

## CHAPTER IV

### RESULTS AND DISCUSSION

The modification of graft copolymerization of methyl methacrylate (MMA) onto natural rubber (NR) latex was prepared using emulsion polymerization. Three different redox initiator systems were used for the graft copolymerization. There are cumene hydroperoxide (CHPO)/tetraethylene pentamine (TEPA), tert-butyl hydroperoxide (TBHPO)/TEPA, and potassium persulfate ( $K_2S_2O_8$ )/sodium thiosulfate ( $Na_2S_2O_3$ ). The influential factors of the initiator concentration, reaction temperature, monomer concentration, and reaction time were investigated.

#### 4.1 Properties of Natural Rubber Latex

The high ammonia natural rubber (HANR) latex was obtained from Thai Rubber Latex Corporation (Thailand) Public Co., Ltd. The dry rubber content and the total solid content of latex were 60.03% and 61.54%, respectively. The typical properties of HANR are shown in Table 4.1.

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**Table 4.1** The properties of natural rubber latex (high ammonia grade)

Properties	Values
Total solid content (TSC), %	61.54
Dry rubber content, %	60.03
Non rubber solids, %	1.51
Ammonia content (on total weight), %	0.70
Ammonia content (on water phase), %	1.82
pH value	10.92
KOH number	0.5610
Volatile fatty acid number (VFA)	0.0194
Mechanical stability time @ 55% TSC, sec	1,100
Specific gravity at 25 <sup>0</sup> C	0.9411
Magnesium content (on solid), ppm	23

#### 4.2 Preparation of the Grafted Natural Rubber

The work described here consists of a study of the graft copolymerization of methyl methacrylate in natural rubber latex by emulsion polymerization technique and using three different redox systems, cumene hydroperoxide(CHPO)/tetraethylene pentamine (TEPA), tert-butyl hydroperoxide (TBHPO)/TEPA, and potassium persulfate ( $K_2S_2O_8$ )/sodium thiosulfate( $Na_2S_2O_3$ ). This study examines the dependence of percentage conversion, percentage grafted natural rubber, and percentage grafting efficiency on the initiator concentration, reaction temperature, monomer concentration, and reaction time.

The appropriate condition, which yielded high percentage conversion, percentage grafted natural rubber, and percentage grafting efficiency were investigated.

#### **4.2.1 The Preparation of the Grafted Natural Rubber using CHPO or TBHPO as Redox Initiator.**

##### **4.2.1.1 Effect of Initiator Concentration**

The graft copolymerization of methyl methacrylate onto natural rubber was initiated by the redox initiator. The oil soluble initiator, CHPO or TBHPO, was used with the amine activator, TEPA. The bipolar redox initiating system was employed at a ratio 1:1.

The effect of initiator concentration at various temperatures on the percentage conversion, percentage grafted natural rubber, and percentage grafting efficiency are shown in Tables 4.2-4.5 and Figures 4.1-4.14. The detail of all data and calculations are shown in Appendix A. The parameters of graft copolymerization were obtained as follows:

MMA concentration	: 100 phr
Initiator concentration	: 0.5-2.0 phr
Reaction temperature	: 30-60°C
Reaction time	: 8 hr

Figures 4.1a-4.8b show the effect of initiator concentration on the percentage conversion, percentage grafted natural rubber, and percentage grafting efficiency at different temperatures. In Figures 4.9-4.14, the percentage conversion increases as the initiator concentration increases at every temperature investigated. Initially, the increase in initiator concentration produces more graft sites for methyl methacrylate to graft. The percentage grafted natural rubber and percentage grafting

efficiency decrease as the initiator concentration increases. The reason is that the homopolymers are formed more readily than the graft copolymer. It can be seen that increasing initiator concentrations up to 0.5 phr are accompanied by a significant increase in the grafting efficiency. Beyond this concentration, the graft efficiency decreases markedly. When higher concentrations of initiator are used, excessive radicals react with each other, leading to a faster rate of termination or primary termination. Upto this point, the grafting efficiency does not increase at all. The highest percentage grafted natural rubber and grafting efficiency were observed at the initiator concentration of CHPO and TBHPO of 0.5 phr and reaction temperature 50°C.

**Table 4.2** Effect of the initiator concentration of TBHPO and CHPO on the percentage conversion, percentage grafting efficiency and percentage grafted natural rubber at 60°C, MMA monomer concentration 100 phr, and reaction time 8 hr.

Reaction properties	TBHPO				CHPO			
	Initiator concentration (phr)				Initiator concentration (phr)			
	0.5	1.0	1.5	2.0	0.5	1.0	1.5	2.0
Conversion (%)	82.5	84.3	91.3	87.9	81.0	81.7	87.3	84.8
Grafting efficiency (%)	68.6	69.1	66.4	60.5	74.4	66.0	62.4	63.2
Graft properties								
Grafted NR (%)	76.1	78.2	77.3	74.5	75.6	71.1	73.6	72.0
Free NR (%)	9.5	7.6	6.5	6.5	12.7	10.8	8.6	9.9
Free PMMA (%)	14.4	14.3	16.3	18.8	11.6	18.2	17.8	17.9

**Table 4.3** Effect of the initiator concentration of TBHPO and CHPO on the percentage conversion, percentage grafting efficiency and percentage grafted natural rubber at 50 °C, MMA monomer concentration 100 phr, and reaction time 8 hr.

