



CHAPTER IV

Results and Discussion

4.1 Preparation and purification of liquid natural rubber

4.1.1 Determination of dry rubber content (DRC)

DRC was determined by the method described previously [19]. It was found that the percentage of DRC in the latex was 59.60 %. This latex was used to prepare liquid natural rubber.

4.1.2 Preparation of LNR by chemical treatment

LNR was prepared by the method called "chemical oxidative degradation" using a phenylhydrazine/oxygen redox system. This technique was described previously by Brosse et al. [5]. Brosse et al. indicated that the reaction was dependent upon phenylhydrazine concentration, temperature and reaction time. The study was conducted by varying phenylhydrazine concentration of about 4-15 % (by wt of DRC), reaction temperature between 50-70 °C and reaction time between 0-100 h.

The results showed the reduction of rubber molecular weight from 200,000 to approximately 10,000.

In this investigation, the depolymerization reaction was carried out at 80 °C with the air flow rate of 2-3 liter/minute, phenylhydrazine concentration of 10 % (by wt of DRC) and reaction time of 0-30 h. The results are tabulated in Table 4.1, and the plot of molecular weight of LNR vs reaction time is shown in Figure 4.1.

The results suggested that the reaction time influenced the degree of depolymerization. The molecular weight of rubber latex decreased rapidly in the first 5 hours and then decreased slowly as the reaction time increased to 30 hours. The reduction in molecular weight of rubber latex by this method was in the range of 140,000 to approximately 10,000.

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Table 4.1 Molecular weight of LNR at different depolymerization time

No	[Phenylhydrazine],% (wt/wt of DRC)	Depolymerization time, h	$\bar{M}_v \times 10^{-3}$	Remark
1	0	0	141.6	Non-degraded rubber
2	10	1	78.5	
3	10	3	37.1	
4	10	5	33.0	
5	10	10	23.0	
6	10	15	18.7	
7	10	20	16.2	
8	10	30	11.0	

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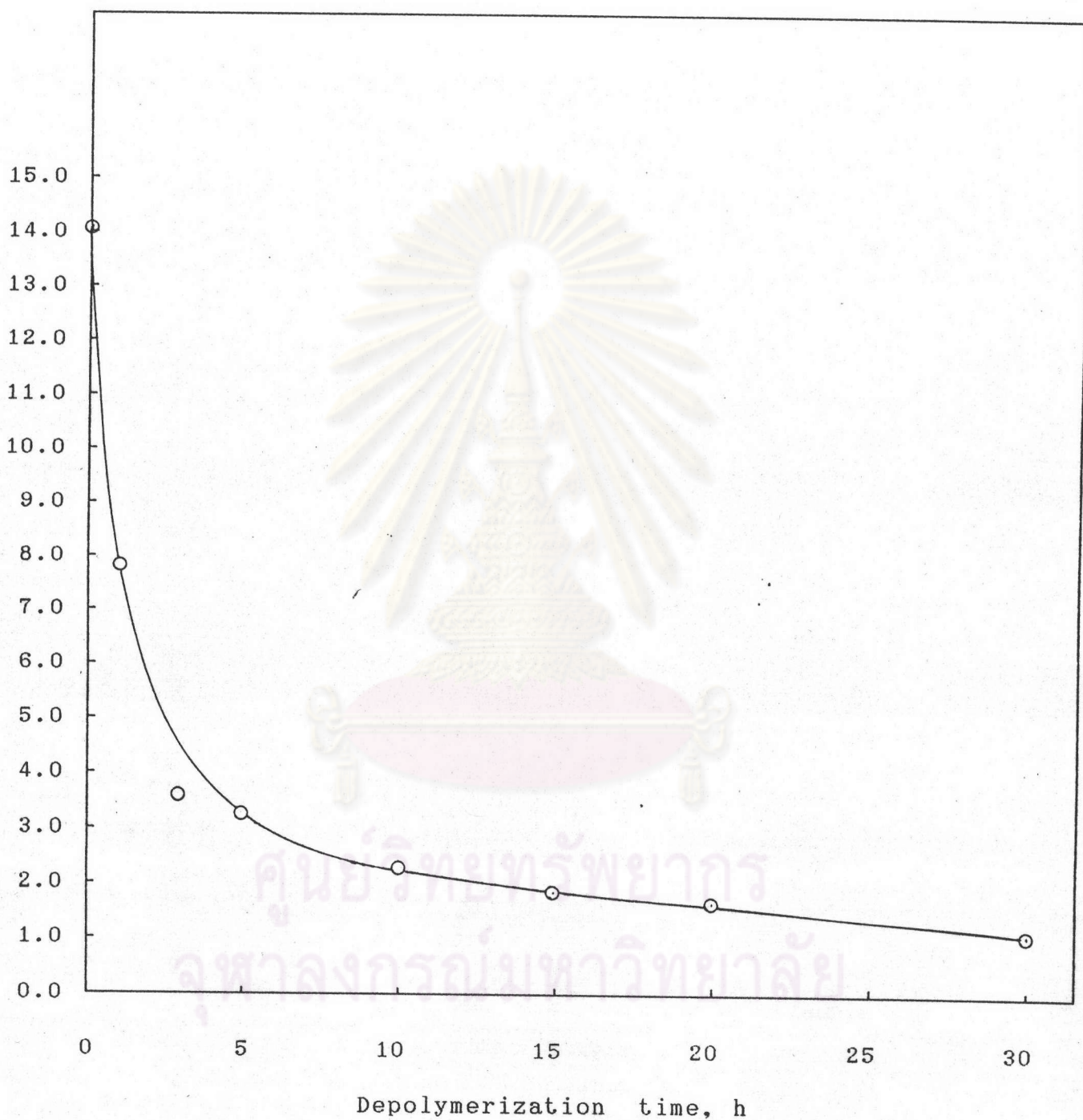
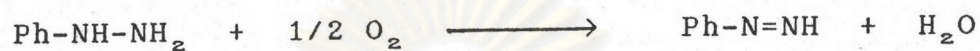
$\bar{M}_v \times 10^{-4}$ 

Fig 4.1 Plot of depolymerization time vs molecular weight of LNR

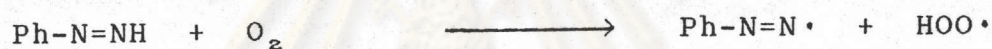
The possible mechanism involved in the depolymerization reaction of natural rubber was proposed previously by Barnard et al. [23] as follows:

1. Oxidation of phenylhydrazine to phenyldiimide

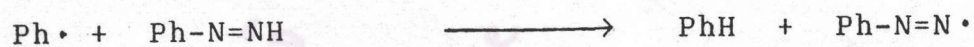


2. Decomposition of phenyldiimide

initiation



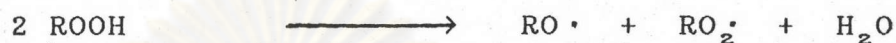
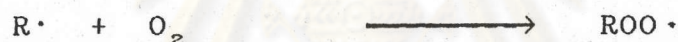
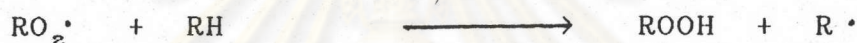
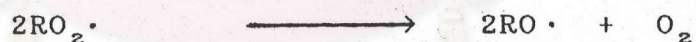
propagation



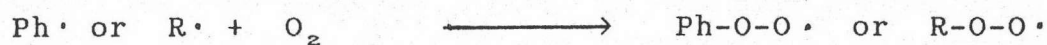
termination

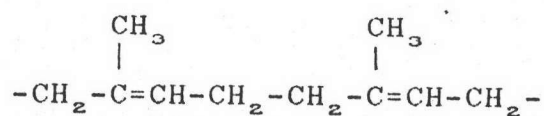


3. Autocatalysed thermal oxidation of hydroperoxide

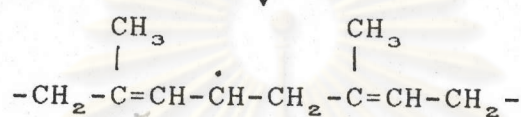
initiationpropagationtermination

4. Oxidation of natural rubber by phenylhydrazine / oxygen system

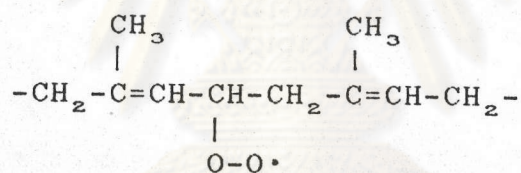
initiation

propagation

↓
ROO·



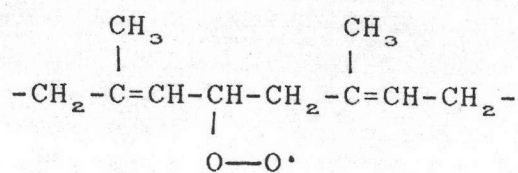
↓
O₂



↓
a. Intramolecular reaction

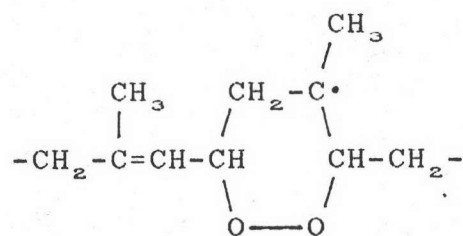
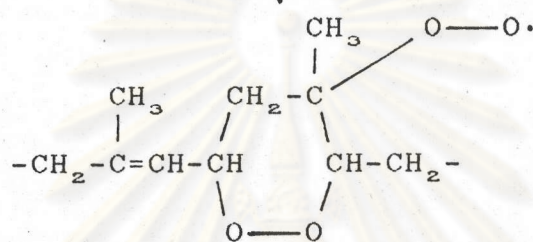
b. Intermolecular reaction

a. Intramolecular reaction

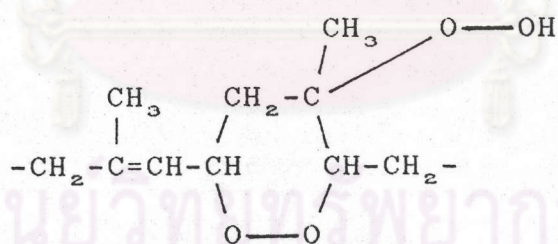


↓
addition to double bond

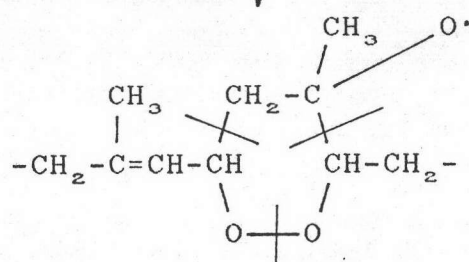
↓


 O_2


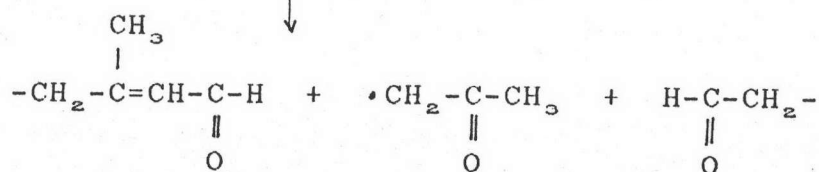
abstraction of hydrogen from
neighbouring molecules



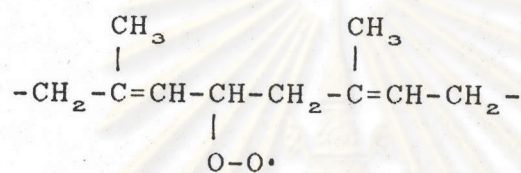
decomposition of hydroperoxide
to alkoxy radical



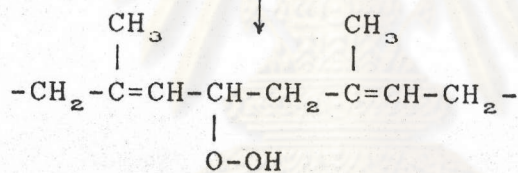
generally accepted decomposition
but not only reaction



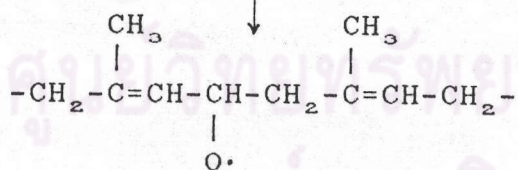
b. Intermolecular reaction



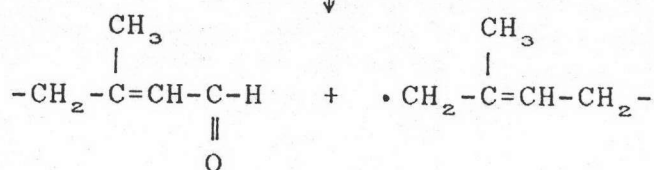
RH



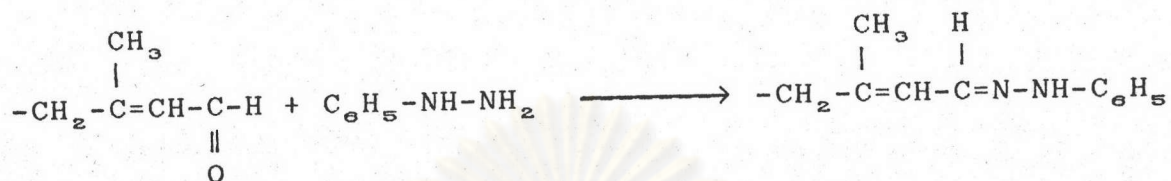
decomposition of hydroperoxide
to alkoxy radical



