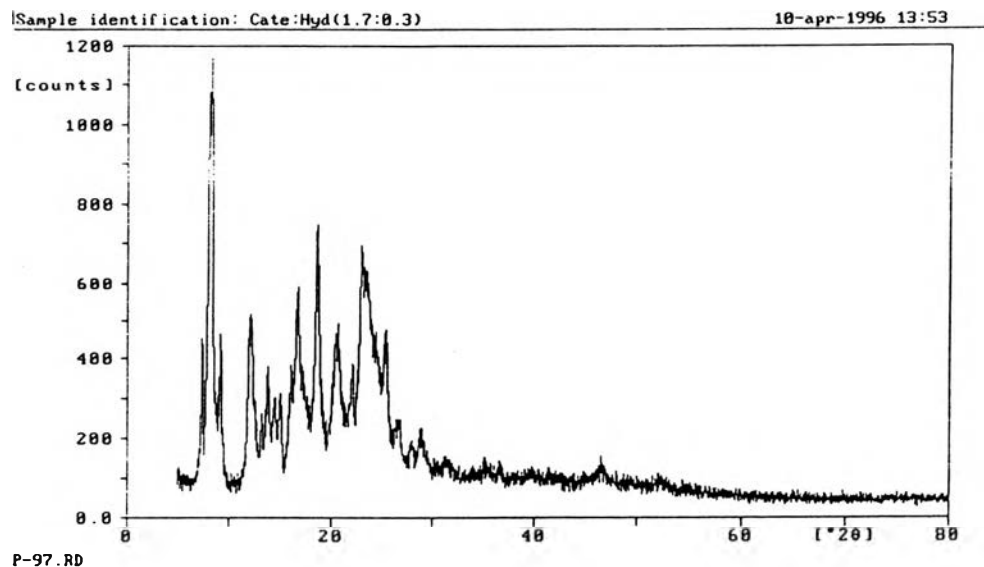


Figure 3.12 XRD pattern of product H3.

The degree of product crystallinity seen by XRD is inversely proportional to the amount of hydroquinone use of content, see in Figure 3.13. The reason is that hydroquinone reduces the remain ladder structure, which is responsible for the crystalline behavior. As seen in Figure 3.13 showing XRD pattern of synthesized products H0-h6 at 5 h reaction time, sample H6 shows broad peaks in the 15 and 25 2θ range, indicating that this copolymer is mostly amorphous. At 4 h and 3 h reaction times, the XRD pattern of each mole ratio shows the same tendency as the 5 h reaction time products, as shown in Figure 3.14.

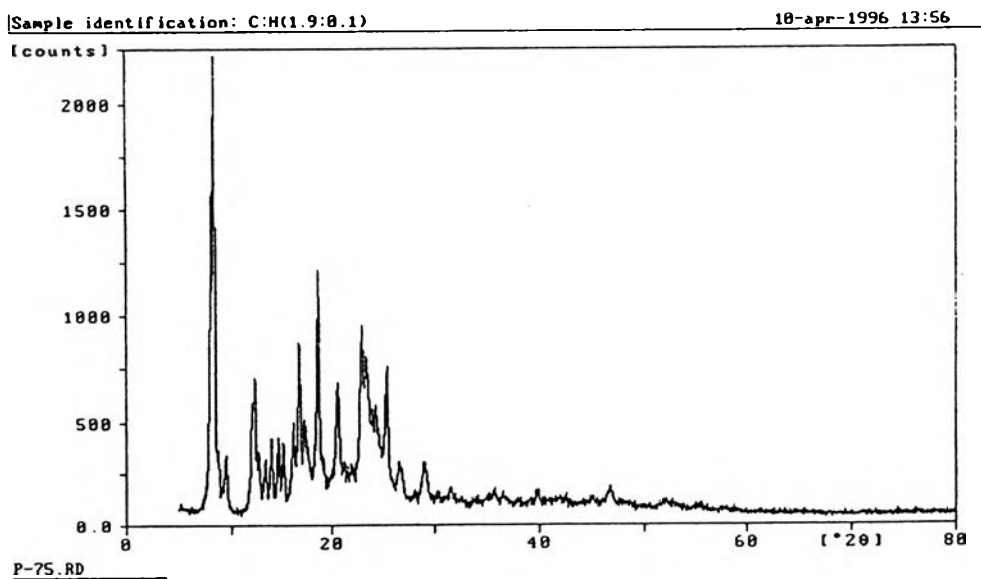


Figure 3.13-A XRD pattern of product H1 at 5 h reaction time.

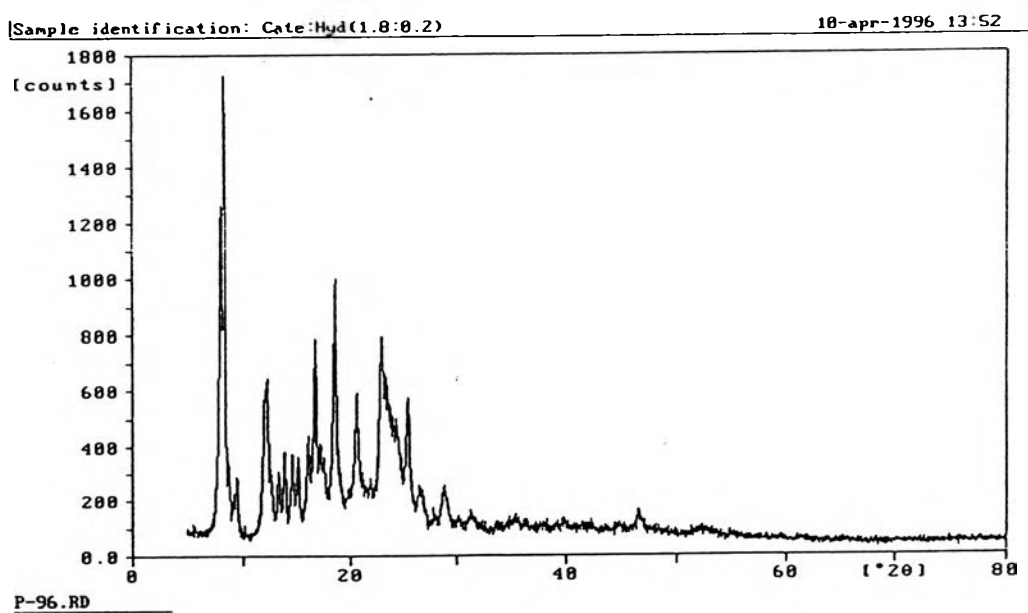


Figure 3.13-B XRD pattern of product H2 at 5 h reaction time.

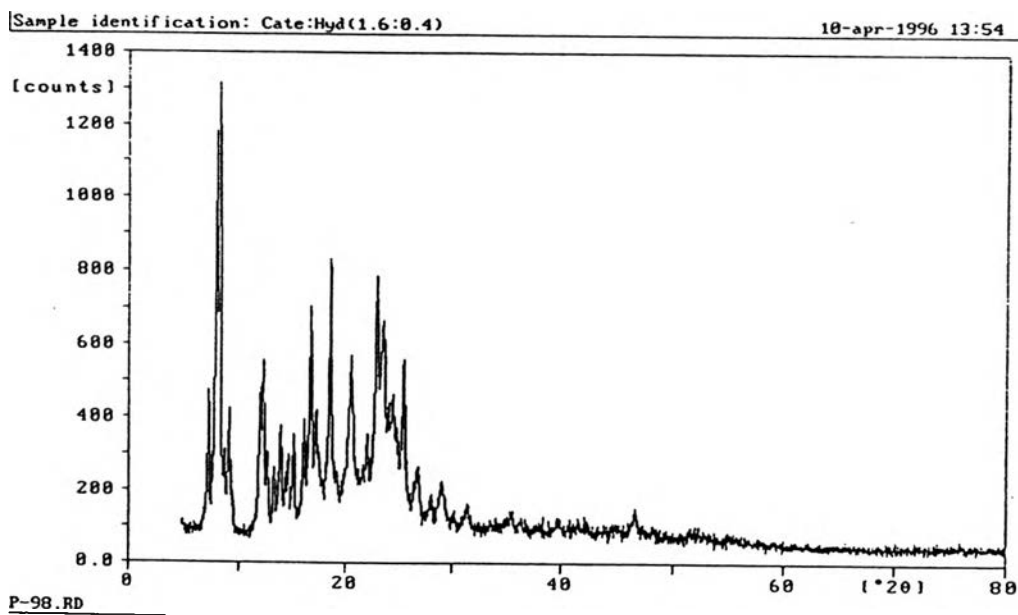


Figure 3.13-C XRD pattern of product H4 at 5 h reaction time.

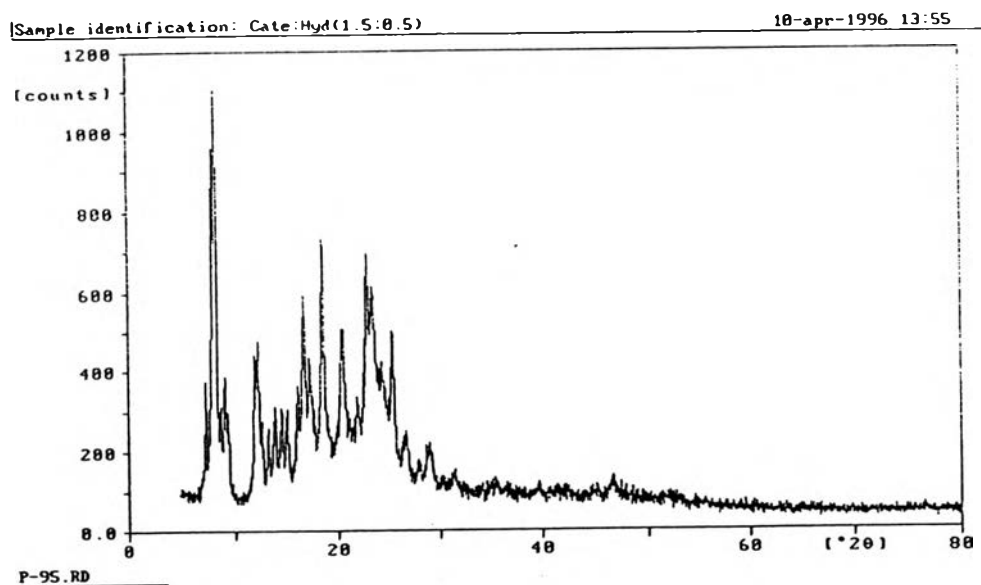


Figure 3.13-D XRD pattern of product H5 at 5 h reaction time.