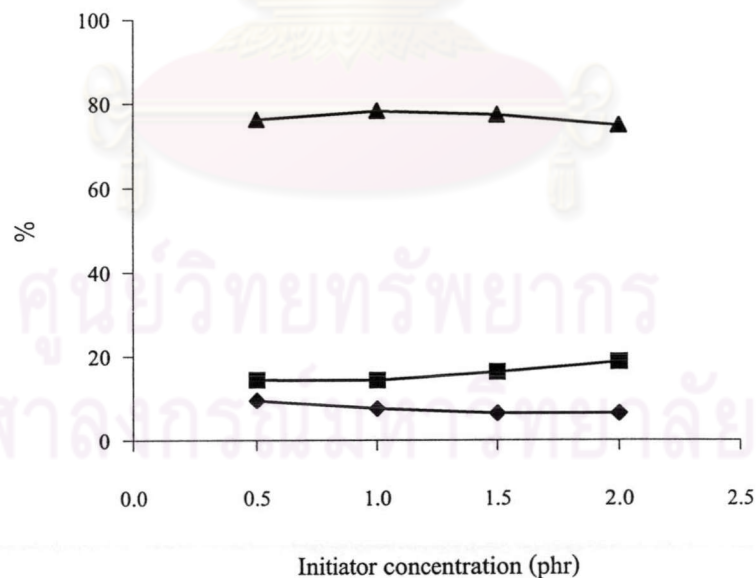
Reaction properties	TBHPO				CHPO			
	Initiator concentration (phr)				Initiator concentration (phr)			
	0.5	1.0	1.5	2.0	0.5	1.0	1.5	2.0
Conversion (%)	82.5	84.3	82.5	87.8	83.8	84.2	88.6	86.3
Grafting efficiency (%)	74.5	61.4	57.6	55.3	84.4	60.7	55.9	53.9
Graft properties								
Grafted NR (%)	80.5	73.8	72.8	73.5	83.9	74.3	71.7	71.0
Free NR (%)	7.5	8.2	6.6	5.3	8.8	7.5	7.3	7.3
Free PMMA (%)	12.1	18.0	19.5	21.2	7.2	18.2	21.0	21.6

**Table 4.4** Effect of the initiator concentration of TBHPO and CHPO on the percentage conversion, percentage grafting efficiency and percentage grafted natural rubber at 40 °C, MMA monomer concentration 100 phr, and reaction time 8 hr.

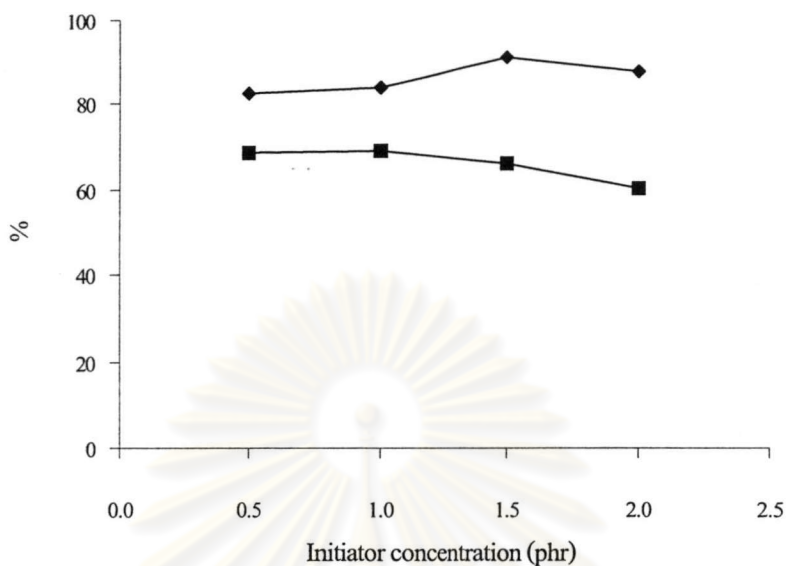
Reaction properties	TBHPO				CHPO			
	Initiator concentration (phr)				Initiator concentration (phr)			
	0.5	1.0	1.5	2.0	0.5	1.0	1.5	2.0
Conversion (%)	61.1	82.4	91.2	87.0	71.7	84.0	84.3	84.5
Grafting efficiency (%)	68.7	61.1	49.3	45.1	78.0	59.6	53.2	49.2
Graft properties								
Grafted NR (%)	81.2	77.8	67.0	62.4	78.0	72.5	71.0	59.4
Free NR (%)	6.8	7.8	8.8	11.0	13.1	8.8	7.3	7.1
Free PMMA (%)	12.1	14.4	24.2	26.6	8.9	18.7	21.7	23.5

**Table 4.5** Effect of the initiator concentration of TBHPO and CHPO on the percentage conversion, percentage grafting efficiency and percentage grafted natural rubber at 30°C, MMA monomer concentration 100 phr, and reaction time 8 hr.