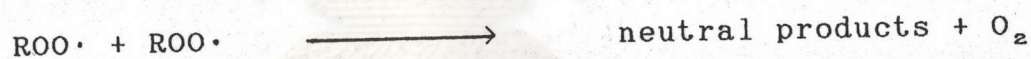
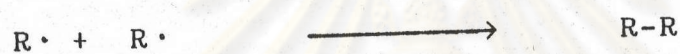
generally accepted decomposition
but not only reaction



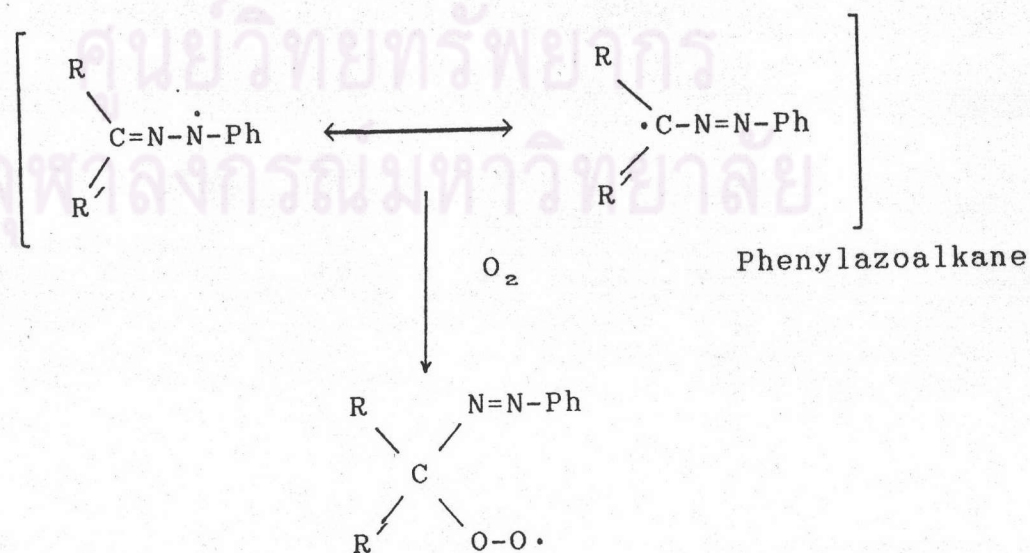
Then the carbonyl group of LNR reacted with an excess of phenylhydrazine to form phenylhydrazone end groups.

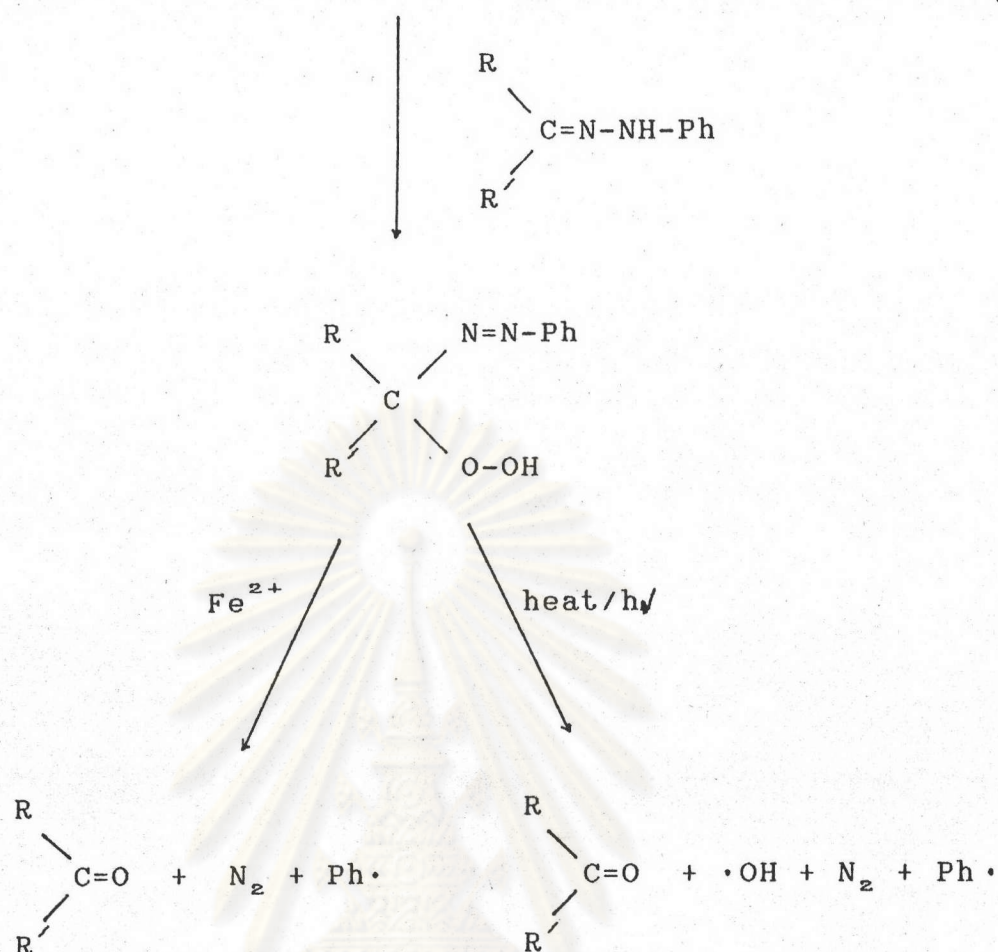


termination



5. Autooxidation of phenylhydrazone





4.1.3 Purification of LNR

In the preparation process of LNR, Teric 16A16 and phenylhydrazine were added to the rubber latex. In order to obtain the purified LNR, these two reagents had to be eliminated. So an appropriate solvent had to be used to dissolve these two reagents but not the LNR. From the experiments, it was found that Teric 16A16 and phenylhydrazine would dissolve completely in methanol while low molecular weight LNR was also slightly soluble in methanol.

Purification process was carried out twice by dissolving LNR in about a tenfold volume of toluene, filtered by means of suction filtration and then precipitated from excess methanol. After drying in an oven at 80 °C for 15 h, the first purified LNR was weighed and the percentage yield was calculated. The second purification process was performed using the same procedure as above but a mixed solvent of methanol/acetone (3/1 v/v) was used instead of pure methanol. The purified LNR was dried in an oven at 80 °C for 15 h and consecutively dried in vacuo at 80 °C for 15 h. The product was weighed and the percentage yield was calculated. The results are shown in Table 4.2.

The results suggested that after each purification step, a large decrease in percentage yield of LNR observed especially the item which used longer depolymerization time. The amount of LNR was decreased by about 13-23 % in the first purification step, and about 14-50 % in the second purification step. The remarkable decrease in percentage yield during the purification steps of LNR obtained from using longer depolymerization time was due to the fact that the longer the depolymerization time, the larger quantity of lower molecular weight LNR was obtained. This low molecular weight LNR is more

Table 4.2 Weight and percentage yield of LNR after each purification step.

No	Depoly- merization time, h	LNR precipitated from MeOH		LNR precipitated from MeOH/Acetone (3/1 v/v)	
		wt of LNR, g	% yield	wt of LNR, g	% yield
1	0	-	-	-	-
2	1	78.1	86.8	77.4	86.0
3	3	76.4	84.9	70.3	78.1
4	5	75.2	83.6	72.0	80.0
5	10	75.5	83.9	68.1	75.7
6	15	71.8	79.8	60.5	67.2
7	20	67.3	74.8	57.6	64.0
8	30	69.6	77.3	45.3	50.3

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soluble in methanol or methanol/acetone mixture than high molecular weight LNR. The mixed solvent of methanol/acetone was used in the second purification step since we wanted to eliminate non-rubber constituents, e.g. fatty acid, sterols, quebrachitol, all of which are soluble in acetone [24]. IR and ^1H NMR spectra are shown in Figure 4.2 and 4.3 respectively.



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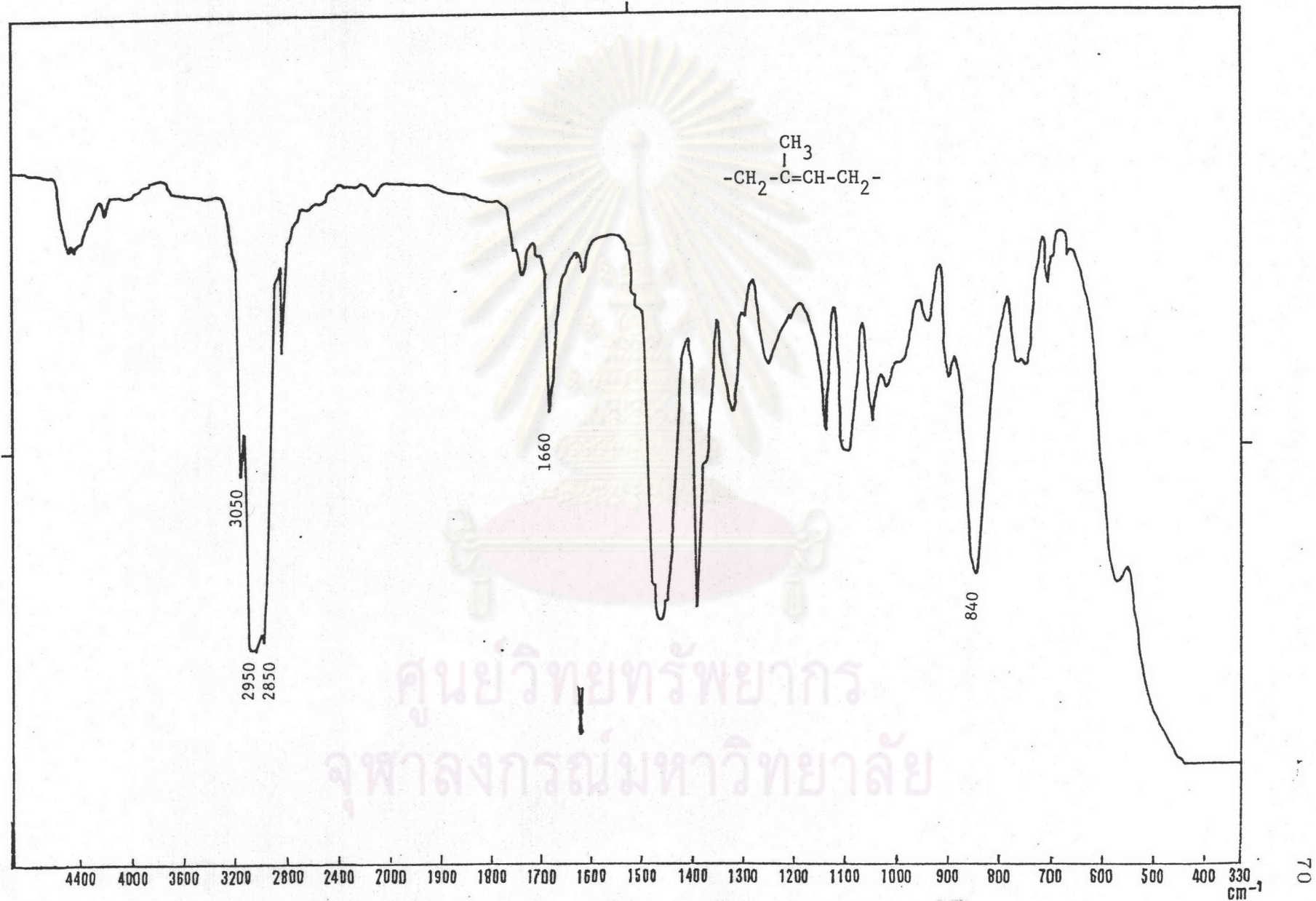