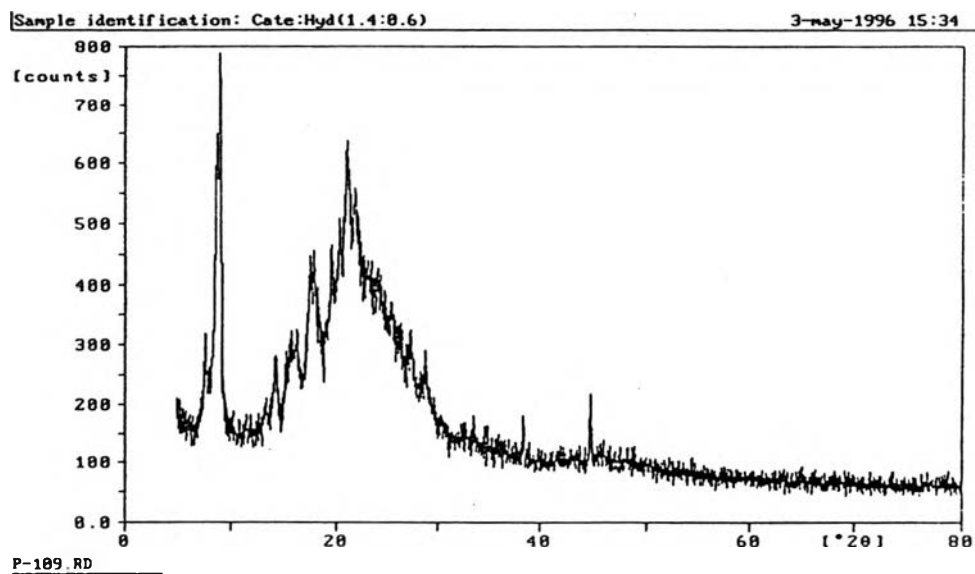


Figure 3.13-E XRD pattern of product H6 at 5 h reaction time.

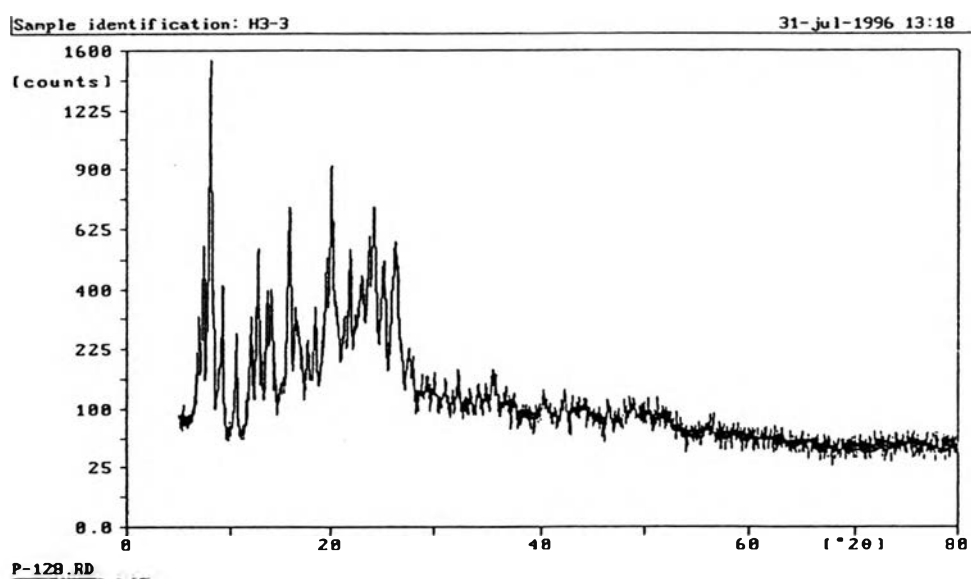


Figure 3.14-A XRD pattern of product H3 at 3 h reaction time.

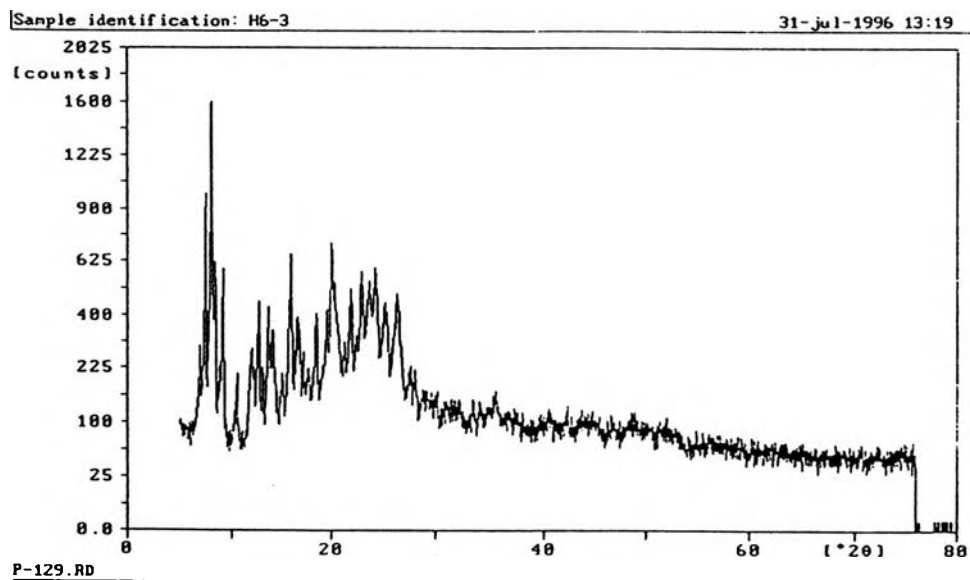


Figure 3.13-B XRD pattern of product H6 at 3 h reaction time.

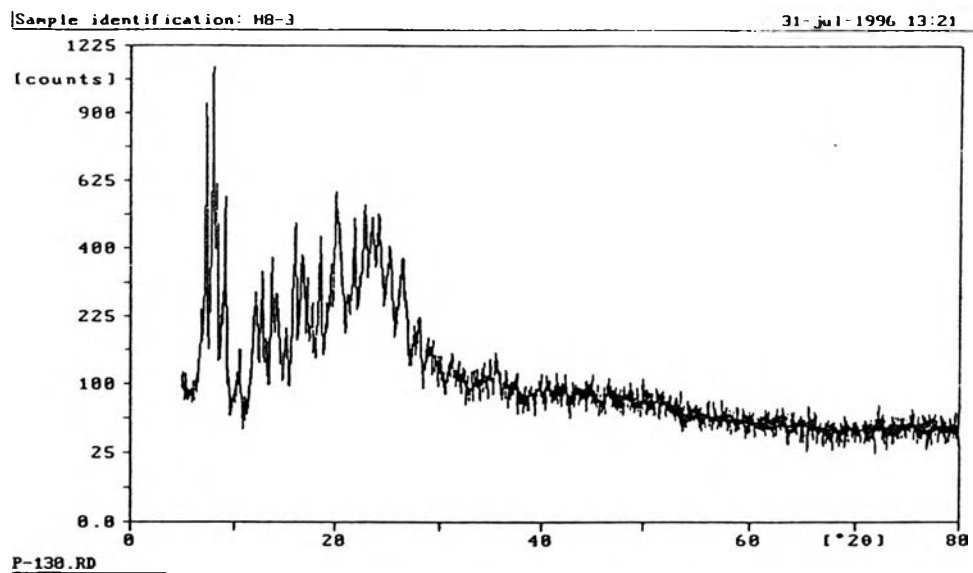


Figure 3.14-C XRD patterns of product H8 at 3 h reaction time.

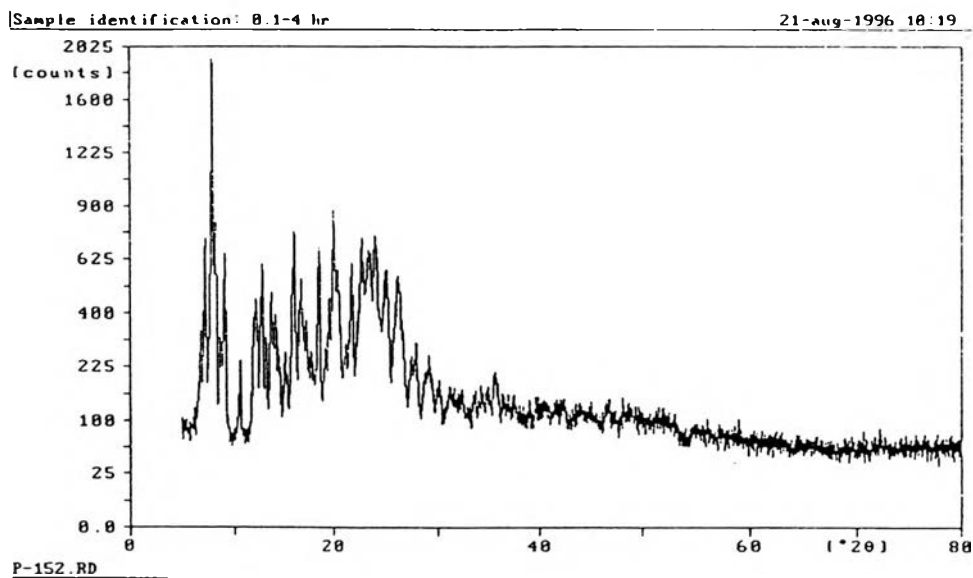


Figure 3.14-D XRD pattern of product H1 at 4 h reaction time.