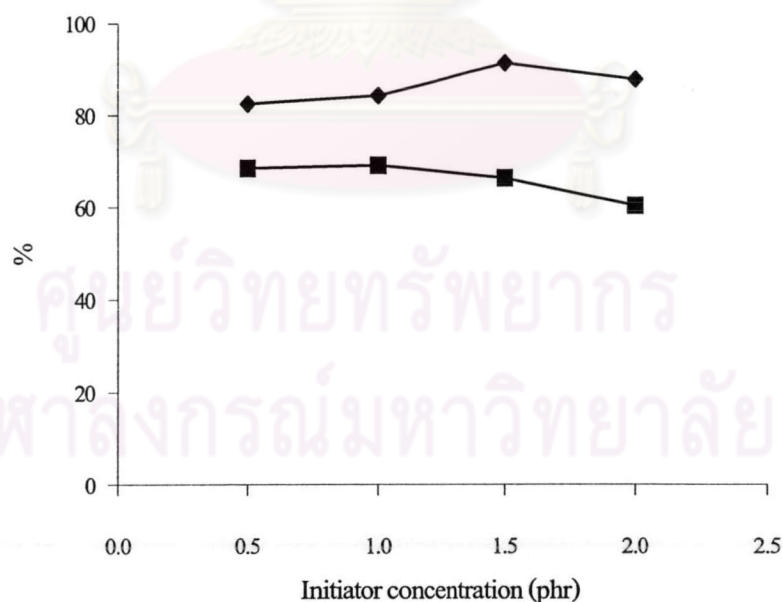
Reaction properties	TBHPO				CHPO			
	Initiator concentration (phr)				Initiator concentration (phr)			
	0.5	1.0	1.5	2.0	0.5	1.0	1.5	2.0
Conversion (%)	44.7	61.5	85.7	90.5	50.1	66.4	84.1	91.4
Grafting efficiency (%)	70.7	55.3	46.6	41.4	73.8	68.4	50.8	43.9
Graft properties								
Grafted NR (%)	71.9	69.5	62.9	60.7	73.8	68.4	50.8	43.9
Free NR (%)	14.3	13.2	12.2	6.1	12.9	12.9	8.6	7.6
Free PMMA (%)	13.9	17.3	25.0	28.2	8.9	1.9	22.8	27.2



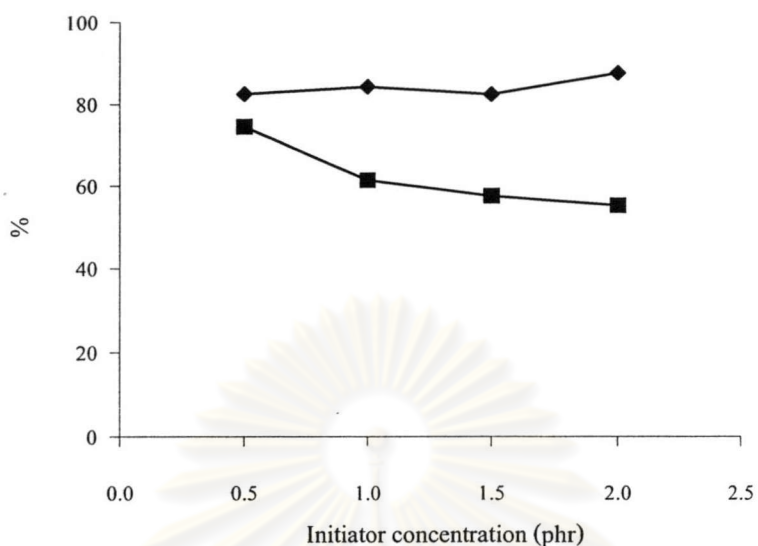
**Figure 4.1a** Effect of the initiator concentration of TBHPO on the percentage free NR (◆), percentage free PMMA (■), and percentage grafted natural rubber (▲) at 60°C, MMA monomer concentration 100 phr, and reaction time 8 hr



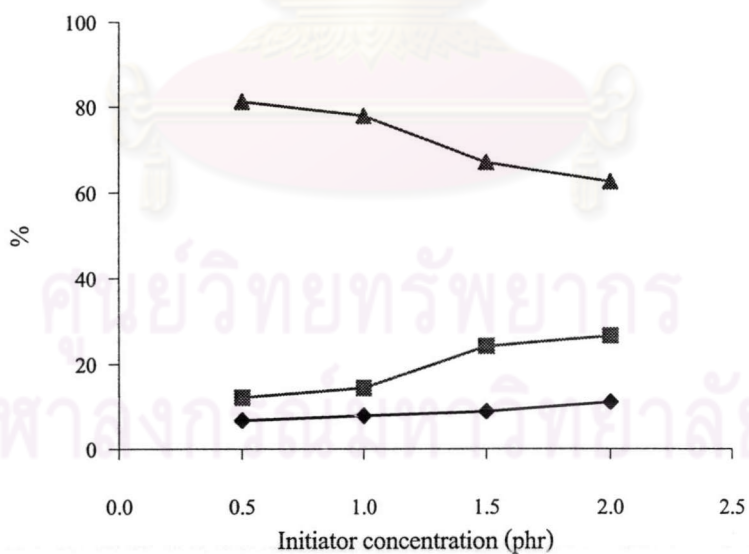
**Figure 4.1b** Effect of initiator concentration of TBHPO on the percentage conversion (▲), and percentage grafting efficiency (■) at 60°C, MMA monomer concentration 100 phr, and reaction time 8 hr



**Figure 4.2a** Effect of the initiator concentration of TBHPO on the percentage free NR (◆), percentage free PMMA (■), and percentage grafted natural rubber (▲) at 50°C, MMA monomer concentration 100 phr, and reaction time 8 hr

