CHAPTER III
RESULTS AND DISCUSSION

3.1 Synthesis

The synthesis of a liquid crystalline copolymer from silica, catechol and 4-*tert*-butylcatechol can be accomplished via one step by the so-called OOPS (oxide one pot synthesis) Process using TETA as the catalyst in EG solvent. Catechol (CAT) and 4-*tert*-butylcatechol (*t*-BUT) acted as nucleophilic anion with the counter ion $TETAH^+$. The nucleophilic attack of $TETAH^+O^-C_6H_4OH$ and $TETAH^+O^-C_6H_3C(CH_3)_3OH$ on Si atom of silica breaks Si-O bonds and forms $Si-O-C_6H_4OH$ and $Si-O-C_6H_3C(CH_3)_3OH$ bond respectively. The by product water is distilled off to drive the reaction forward.

The synthesized product is supposed to show LC properties; nevertheless, its properties depend on the composition proportion of raw materials, the amount of TETA catalyst and the reaction time which were studied in this research. Thus, the characteristic properties of the products will be compared as a function of each variable. The bis(catechol)silane polymer is a ladder polymer which is highly crystalline. The molecules are packed too tightly to exhibit LC behavior; thus, it is interesting to add some substitutes onto the molecules to obstruct the dense packing. The *t*-butyl group in 4-*tert*-butylcatechol has been shown to work this way. *t*-BUT groups appear to force the molecules to pack lossely.

After all the chemical substances were mixed together and heated for a while, a clear yellow solution is obtained. As the reaction was completed and cooled down to room temperature, a fluffy precipitate was obtained. The

powder obtained from washing with methanol and acetonitrile was slightly yellow in general. The color of the product became darker with the increasing of the amount of *t*-BUT until it reached the ratio of 1.0:1.0 of CAT:*t*-BUT when it started to give light brown powder. Surprisingly, it then returned to be lighter in color when the amount of *t*-BUT was further increased, and the most pearl white powder was obtained from the reaction with no CAT.

The typical yield obtained was the highest when the amount of *t*-BUT was 0.1, and trended to decrease with the *t*-BUT increment in the reaction up to the ratio of 1.0:1.0 which gave the least yield of the product. When the amount of *t*-BUT was further increased, the amount of gained product gradually increased again. From this result, it can be implied that maybe there is more competition between CAT and *t*-BUT to join in the reaction when the mole ratio of them is equivalent, the amount of gained product is consequently less. The variation of the reaction time at 3, 4 and 5 hours gave more or less the same weight of the product. Typically, the longer the reaction time, the more time to break Si-O bonds, the slightly more weight of gained product. However, the 1- and 2-hour reactions gave much less weights than those of 3-, 4- and 5-hour ones, and the product weight decreased when the reaction time was prolonged to 7 and 9 hours.

By considering the variation of the catalyst amount, the more TETA used in the reaction, the more weight of the product obtained. The products from different amount of TETA showed the same shade in color, but a little bit lighter with the 16.66% and 33.33% TETA products. The function of TETA was to help the reaction to go forth by catching proton and acting as counter ion with nucleophilic anion of CAT or *t*-BUT. The color shade and the weight gain of the products are shown in Tables 3.1-3.5.

Table 3.1 The weight gain of the product for each mole ratio at 5-hour reaction time

t-BUT:CAT	Weight gain (g)
0.1:1.9	9.5
0.2:1.8	7.5
0.3:1.7	9.0
0.4:1.6	7.9
0.5:1.5	6.5
0.6:1.4	6.6
0.7:1.3	6.7
0.8:1.2	5.5
0.9:1.1	3.0
1.0:1.0	2.3
1.1:0.9	2.8
1.2:0.8	2.8
1.3:0.7	3.2
1.4:0.6	3.2
1.5:0.5	2.9
1.6:0.4	3.4
1.7:0.3	3.8
1.8:0.2	3.5
1.9:0.1	3.4
2.0:0.0	3.4

Table 3.2 The weight gain of the product for each mole ratio at
4-hour reaction time

t-BUT:CAT	Weight gain (g)
0.1:1.9	8.6
0.2:1.8	8.6
0.3:1.7	7.5
0.4:1.6	8.6
0.5:1.5	7.0
0.6:1.4	6.0
0.7:1.3	4.6
0.8:1.2	4.3
0.9:1.1	2.0
1.0:1.0	2.4
1.1:0.9	2.6
1.2:0.8	2.7
1.3:0.7	2.8
1.4:0.6	2.5
1.5:0.5	2.9
1.6:0.4	3.6
1.7:0.3	3.5
1.8:0.2	3.2
1.9:0.1	3.2
2.0:0.0	3.4

Table 3.3 The weight gain of the product for each mole ratio at
3-hour reaction time

t-BUT:CAT	Weight gain (g)
0.1:1.9	7.8
0.2:1.8	8.4
0.3:1.7	8.0
0.4:1.6	5.2
0.5:1.5	3.2
0.6:1.4	4.5
0.7:1.3	5.2
0.8:1.2	3.1
0.9:1.1	3.0
1.0:1.0	2.7
1.1:0.9	2.8
1.2:0.8	2.9
1.3:0.7	3.2
1.4:0.6	3.6
1.5:0.5	3.3
1.6:0.4	3.4
1.7:0.3	3.6
1.8:0.2	3.6
1.9:0.1	3.4
2.0:0.0	3.7

Table 3.4 The weight gain of the product at mole ratio of 1.2:0.8,
CAT:t-BUT, 5-hour reaction time for each mole%TETA

mole%TETA	Weight gain (g)
16.66	1.6
33.33	1.9
50.00	2.0
66.68	2.0
83.33	2.1
100.00	5.5

Table 3.5 The weight gain of the product at mole ratio of 1.2:0.8,
CAT : t-BUT, with 100 mole% TETA for each reaction time

Reaction Time (hrs)	Weight gain (g)
1	1.2
2	1.2
3	2.1
4	4.3
5	5.5
7	4.2
9	1.8

3.2 Characterization

3.2.1 Mass Spectroscopy

The product was proposed to be the random copolymer of bis(1,2-dioxyphenyl)silane monomer (m/z = 244), (1,2-dioxyphenyl-1',2'-dioxy-4'-*tert*-butylphenyl)silane monomer (m/z = 300), and bis(1,2-dioxy-4-*tert*-butylphenyl)silane monomer (m/z = 356). There were also the peaks of free catechol (m/z = 110) and *t*-butylecatechol (m/z = 166) from the hydrolysis of the product, and the fragment of *t*-butylcatechol from the loss of a methyl group (m/z = 151) to form a stable 3°-radical ion. The spectra show the base peak at m/z = 244 when the ratio of *t*-BUT in the reaction was varied from 0.1 to 0.9, and the base peak changed to m/z = 151 for the latter higher ratios. The mass spectrum of a product is shown in Figure 3.1.

The higher oligomers and polymers were not observed because they were broken into monomers and fragments by the bombardment of high electron energy. The structures of each fragment are shown in Table 3.6. The product of m/z = 244 (species I) came from two CAT's, and the one at m/z = 300 (species III) derived from one CAT and one *t*-BUT, whereas the one of m/z = 356 (species V) was the consequence from the composition of two molecules of *t*-BUT. As the ratio of *t*-BUT increased, the amount of m/z = 244 decreased while those of m/z = 300 and m/z = 356 increased.
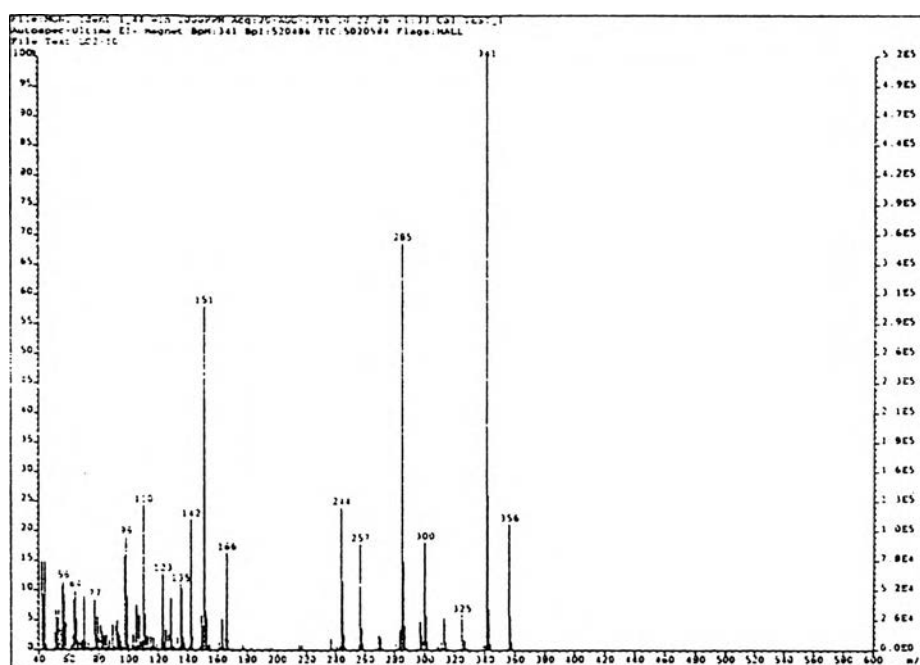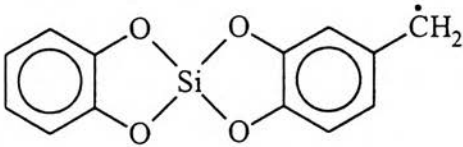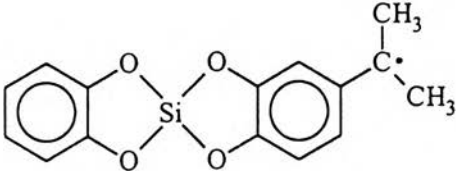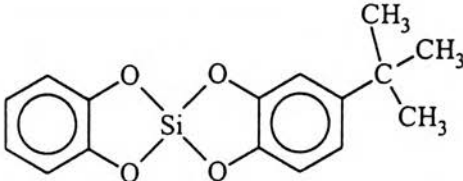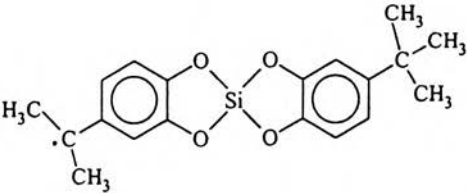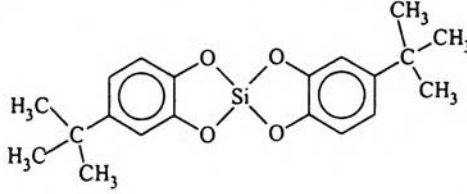
Figure 3.1 Mass spectrum of the 1.2:0.8 mole ratio of CAT:*t*-BUT at
5-hour reaction time.

Table 3.6 The proposed structures of the product fragments

m/z	Species
110	
136	
151	
166	
244	 (I)

m/z	Species
257	
285	 (II)
300	 (III)
341	 (IV)
356	 (V)

Surprisingly the fragment of m/z 285 (species II) and of m/z 341 (species IV), derived from the loss of a methyl group from those of m/z 300 and 356 respectively, had higher amount than ones without any loss of methyl

group in every ratio. This observation suggests that they were more stable with the lost of a methyl group from the structure and being as free radical fragments in the high electron energy chamber.

From the reason that species II is more stable than species III, and species IV is more stable than species V, the amounts of CAT and *t*-BUT reacted in the reaction for each ratio were determined by the proportion of species II to species I, and of species IV to species I, respectively. Both proportions trend to increase with the increment of *t*-BUT, see figures 3.2-3.4. The latter proportion increases at a faster rate from the result of the increasing of species IV and the decreasing of species II as the amount of *t*-BUT was increased.

3.2.2 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 3.5 displays the FTIR spectrum of a raw material silica and Figure 3.6-3.8 show the FTIR spectra of the products for each condition variations. The absorption peak assignments of functional groups in the product were listed in Table 3.7. The products show similar peaks in general, for instance; aromatic C=C stretching at 1590 and at 1500 cm^{-1}, C-O stretching at 1250 cm^{-1}, and Si-O-C stretching at 1100 and 1018 cm^{-1}. Out-of-plane C-H bending of 4 adjacent hydrogens of 1,2-disubstituted aryl shows the peak at 747 cm^{-1} while the 1,2,4-trisubstituted aryl shows the peak at 817 cm^{-1} resulted from 2 adjacent hydrogens. The in-plane C-H bending of 1,2-disubstituted and 1,2,4-trisubstituted aryl appear at 1000 and 1125 cm^{-1}, respectively. All these C-H bending deformations show weak peaks. C-H bending of CH_3 in *t*-butyl group shows weak doublet peaks at around 1360 cm^{-1}. The peak at 2958 cm^{-1} represents the asymmetric C-H stretching of methyl group.
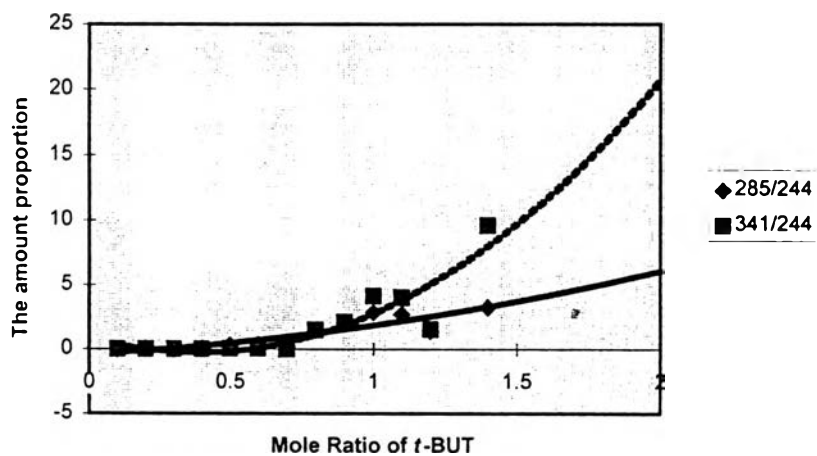
Figure 3.2 The amount proportion of m/z 285 and m/z 244 and of m/z
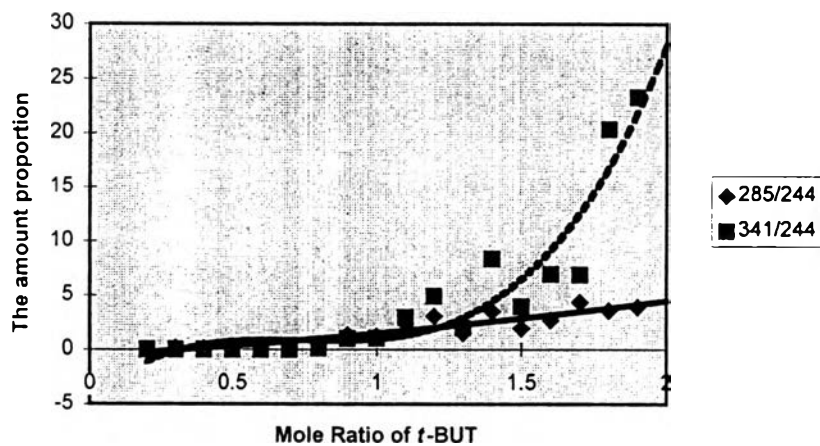
341 and m/z 244 of 3-hour reaction time products.

Figure 3.3 The amount proportion of m/z 285 and m/z 244 and of m/z
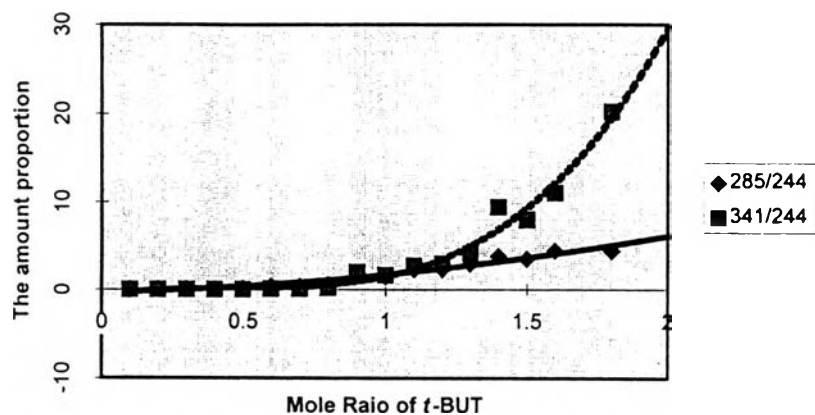
341 and m/z 244 of 4-hour reaction time products.