Fig 4.2 IR (neat) spectrum of liquid natural rubber

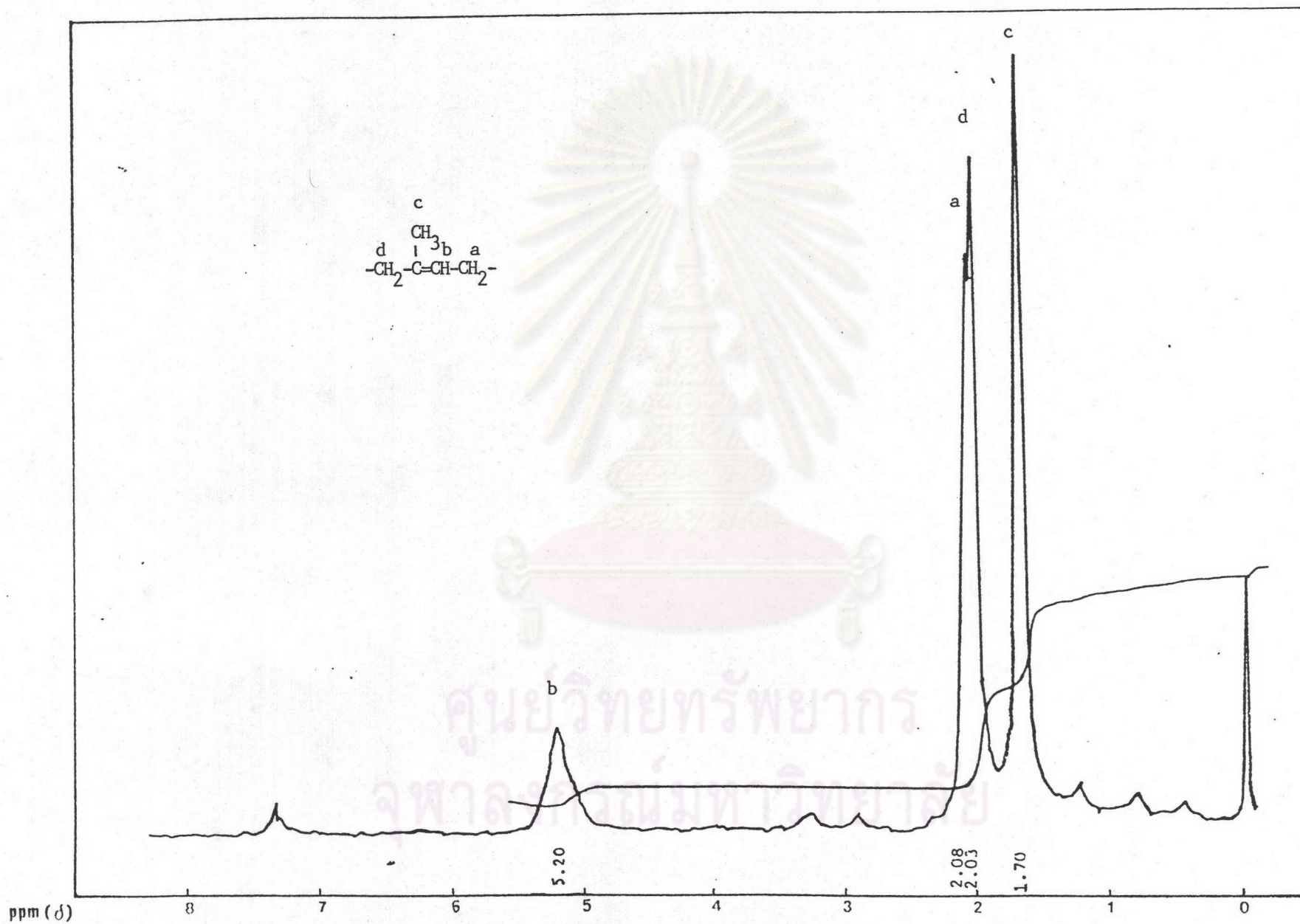


Fig 4.3 ^1H NMR (CCL_4) spectrum of liquid natural rubber

4.1.4 Molecular weight determination of LNR

The molecular weight of LNR was determined by viscosity measurement. The flow time of rubber solution was measured at 25°C using Ubbelohde viscometer. The concentrations of rubber solutions were varied from 0.6 to 1.0 % (wt/v) in toluene. The flow times of pure toluene were measured in the manner mentioned above.

The viscosity average molecular weight (\bar{M}_v) was calculated from the intrinsic viscosity, $[\eta]$, of the polymer solution using the Mark-Houwink relationship :

$$[\eta] = K (\bar{M}_v)^a$$

where the intrinsic viscosity, $[\eta]$, was obtained from the linear extrapolation of the plot of η_{sp}/c vs c to zero concentration as shown in Figure 4.4.

The values of K and a of cis-1,4-polyisoprene rubber in toluene at 25 °C were 5.0×10^{-4} dL/g and 0.67 respectively [25].

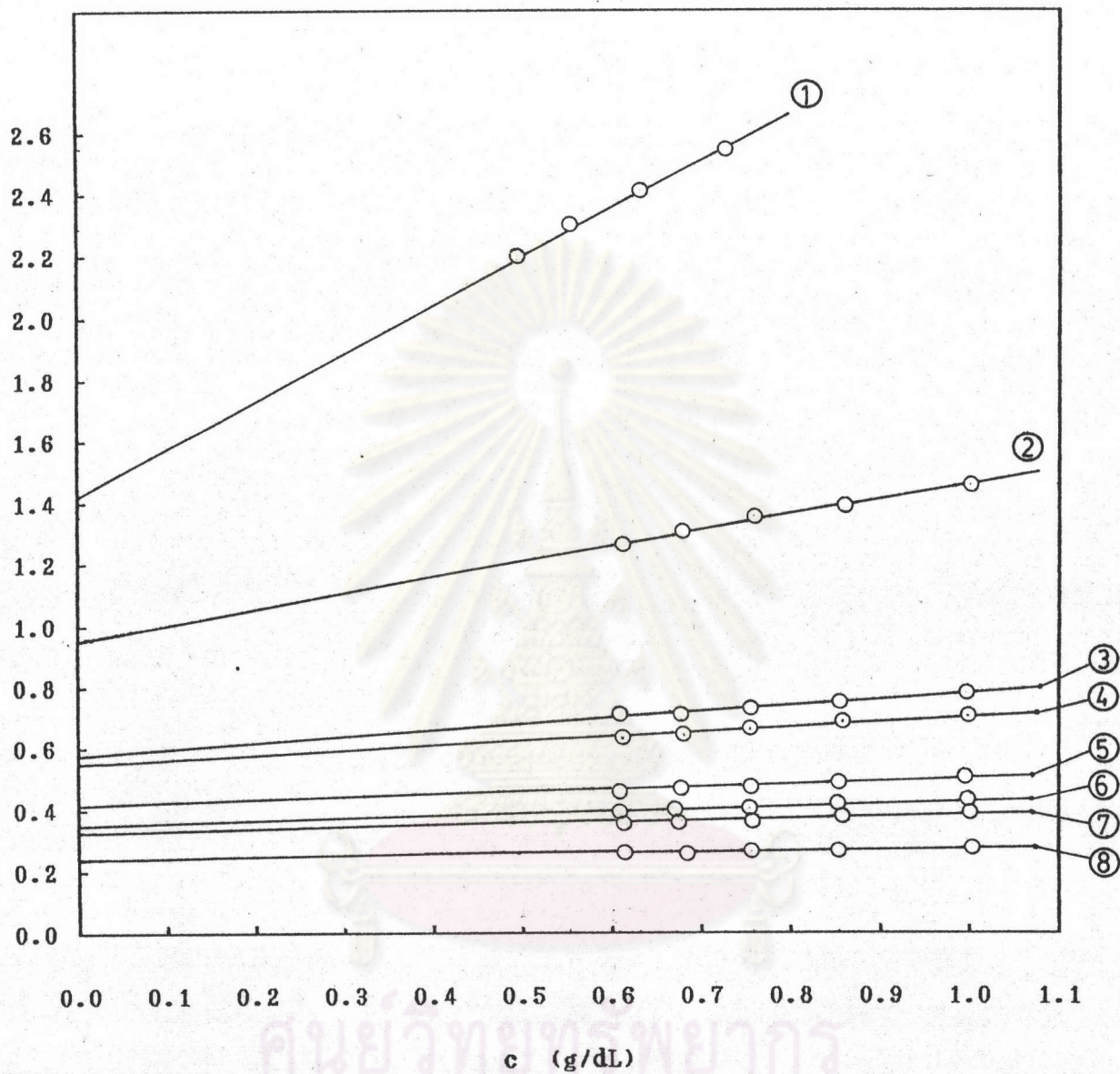
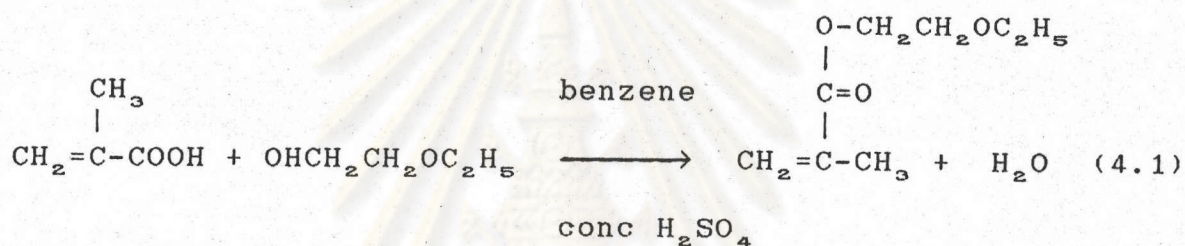
η_{sp}/c 

Fig 4.4 Plot of η_{sp}/c vs concentration of rubber solutions of different depolymerization times (t_d): $t_{d1} = 0$ h; $t_{d2} = 1$ h; $t_{d3} = 3$ h; $t_{d4} = 5$ h; $t_{d5} = 10$ h; $t_{d6} = 15$ h; $t_{d7} = 20$ h and $t_{d8} = 30$ h.

4.2 Preparation of 2-ethoxyethyl methacrylate

2-Ethoxyethyl methacrylate (2-EEMA) was prepared from the reaction of methacrylic acid with 2-ethoxyethanol in benzene using sulfuric acid as a catalyst and phenothiazine and 2,6-di-*tert*-butyl-p-cresol as inhibitors. The condensation reaction occurred under refluxing condition.



Methacrylic acid	2-Ethoxyethanol	2-Ethoxyethyl methacrylate
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The by-product, water, was removed as a binary azeotrope with benzene. Thus the condensation reaction could be driven almost to completion by this technique. The inhibitors system also prevented polymerization from occurring effectively since only a small amount of polymer was formed in the reaction flask during the removal of benzene and the purification step. This procedure gave more than 80 % yield of the desired monomeric ester. The IR and NMR spectra of this ester are shown in Figures 4.5 and 4.6, respectively.