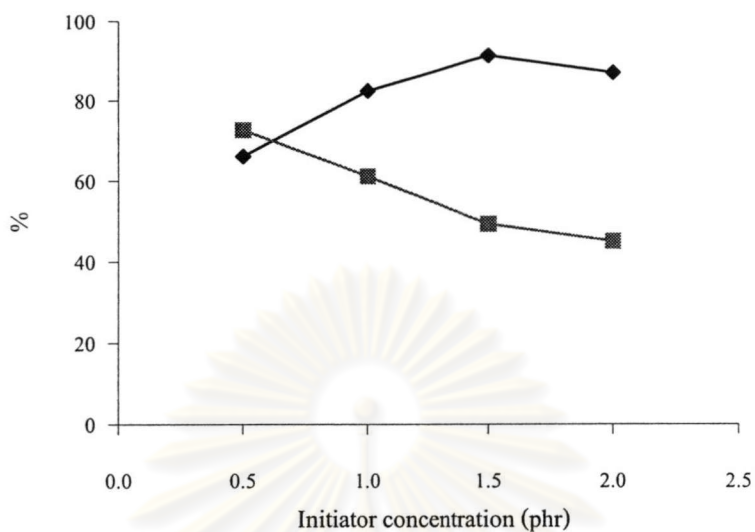


**Figure 4.3a** Effect of the initiator concentration of TBHPO on the percentage conversion (◆), and percentage grafting efficiency (■) at 50°C, MMA monomer concentration 100 phr, and reaction time 8 hr

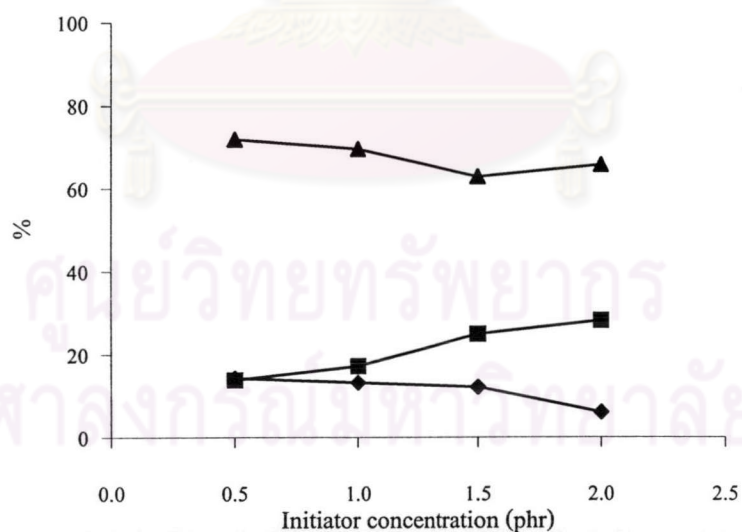


**Figure 4.3a** Effect of the initiator concentration of TBHPO on the percentage free NR (◆), percentage free PMMA (■), and percentage grafted natural rubber (▲) at 40°C, MMA monomer concentration 100 phr, and reaction time 8 hr

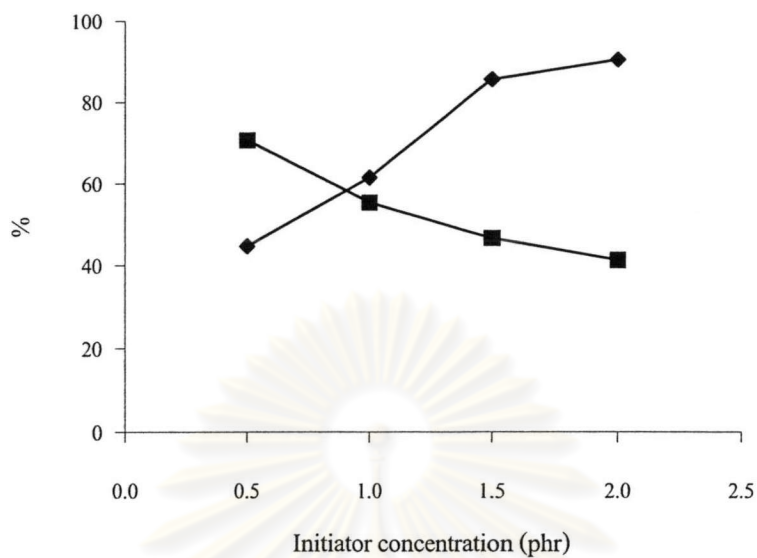




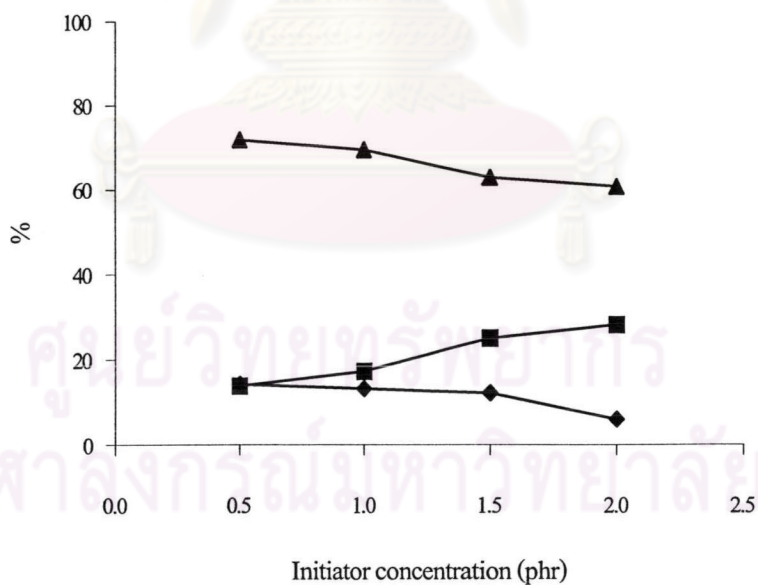
**Figure 4.3b** Effect of initiator concentration of TBHPO on the percentage conversion (◆), and percentage grafting efficiency (■) at 40°C, MMA monomer concentration 100 phr, and reaction time 8 hr