Figure 3.4 The amount proportion of m/z 285 and m/z 244 and of m/z
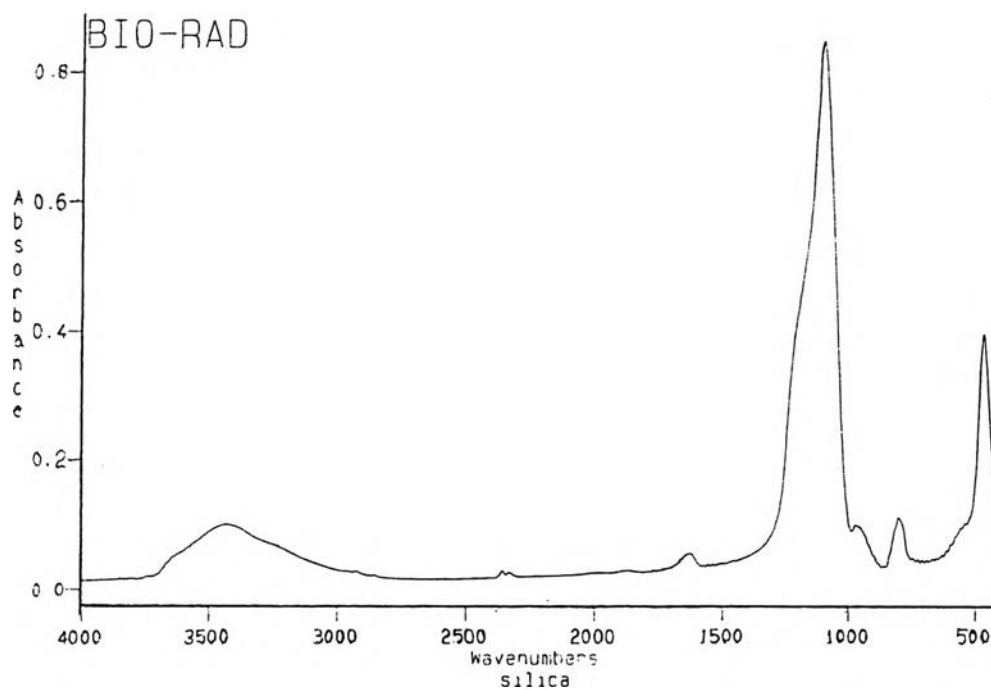341 and m/z 244 of 5-hour reaction time products.

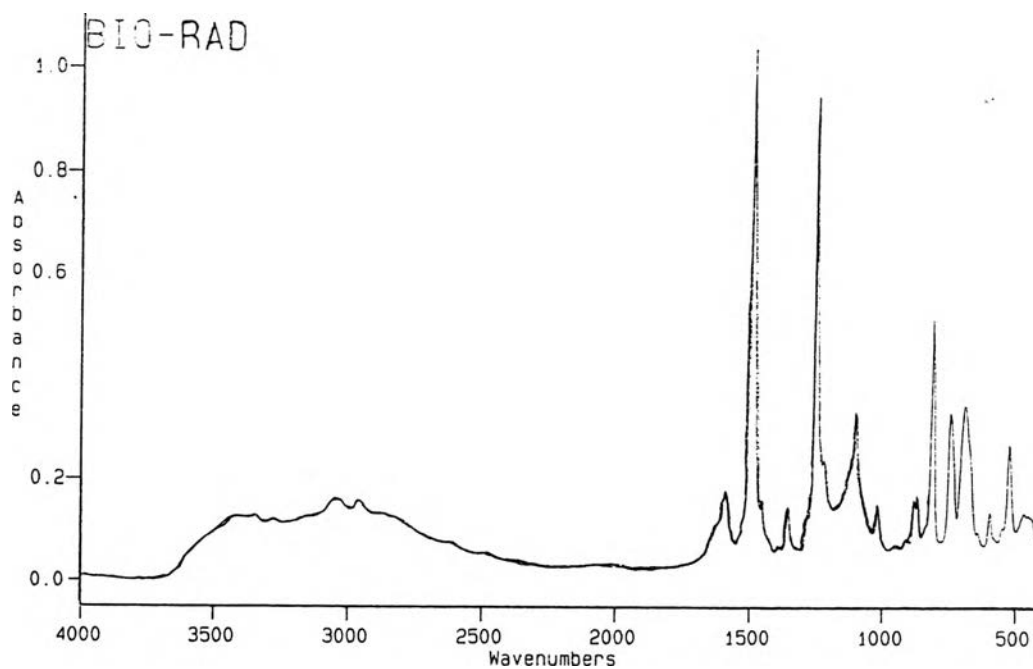Figure 3.5 FTIR spectrum of a raw material silica.

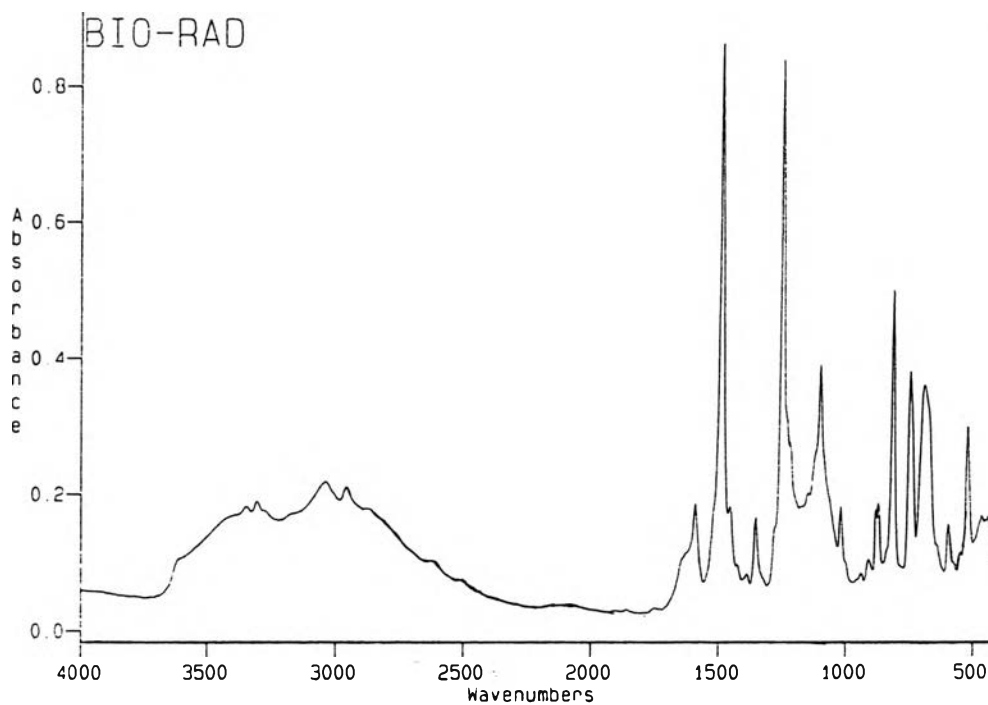Figure 3.6a FTIR spectrum of the product at the mole ratio of

CAT:*t*-BUT = 1.9:0.1.

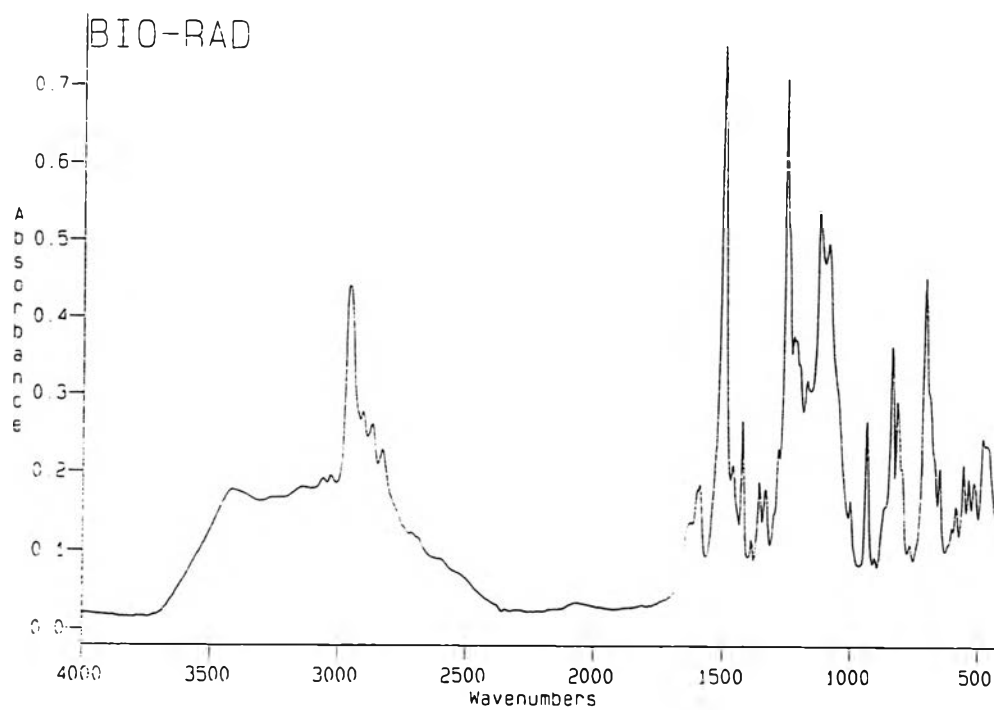Figure 3.6b FTIR spectrum of the product at the mole ratio of
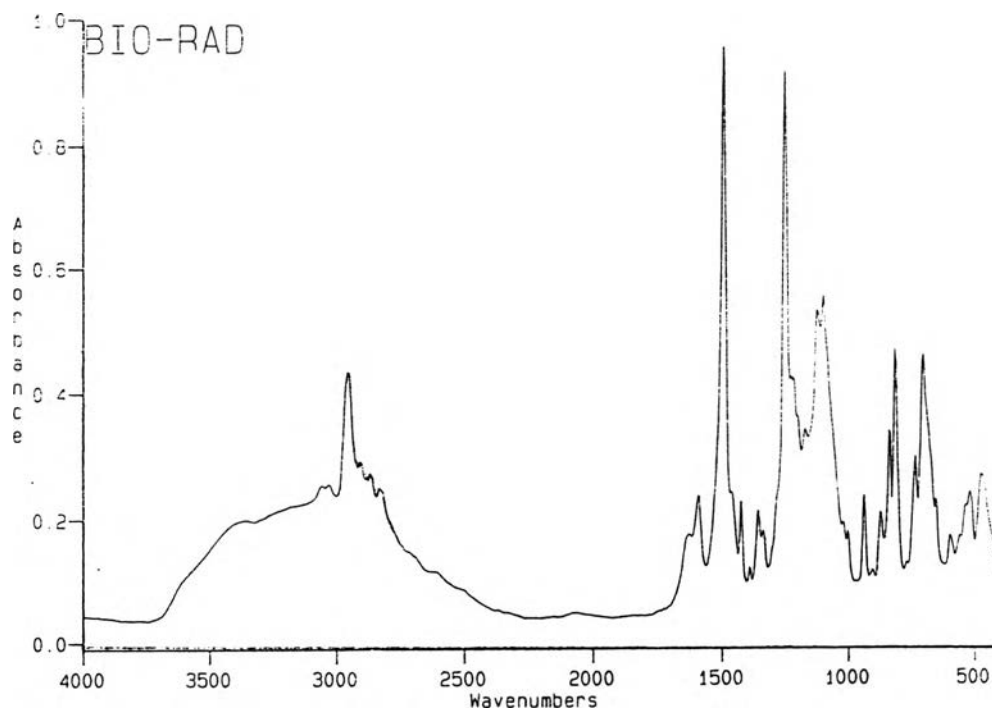
CAT:*t*-BUT = 1.5:0.5.

Figure 3.6c FTIR spectrum of the product at the mole ratio of
CAT:*t*-BUT = 1.0:1.0.
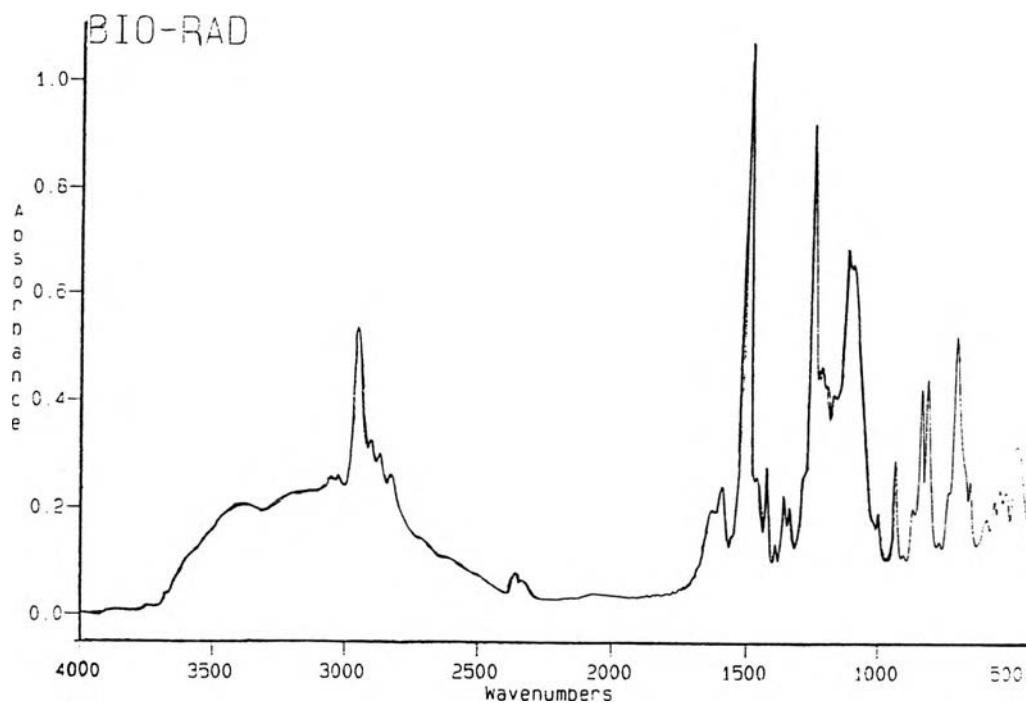
Figure 3.6d FTIR spectrum of the product at the mole ratio of
CAT:*t*-BUT = 0.5:1.5.

Figure 3.6e FTIR spectrum of the product at the mole ratio of
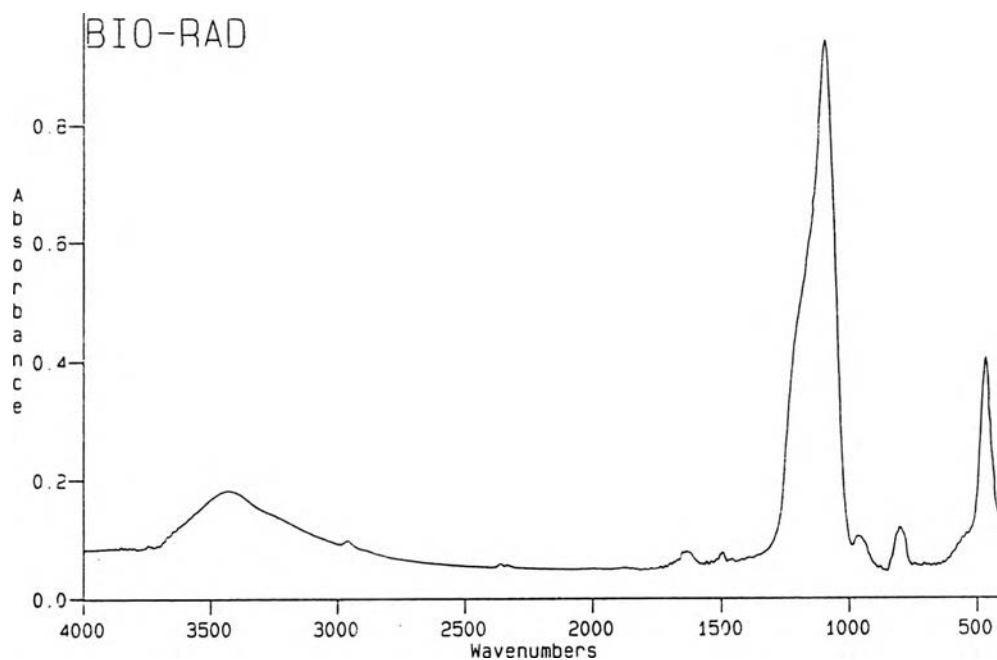
CAT:*t*-BUT = 0.0:2.0.