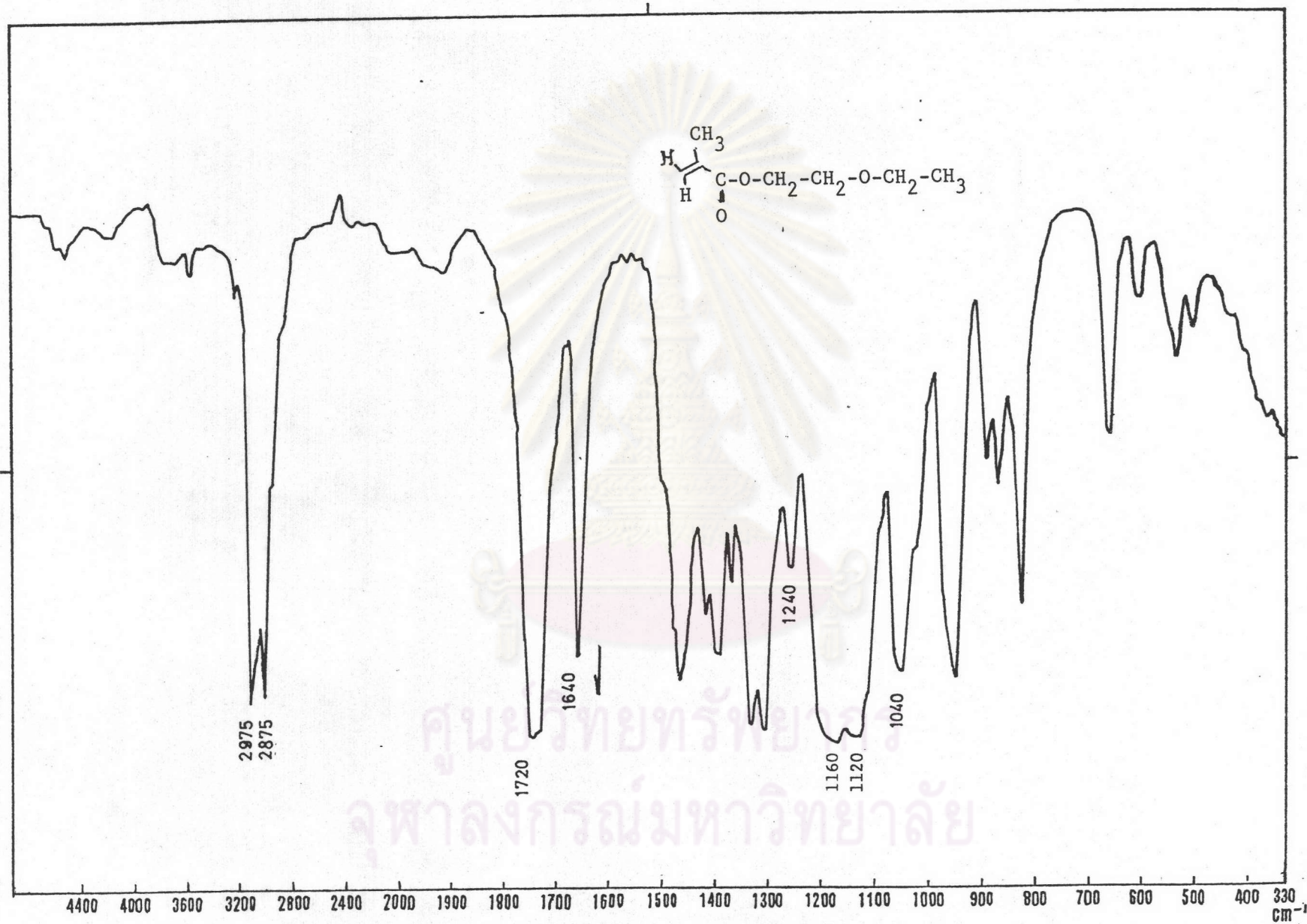


Fig 4.5 IR (neat) spectrum of 2-ethoxyethyl methacrylate

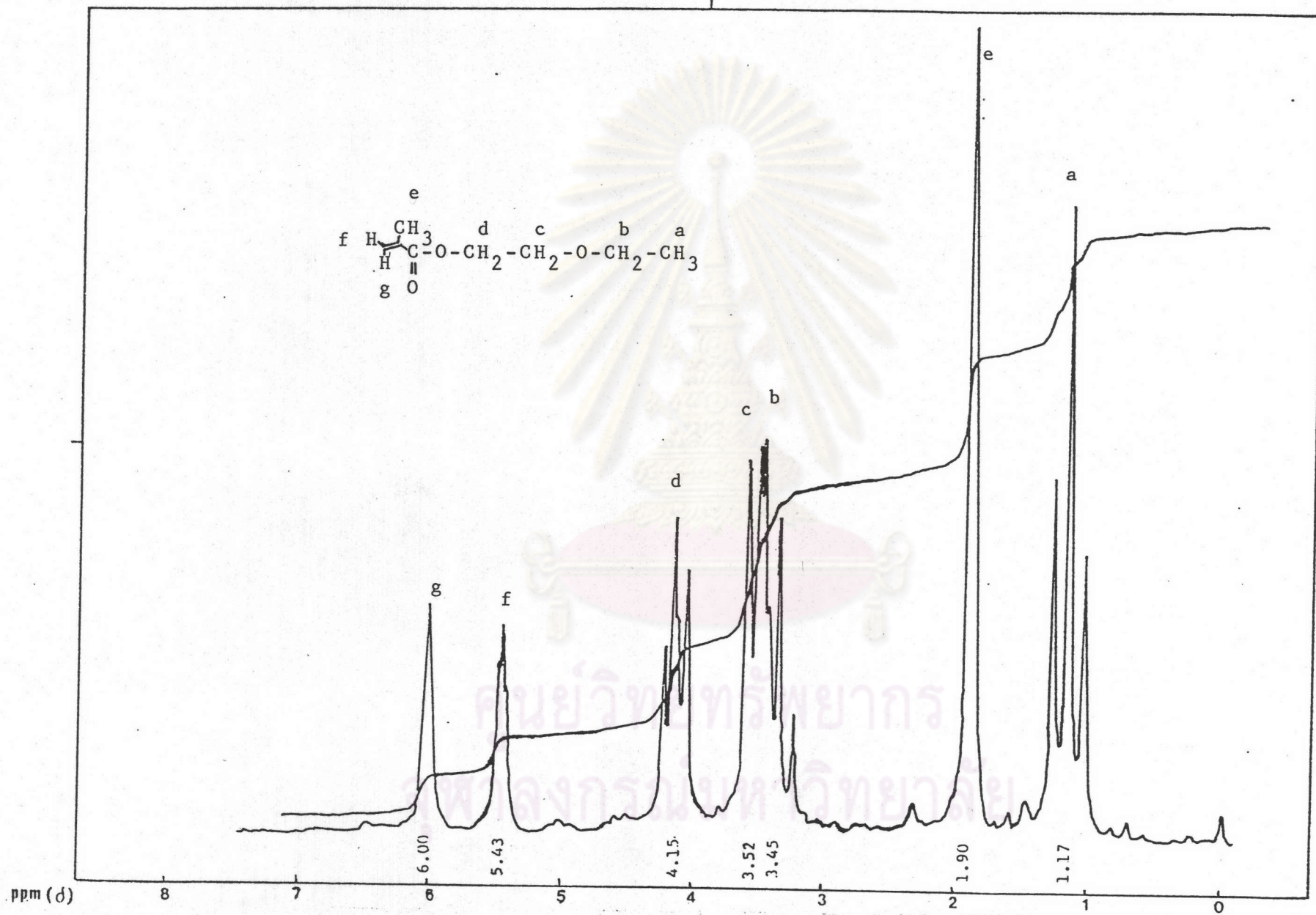
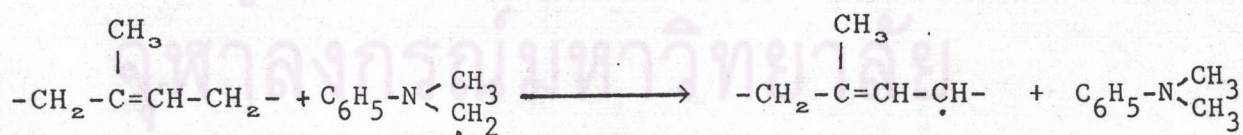
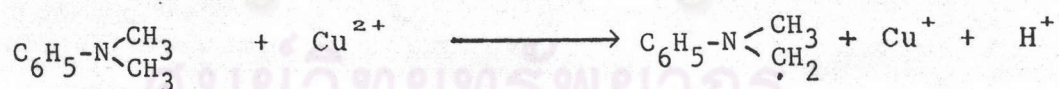


Fig 4.6 ¹H NMR (CCl₄) spectrum of 2-ethoxyethyl methacrylate

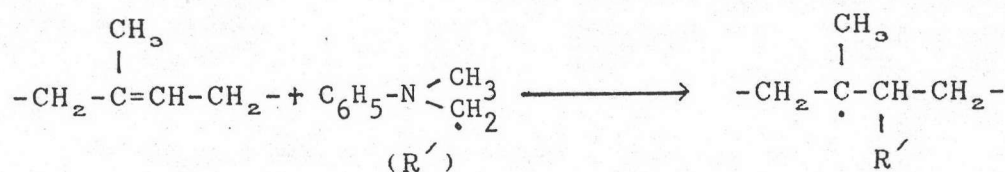
4.3 Preparation of graft copolymer of LNR

The grafting process by Lenka et al. [17] was used with some modification. In this method DMA/Cu²⁺ system was used as a redox initiator. Graft copolymerization starts by the reaction between DMA and Cu²⁺ to form methyl anilinomethyl radical which can abstract a hydrogen atom from rubber backbone, and results in a rubber macroradical. This rubber macroradical then interacts with 2-ethoxyethyl methacrylate (2-EEMA) to produce graft copolymer. The mechanism is suggested as follows:

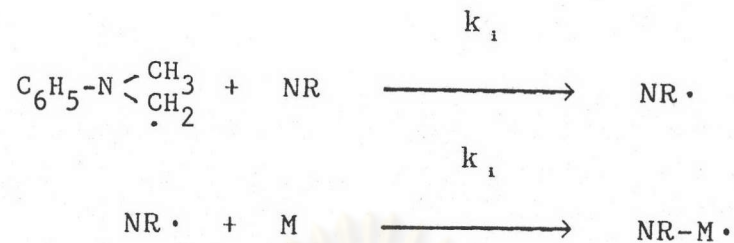
initiation



or

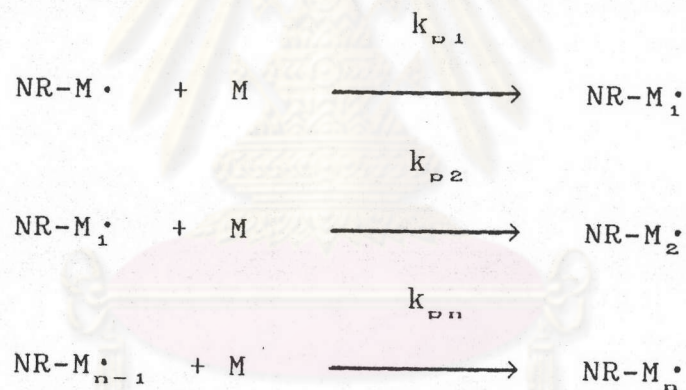


The initiation step can generally be represented as:

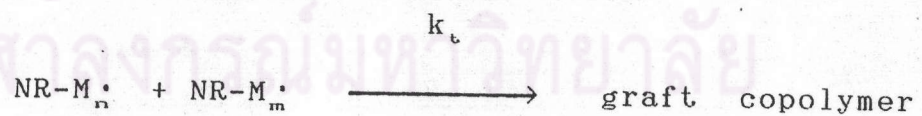


where NR is natural rubber and
M is monomer

propagation



termination



In the preparation of graft copolymer of LNR ($\bar{M}_v = 3.3 \times 10^4$), appropriate conditions which can produce high percentage yield of grafting were investigated. The parameters that were chosen to study are:

- 4.3.1 Effect of reaction temperature
- 4.3.2 Effect of monomer concentration
- 4.3.3 Effect of CuSO_4 concentration
- 4.3.4 Effect of DMA concentration
- 4.3.5 Effect of type of copper salt
- 4.3.6 Effect of acid concentration
- 4.3.7 Effect of type of solvent
- 4.3.8 Effect of reaction time

4.3.1 Effect of reaction temperature

The graft copolymerization was carried out at six different temperatures ranging from 40-100 °C, keeping the concentrations of all other reagents and conditions constant. The results of the graft copolymerization are summarized in Table 4.3. The effect of reaction temperature on % grafting is shown in Figure 4.7. A perusal of the results indicates that the percentage of grafting-on increases slightly with increasing reaction temperature from 40-70 °C. But when the reaction temperature is further increased, the extent of grafting increases remarkably and reaches the maximum value at 80°C. As the reaction temperature rises above 80°C the extent of grafting-on decreases.

Table 4.3 Effect of reaction temperature on % grafting

No	Temperature, °C	Wt of homopolymer, g	Wt of graft copolymer, g	% Grafting
1	40	0.02	0.88	3.4
2	50	0.02	0.92	8.3
3	60	0.11	0.92	7.8
4	70	0.67	0.93	9.4
5	80	1.81	1.54	81.5
6*	90	1.89	1.26	47.8
7*	100	1.97	1.20	41.3

--* Gel formation took place in the reaction flask

The increases in percentage of grafting with the increasing of reaction temperature ranging from 40-80°C may be due to the fact that high temperatures provide a larger number of molecules with greater energy, swellability of rubber and a high diffusion rate of monomer to the rubber matrix. The adsorption of 2-EEMA on rubber is also increased with temperature and therefore its complexation with rubber enhances its reactivity. At higher temperature the formation rate of homopolymerization is favored and

the crosslinking reaction of the rubber chain can also take place to produce gel that cannot dissolve in any solvent. The similar result was also observed by Lenka et al. [13, 15-17] when they investigated the graft copolymerization of MMA onto natural rubber using several redox systems including DMA/Cu²⁺ system. IR and ¹H NMR spectra of the reaction products are shown in Figure 4.8 - 4.11.



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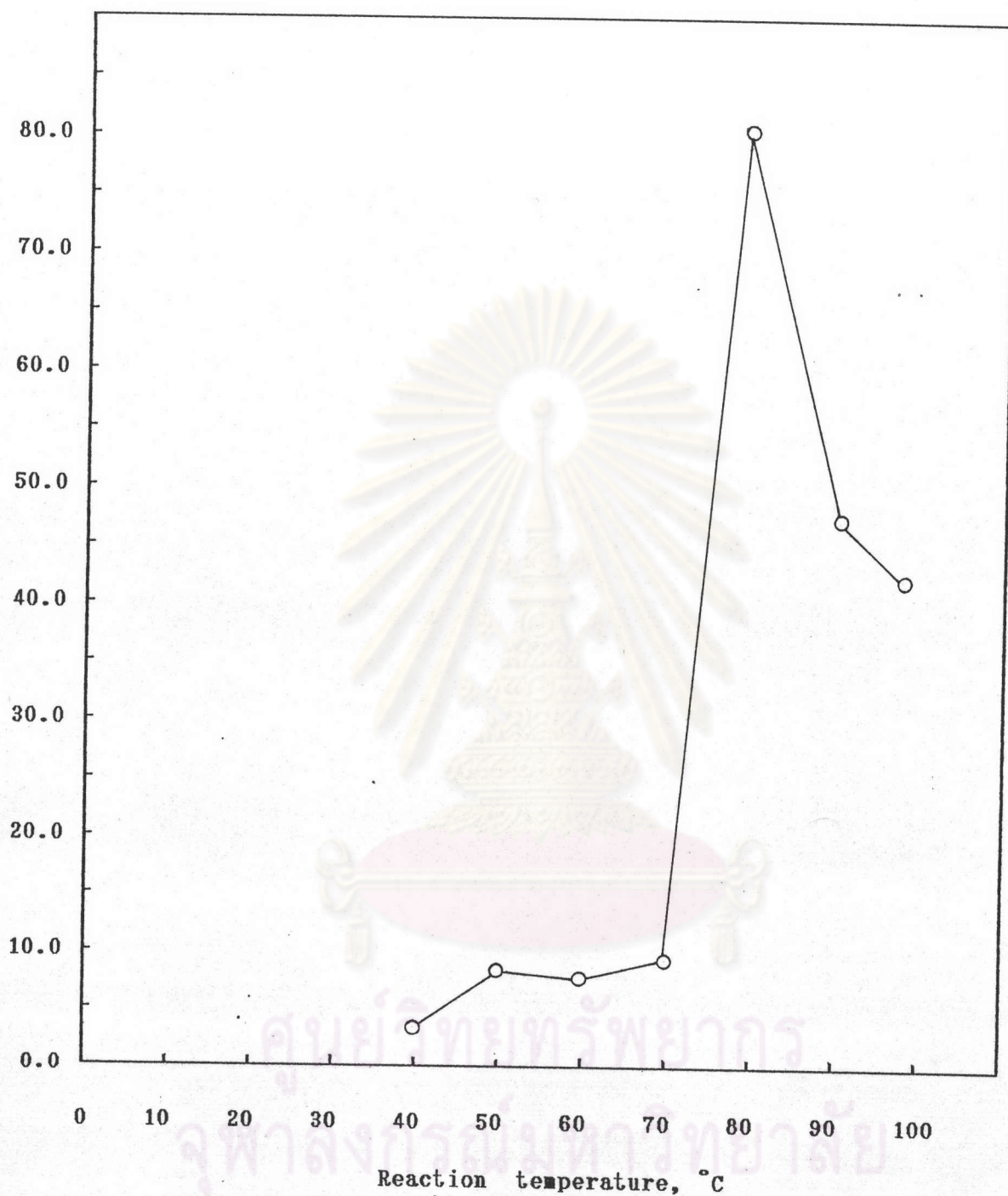


Fig 4.7 Effect of the reaction temperature on % grafting. The reaction of LNR (5.0×10^{-3} M) in CCl_4 with 2-EEMA (7.5×10^{-1} M) using initiator which consisted of CuSO_4 (2.0×10^{-3} M) and DMA (2.0×10^{-3} M) in the presence of conc H_2SO_4 (7.5×10^{-4} M) was carried out at six different temperatures for 30 h.