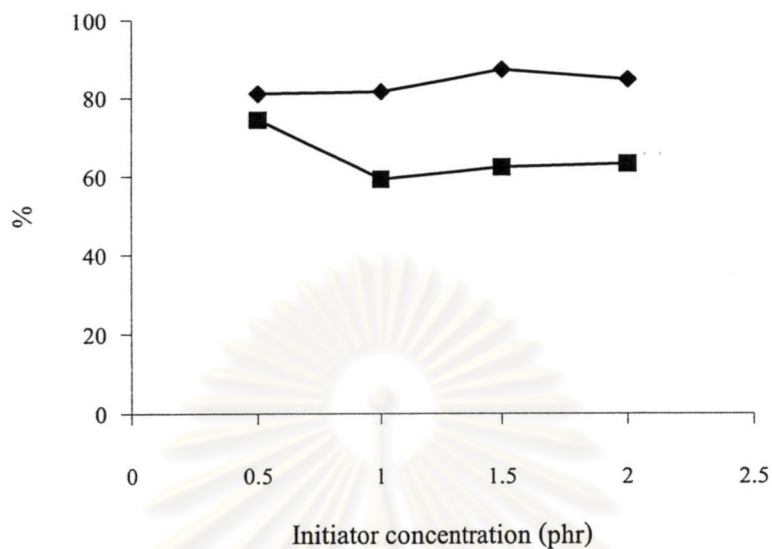
**Figure 4.4a** Effect of the initiator concentration of TBHPO on the percentage free NR (◆), percentage free PMMA (■), and percentage grafted natural rubber (▲) at 30°C, MMA monomer concentration 100 phr, and reaction time 8 hr



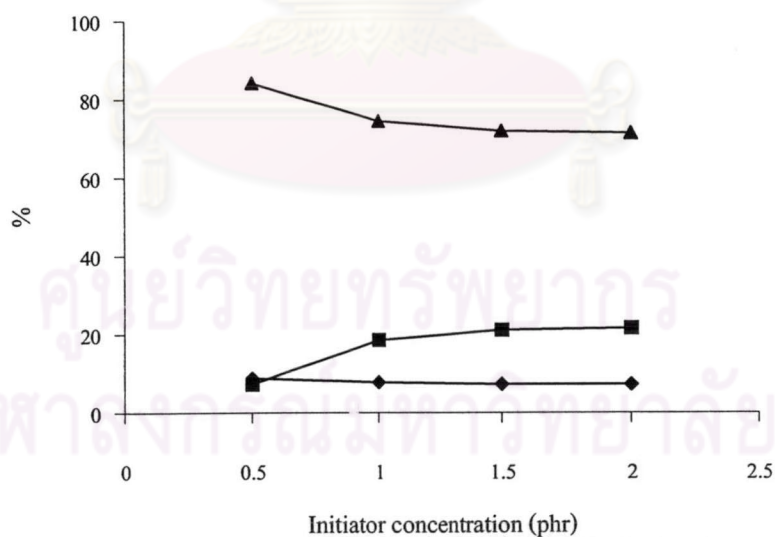
**Figure 4.4b** Effect of initiator concentration of TBHPO on the percentage conversion (◆), and percentage grafting efficiency (■) at 30°C, MMA monomer concentration 100 phr, and reaction time 8 hr



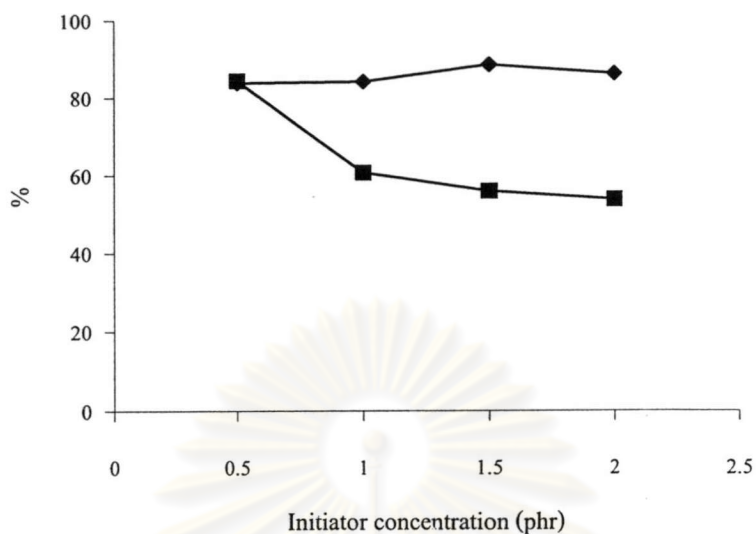
**Figure 4.5a** Effect of the initiator concentration of CHPO on the percentage free NR (◆), percentage free PMMA (■), and percentage grafted natural rubber (▲) at 60°C, MMA monomer concentration 100 phr, and reaction time 8 hr



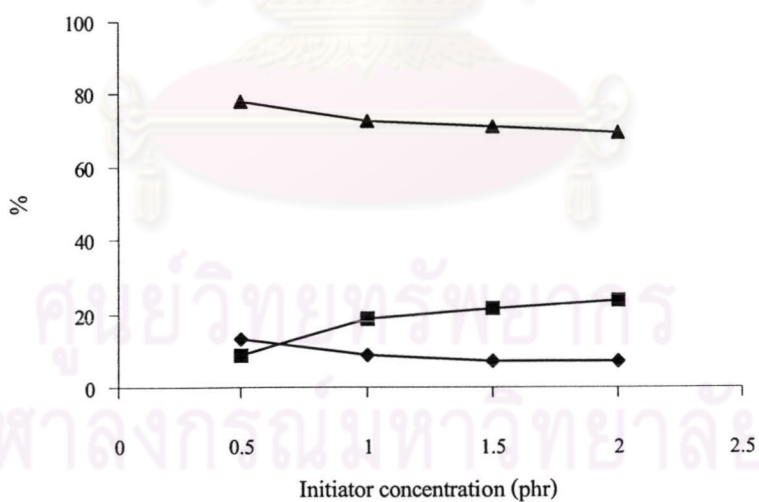
**Figure 4.5b** Effect of initiator concentration of CHPO on the percentage conversion (◆), and percentage grafting efficiency (■) at 60°C, MMA monomer concentration 100 phr, and reaction time 8 hr