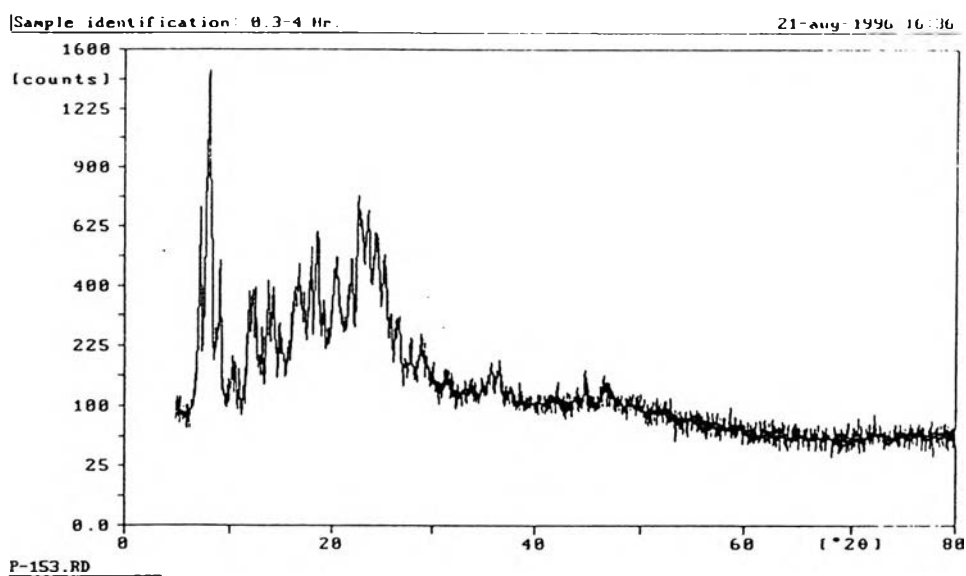


Figure 3.14-E XRD pattern of product H3 at 4 h reaction time.

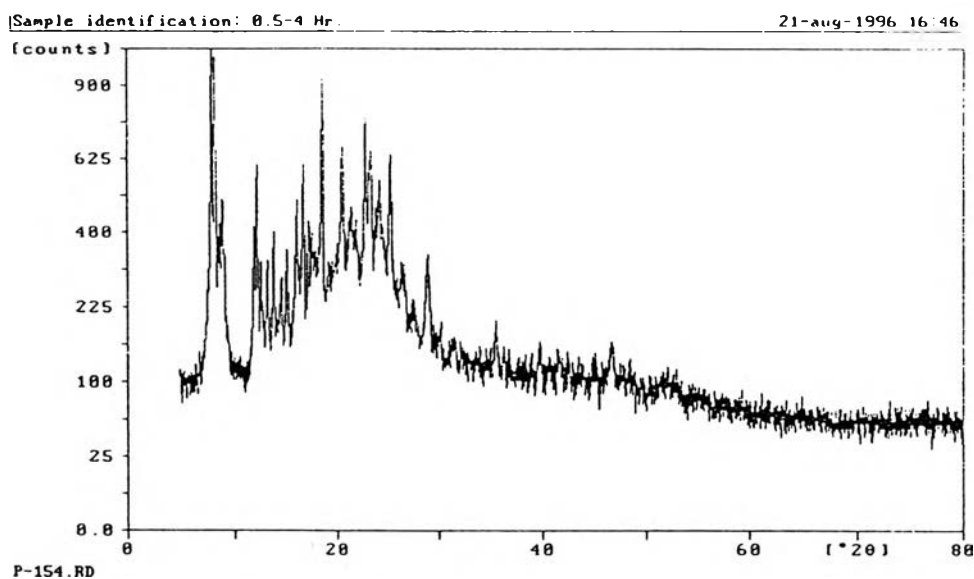


Figure 3.14-F XRD pattern of product H5 at 4 h reaction time.

XRD patterns of synthesized product obtained by varying the TETA concentration are shown in Figure 3.15. It indicates that the product at 16.67%mol Si TETA is not the ladder copolymer because the XRD spectrum looks like amorphous. This assumption is supported by the TGA results which show the percent ceramic yield 76.5% by weight. The difference in the XRD patterns with different quantities of TETA is in the range of 2θ peak between 15 and 25 degree 2θ .

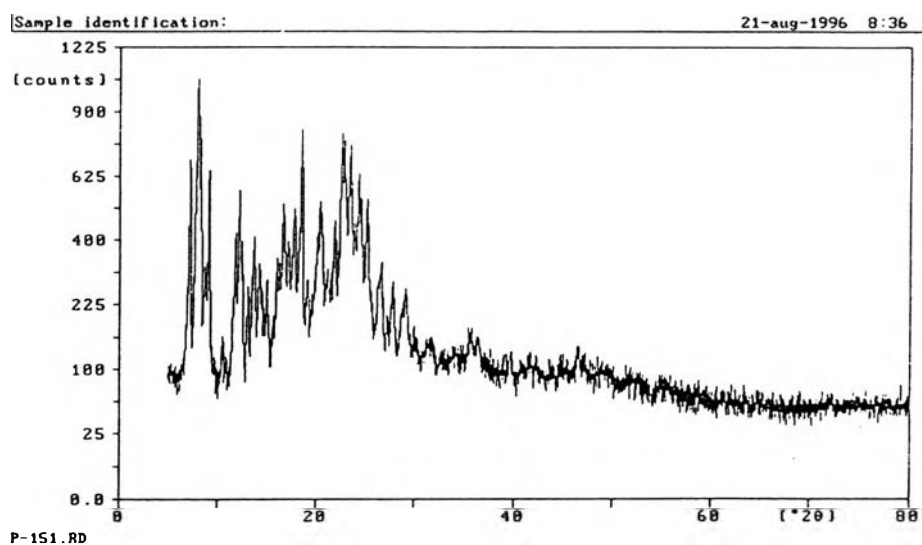


Figure 3.15-A XRD pattern of product 100% mol Si of TETA.

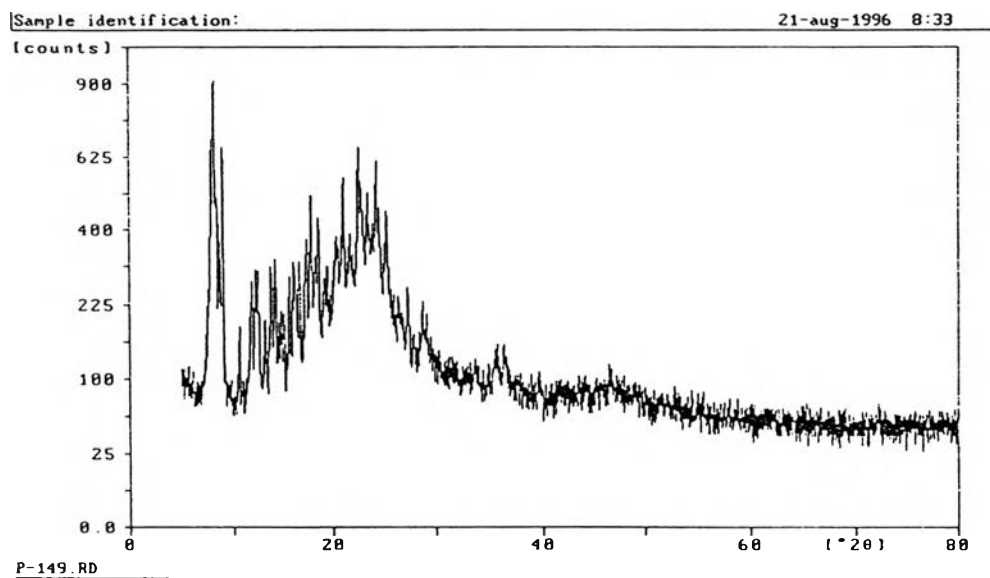


Figure 3.15-B XRD pattern of product 84% mol Si of TETA.

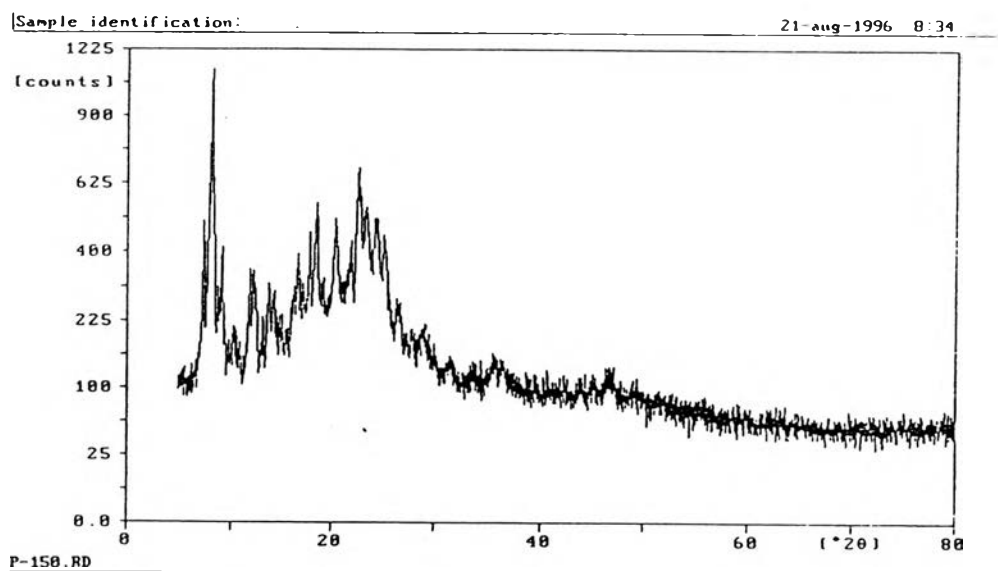


Figure 3.15-C XRD pattern of product 67% mol Si of TETA.

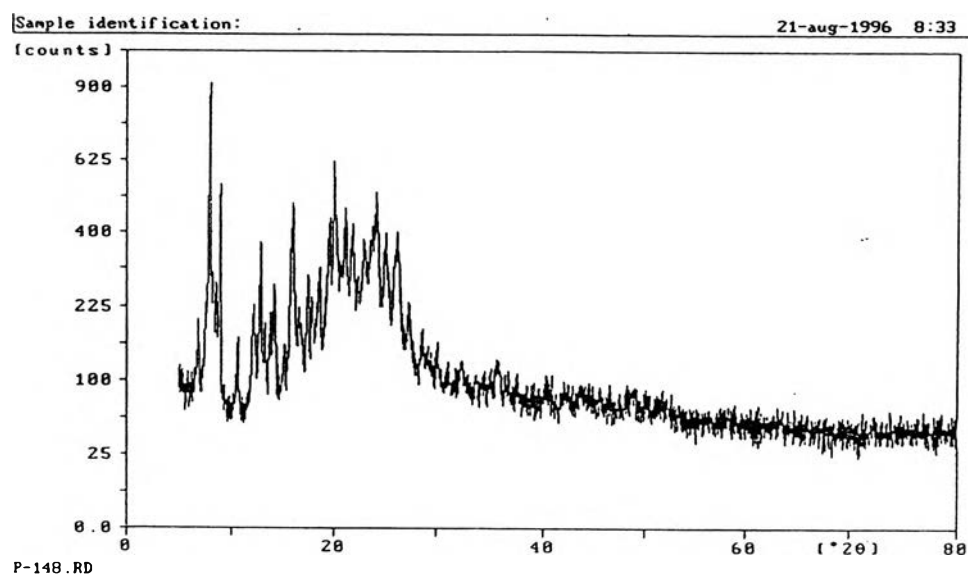


Figure 3.15-D XRD pattern of product 33% mol Si of TETA.