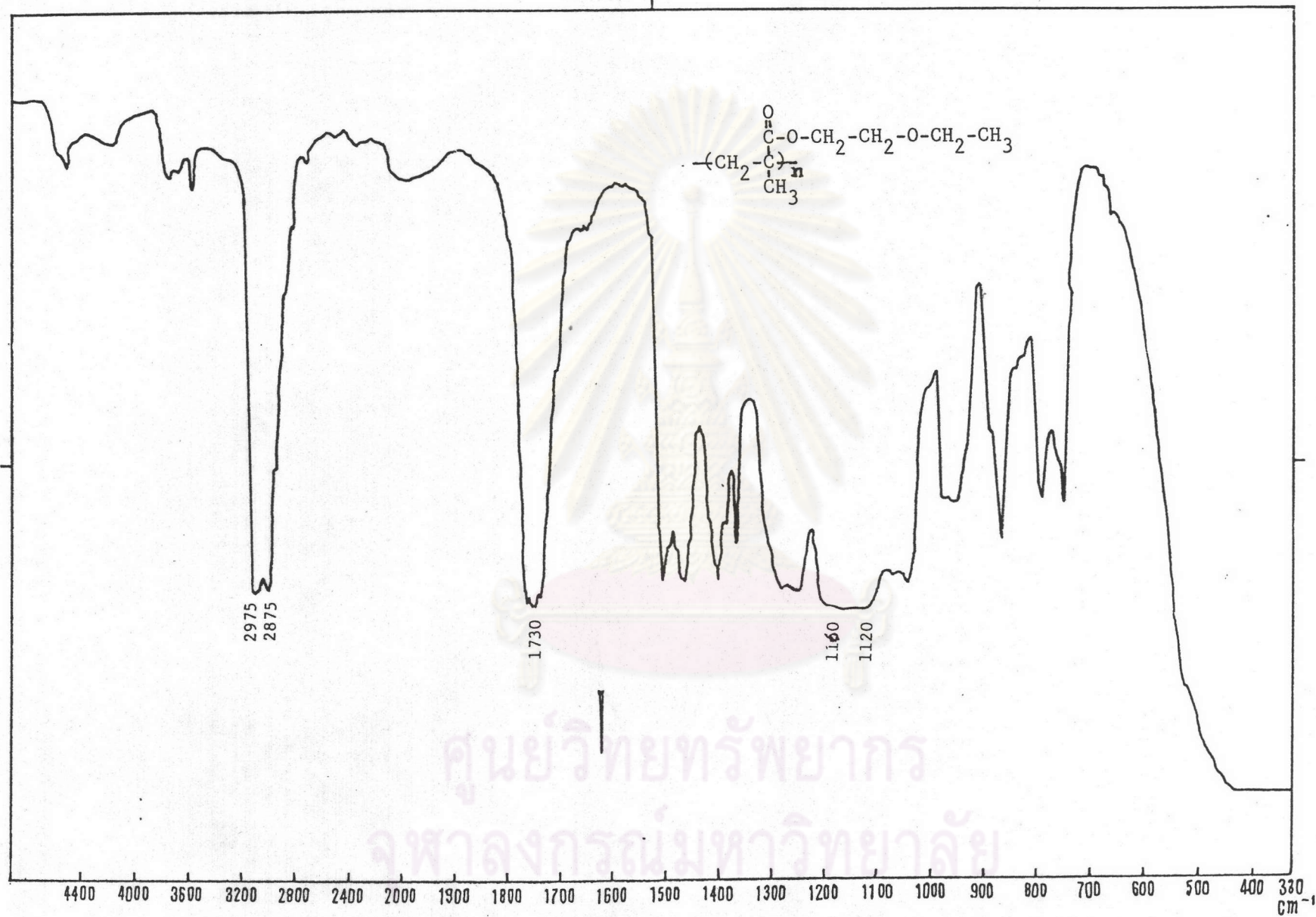


Fig 4.8 IR (neat) spectrum of poly(2-ethoxyethyl methacrylate)

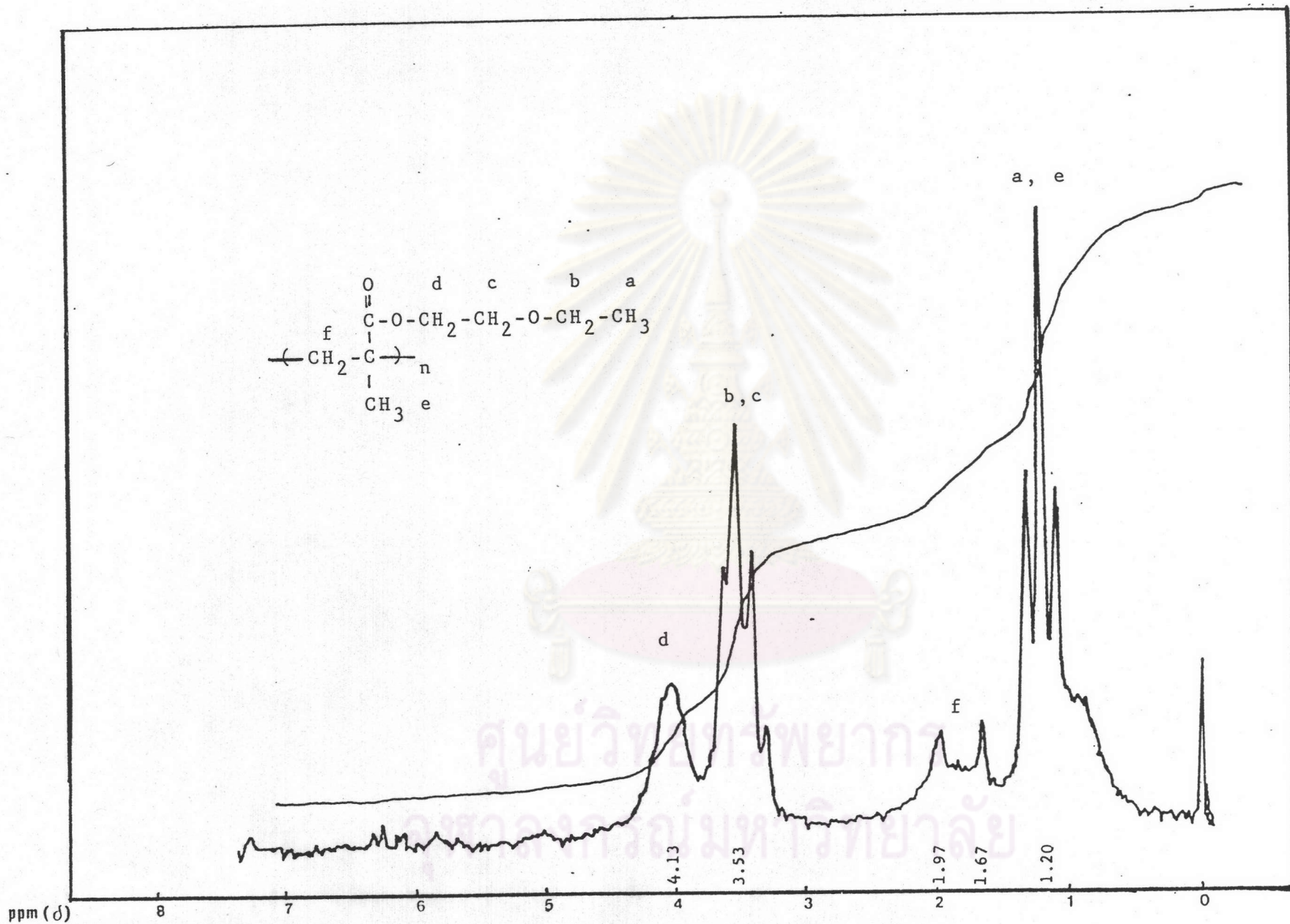


Fig 4.9 ^1H NMR (CCl_4) spectrum of poly(2-ethoxyethyl methacrylate)

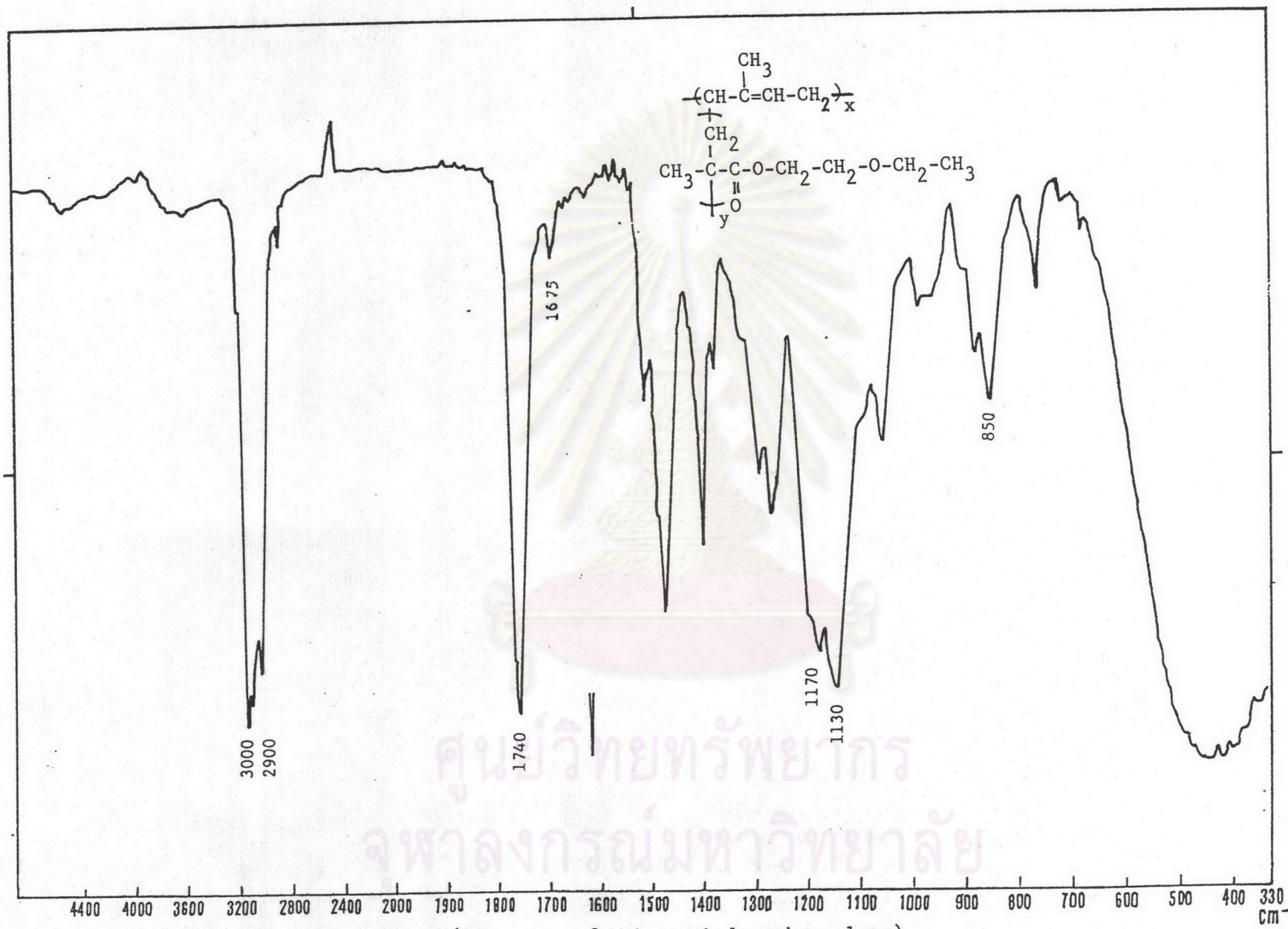


Fig 4.10 IR (neat) spectrum of poly(isoprene-g-2-ethoxyethyl methacrylate)