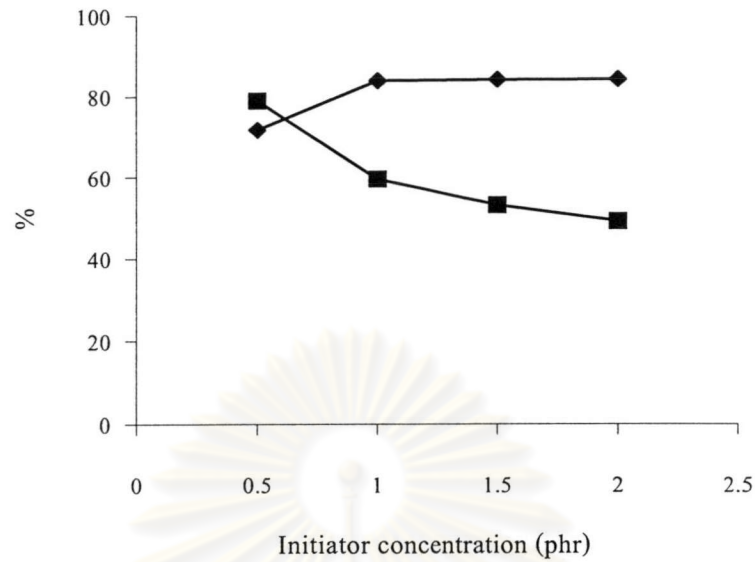
**Figure 4.6a** Effect of the initiator concentration of CHPO on the percentage free NR (◆), percentage free PMMA (■), and percentage grafted natural rubber (▲) at 50°C, MMA monomer concentration 100 phr, and reaction time 8 hr



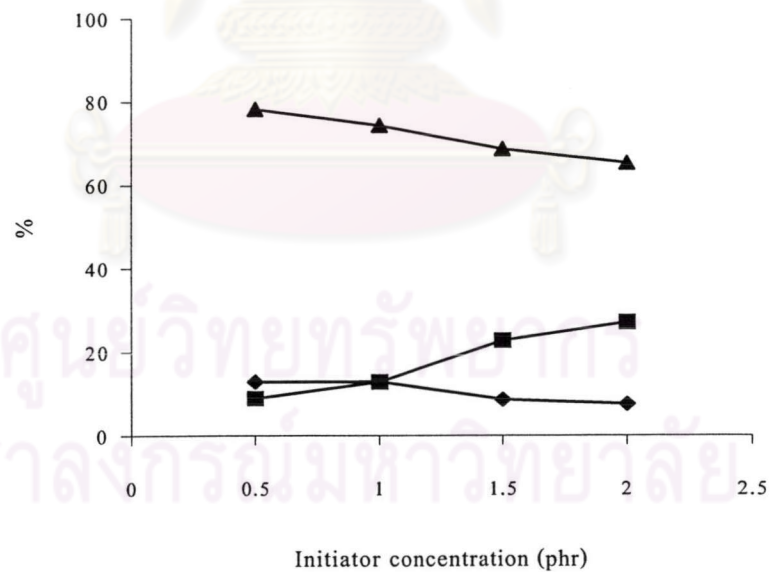
**Figure 4.6b** Effect of initiator concentration of CHPO on the percentage conversion (◆), and percentage grafting efficiency (■) at 50°C, MMA monomer concentration 100 phr, and reaction time 8 hr



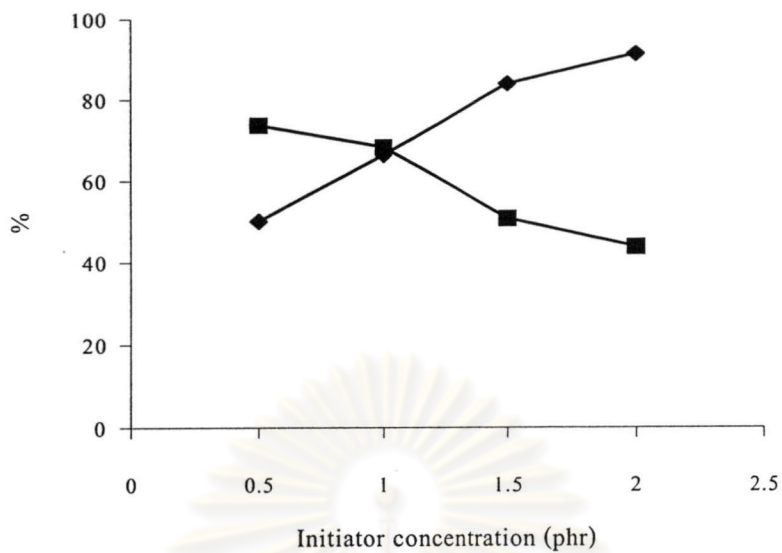
**Figure 4.7a** Effect of initiator concentration of CHPO on the percentage free NR (◆), percentage free PMMA (■), and percentage grafted natural rubber (▲) at 40°C, MMA monomer concentration 100 phr, and reaction time 8 hr