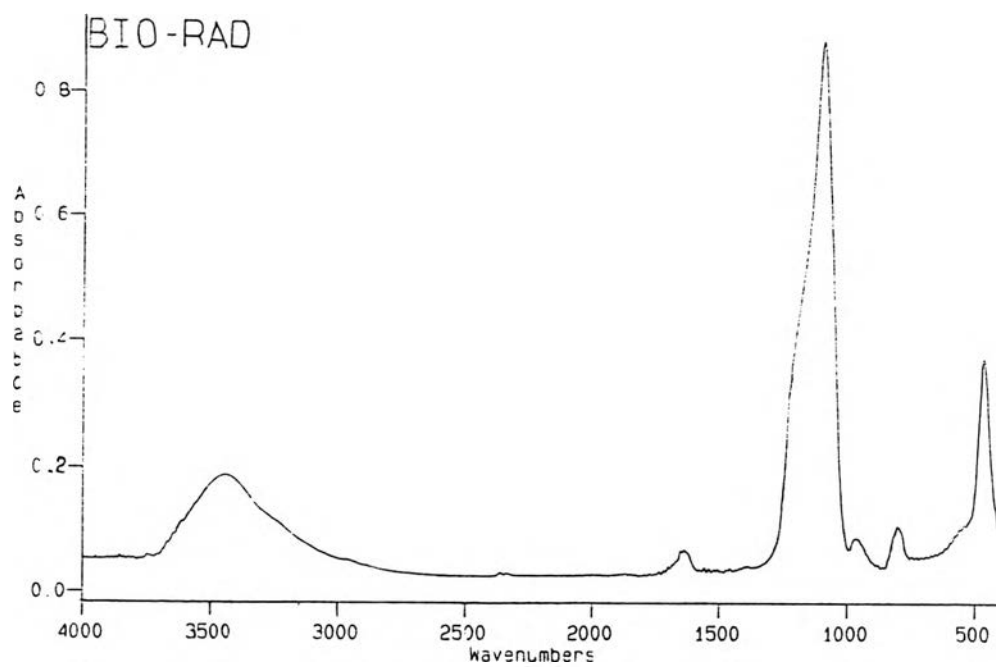Figure 3.7a FTIR spectrum of the product at 1-h reaction time.

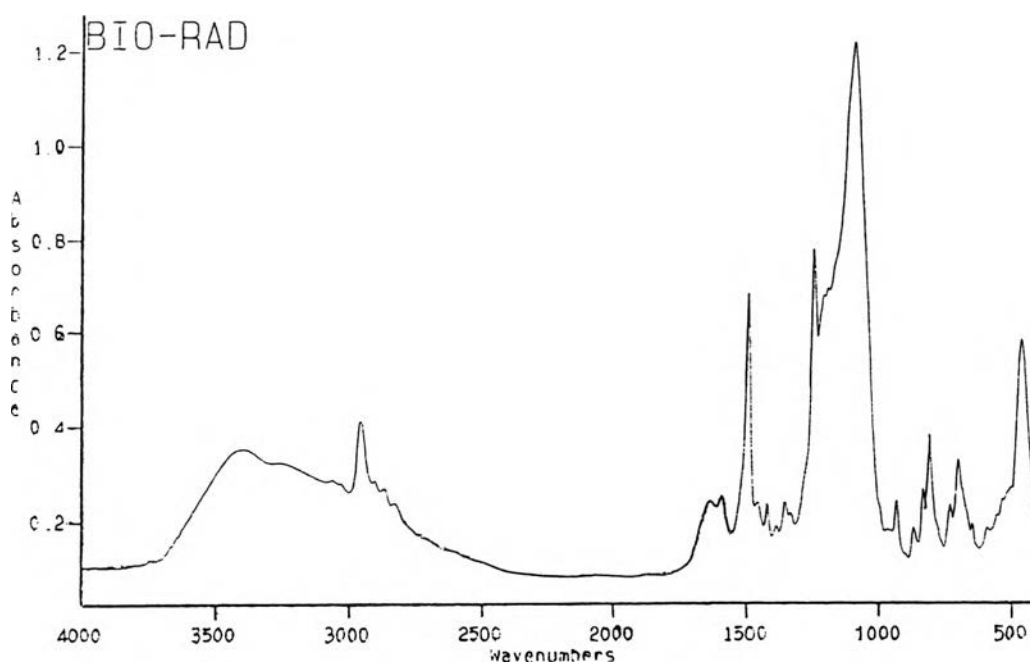Figure 3.7b FTIR spectrum of the product at 2-h reaction time.

Figure 3.7c FTIR spectrum of the product at 3-h reaction time.
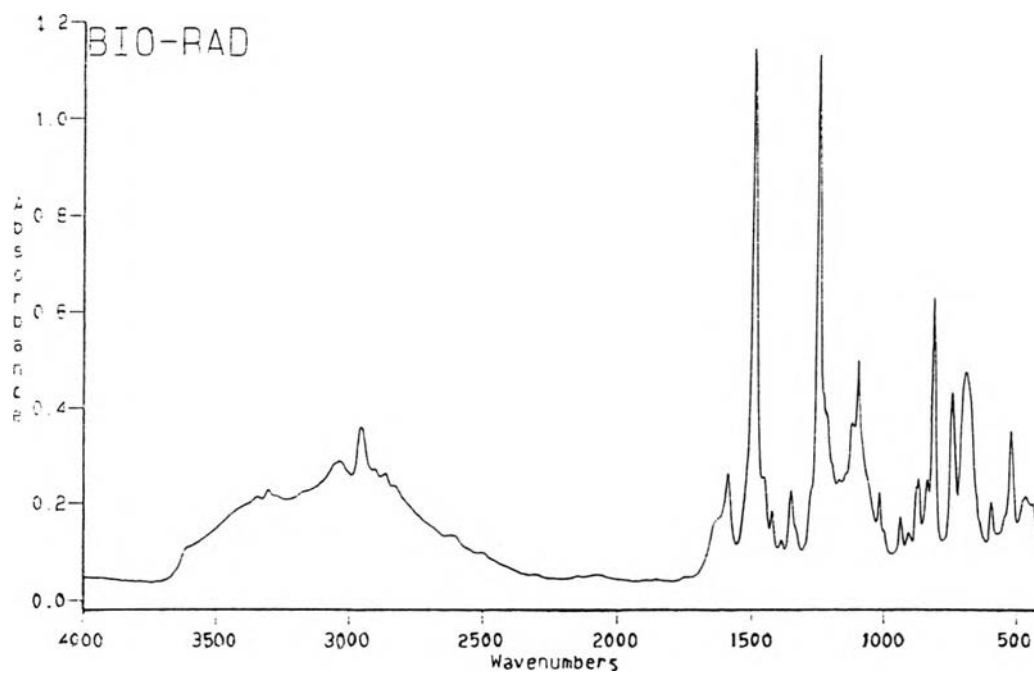
Figure 3.7d FTIR spectrum of the product at 4-h reaction time.
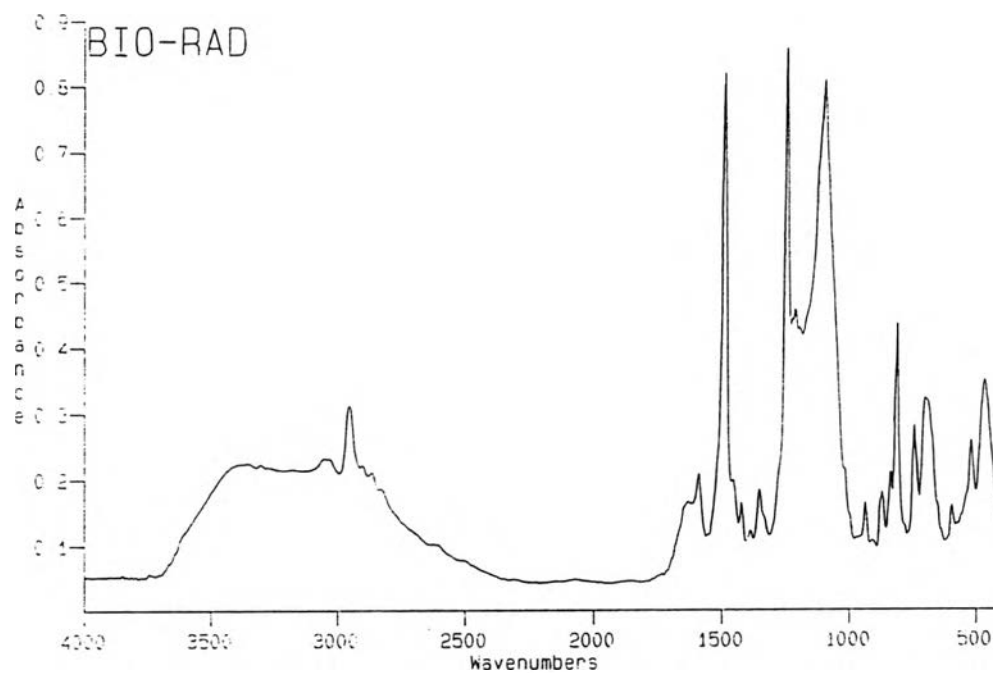

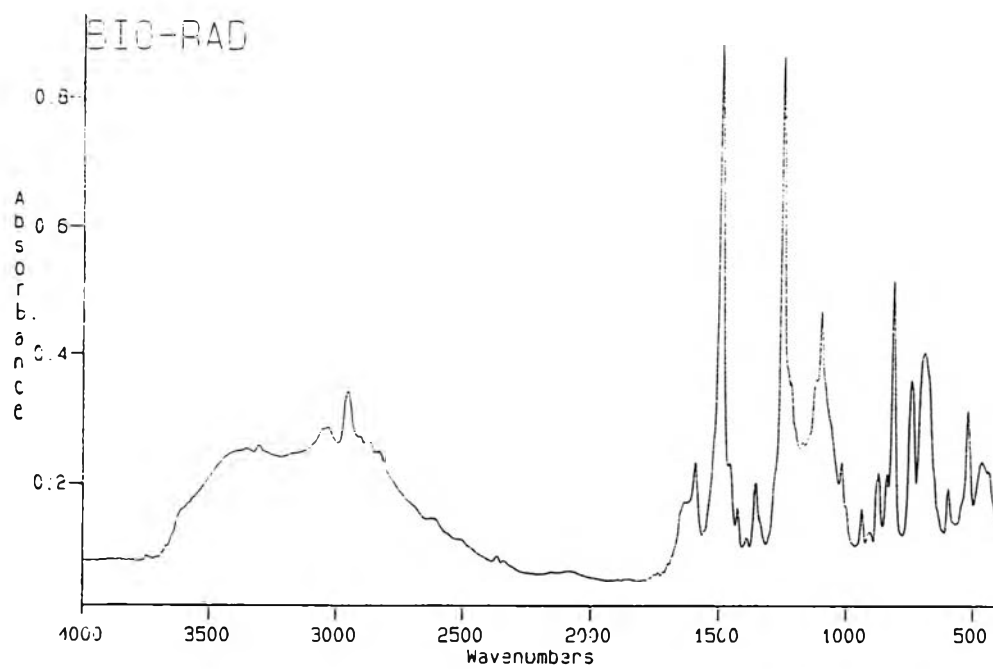Figure 3.7e FTIR spectrum of the product at 5-h reaction time.

Figure 3.7f FTIR spectrum of the product at 7-h reaction time.
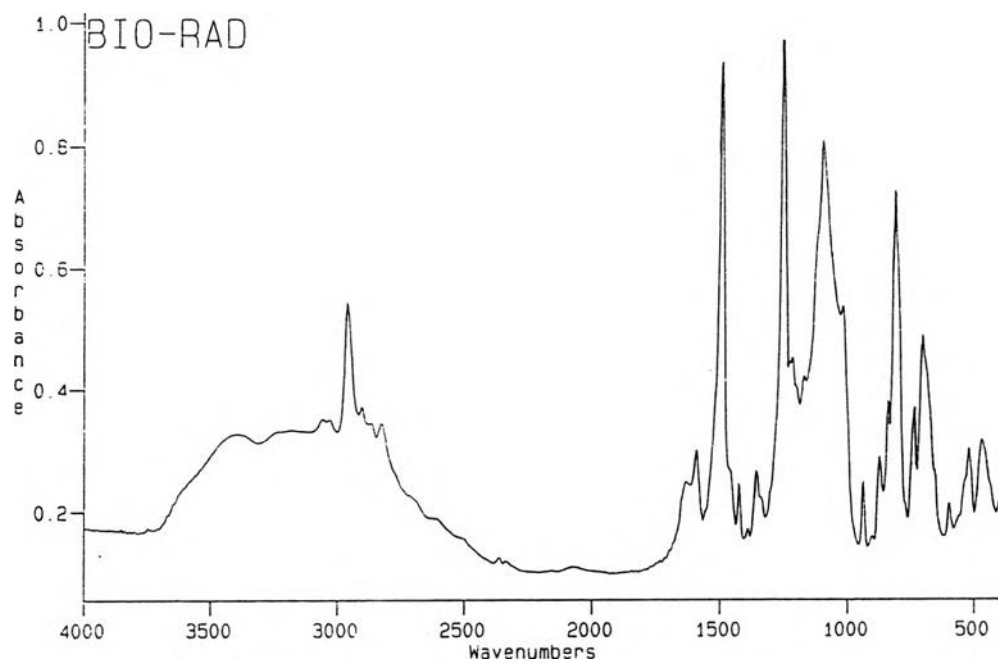

Figure 3.7g FTIR spectrum of the product at 9-h reaction time.
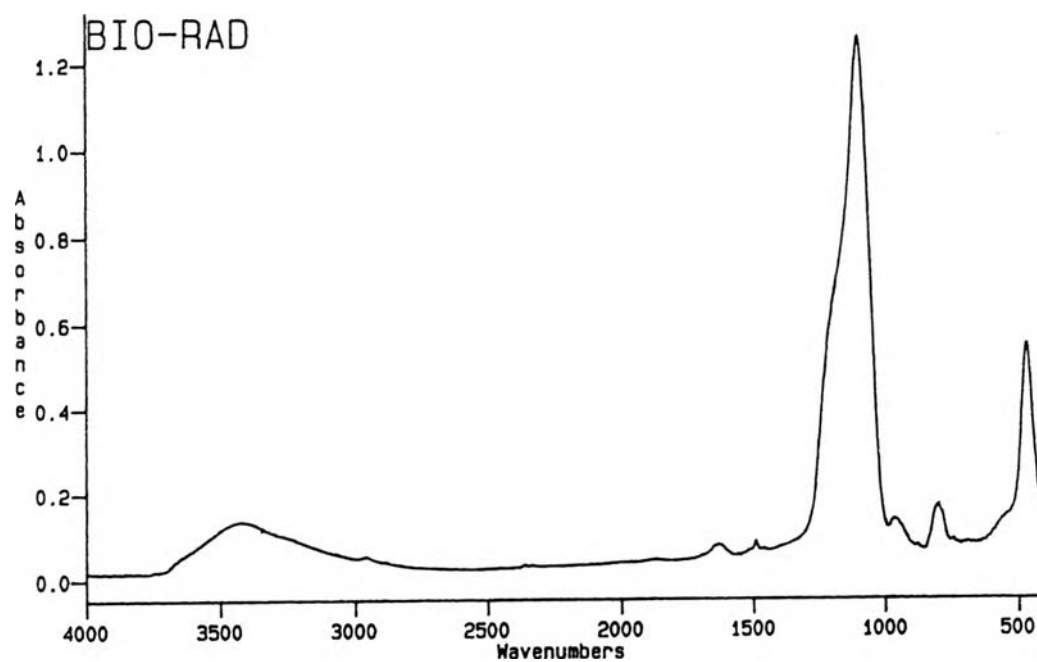
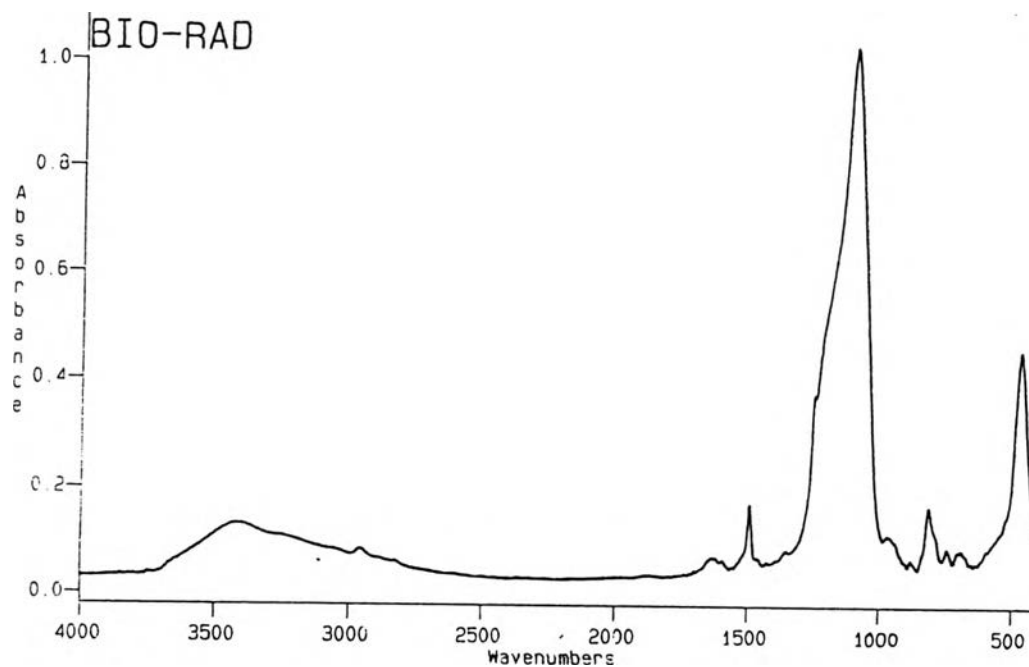Figure 3.8a FTIR spectrum of the product at 16.67% TETA.