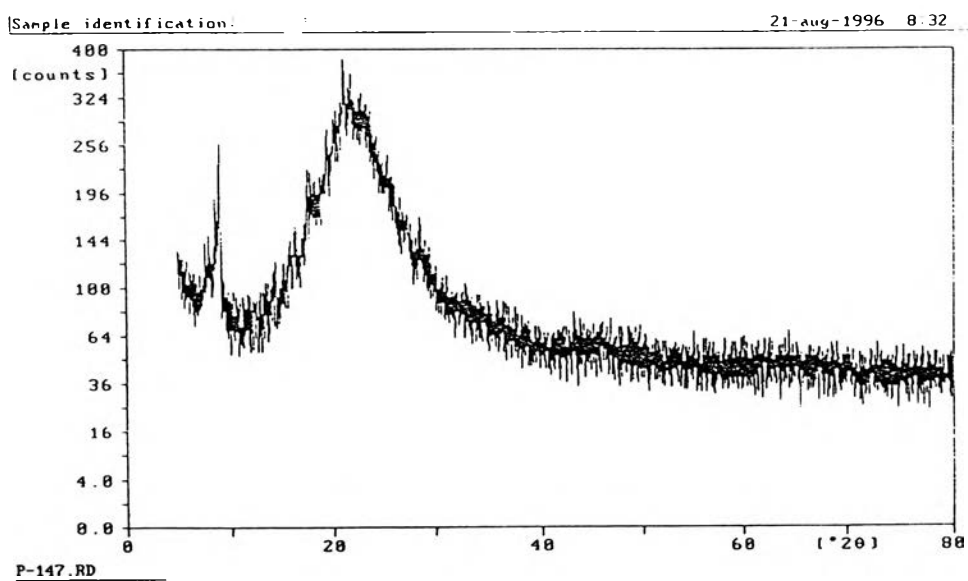


Figure 3.15-E XRD pattern of product 17% mol Si of TETA.

3.2.4 Mass Spectrometry (MS)

The EI⁺-MS of sample H3 powder is shown in Figure 3.16. This fragmentation pattern could be employed to elaborate this product structure. Although the product contains some hydroquinone, this MS spectrum shows m/z 244 peak as the base molecular ion peak, and m/z 110 peak corresponding to catechol and hydroquinone.

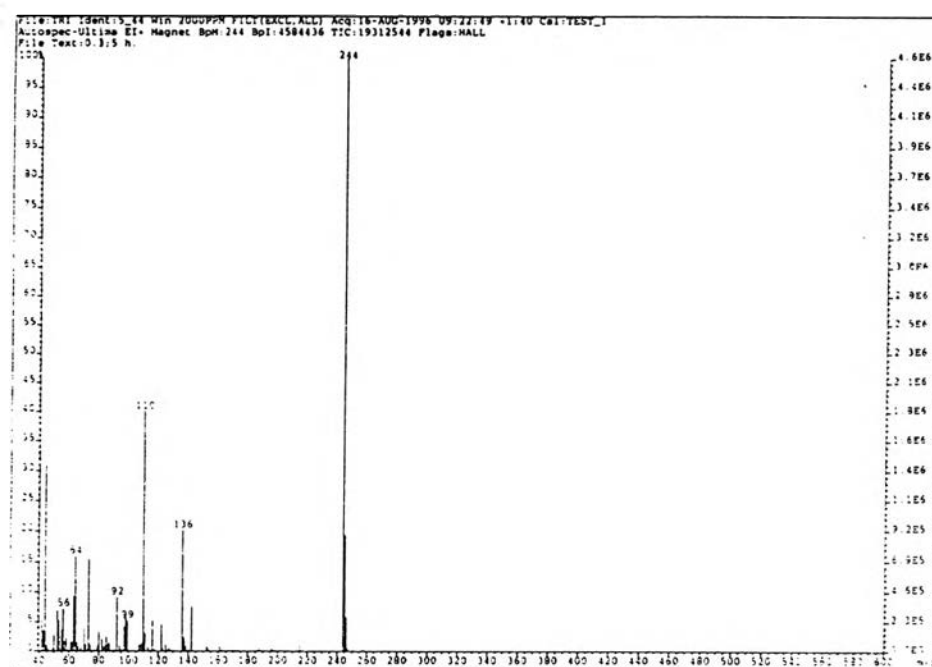
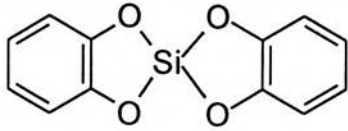
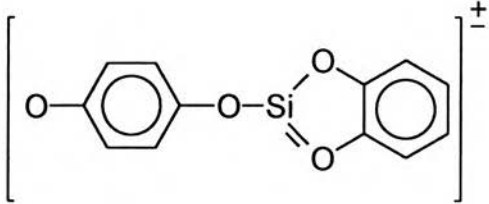
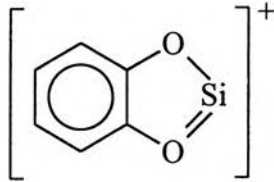
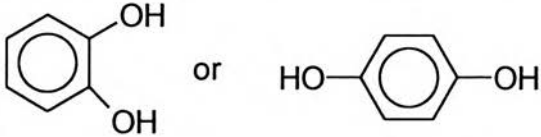
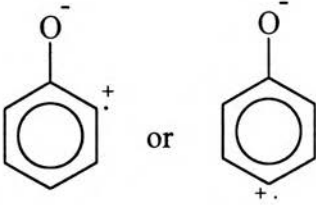



Figure 3.16 EI⁺-MS spectrum of product H3.

Apparently, TETA fragmentation is not seen. Hence, it is assumed that only trace amounts of TETA still remains in the product, as indicated by ¹H-NMR. Table 3.4 shows the proposed structure of the product, according to the fragmentation pattern in Figure 3.16.

Table 3.4 Purposed fragmentation structure of product H3 from EI⁺-MI spectra

m/z	Intensity	Species
224	100	 or 
136	20	
110 (108+2H ⁺)	40	
92	9	
64	16	

Although the amount of hydroquinone used varied, mass spectra did not change. Figure 3.17 illustrates the fragmentation pattern of each mole ratio at 5 h reaction time. The same species of fragments were observed in each mole ratio which the same results were obtained at 3 h and 4 h reaction time.

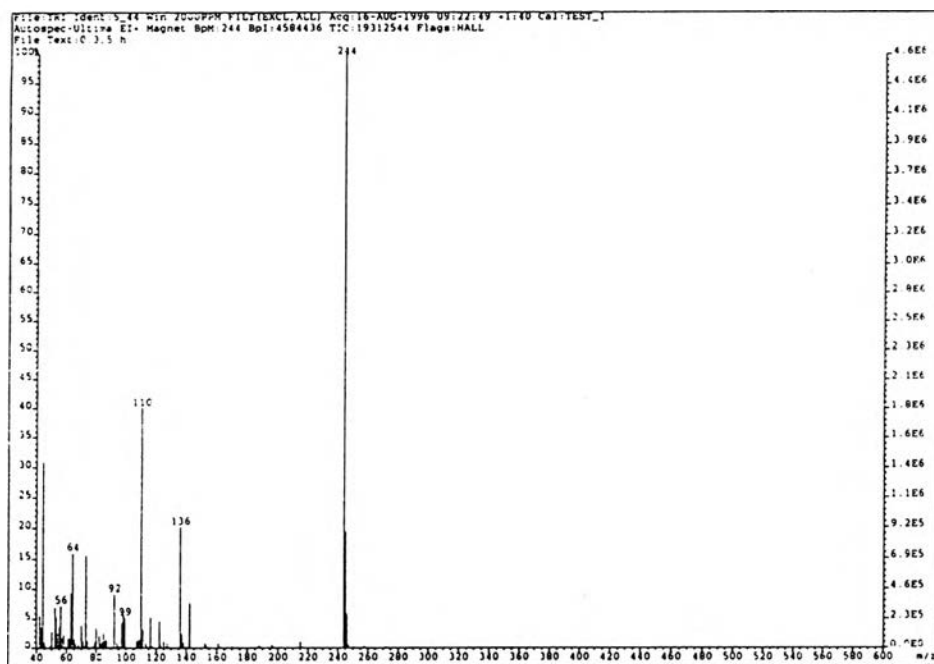


Figure 3.17-A MS spectra of product H1.

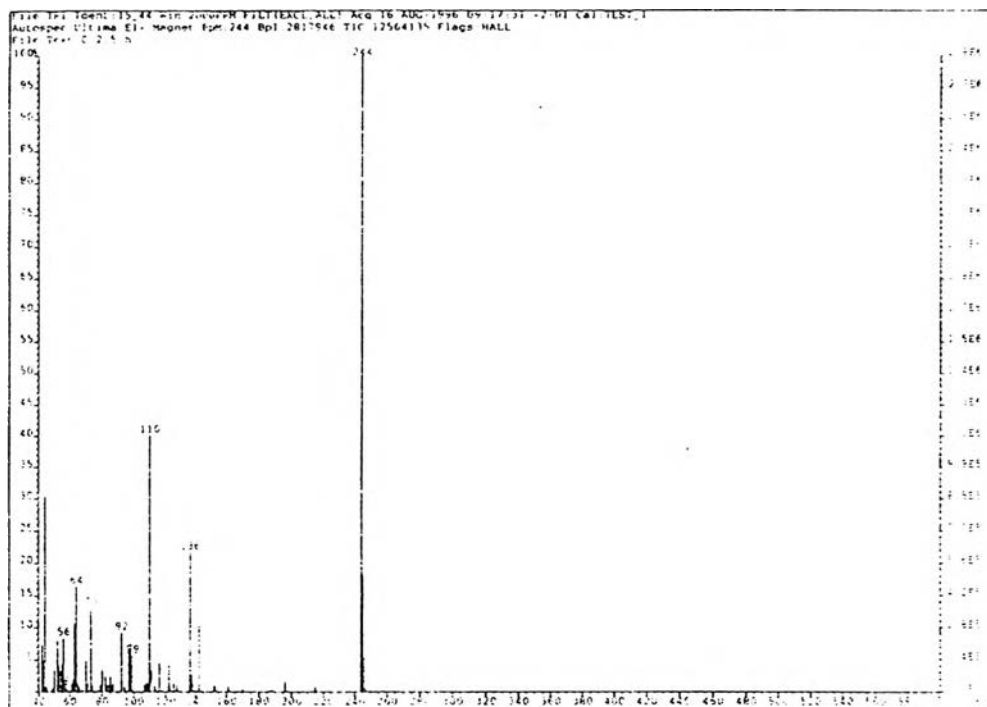


Figure 3.17-B MS spectra of product H2.