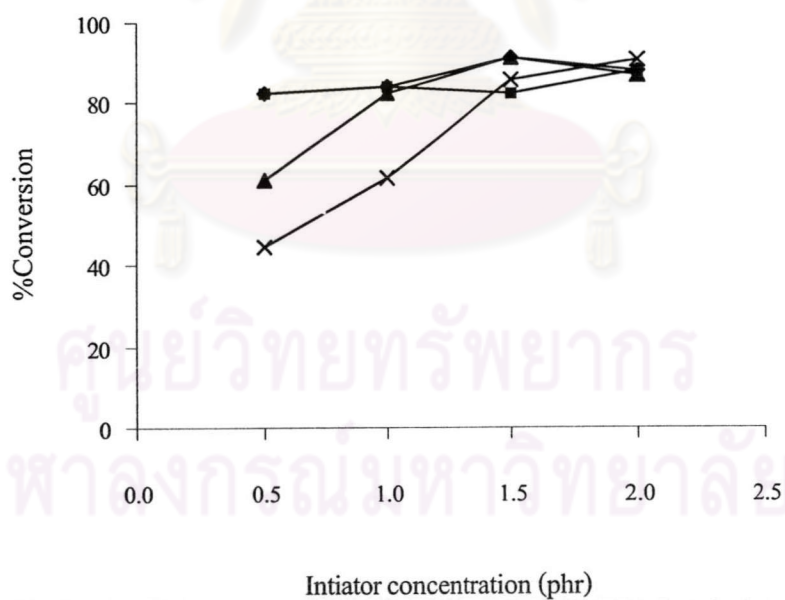
**Figure 4.7b** Effect of initiator concentration of CHPO on the percentage conversion (◆) and percentage grafting efficiency (■) at 40°C, MMA monomer concentration 100 phr, and reaction time 8 hr



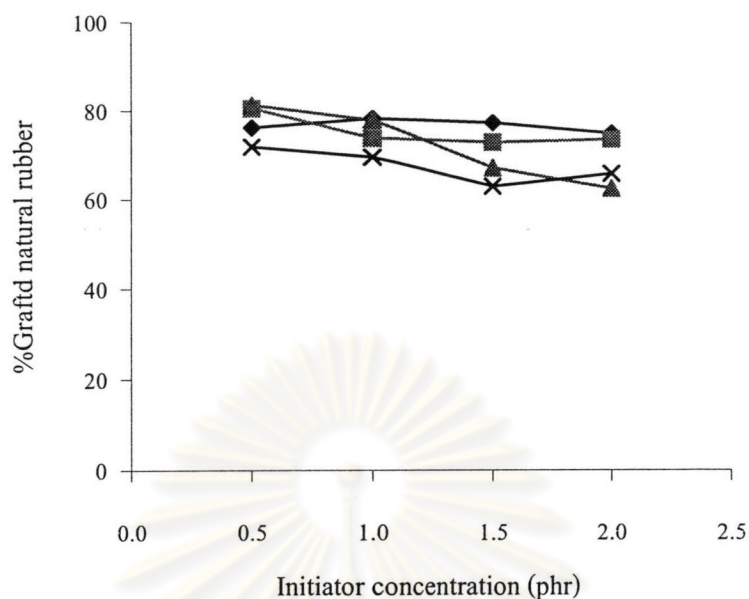
**Figure 4.8a** Effect of initiator concentration of CHPO on the percentage free NR (◆), percentage free PMMA (■), and percentage grafted natural rubber (▲) at 30°C, MMA monomer concentration 100 phr, and reaction time 8 hr



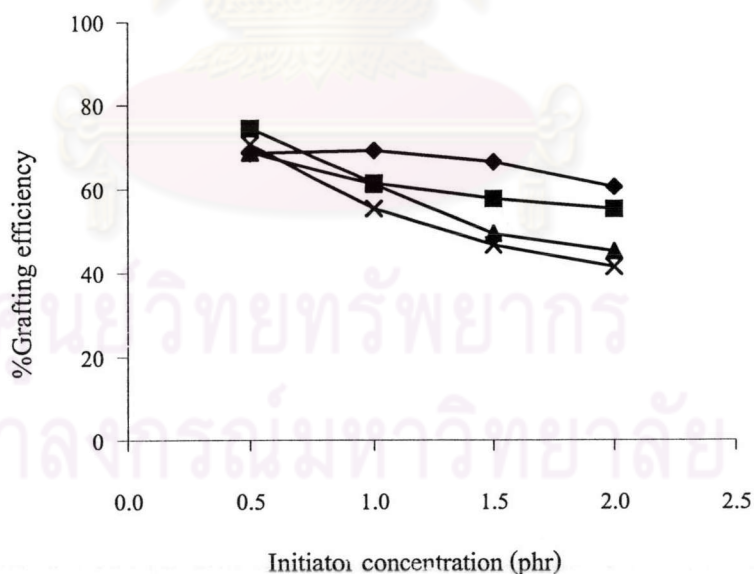
**Figure 4.8b** Effect of initiator concentration of CHPO on the percentage conversion (◆), and percentage grafting efficiency (■) at 30°C, MMA monomer concentration 100 phr, and reaction time 8 hr