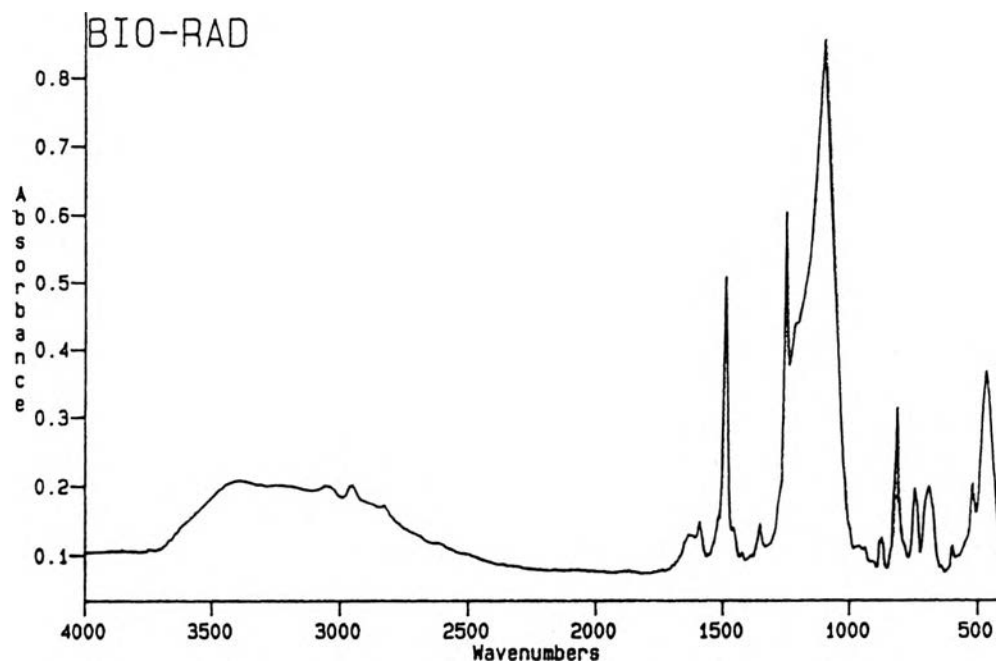Figure 3.8b FTIR spectrum of the product at 33.33% TETA.

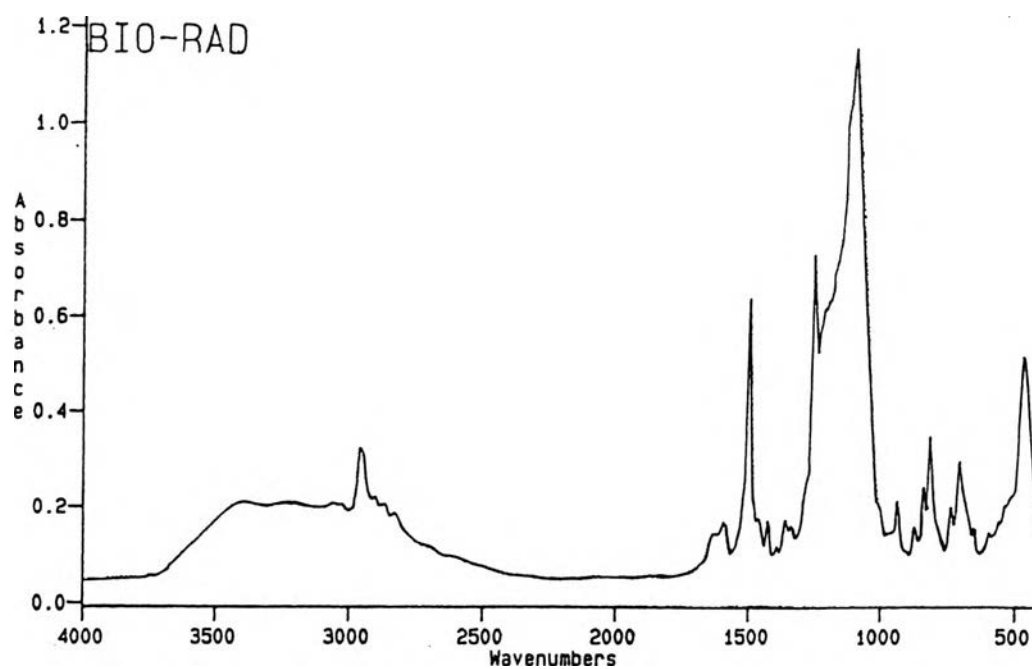Figure 3.8c FTIR spectrum of the product at 50% TETA.

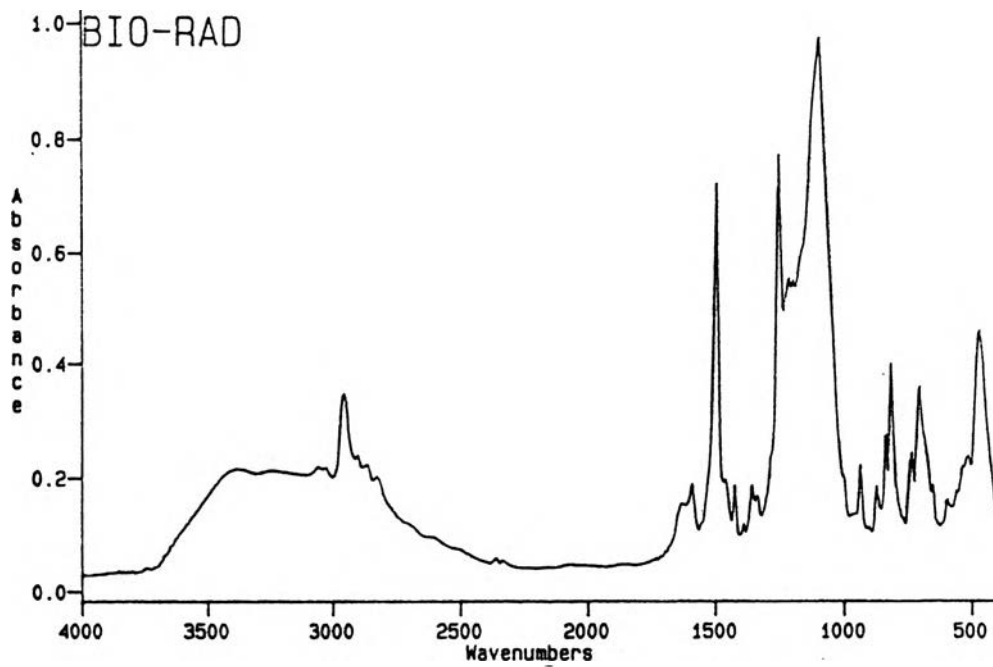Figure 3.8d FTIR spectrum of the product at 66.68% TETA.

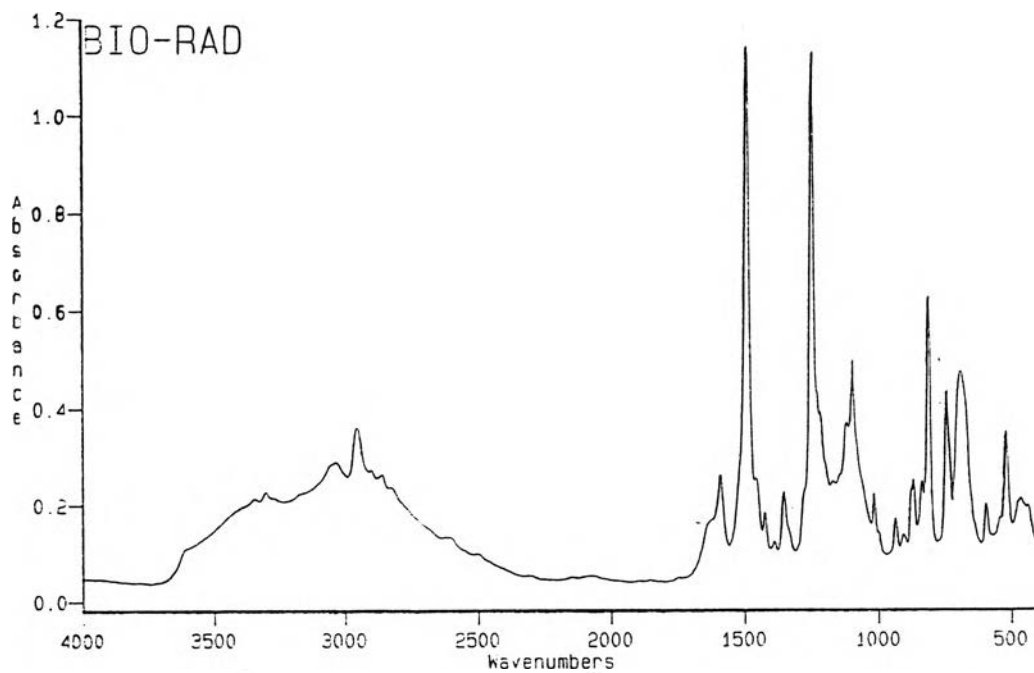Figure 3.8e FTIR spectrum of the product at 83.33% TETA.

Figure 3.8f FTIR spectrum of the product at 100% TETA.

Table 3.7 The peak assignments of absorption of functional

groups in the product

Assignment	Wave Number (cm^{-1})	
υ O-H	3600-3300	(broad)
υ$_{as}$ C-H (CH$_3$)	2958	(medium)
υ C-H (aromatic)	3058	(doublet, weak)
υ C=C (aromatic)	1590	(weak)
	1500	(strong)
σs C-H (CH$_3$)	1360	(doublet, weak)
υ C-O (aromatic)	1250	(strong)
υ Si-O-C	1100	(medium)
	1015	(weak)
σ C-H (1,2,4-trisubstituted aryl)	817	(medium)
σ C-H (1,2-disubstituted aryl)	747	(medium)

The OH stretching broad band appears in the 3500-3300 cm^{-1} region. These OH groups may be of the unsubstituted hydroxyl group of CAT and of t-BUT in the product or be of the free CAT and/or free t-BUT from the hydrolysis of the products.

Although the FTIR technique is not quite suitable for quantitative analysis, it can be observed that as the proportion of t-BUT in the reaction was increased, the height of the peak at 2958 cm^{-1} which represents the methyl group increased as well. The trend of the intensity increment of this peak is demonstrated in Figure 3.9. Each point derived from plotting the ratio of this peak intensity and the intensity of the peak at 1500 cm^{-1}, the strongest one, of each mole ratio.

The FTIR spectra of 1-hand 2-h reaction time products look like that of silica. At longer reaction times, the spectra differ more from silica. The proposed product does not obtain if the reaction time is less than 3 hours, and the longer the reaction time, the faster the reaction is completed. The spectra of 7-h and 9-h reaction time products however become broader in the region of 1300-1100 cm^{-1} indicating that there are more silica left in the product when the reaction time is more than 5 hours. The reason may be derived from the backward of the reaction when the reaction is let undergo for more than the proper reaction time.

In case of the catalyst TETA variation, the spectra of 16.67 and 33.33 mole%TETA products look the same as that of silica. In the 50% TETA spectrum, we can observed the peaks at 747, 817 and 1500 cm^{-1}. The peak at 2958 cm^{-1} was first noticed at the 66.68%TETA. However, the spectra of all 16.67, 33.33, 50, 66.67 and 83.33%TETA products suggest that there is still much of unreacted silica in the product. It looks the best in the spectra of the 100%TETA product.
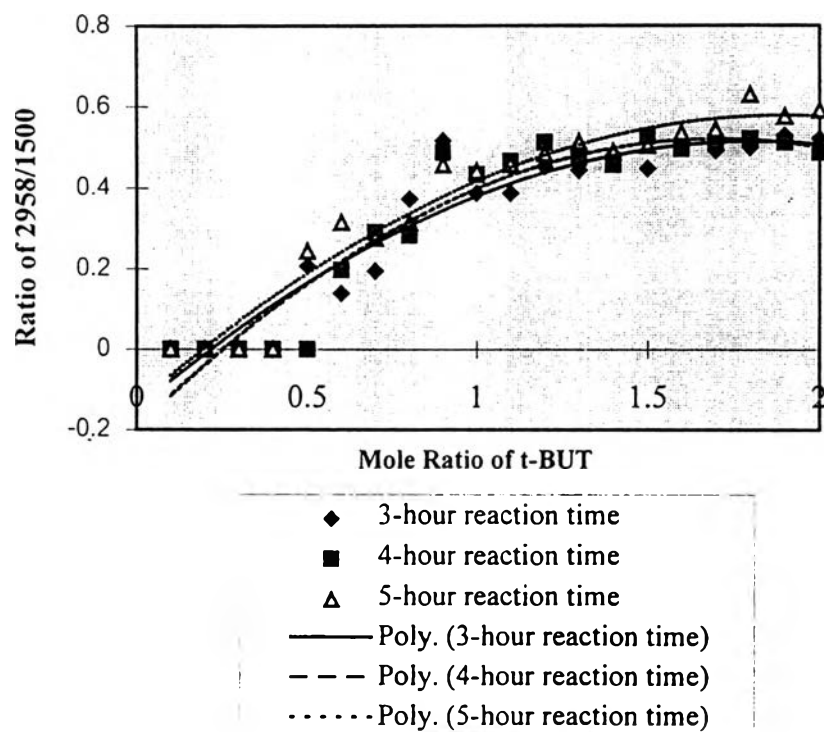
Figure 3.9 The height ratio of the peak at 2958 cm⁻¹ and at 1500 cm⁻¹.