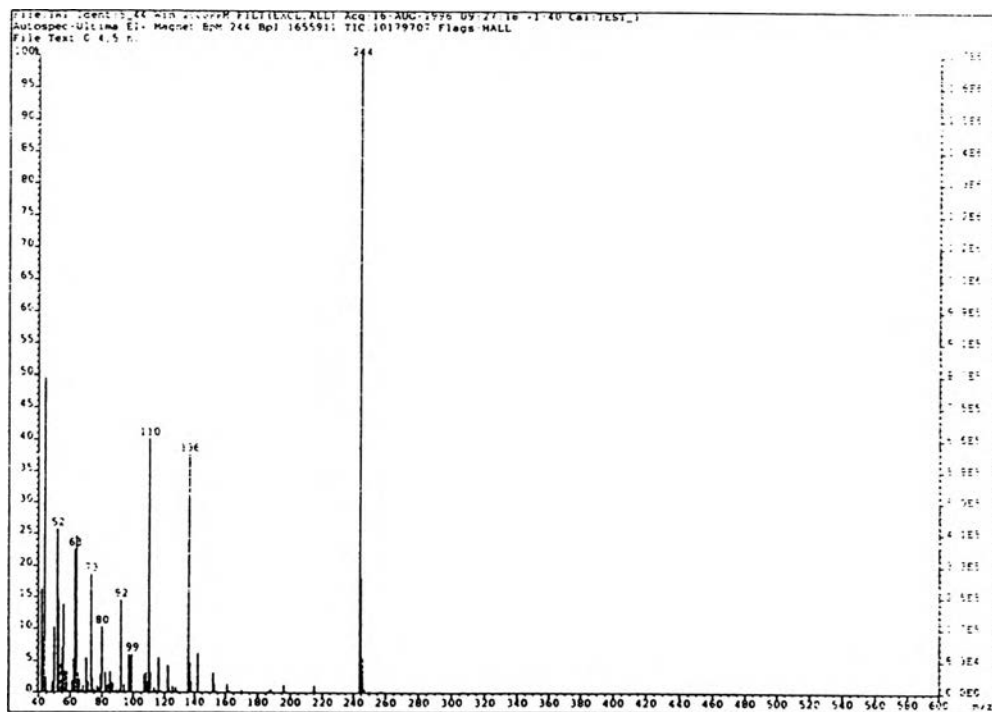


Figure 3.17-C MS spectra of product H4.

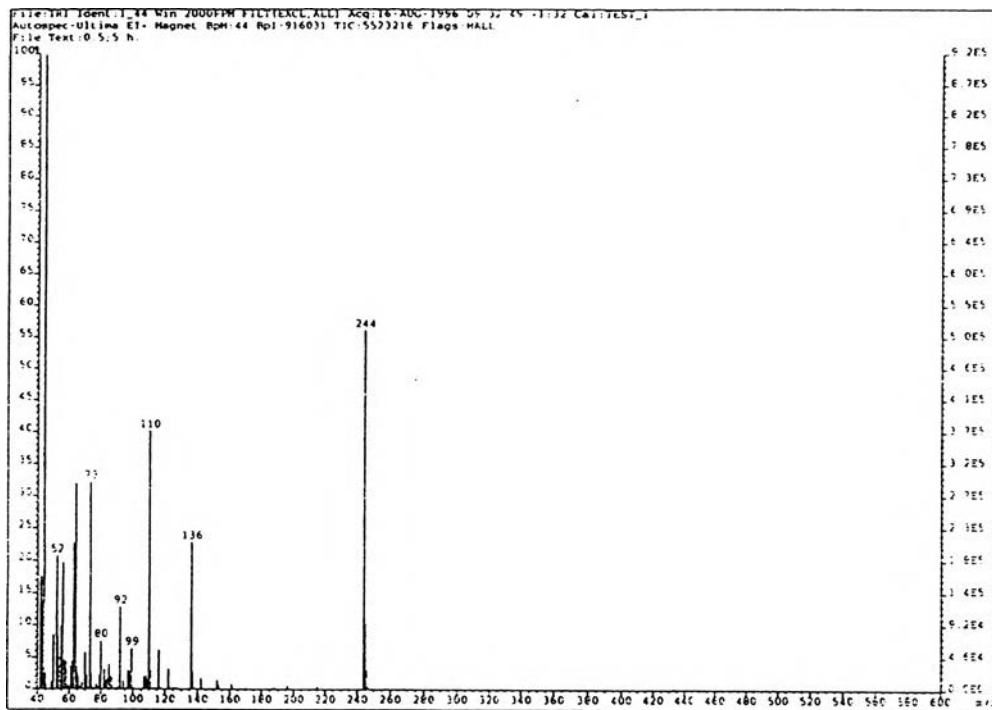


Figure 3.17-D MS spectra of product H5.

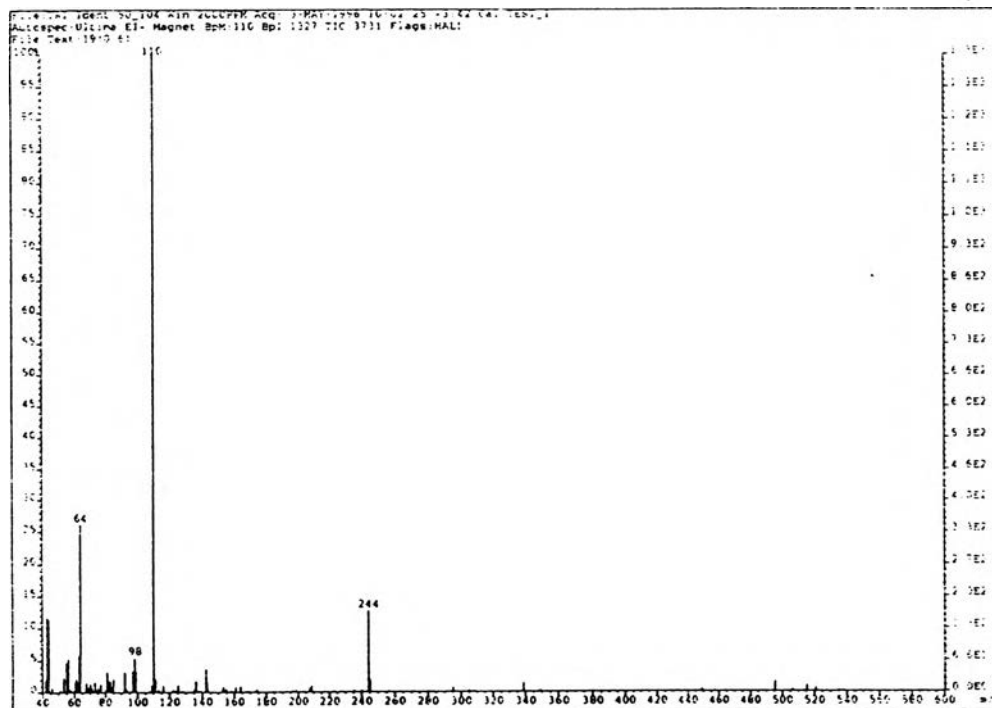


Figure 3.17-E MS spectra of product H6.

The fragment intensities are listed in table 3.5. The intensity of $m/e=244$ mostly are 100% relative height because the molecule of the product is impacted instantly by high energy of electron beam to result in the biggest fragment which is $m/e=244$. The base peak of sample H6 at 4 h and 5 h reaction time are $m/e=110$. This fragment might be unreacted hydroquinone / catechol and a fragment of the product. At 3 h reaction time, every sample shows base peak at m/e 244. Samples H3-H5 give lower intensity at m/e 110 than the others. Again the high intensity at m/e 110 might correspond to unreacted catechol and hydroquinone.

The same fragmentation patterns are also obtained from TETA and reaction time variations. At 1 h and 2 h reaction times and 17% mol Si TETA, the base peak is at m/e 110, meaning that these conditions are not suitable for producing the copolymer. It should be more than 2 h and the catalyst ought to be more than 17% mol Si. For the other samples, The base peak shows 100% relative height at m/z 244, except the condition of 67% mol Si of TETA which gives m/z 244 about 88 % relative height.

Table 3.5 Relative height intensity of fragments from MS spectra

m/e	% Height Relative Intensity																				
	3 hours reaction time									4 hours reaction time						5 hours reaction time					
	H1	H2	H3	H4	H5	H6	H7	H8	H9	H1	H2	H3	H4	H5	H6	H1	H2	H3	H4	H5	H6
244	100	100	100	100	100	100	100	100	100	100	100	100	100	100	77.39	100	100	100	100	56.31	12.83
136	41.68	77.68	18	25.11	26.65	22.86	30.7	33.99	22.78	20.39	19.29	20.56	24.35	33.65	22.07	32.03	21.75	20.2	37.8	43.31	-
110	64.99	51.18	37.64	33.52	36.88	71.27	85.26	47.46	49.48	33.33	28.5	16.84	36.58	40.24	100	54.11	40.26	40.11	40.24	12.98	100
92	17.21	26.4	8.04	8.86	9.42	14.04	15.57	12.15	11.02	8.27	7.69	11.32	9.14	17.49	18.35	12.97	9.28	9.18	14.68	12.98	3.27
64	33.98	59.89	13.03	12.31	13.01	25.58	28.06	9.93	19.66	13.36	12.51	7.12	13.15	28.16	46.81	20.39	16.57	16.03	24.92	32.19	26.25

3.2.5 Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra of the precipitated products are shown in Figure 3.18. The peak positions and assigned functional groups are listed in Table 3.8. The aromatic ν C=C band are found at 1590 and 1500 cm^{-1} . The single peak at 1250 cm^{-1} results from ν C-O aromatic. The ν Si-O symmetric appears at 1100 cm^{-1} , while ν Si-O asymmetric occurs at 1015 cm^{-1} . The C-H out of plane bending of ortho and para substitution on benzene ring are found at 750 cm^{-1} and 810 cm^{-1} , respectively.