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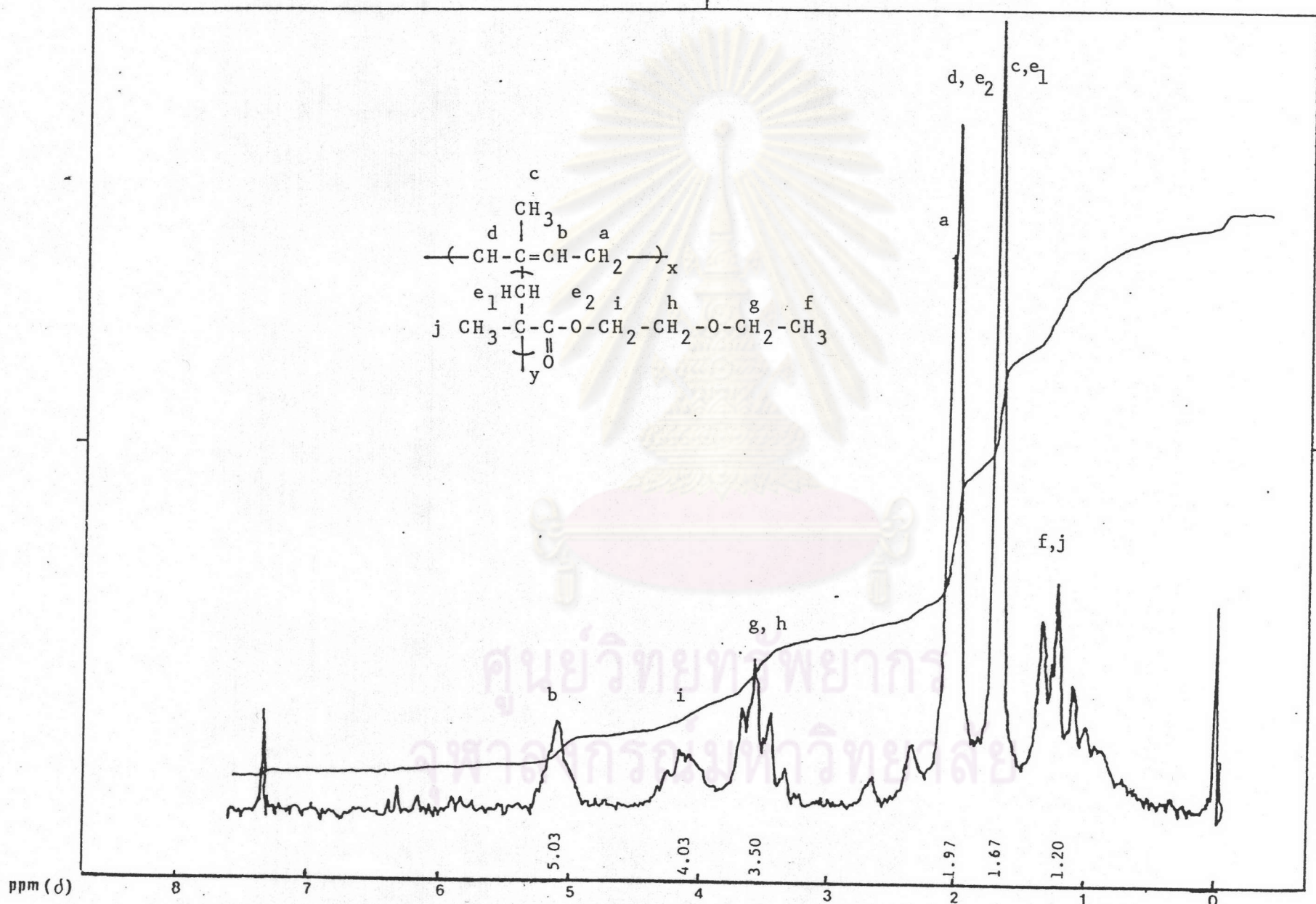


Fig 4.11 ^1H NMR (CCl_4) spectrum of poly(isoprene-g-2-ethoxyethyl methacrylate)

4.3.2 Effect of monomer concentration

The effect of monomer concentration on the extent of grafting was investigated by changing the monomer concentration within the range of 0.1 mol/L to 2.5 mol/L and keeping the concentrations of all other reagents and conditions constant. The results are summarized in Table 4.4. The effect of monomer concentration on percentage of grafting is shown in Figure 4.12. The results reveal that as the monomer concentration increases from 0.1 mol/L to 0.75 mol/L, the percentage of grafting-on increases, and it reaches a maximum value at the monomer concentration of 0.75 mol/L; thereafter it decreases. The reason is that at higher monomer concentration, homopolymerization is more favored than grafting. So the formation of graft copolymer is decreased.

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Table 4.4 Effect of monomer concentration on % grafting

No	[2-EEMA], mol/L	Wt of homopolymer, g	Wt of graft copolymer, g	% Grafting
8	0.10	0.10	0.93	9.2
9	0.25	0.48	1.10	28.9
10	0.50	1.09	1.30	53.0
(5)	0.75	1.81	1.54	81.5
11	1.00	2.36	1.43	68.1
12	2.50	8.62	0.96	13.3

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% Grafting

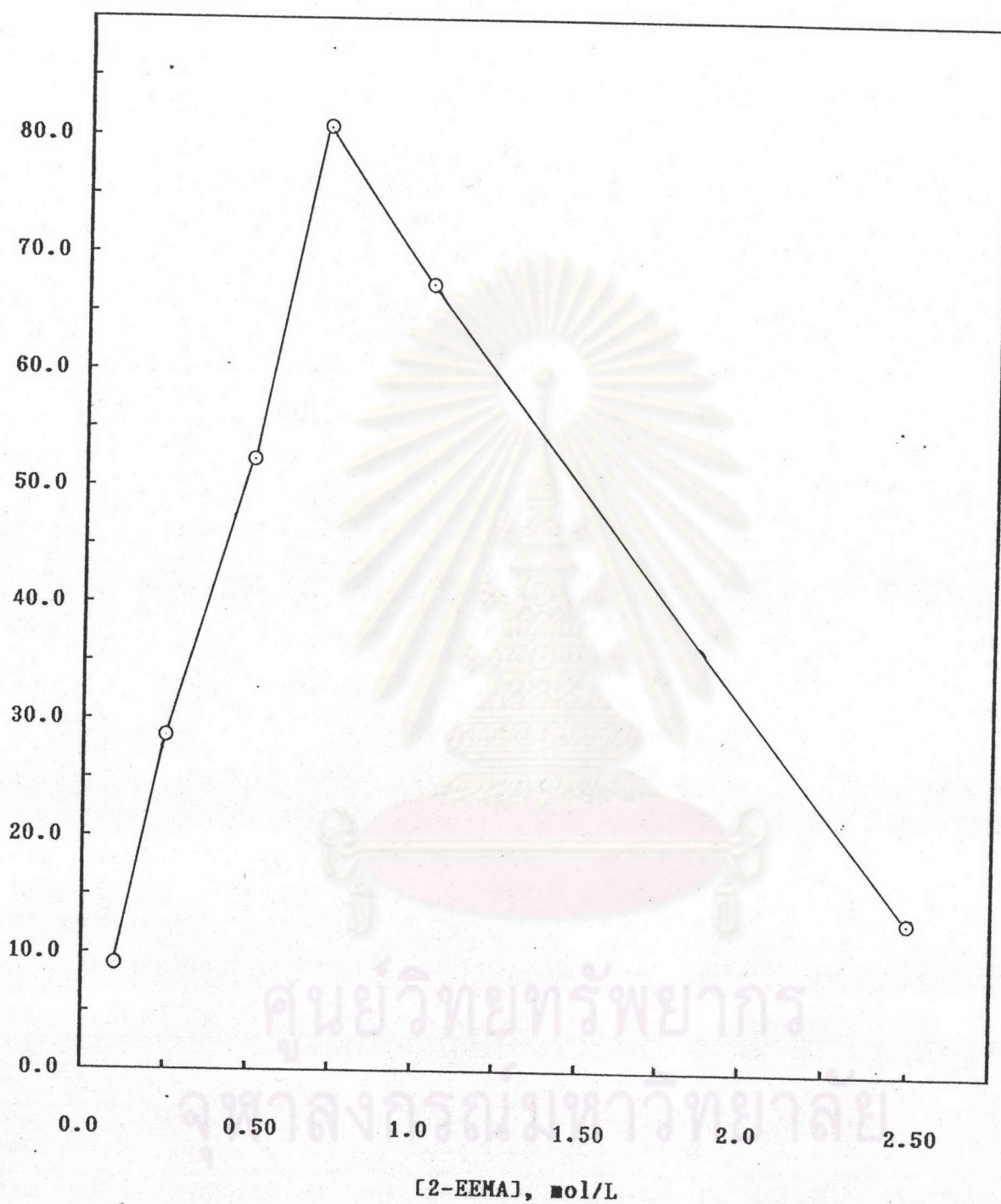


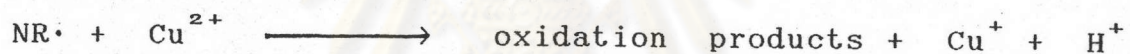
Fig 4.12 Effect of [2-EEMA] on % grafting. The graft copolymerization of LNR ($5.0 \times 10^{-1} \text{ M}$) in CCl_4 using redox initiator which consisted of CuSO_4 ($2.0 \times 10^{-3} \text{ M}$) and DMA ($2.0 \times 10^{-3} \text{ M}$) in the presence of conc H_2SO_4 ($7.5 \times 10^{-4} \text{ M}$) and 2-EEMA at six different concentrations was carried out at 80°C for 30 h.

4.3.3 Effect of CuSO₄ concentration

The effect of CuSO₄ concentration on the percentage of grafting was studied by varying the concentration of CuSO₄ in the range of 1.0×10^{-3} mol/L to 6.0×10^{-3} mol/L while keeping the concentrations of all other reagents and reaction conditions constant. The results are summarized in Table 4.5 and the effect of CuSO₄ concentration on % grafting is shown in Figure 4.13. In the experiments, it was observed that with an increase of CuSO₄ concentration up to 2.0×10^{-3} mol/L, the graft yield increases and becomes maximum at the concentration 2.0×10^{-3} mol/L, and thereafter it decreases. The increase of graft yield at the initial state may be associated with the presence of Cu²⁺ ions in the vicinity of rubber molecules inducing easy formation of rubber-monomer complex. Furthermore, the creation of methyl anilinomethyl radical by the effect of Cu²⁺ ions occurred in the proximity of rubber molecules, thus assisting the ease of formation of rubber macroradicals. Therefore, the extent of grafting is increased. The drop in graft yield at higher concentrations of CuSO₄ could be attributed to many reasons such as the termination of free radicals in solution by the interaction between Cu²⁺ ions and homopolymer and/or rubber radicals.

Table 4.5 Effect of CuSO_4 concentration on % grafting

No	$[\text{CuSO}_4]$, mol/L	Wt of homopolymer, g	Wt of graft copolymer, g	% Grafting
13	1.0×10^{-3}	2.11	1.27	49.6
(5)	2.0×10^{-3}	1.81	1.54	81.5
14	4.0×10^{-3}	1.16	1.36	60.6
15	10.0×10^{-3}	1.46	1.29	50.8



In this case, the Cu^{2+} ion seems to act as a radical trap. Furthermore, a particularly high level of $[\text{Cu}^{2+}]$ ions may perturb the complexation of monomer with rubber. Similar observations have also been noticed by Lenka et al. in graft copolymerization of natural rubber with MMA using DMA/ Cu^{2+} redox system [17] and in the system using potassium peroxydisulphate/ Ag^+ as a redox system [15].