3.2.3 Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR is one of the most useful instrument techniques to study the structural formula of both organic and inorganic materials. In this thesis, ^{1}H, ^{13}C and ^{29}Si NMR of the samples have been investigated. ^{1}H NMR spectra of t-butylcatechol, catechol and the synthesized product are shown in Figures 3.10, 3.11 and 3.12, respectively.
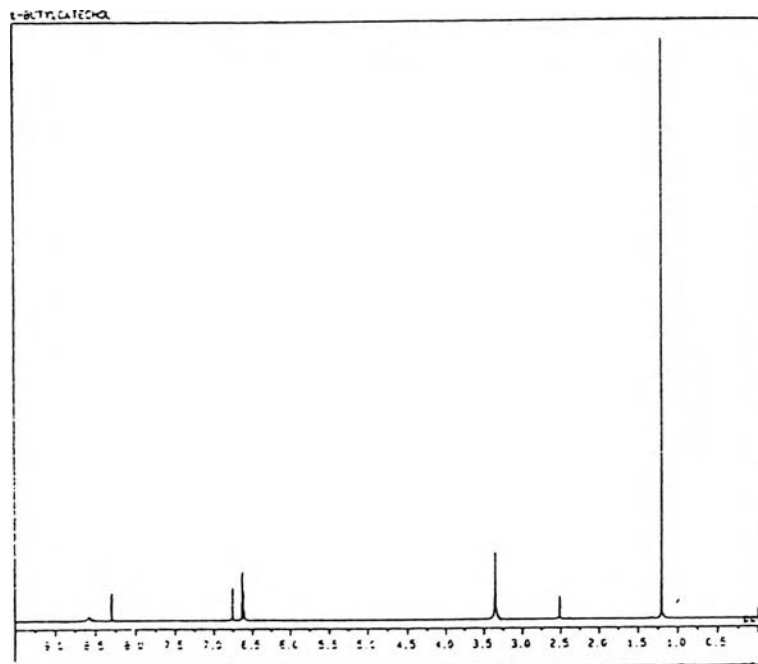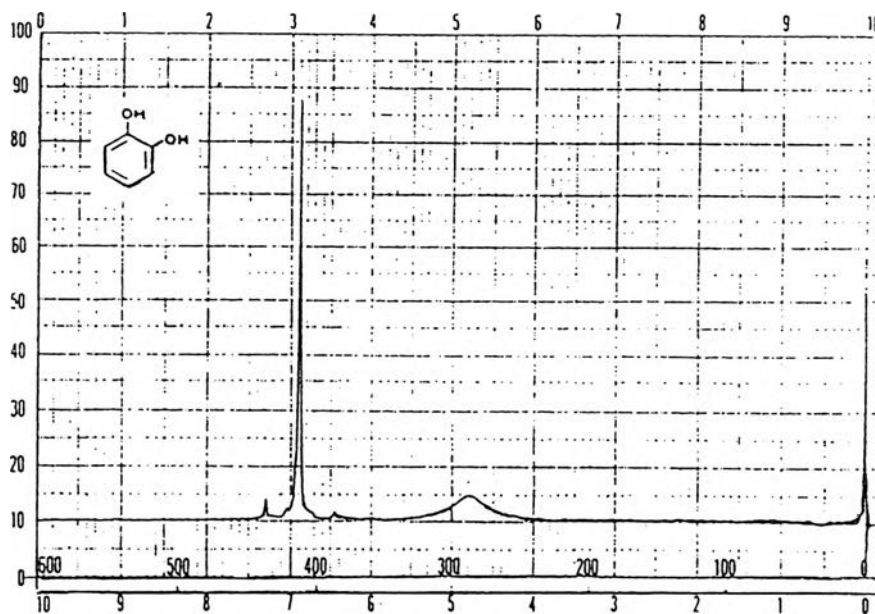
Figure 3.10 ¹H NMR spectrum of *t*-butylcatechol.
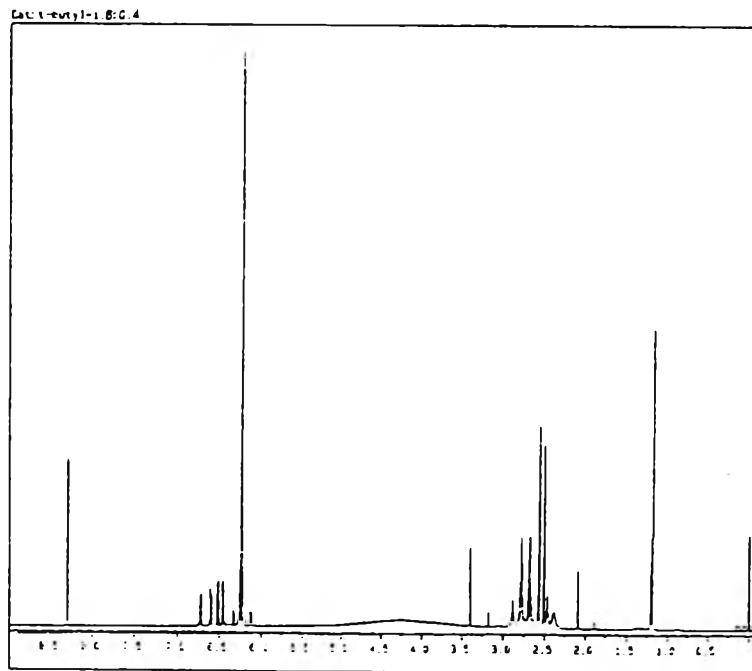

Figure 3.11 ¹H NMR spectrum of catechol.

Figure 3.12 ¹H NMR spectrum of a synthesized product.

In the product spectrum, the multiplet peaks at 6.2 ppm represent the proton on benzene ring of catechol. The two multiplet peaks at 6.58-6.62 and 6.70-6.75 ppm come from the protons on benzene ring of t-butylcatechol as they appear at the same position as those in the t-butylcatechol spectrum in figure 3.10. The other two multiplet peaks at 6.58-6.62 and at 6.70-6.75 ppm are from the protons on benzene ring of t-butylcatechol in the product as well. The reason for the appearing at lower chemical shift of these peaks may be from the effect of Si in the product. The Si atom has d-orbital offering free space for unbonded electrons of the close-by atoms, oxygen, to reside. Therefore, oxygen can give less electrons to benzene ring. The magnetic anisotropy effect from the interaction of π electrons in aromatic with the applied magnetic field will be reduced. Hydrogen attached to benzene ring are in the deshield area. When the second magnetic field generated by circulating

π electrons is reduced, more applied magnetic field has to be used. As a consequence, the resonance happened at lower chemical shift.

Protons of *t*-butylcatechol produce multiplet peaks at higher chemical shift than the protons in catechol because they have the effect from *t*-butyl group which can slightly give electrons to benzene ring. The more electrons inductively donated to benzene enhance the second magnetic field, so less applied magnetic field is needed. Furthermore, the product contains many species of monomers, oligomers and polymers, a particular hydrogen may be coupled to two or more sets of hydrogens of different chemical shifts that result in the appearance of a number of resonance lines instead of only a single resonance line.

The peak at 1.18 ppm are produced by the protons in *t*-butyl group. There are also two other peaks beside it at slightly higher chemical shift that might be resulted from the effect of having minor products. We can notice a group of the multiplet peaks at 2.3-2.9 ppm which display protons of TETA left in the product. A peak at 2.5 ppm is from the proton in solvent, DMSO-d_6, and the singlet peak at 3.3 ppm corresponds to the water absorbed in the solvent. In addition, the singlet peak at 8.3 represents the protons in hydroxy group on benzene ring.

Figure 3.13 shows ^{13}C NMR spectrum of the product. The peaks at 145, 115 and 109 ppm result from carbon atoms on the benzene ring of catechol in the product, while the appearance of the peaks at 151 and 115 ppm is due to the carbon atoms on benzene ring of *t*-butylcatechol.

The methyl group carbons and the tertiary carbon in *t*-butylcatechol show few little peaks at ~ 33 ppm. The multiplet peaks at 39 ppm are from the solvent, DMSO-d_6. The spectrum also shows that there is a little bit of TETA, at 47 and 46 ppm, left in the product.
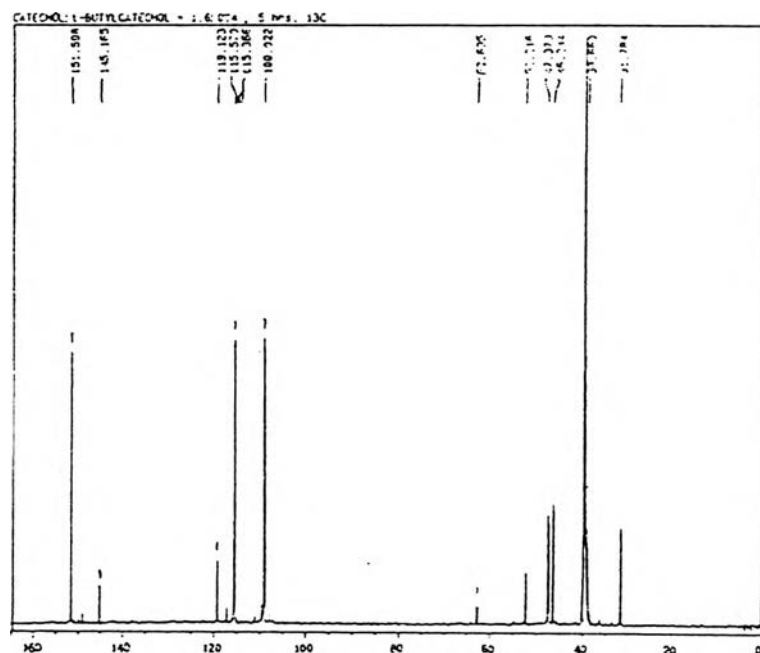
Figure 3.13 ^{13}C NMR spectrum of a synthesized product.

Figure 3.14 demonstrates ^{29}Si NMR spectrum of the product. The chemical shift reference for ^{29}Si is the same compound as that for ^{1}H and ^{13}C, tetramethylsilane (TMS). One of the major factors influencing chemical shifts is substitutent electronegativity. However, there is an inductive effect; even oxygen (EN 3.5) has higher EN than silicon (EN 1.7), silicon has d-orbital lacking electron, so lone pair electrons from oxygen trend to be around silicon atom instead. Moreover, benzene ring also gives its crowded electrons to oxygen which are further to silicon. The NMR resonance of silicon in this product consequently occurs at much upfield—low chemical shift—because of shielding. The shift of Si atom in the the product occurs at -140 ppm as compared with that of the Si atom in the tetramethylsiloxane (($CH_3O)_4Si$) which appears at -79.2 ppm.
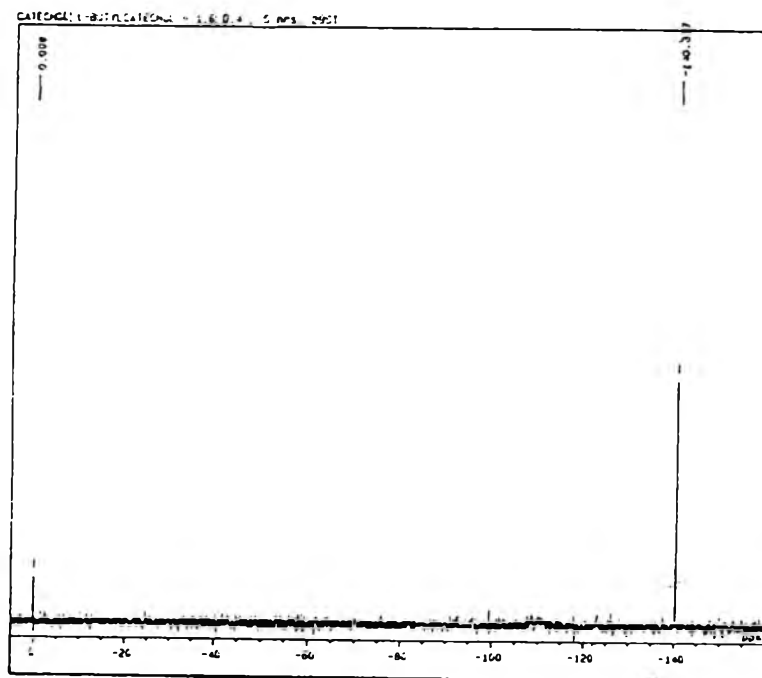
Figure 3.14 ^{29}Si NMR spectrum of a synthesized product.

3.2.4 X-Ray Diffraction (XRD)

X-ray diffraction is the traditional method of crystallographic structure determination. The scattering from an individual atom can be represented by its own particular "scattering factor" to represent the scattered amplitude, which will be a function of direction, f(θ), where 2θ is the angle between the direction in which the amplitude is measured and the direction of the incident radiation. The XRD patterns of starting material, silica, and one of the product are demonstrated in figures 3.15 and 3.16, respectively. The pattern of the product showing sharp peaks indicates that the product is in crystalline whereas silica shows broad peaks of an amorphous material. The maximum intensity 2θ peak is at 8.3. The other prominent peaks are at 12.1, 13.9, 15.9, 16.7, 18.5, 20.6, 22.8, 23.5 and 25.3.
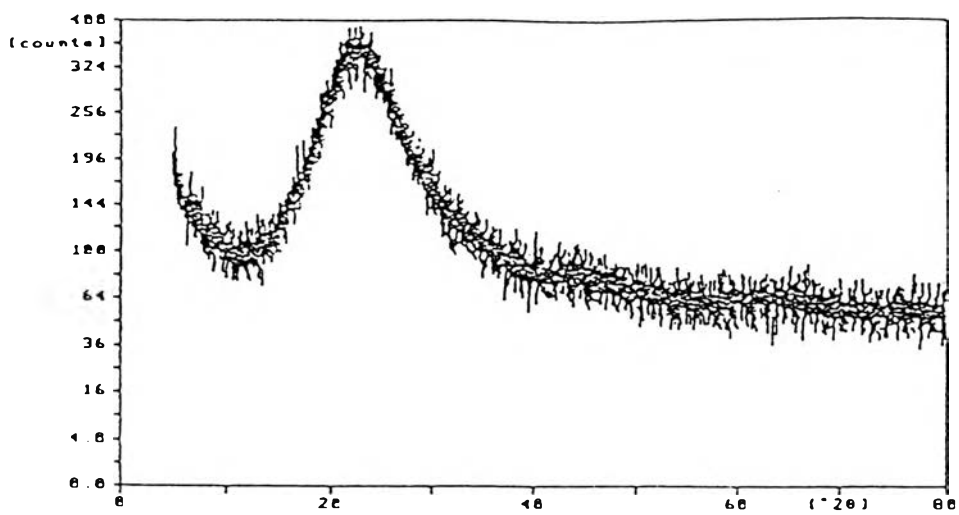
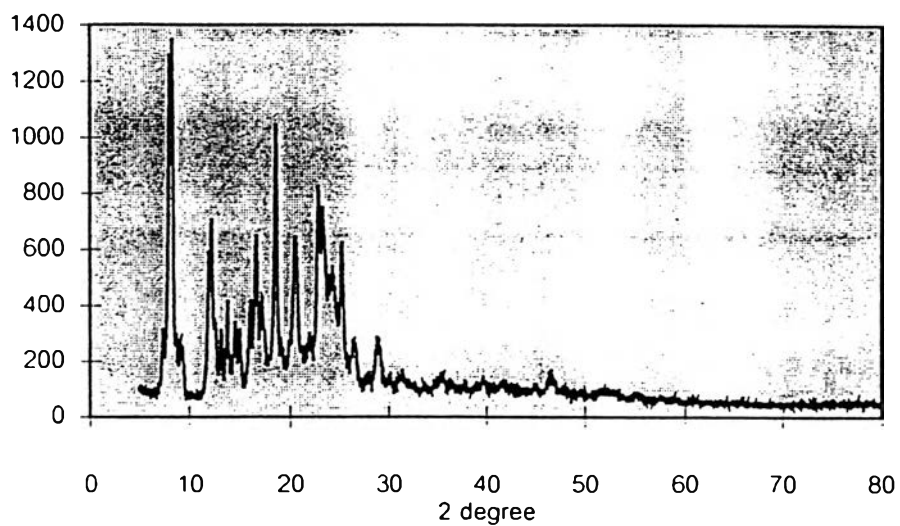Figure 3.15 XRD pattern of starting material, silica.

Figure 3.16 XRD pattern of a synthesized product.

Figure 3.17 demonstrates the XRD pattern of synthesized products in some mole ratios at 5-hour reaction time. The 2θ peak at 5.7 appears when the mole proportion of t-BUT is increased over than the ratio of CAT:t-BUT = 1.5:0.5, and the intensity of the maximum peak at 8.3 decreases. The maximum peak disappears at the mole ratio more than 1.0:1.0; and the peak at 5.7 becomes the maximum one instead. Moreover, as the amount of t-BUT is increased, the peak pattern of the product becomes broader, indicating more amorphous behavior. This results from the obstruction of ladder structure, which displays crystalline behavior, by the bulky group, t-butyl. The product without any CAT in the reaction shows the broadest pattern as the result from the most amount of bulky group. The reaction time affects the product characteristic as well, see figure 3.15. The more the reaction time is used, the more the product displays crystalline phase until the reaction time reaches 5 hours, which can be affirmed by TGA and FTIR. 7- and 9-hour reaction time products reveal broader peaks indicating more silica left in the products. Again, the backward reaction might occur when the reaction was let undergo after the proper reaction time was reached.