The hydrolysis of this product is observed by the presence of O-H stretching. It also implies that this product has some partially substituted hydroxyl group of catechol / hydroquinone or it could be untreated material.

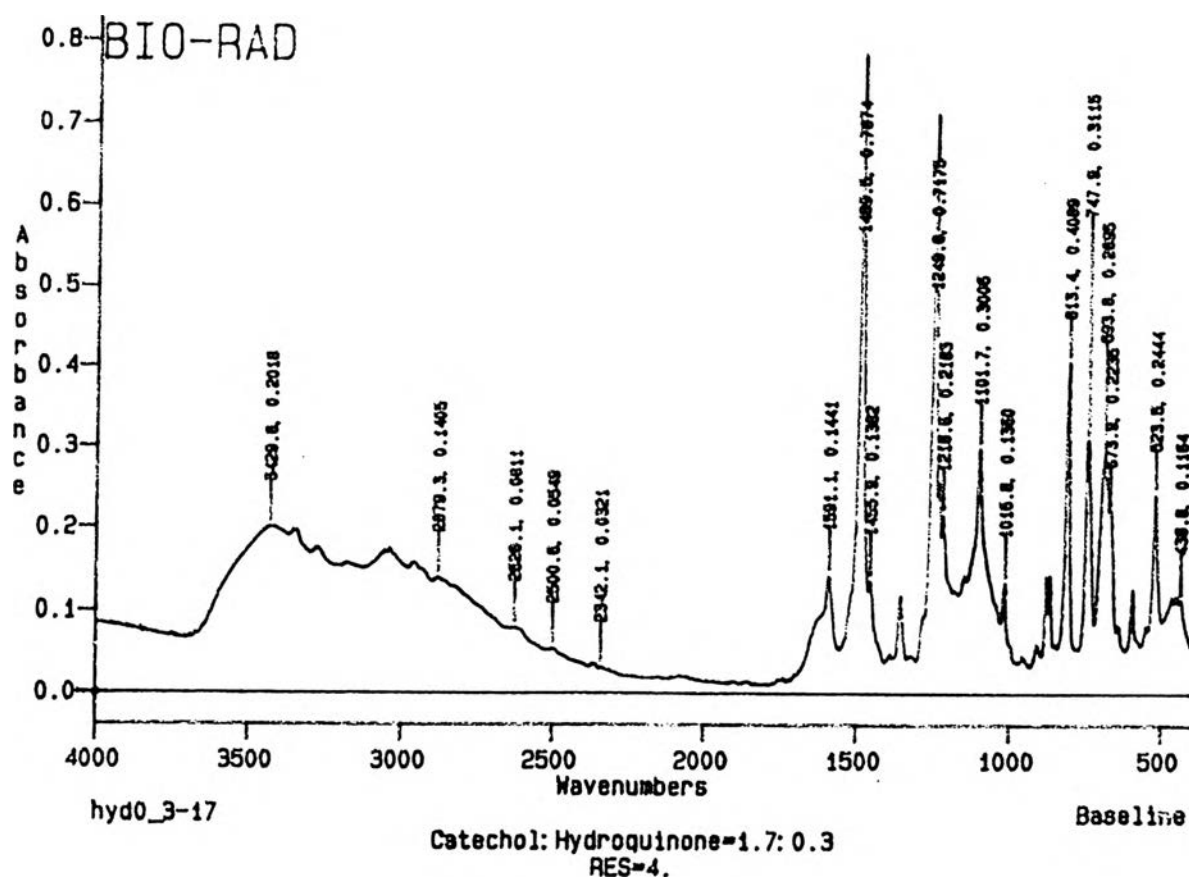


Figure 3.18 FTIR Spectrum of product H3.

Table 3.6 Frequency vibration and suggested functional group of product H3

Functional group	Peak position
ν O-H stretching	3500-3300 (broad)
C-H aromatic stretching	2824 (weak)
C=C aromatic stretching	1590 (weak)
C-C aromatic stretching	1490 (strong)
Si-O-C stretching	1102 (strong)
Si-O-C stretching	1016 (weak)
Para-disubstituted benzene ring	813 (medium)
Ortho-disubstituted benzene ring	747 (medium)

When the ratio of catechol to hydroquinone was changed, the significant peaks at about 810 cm^{-1} and 750 cm^{-1} must be considered. These peaks correspond specifically to para- and ortho- substitution on benzene rings in the product, respectively. FT-IR can be used to roughly estimate the quantity of each component in the product, especially when hydroquinone increase. We observe both intensity increment at 810 cm^{-1} and intensity decrement at 750 cm^{-1} in the products which were synthesized at 5 reaction time as shown in Figure 3.19.

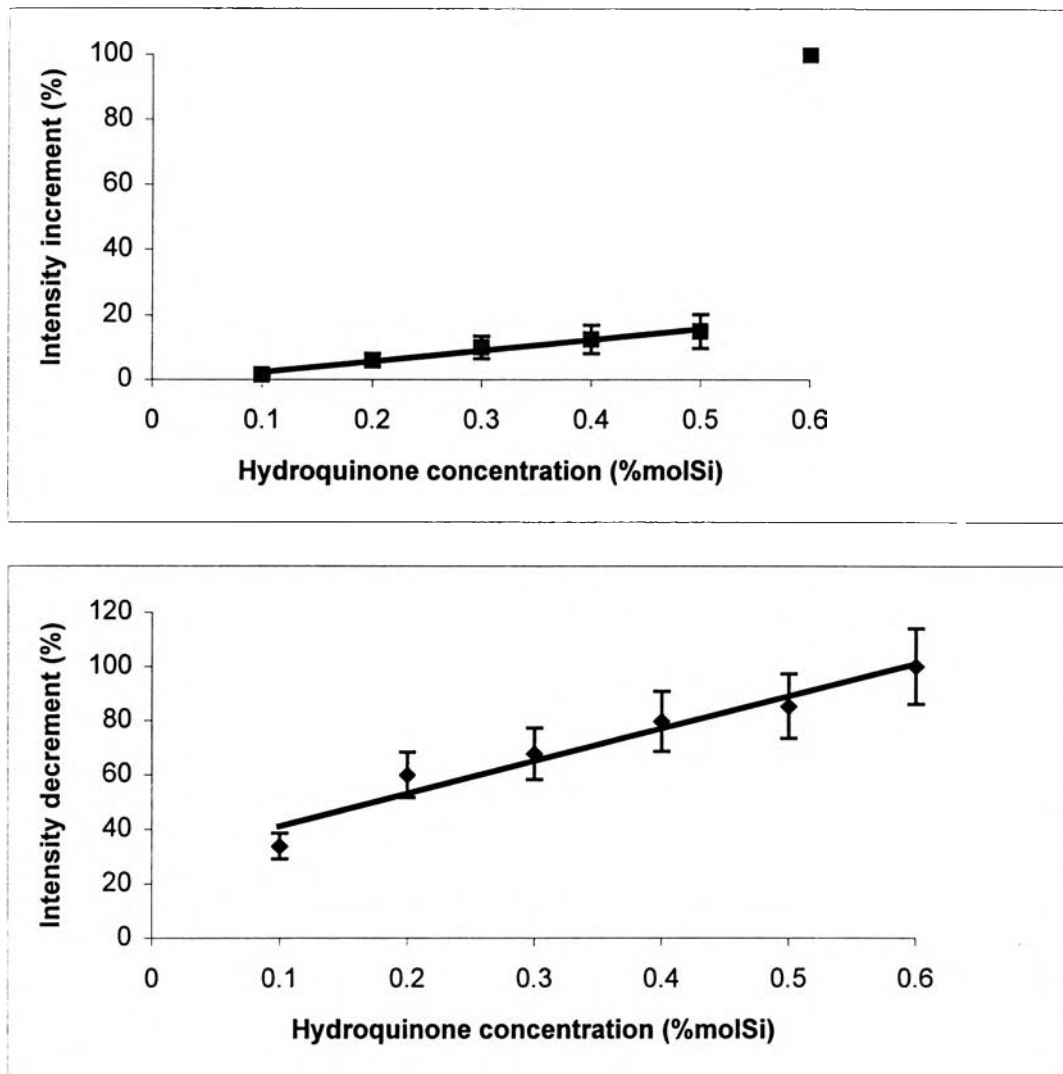


Figure 3.19 Percent Increment at 813 cm^{-1} and %decrement at 750 cm^{-1} with the increment of hydroquinone.

At 3 h and 4 h reaction times, although surface area of silica is high, the different absorbance intensity could not be used for quantitative analysis because the reaction was not complete, as compared to those at 5 h reaction time.

3.2.6 Nuclear Magnetic Resonance spectroscopy (NMR)

The magnetic environment for individual atom affects the pattern of proton signal in the NMR. The proton splitting pattern for aromatic compounds often distinguished by the position of substitution on the benzene ring. Figures 3.20 and 3.21 show the pattern of hydroquinone and para-chloroanisole. Interestingly, hydroquinone gives a singlet peak at 6.8 ppm whereas para-chloroanisole, with different para substituents, gives 2 singlet peaks at 6.8 - 7.4 ppm. The compound that has different substituted group on benzene ring, gives 2 doublet peaks. The chemical shift of ortho-substituted benzene ring, catechol, gives multiplets centered at 7.0 ppm (see Figure 3.22).