% Grafting

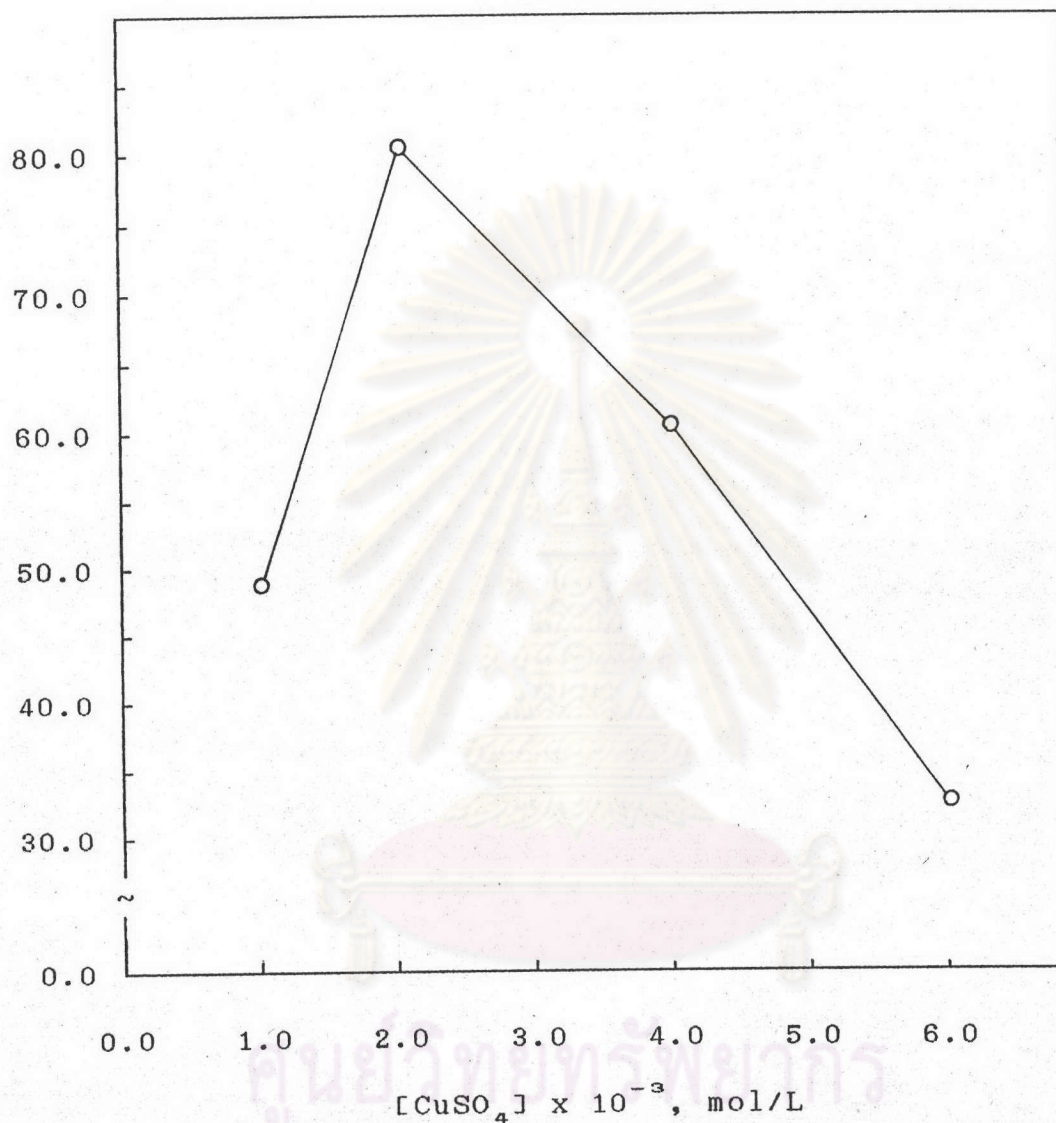
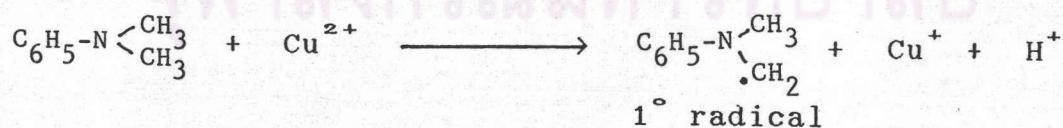


Fig. 4.13 Effect of $[CuSO_4]$ on % grafting. The reaction of LNR (5.0×10^{-1} M) in CCl_4 with 2-EEMA (7.5×10^{-1} M) and conc H_2SO_4 (7.5×10^{-4} M) in the presence of DMA (2.0×10^{-3} M) and $CuSO_4$ at six different concentrations was carried out at $80^\circ C$ for 30 h.

4.3.4 Effect of N,N-dimethyl aniline concentration

The effect of DMA concentration on the extent of grafting was studied by varying the concentration within the range of 1.0×10^{-3} mol/L to 1.0×10^{-2} mol/L and keeping the concentrations of all other reagents and reaction conditions constant. The results are summarized in Table 4.6. The curve of DMA concentration vs the percentage of grafting is shown in Figure 4.14. The curve indicates that as the concentration of DMA increases from 1.0×10^{-3} mol/L to 2.0×10^{-3} mol/L, the extent of grafting also increases and becomes maximum at the concentration of DMA 2.0×10^{-3} mol/L. But when the concentration of DMA is higher than 2.0×10^{-3} mol/L, it is found that the percentage of grafting decreases. The reason is probably due to the fact that in the DMA/ Cu^{2+} system, a Cu^{2+} ion abstracts a hydrogen atom from DMA and generate a radical species as follows:



At higher concentrations of DMA, a large quantity of methyl anilinomethyl radicals which are generated can undergo hydrogen atoms abstraction at high rates from

Table 4.6 Effect of the concentration of N,N-dimethylaniline on % grafting

No	[DMA], mol/L	Wt of homopolymer, g	Wt of graft copolymer, g	% grafting
16	1.0×10^{-3}	1.95	1.46	72.2
(5)	2.0×10^{-3}	1.81	1.54	81.5
17	4.0×10^{-3}	1.53	1.29	52.0
18	6.0×10^{-3}	1.58	1.17	38.1
19	1.0×10^{-2}	0.62	1.02	19.7

the backbone of rubber. This means that more active sites are generated and can interact with monomers to yield higher percentage of grafted product. But when higher concentration of DMA was used in the system, a complex formation reaction of DMA with Cu^{2+} occurs instead of rubber. The result of that reaction yields 1° radical which may interact with each other or with other substances. This then depresses the reaction of rubber, so the extent of grafting decreases. Similar results have been observed by Lenka et al. [17].

% Grafting

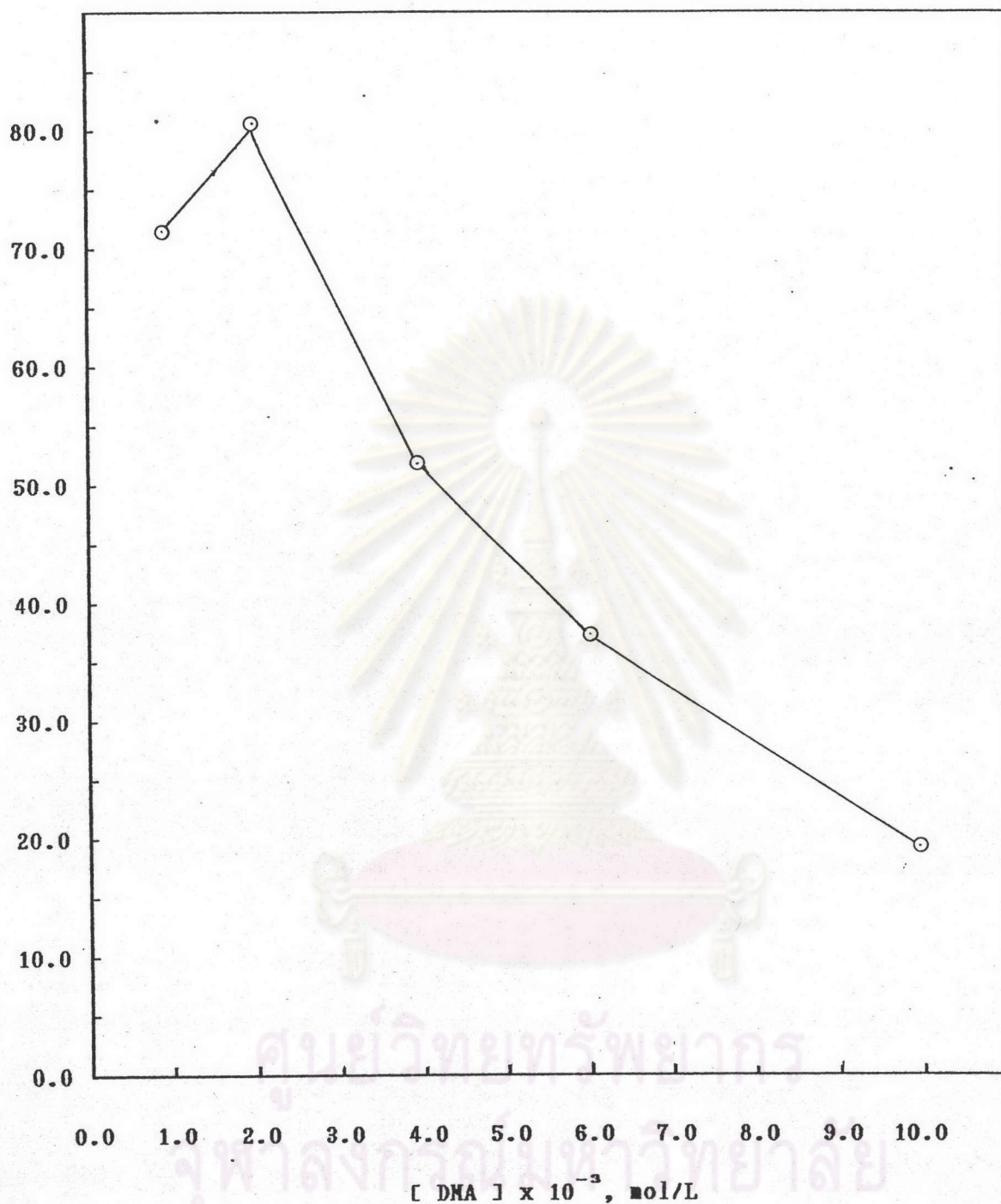
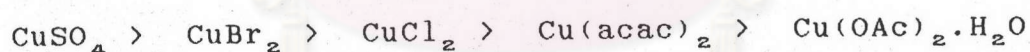


Fig 4.14 Effect of $[DMA]$ on % grafting. The reaction of LNR ($5.0 \times 10^{-1} \text{ M}$) in CCl_4 with 2-EEMA ($7.5 \times 10^{-1} \text{ M}$) in the presence of conc H_2SO_4 ($7.5 \times 10^{-4} \text{ M}$) using redox initiator which consisted of CuSO_4 ($2.0 \times 10^{-3} \text{ M}$) and DMA at five different concentrations was carried out at 80°C for 30 h.

4.3.5 Effect of type of copper salt

The effect of type of copper salt on the percentage of grafting was studied by using five different types of copper salt: anhydrous copper sulphate, anhydrous copper chloride, copper acetylacetonate, copper acetate monohydrate and copper bromide. The concentration of all other reagents and conditions were kept constant. The effect of type of copper salt on the percentage of grafting are summarized in Table 4.7. The curve of % grafting vs type of copper salt is shown in Figure 4.15. The results indicate that the anion of copper salt plays an important role on the percentage of grafting. The order of reactivity is found to obey the following sequence:



The result indicates that anions of cupric salt have an important role on the percentage of grafting by controlling the initiation and termination steps of graft copolymerization reaction. Since SO_4^{2-} , Br^- , Cl^- , acac^- and OAc^- anions have different sizes and basicities, their abilities in controlling those steps are different.

Table 4.7 Effect of type of copper salt on % grafting

No	Type of copper salt	Wt of homopolymer, g	Wt of graft copolymer, g	% Grafting
(5)	Anhy CuSO_4	1.81	1.54	81.5
20	Anhy CuCl_2	1.66	1.17	37.4
21	$\text{Cu}(\text{acac})_2$	1.32	1.12	31.4
22	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	0.99	1.03	21.2
23	CuBr_2	1.89	1.42	66.8

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4.3.6 Effect of acid concentration

The effect of acid concentration on the percentage of grafting was investigated by changing the acid concentration from 0.0 - 5.0×10^{-3} mol/L while the concentrations of all other reagents and conditions were kept constant. The results are summarized in Table 4.8. The relation between % grafting vs acid concentration is shown in Figure 4.15. The results indicate that the extent of grafting increases with acid concentration and becomes maximum at acid concentration of 7.5×10^{-4} mol/L, and thereafter it decreases.

The increase of percentage of grafting with an increase in acid concentration may be due to the ability of acid to accelerate the auto-oxidation of DMA via hydrogen-bonded complex formation to yield amino-hydroperoxide which functions as chain carrier in the auto-oxidation. But high concentration of acid suppresses the formation of methyl anilinomethyl radicals and consequently the graft yield decreases. Similar observations have been noted by Lenka et al. for the case of grafting of natural rubber using Mn (III) acetylacetonate [14] and DMA/Cu²⁺ redox system [17].