The amount of catalyst, TETA, has also an influence on the product properties as well, see figure 3.16. The XRD patterns of less than 50 mole%TETA products look similar to that of silica. Although the 66.68% and the 83.33%TETA ones show sharper peaks, their 2θ peaks between 15-30 degree are still broad meaning that there is still some remaining silica. This supposition can be assured by TGA results which shows higher percent ceramic yield, except the 100%TETA one. The product is in crystalline phase, meaning that the amount of catalyst should not be less than 100 mole%TETA.
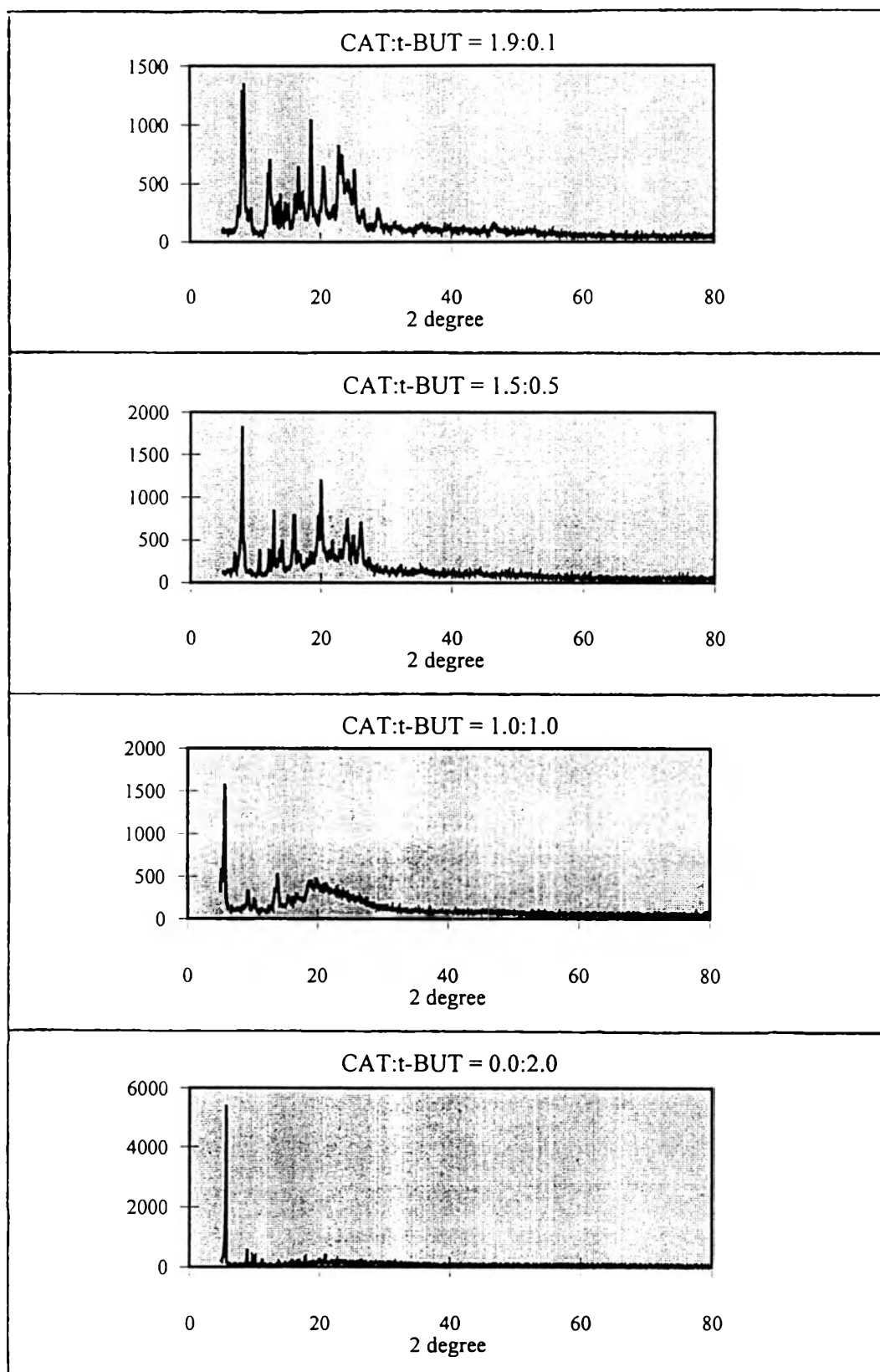
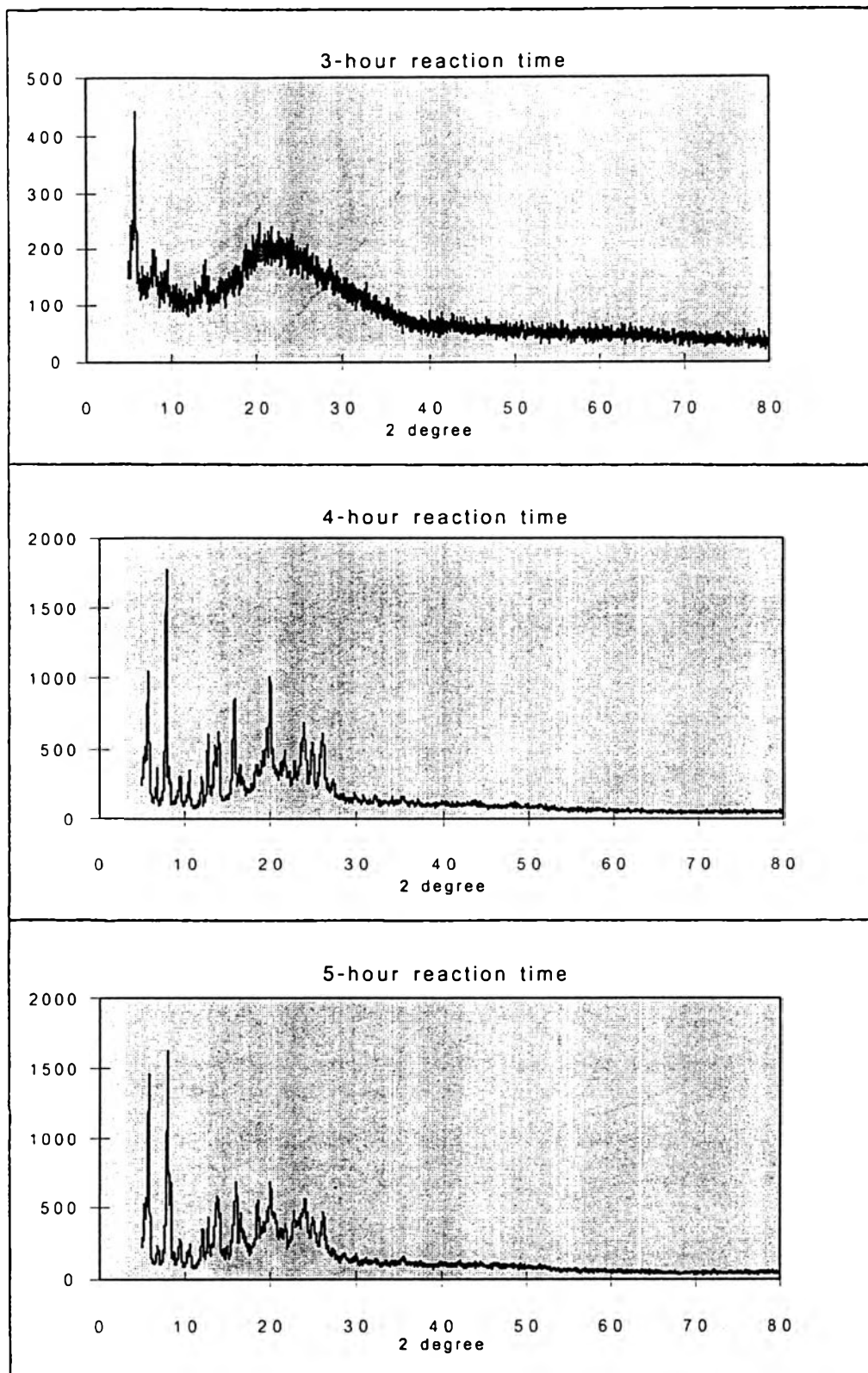Figure 3.17 XRD pattern of some mole ratio variation products.

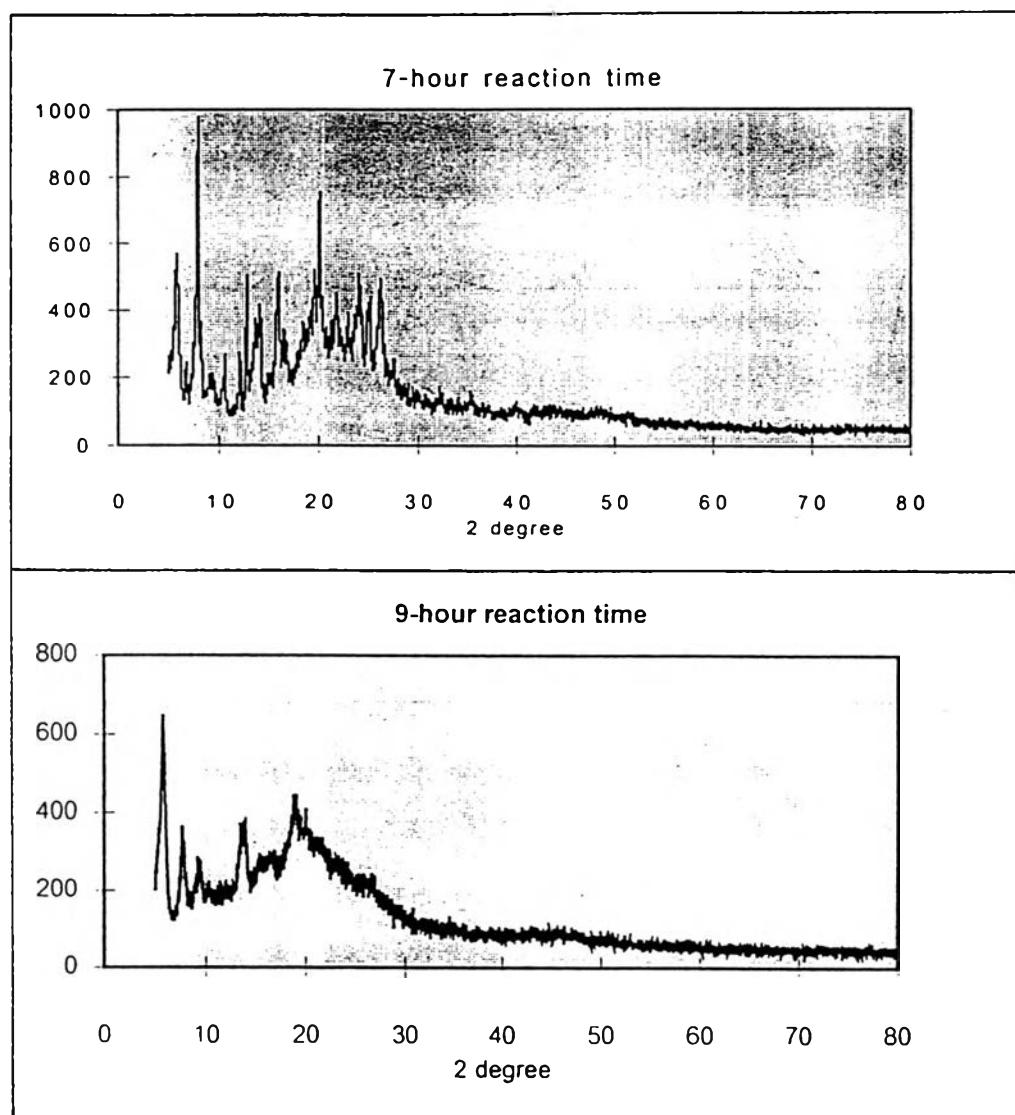Figure 3.18a XRD pattern of reaction time variation products.

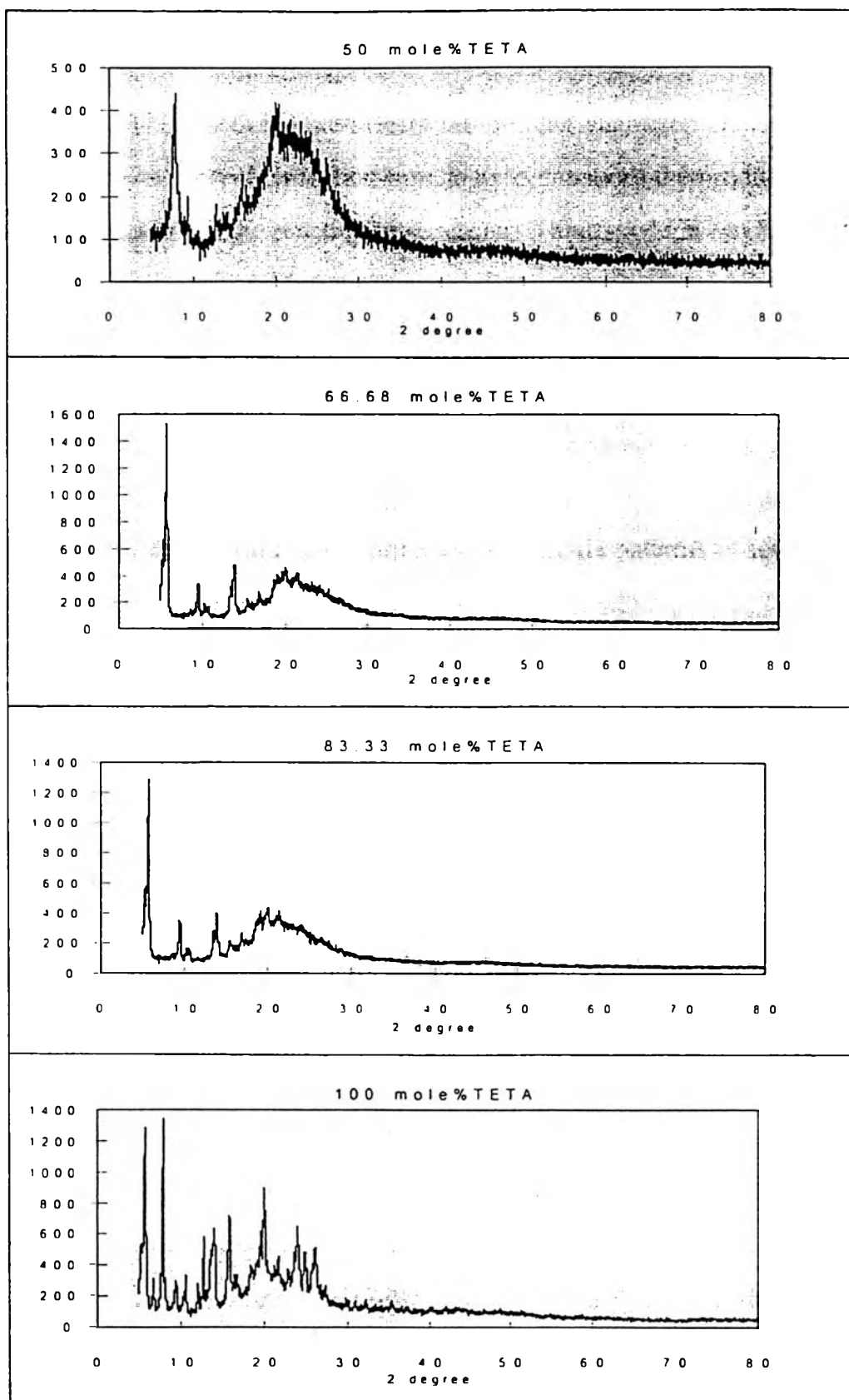Figure 3.18b XRD pattern of reaction time varition products.

Figure 3.19 XRD patterns of TETA variation products.

The reaction time affects the product characteristics as well, see figure 3.18. The longer reaction time, the more the product displays crystalline phase until the reaction time reaches 5 hours, which can be affirmed by TGA and FTIR. 7- and 9-h reaction time products reveal broader peaks indicating more silica left in the products. Again, the backward reaction might occur when the reaction was let undergo after the proper reaction time was reached.

The amount of catalyst, TETA, has also an influence on the product properties as well, see figure 3.19. The XRD patterns of less than 50 mole%TETA products look similar to that of silica. Although the 66.68% and the 83.33%TETA ones show sharper peaks, their 2θ peaks between 15-30 degree are still broad meaning that there is still some remaining silica. This supposition is supported by the TGA results which show higher percent ceramic yield, except the 100%TETA one. The product is in crystalline phase, meaning that the amount of catalyst should not be less than 100 mole%TETA.

3.2.5 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry is a standard technique used for measuring transition temperatures. Phase transitions, such as liquid crystal $\longrightarrow$ isotropic, or crystal$\longrightarrow$ nematic, which require the input of additional thermal energy, show up as endothermic peaks on heating. The position of the maximum of the peak is commonly taken as the transition temperature. [Donald, A.M.; 1992] Figures 3.20-3.22 show DSC profiles of each mole ratio at 5-h reaction time. Generally, the product shows 3 endothermic peaks on heating, but no exotherm appears on cooling at all because of the degradation of the product at elevated temperature with slow heating rate. The first endotherm occurs at around 250-285 °C, and the second one appears in the range of 285-315 °C, as well as the last one exhibits between 355 °C and 380 °C. Note that the peaks shift to slightly higher temperatures at higher mole ratio of t-BUT.

The first two endotherms are probably identified with the crystal-nematic and the nematic-isotropic transitions while the last one may due to the phase transition of the amorphous portion which contains too much *t*-BUT in molecules. Moreover, the endotherms of *t*-BUT variation products look different in appearance. The products from lower *t*-BUT amount (CAT:*t*-BUT = 1.9:0.1 to 1.2:0.8) give broad thermograms while those from higher amount of *t*-BUT show sharper ones. The third endothermic peaks is obviously higher as the amount of *t*-BUT is increased while the XRD results show that the products are more amorphous. In the ratio of 1.1:0.9 to 0.8:1.2, the first peak seems to merge into the second one, and consequently shows only two chief peaks. This could be only a tentative interpretation of the phase transitions of each endotherm.