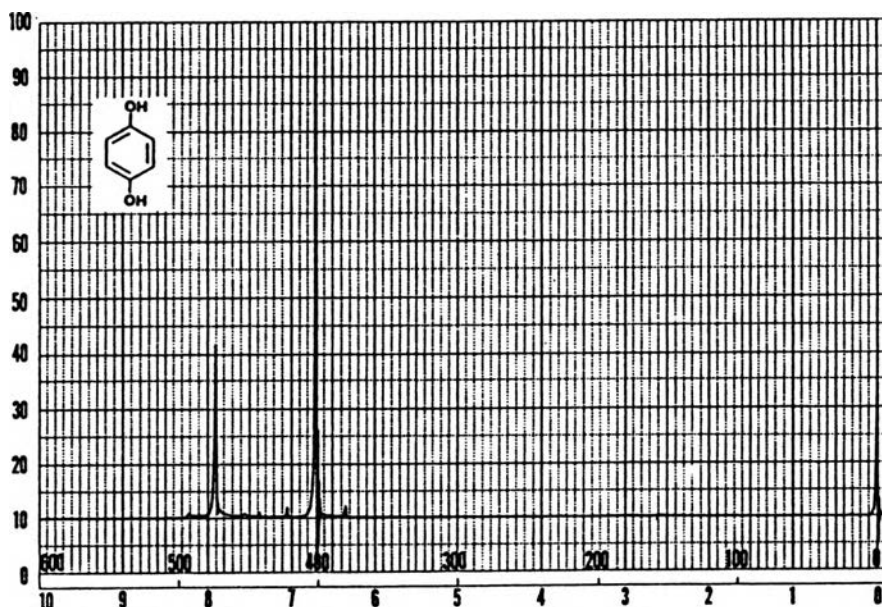


Figure 3.20 ¹H-NMR pattern of para substituted benzene ring of hydroquinone.

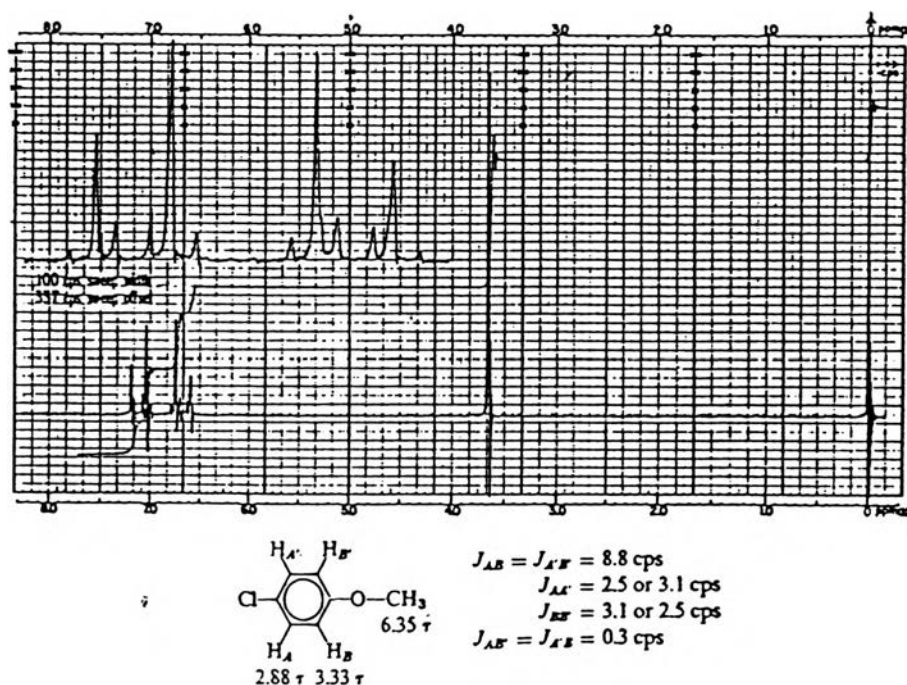


Figure 3.21 $^1\text{H-NMR}$ pattern of p-chloroanisole.

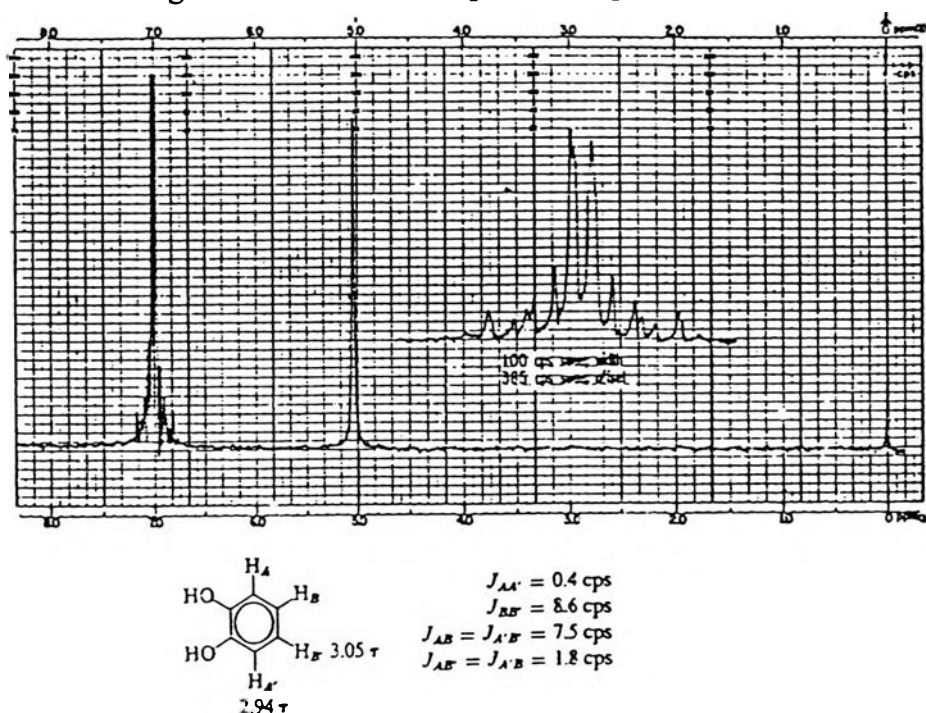


Figure 3.22 $^1\text{H-NMR}$ pattern of catechol.

The $^1\text{H-NMR}$ spectrum of product H3 is shown in Figure 3.23. The peak at 6.2 ppm, which is multiplet peaks, corresponds to the proton on catechol, ortho-substituted on benzene ring. This spectrum reveals identically two splitting pattern signals at 6.42-6.52 ppm and 6.58-6.72 ppm. Both signals are similar to p-chloroanisole pattern, meaning that the two signals are protons of para-substituted

benzene ring. In addition, the singlet signal at 8.3 ppm might be O-H signal on benzene ring.

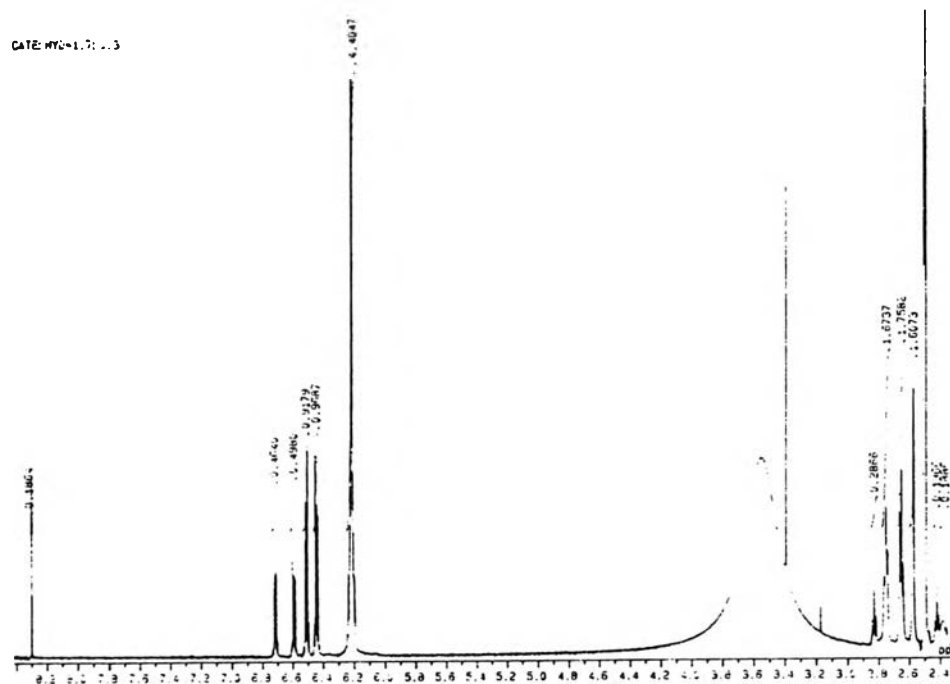


Figure 3.23-A ^1H -NMR spectrum of product H3.

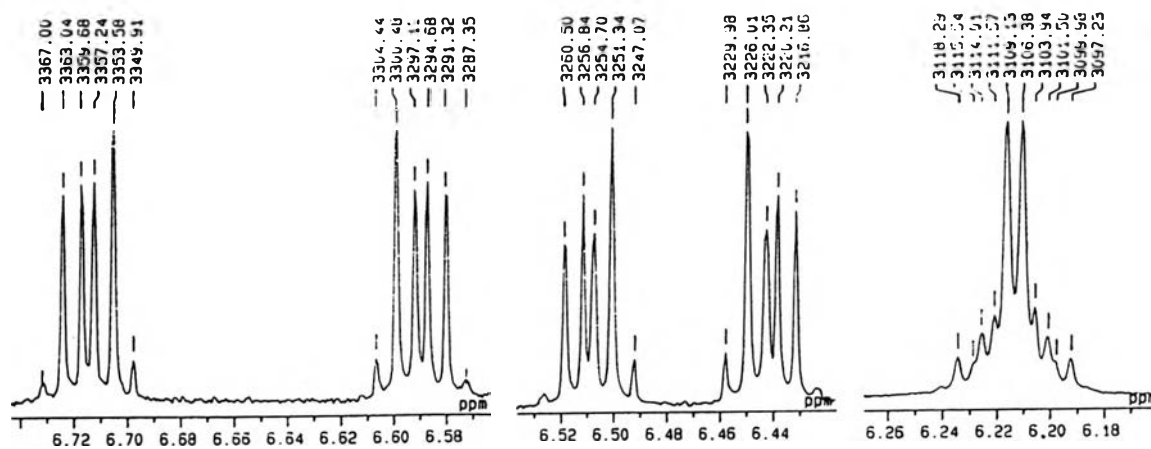


Figure 3.23-B Maximized spectra at 6.00-6.80 ppm.