Table 4.8 Effect of acid concentration on % grafting

No	[H ⁺], mol/L	Wt of homopolymer, g	Wt of graft copolymer, g	% Grafting
24	0.0	1.81	1.11	30.1
(5)	7.5×10^{-4}	1.81	1.54	81.5
25	1.5×10^{-3}	1.89	1.29	51.4
26	5.0×10^{-3}	2.45	1.14	33.9

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% Grafting

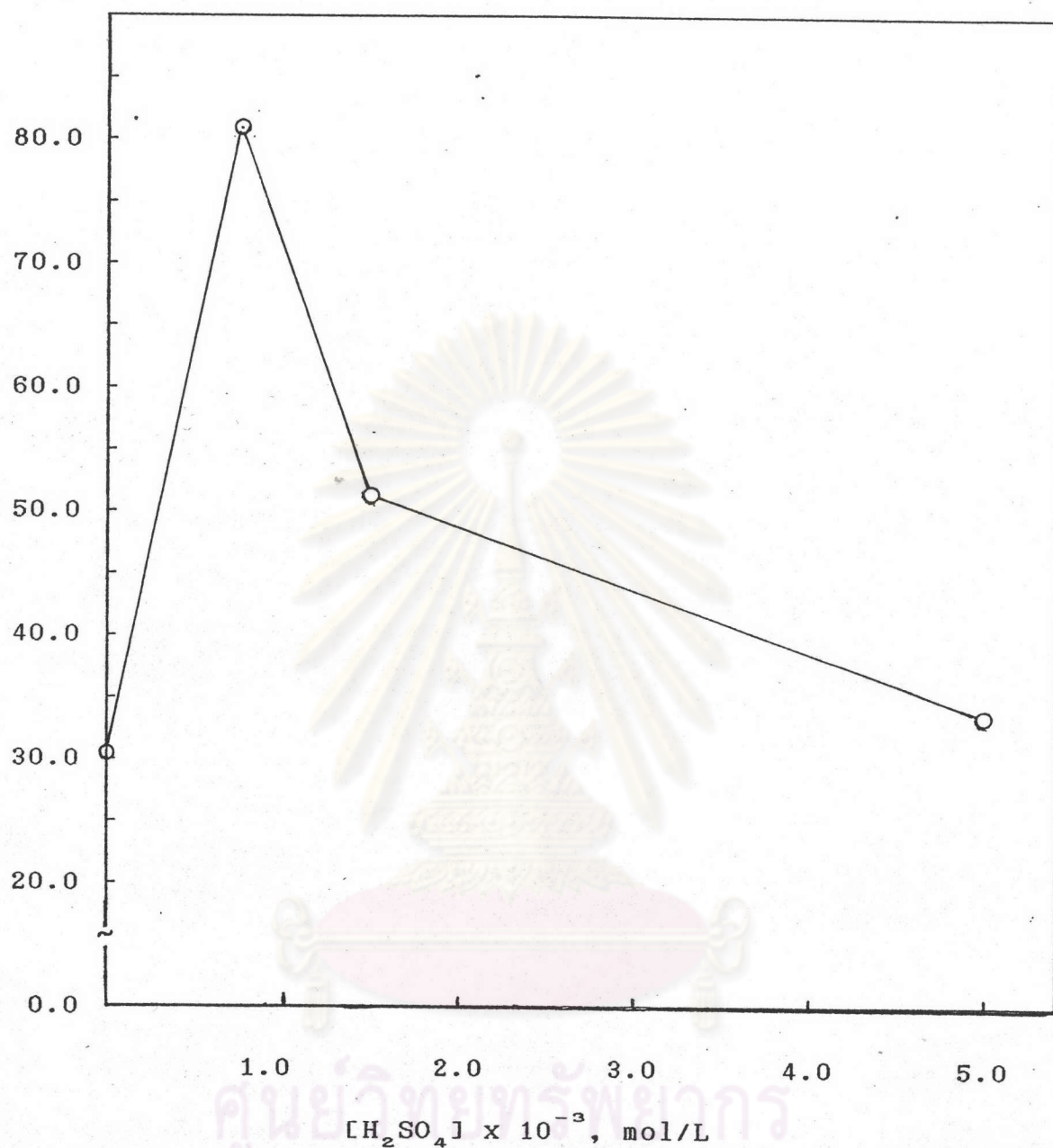
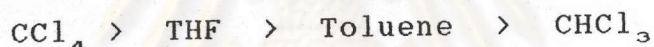


Fig 4.15 Effect of $[H_2SO_4]$ on % grafting. The reaction of LNR (5.0×10^{-1} M) dissolved in CCl_4 with 2-EEMA (7.5×10^{-1} M) using redox initiator which consisted of $CuSO_4$ (2.0×10^{-3} M) and DMA (2.0×10^{-3} M) in the presence of conc H_2SO_4 at four different concentrations was carried out $80^\circ C$ for 30 h.

4.3.7 Effect of type of solvent

The effect of type of solvent on % grafting was studied by using four different types of reaction medium: carbon tetrachloride, tetrahydrofuran, toluene and chloroform while keeping the concentrations of all other reagents and conditions constant. The results are summarized in Table 4.9. The results indicate that the extent of grafting is highly dependent on the type of solvent. The order of reactivity follows the sequence:



The extent of grafting of 2-EEMA onto LNR in organic solvent is probably due to the solubility of rubber and miscibility of monomer in an organic phase. From Table 4.9, the solubility parameters of rubber and CCl_4 are very close compared to the other three solvents. So a rubber molecule should expand most in CCl_4 due to the highest solubility. Therefore, 2-EEMA can diffuse into the rubber matrix and can interact with rubber molecules easily. THF and toluene have almost equal solubility parameters, and therefore they yield about the same percentage of grafting. The solubility parameter of CHCl_3 is

Table 4.9 Effect of type of solvent on % grafting

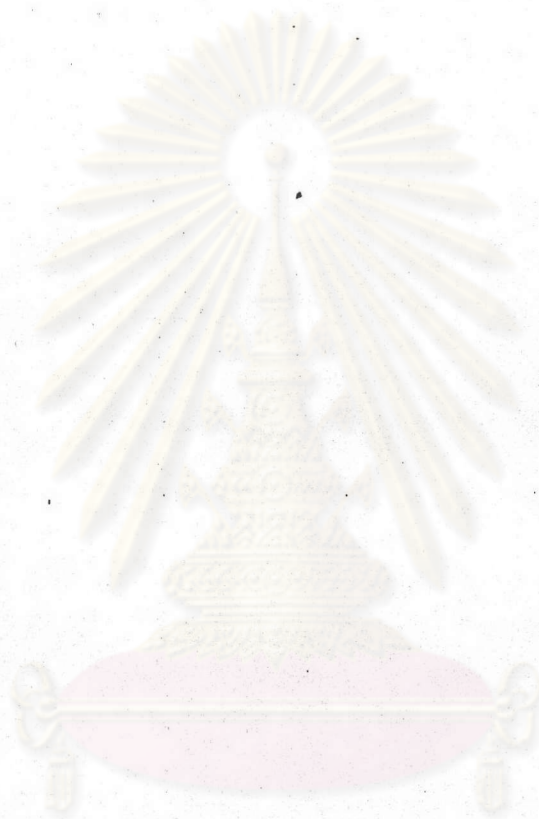
No	Type of solvent (solubility parameter)	Wt of homopolymer, g	Wt of graft copolymer, g	% Grafting
(5)	CCl_4 (17.6)	1.81	1.54	81.5
27	THF (18.6)	1.14	0.93	9.7
28	Toluene (18.2)	0.19	0.91	7.5
29*	CHCl_3 (19.4)	0.68	0.86	1.4

---* Gel formation took place in this reaction medium.

Solubility parameters of natural rubber and 2-EEMA are 16.0 and 18.0, respectively.

Solubility parameter see [25]

significantly different from rubber, so it yields the lowest extent of grafting. In addition, gel formation is observed in this reaction medium.



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4.3.8 Effect of reaction time

The effect of reaction time was investigated by changing the reaction time in the range of 15-60 hours while keeping the concentrations of all other reagents and conditions constant. The effect of reaction time on % grafting are summarized in Table 4.10 and the curve of reaction time vs % grafting is illustrated in Figure 4.16. The results show that in the first 30 hours the extent of grafting increases with an increase in reaction time and becomes maximum at reaction time of 30 hours. A further increase of reaction time causes decreases in the extent of grafting. The reason may be due to an increase in homopolymerization with time and/or gel formation which possibly could take place in the reaction at longer reaction time; therefore the percentage of grafting is depressed.

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Table 4.10 Effect of reaction time on % grafting

No	Reaction, h	Wt of homopolymer,g	Wt of graft copolymer,g	% Grafting
30	15	1.46	1.15	35.0
31	25	1.73	1.26	48.4
(5)	30	1.81	1.54	81.5
32	35	1.93	1.53	80.5
33	45	2.17	1.35	58.8
34	60	2.24	1.27	49.2

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% Grafting

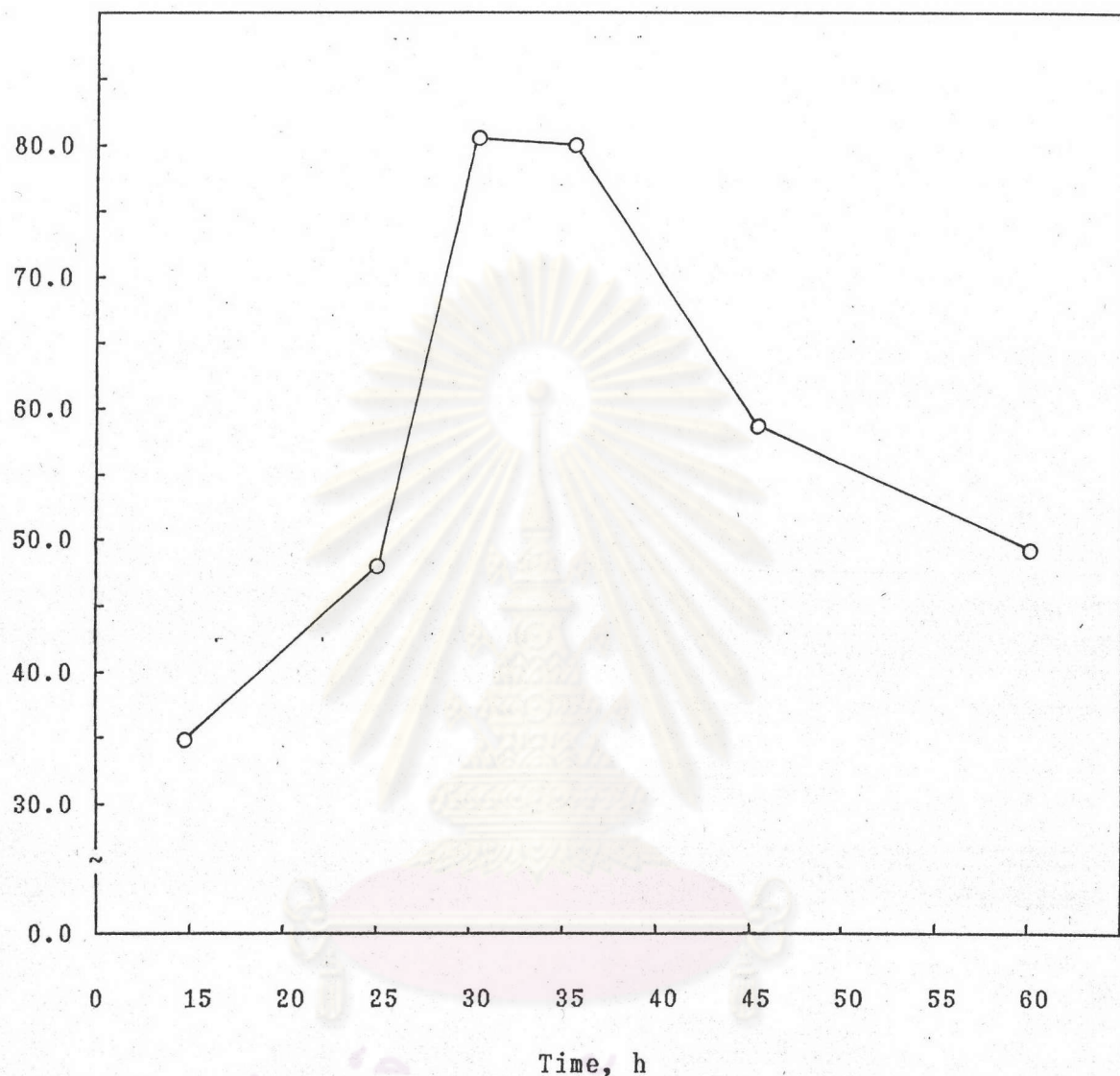


Fig 4.16 Effect of the reaction time on % grafting. The reaction of LNR (5.0×10^{-1} M) dissolved in CCl_4 with 2-EEMA (7.5×10^{-1} M) using redox initiator which consisted of CuSO_4 (2.0×10^{-3} M) and DMA (2.0×10^{-3} M) in the presence of conc H_2SO_4 (7.5×10^{-4} M) was carried out at 80°C . for six different reaction time.

4.4 Adhesive property of the grafted products

The adhesive property of the grafted liquid natural rubber with 40 % and 50 % grafting was measured by the method described previously [22]. These grafted products were prepared from LNR with viscosity average molecular weight of 4.0×10^4 . The results of the measurements are shown in Table 4.11.

Table 4.11 Adhesive property of grafted products

No	% Grafting	Peeling strength (N/25 mm)
1*	40.0	30.6
2*	50.0	18.0

---* These grafted products are crude grafted LNR with no separation of homopolymer.

The result indicates that as the percentage of grafting increases, the peeling strength decreases. This is due to the fact that as the percentage of grafting increases, the softness of the grafted chain increases. So the adhesion power of the grafted product decreases.



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