With the reaction time variation, no peak appears at all by heating from room temperature to 450 °C for 1-h and 2-h reaction times which is the same as that of silica. The peaks are first observed when the reaction time reached 3 hours, and they look broader for 4-h and 5-h products. Amazingly, 7-h and 9-h products give sharper and higher peaks of DSC profiles, see figure 3.23.

The variation of TETA was also investigated by DSC. The 16.67% TETA product does not give any peak at all like that of silica. The peaks start appearing at 33.33% TETA and are more obviously observed at 50% TETA. 66.68% and 83.33% TETA show sharper and higher peaks than those of 100%TETA. Figure 3.24 demonstrates DSC profiles of the products at varied amount of TETA.
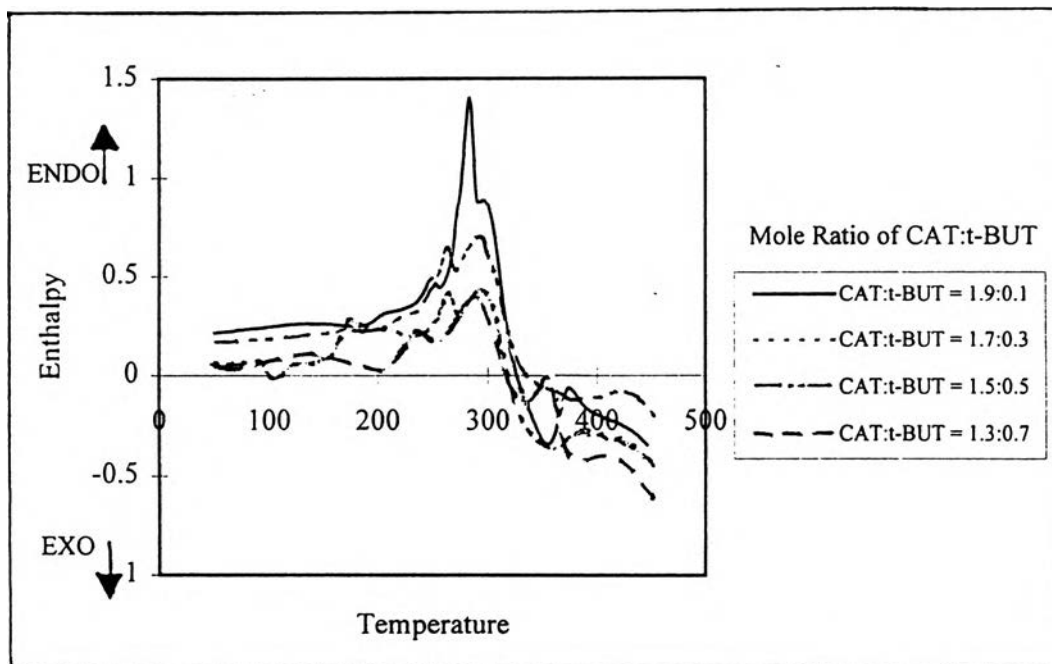
Figure 3.20 DSC profiles of some mole ratio variation products.
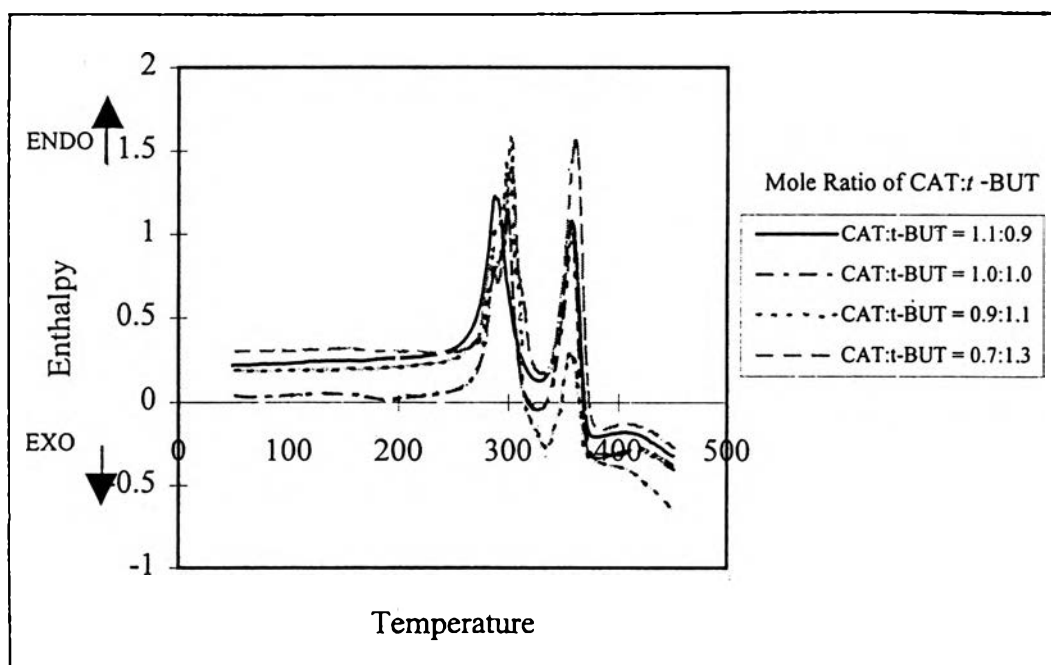

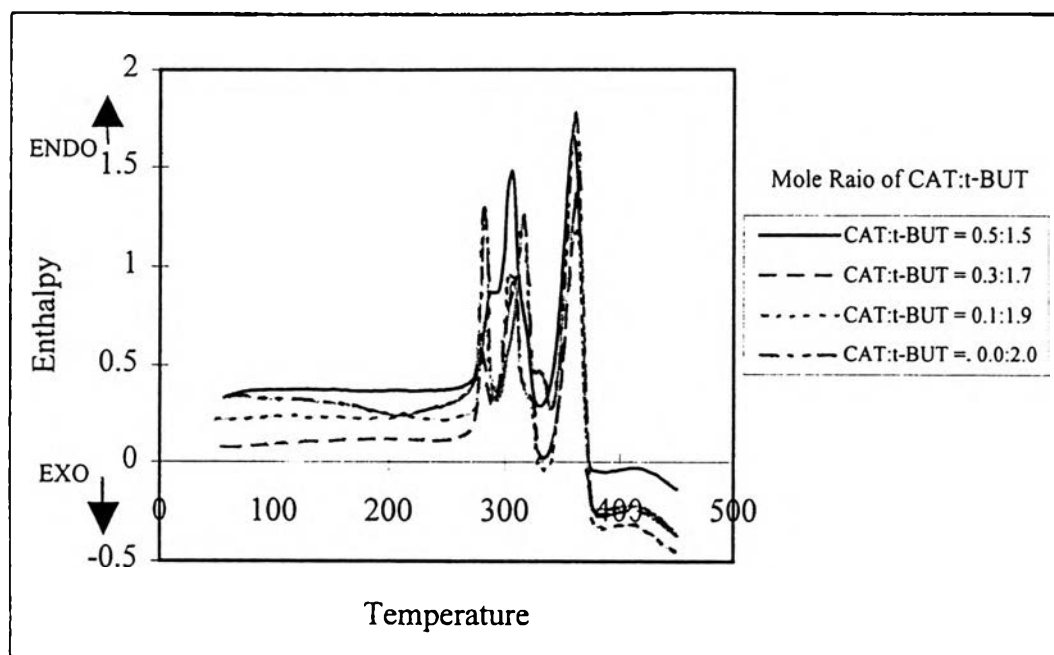Figure 3.21 DSC profiles of some mole ratio variation products.

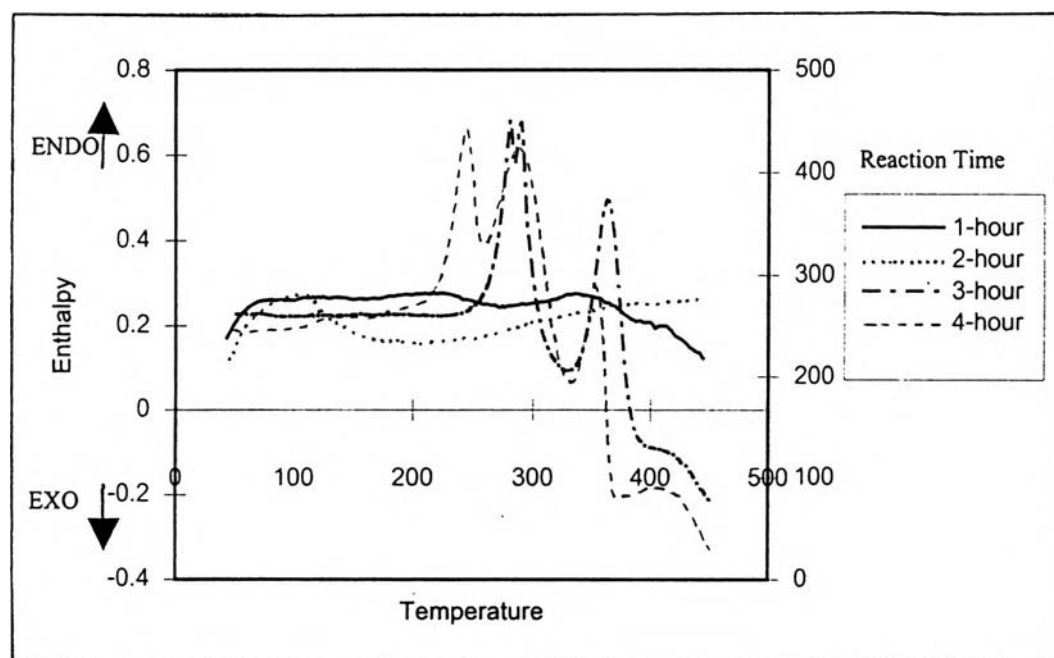Figure 3.22 DSC profiles of some mole ratio variation products.

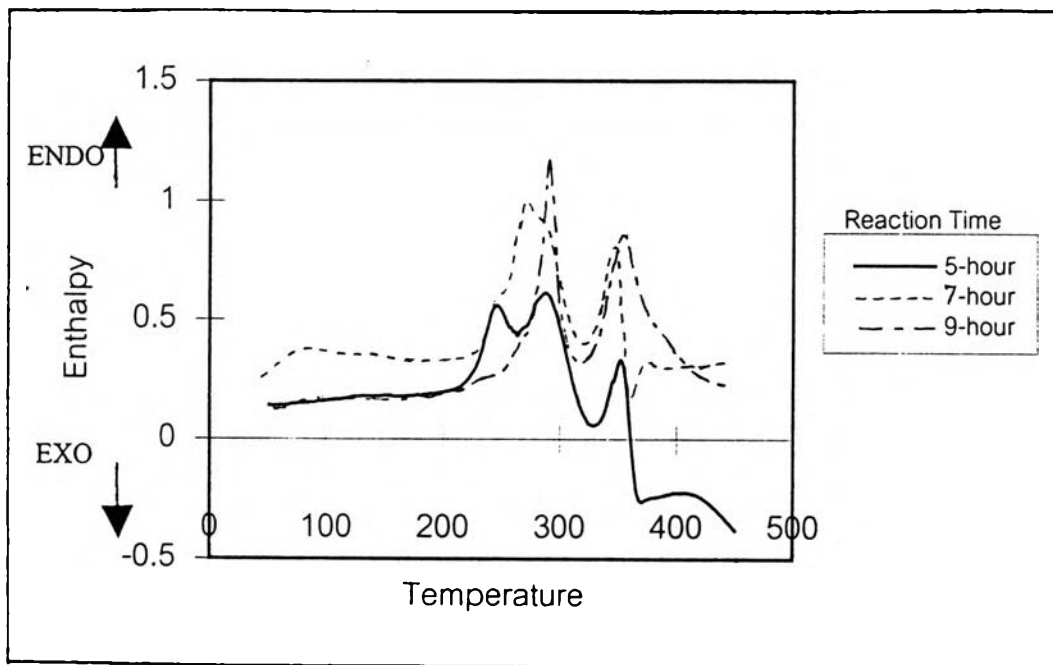Figure 3.23 DSC profiles of some reaction time variation products.

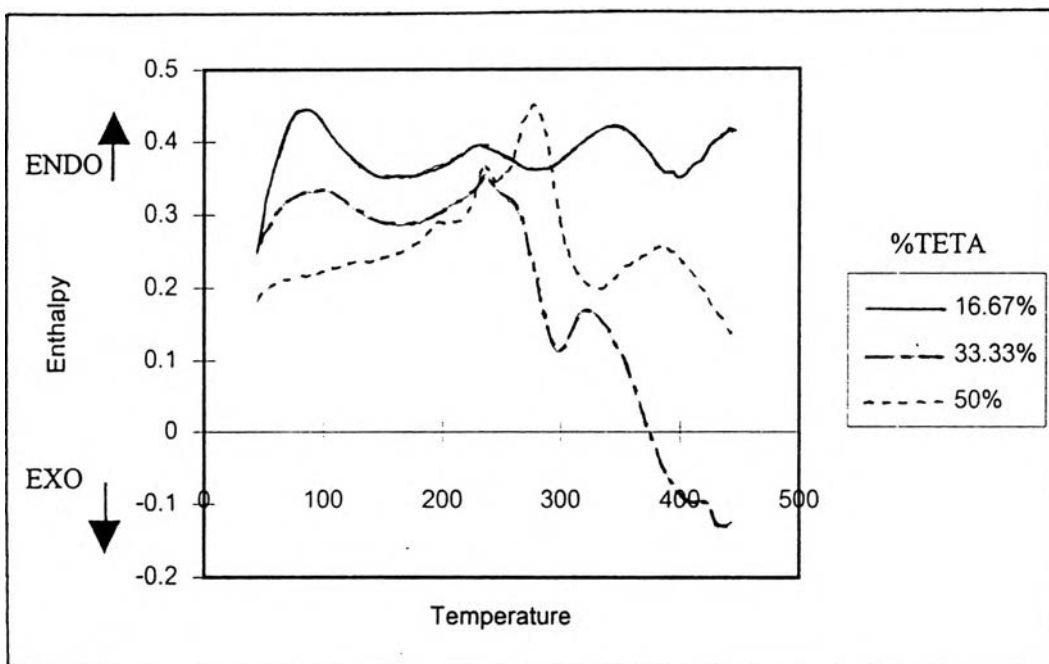Figure 3.24 DSC profiles of some reaction time variation products.

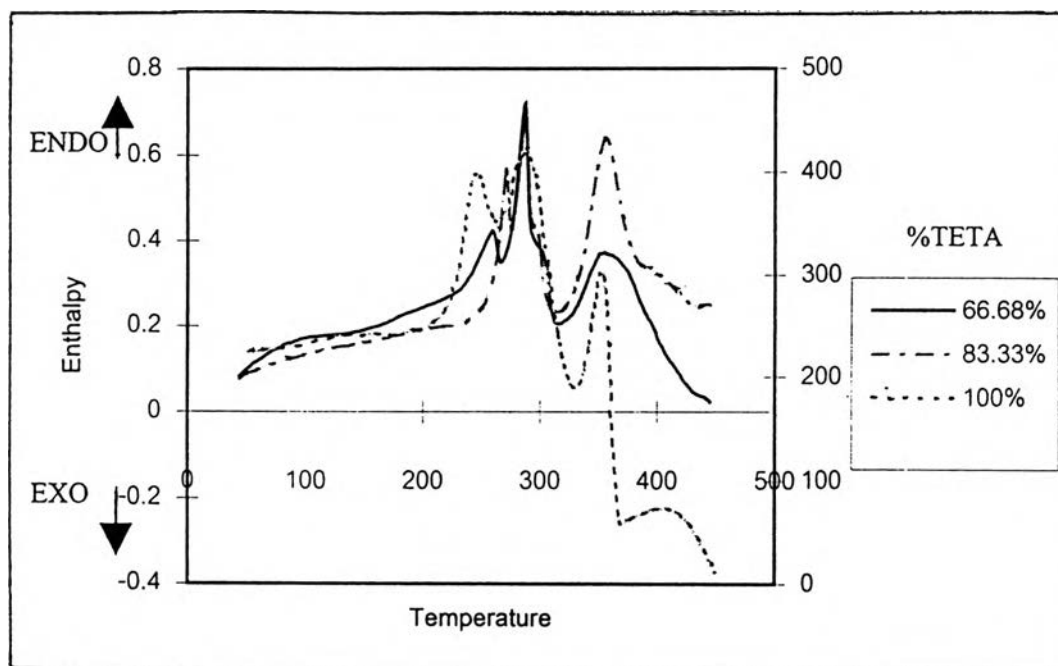Figure 3.25 DSC profiles of some %TETA variation products.