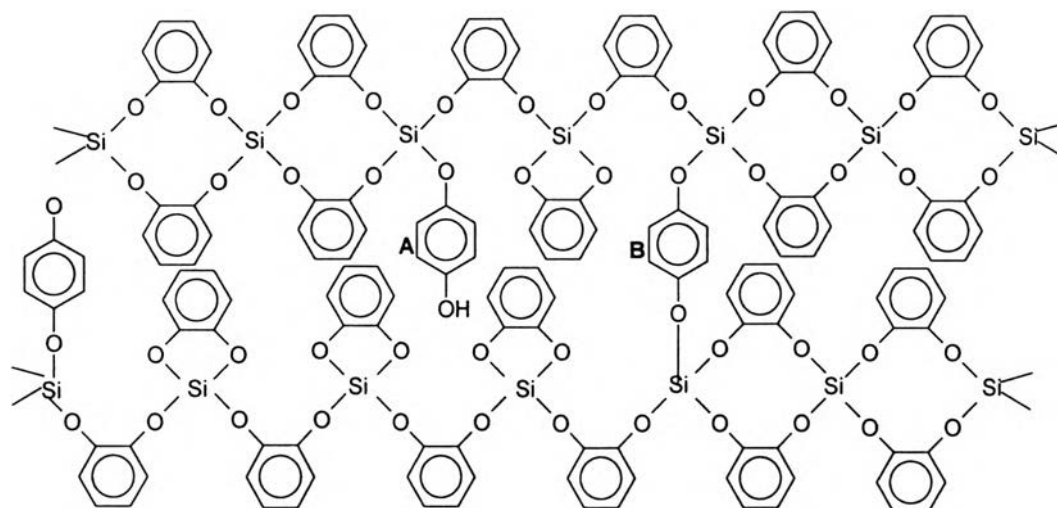


Figure 3.24 Suggested structure of synthesized product.

The structure in Figure 3.24 is proposed to elucidate two group signals of para-substituted on benzene ring. The signals of para-substituted on ring A differ from those of ring B because the environments are different. Therefore, the NMR spectrum for this type of product show two types of para-substitution.

For the ^{13}C -NMR spectrum of synthesized product H3, contains peaks at 152, 115 and 109 ppm which are assigned to benzene carbons of bis(1,2-dihydroxyphenyl)silane polymer which was studied by Rangsitphol J. (1995). Addition of hydroquinone in the reaction influences the ladder structure of bis(1,2-dihydroxyphenyl)silane. Other peaks are seen at 119, 117, and 62 ppm. The 115 and 109 ppm peaks appear close to the original peak in both position as shown in Figure 3.24. All results are present in Table 3.7.

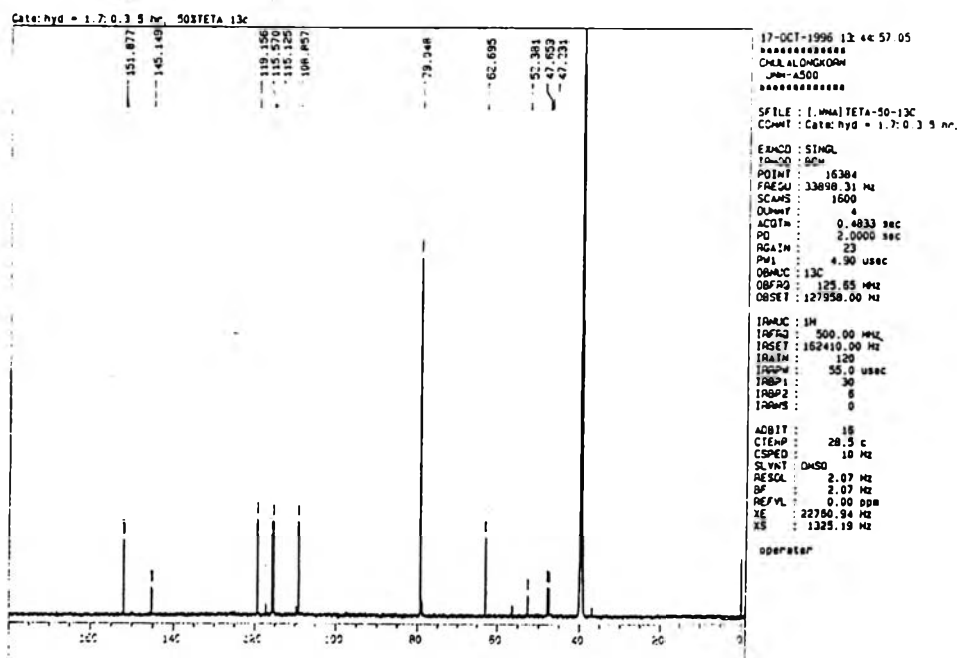


Figure 3.24 ^{13}C -NMR of product H3.

^{29}Si -NMR spectra of precipitated product reveals the peak at substantially low field as shown in Figure 3.24. The ^{29}Si NMR chemical shift assigned to the tetracoordinate silicate at -140 ppm, as shown in Figure 3.25, can be compared with that for the acyclic species $(\text{Pr}^i\text{O})_4\text{Si}$ which appears at -84.7 ppm [Kemmitt, J. et al., 1995]. The reason for the signal appearing at lower field is that the silicon nuclei are deshielded by those aromatic rings. Even though electronegativity of oxygen (EN = 3.5) is normally higher than silicon (EN = 1.7), *d*-orbital lacking electron of Si atom has effected to lone pair electron of oxygen therefore electron cloud inclines to silicon atom and further to aromatic rings which make the silicon nuclei extremely be shielded; see Figure 3.26.

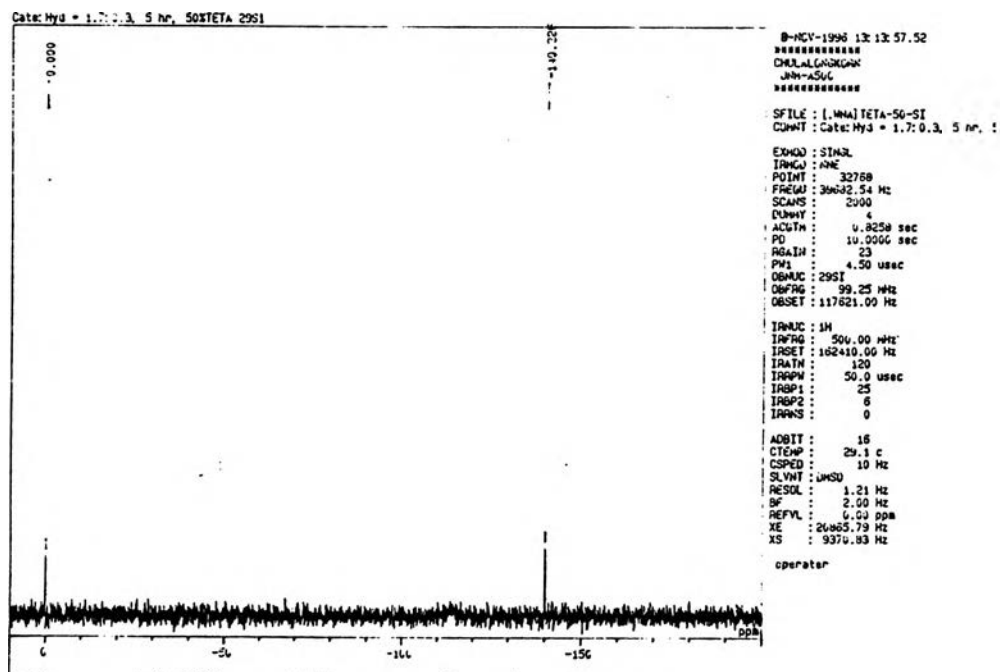
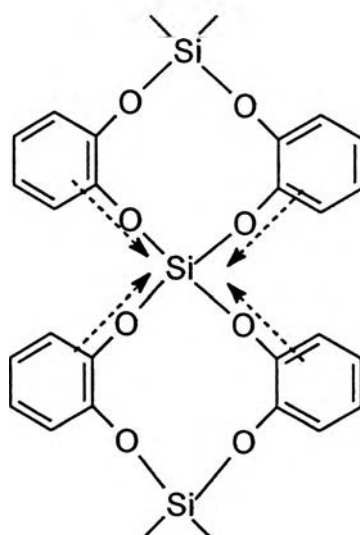
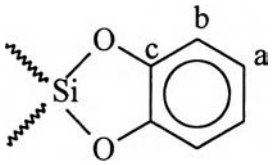
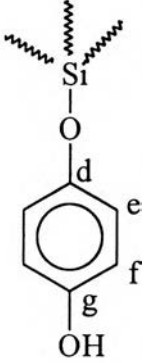
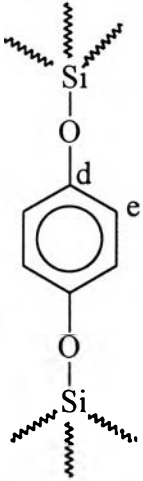
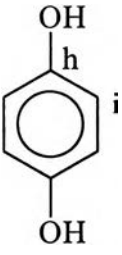


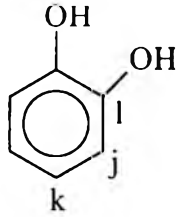
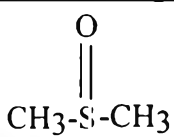
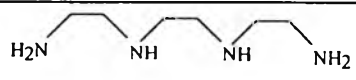
Figure 3.25 ^{29}Si -NMR of product H3.



Scheme 3.3 Direction of electron induced by Si atom.

Table 3.7 ^1H - and ^{13}C - NMR chemical shift of H3 product

Assigned Structure	^1H -NMR (ppm)	^{13}C -NMR (ppm)
	6.2 (multiplet) ortho-sub ⁿ	115 (a) 109 (b) 142 (c)
	6.3-6.5 (doublet) para-sub ⁿ 8.3 (O-H signal)	152 (d) 115.5 (e) 109.5 (f) 119 (g)
	6.5-6.75 (doublet) para-sub ⁿ	152 (d) 115.5 (e)
	6.4 (singlet) para-sub ⁿ 8.5 (O-H signal)	145 (h) 117 (i)

Assigned Structure	$^1\text{H-NMR}$ (ppm)	$^{13}\text{C-NMR}$ (ppm)
	7.0 (multipet) ortho-sub π 5.1 (O-H signal)	117 (j) 122 (k) 145 (l)
HOCH ₂ CH ₂ OH	2.3-2.4 (minor)	62 (minor)
	2.5 (CH ₃ signal)	40
	2.6-2.8 (minor)	46 , 47 (minor)