Figure 3.26 DSC profiles of some %TETA variation products.

3.2.6 Thermogravimetric Analysis (TGA)

TGA is used to characterize the decomposition temperature and thermal stability of materials. The TGA profile of the product gives two regions of mass loss during heating process from room temperature to 950 °C under N_2/O_2 atmosphere. The first mass loss, occuring between 250°-350 °C, results from oxidative decomposition of organic ligands. The other mass loss, between 400°-800 °C, corresponds to the oxidative decomposition of remaining organic residue in the product.

The theoretical percent ceramic yield is expected to be from 25% to 17% with the mole ratio increment of t-BUT from 0.1 to 2.0. The experimental percent ceramic yield of 0.1 mole ratio t-BUT product is about 19% which is less than the theoretical one. It might be because there is some unreacted organic raw material left in the product. Surprisingly, the percentage

ceramic yield increases as the amount of t-BUT is increased until the mole ratio reach 0.9:1.1 of CAT:t-BUT which gives the highest yield, ~40%. The percent ceramic yield trends to increase because when t-BUT attaches to SiO_2, its bulky t-butyl group, even enchancing nucleophilic feature, obstructs other molecules of both CAT and t-BUT from reacting with SiO_2. Consequently the more t-BUT in the reaction, the more difficult for both CAT and t-BUT to join in the reaction. Until the amount of t-BUT is further increased much more than that of CAT, %ceramic yield trends to decrease as expected. Nevertheless, the experimental percent ceramic yield is more than the theoretical ones from the result of the obstruction by t-butyl group as well. Figure 3.25-3.26 and figure 3.27 show TGA profiles and the trend of %ceramic yield of some mole ratio variation products respectively.

In the case of reaction time variation, ceramic yields are very high for the first two hours and trends to decrease when the reaction was let to continue for a long time, see figure 3.28 and figure 3.29. Anyway too long reaction times, 7 h and 9 h, give a reversed trend meaning that there is more silica left probably from the backward reaction verified by the results of FTIR and XRD which are discussed above. The amount of the catalyst TETA also affects the ceramic yield of the product. The more the TETA used, the less the ceramic yield as seen in figure 3.30 and figure 3.31.
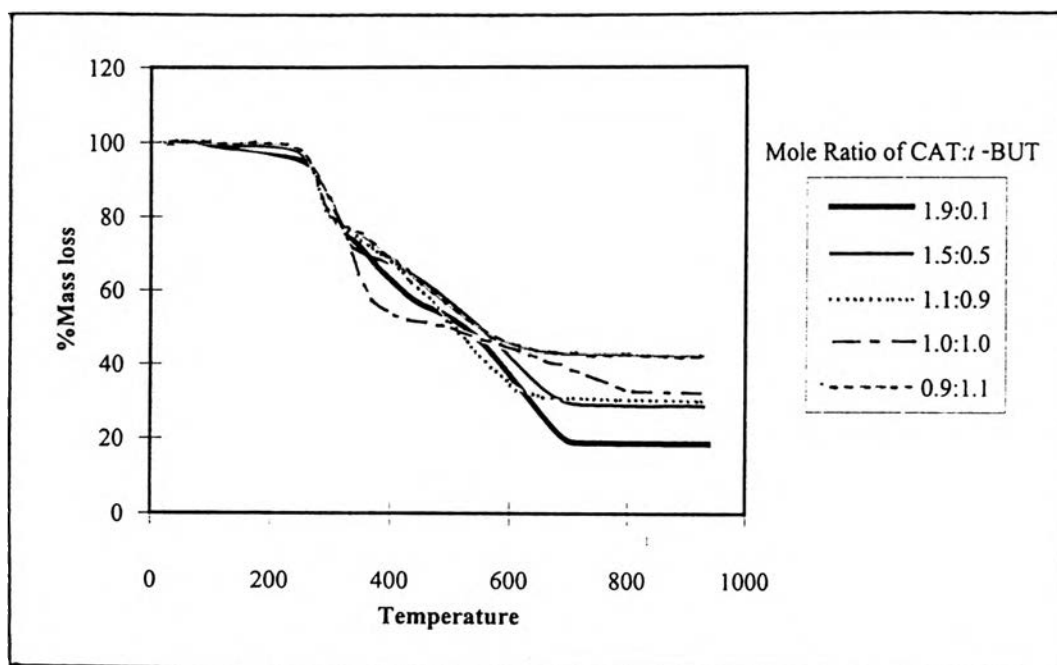
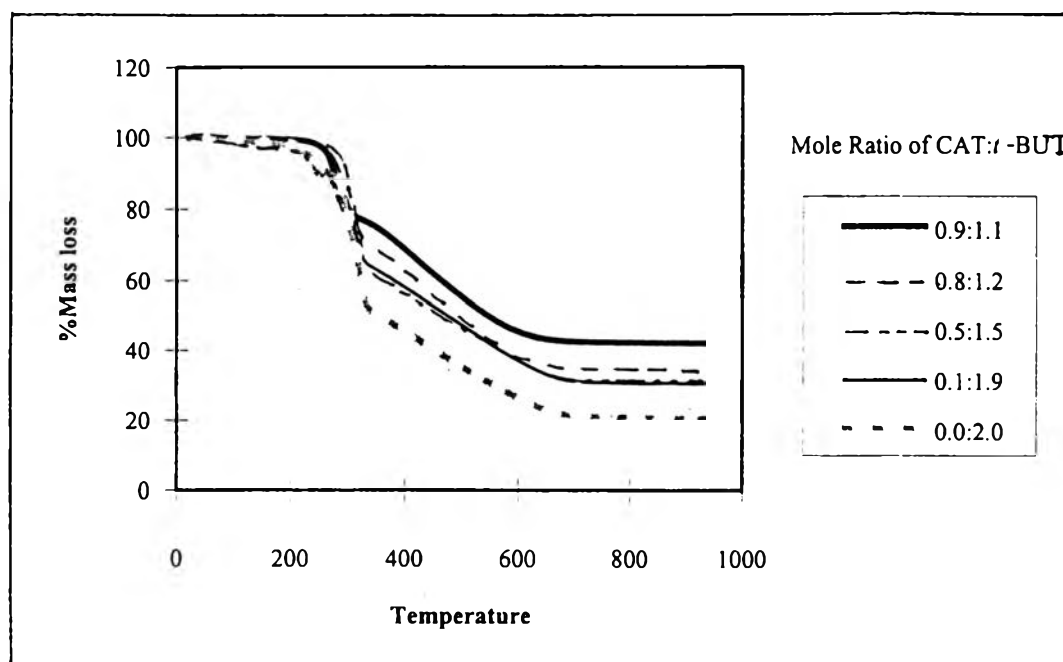Figure 3.25 TGA profiles of some mole ratio variation products.

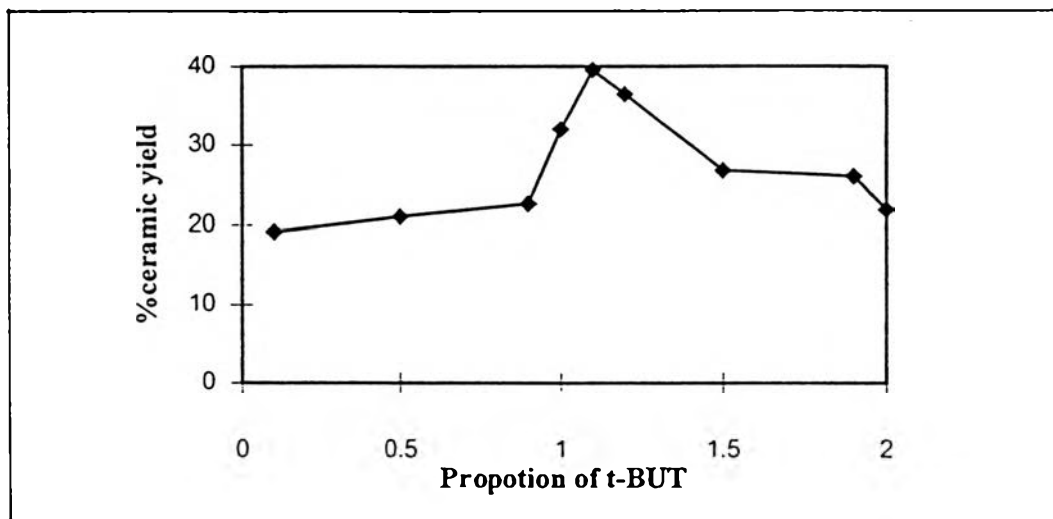Figure 3.26 TGA profiles of some mole ratio variation products.

Figure 3.27 Percent ceramic yield of some mole ratio variation
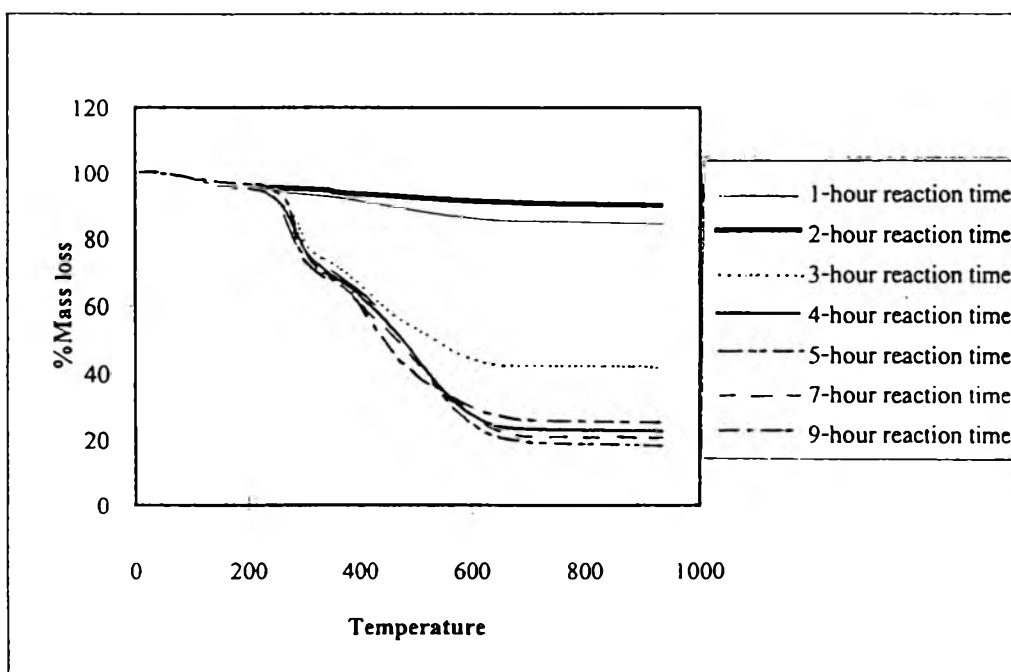products.

Figure 3.28 TGA profiles of reaction time variation products.
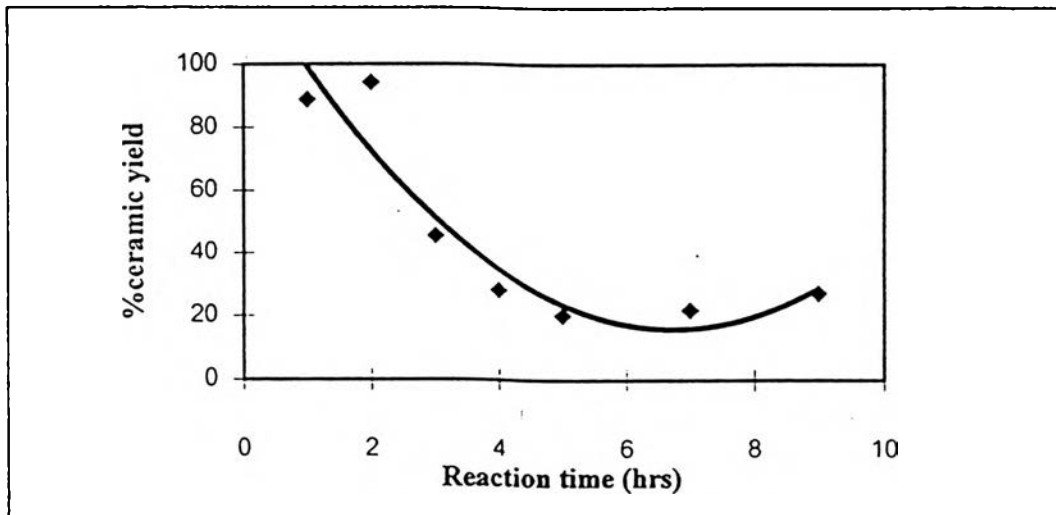
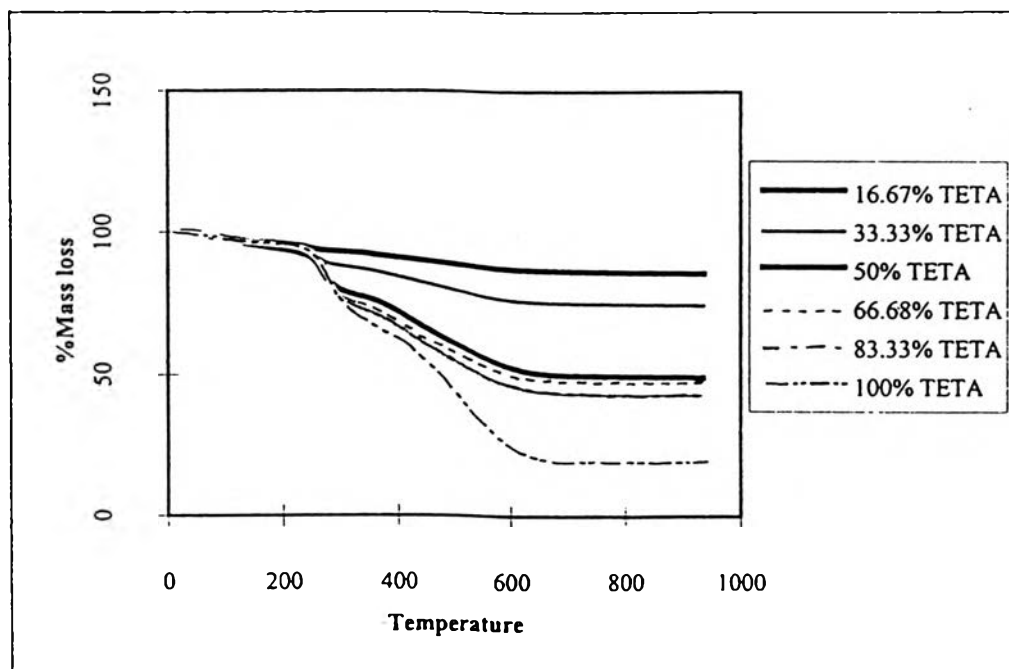Figure 3.29 Percent ceramic yield of reaction time variation products.

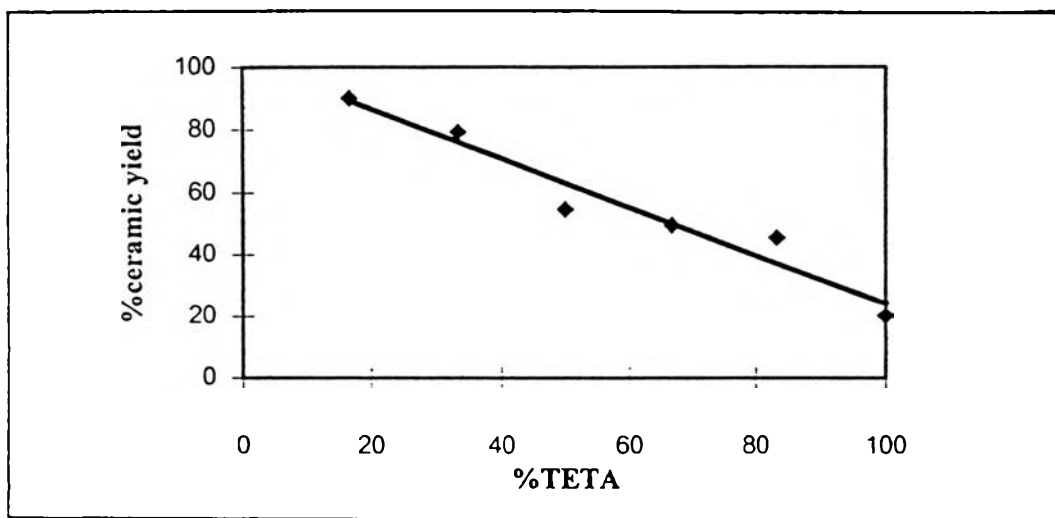Figure 3.30 TGA profiles of %TETA variation products.

Figure 3.31 Percent ceramic yield of %TETA variation products.