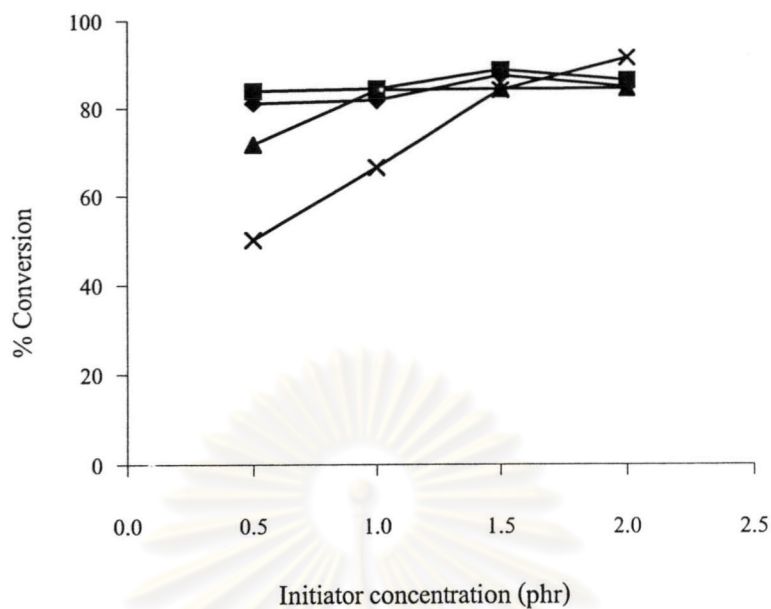
**Figure 4.9** Effect of the initiator concentration of TBHPO on the percentage conversion (30-60°C, MMA monomer concentration 100 phr, reaction time 8 hr) : (◆) 60°C; (■) 50°C; (▲) 40°C; and (X) 30°C



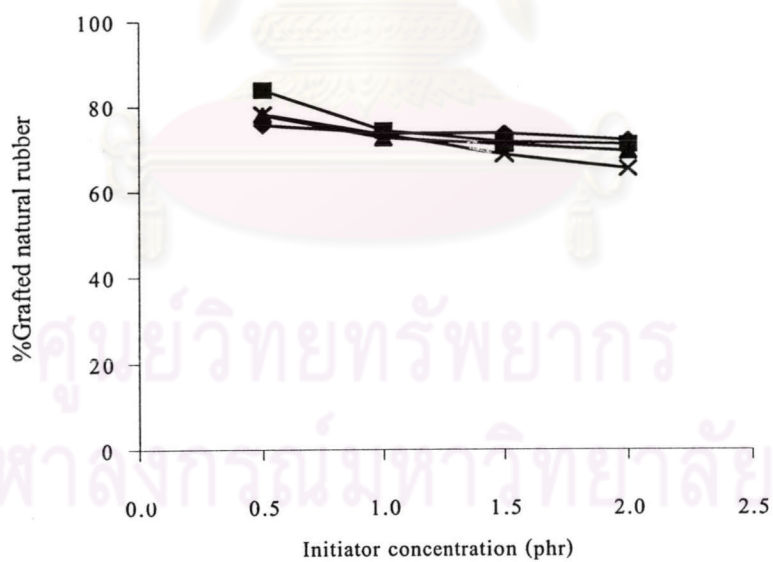
**Figure 4.10** Effect of the initiator concentration of TBHPO on the percentage grafted natural rubber (30-60°C, MMA monomer concentration 100 phr, reaction time 8 hr) : (◆) 60°C; (■) 50°C; (▲) 40°C; and (X) 30°C



**Figure 4.11** Effect of the initiator concentration of TBHPO on the percentage grafting efficiency (30-60°C, MMA monomer concentration 100 phr, reaction time 8 hr) : (◆) 60°C; (■) 50°C; (▲) 40°C; and (X) 30°C

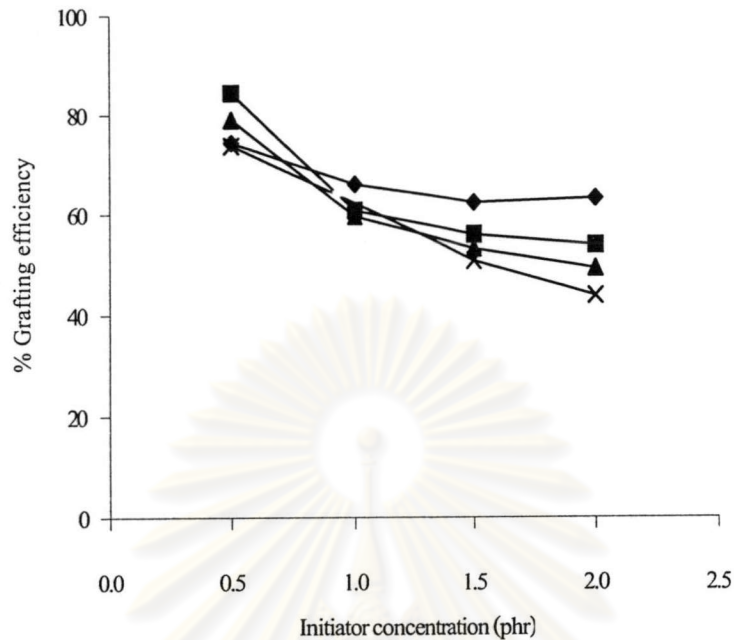


**Figure 4.12** Effect of the initiator concentration of CHPO on the percentage conversion (30-60°C, MMA monomer concentration 100 phr, reaction time 8 hr) : (◆) 60°C; (■) 50°C; (▲) 40°C; and (x) 30°C



**Figure 4.13** Effect of the initiator concentration of CHPO on the percentage grafted natural rubber (30-60°C, MMA monomer concentration 100 phr, reaction time 8 hr) : (◆) 60°C; (■) 50°C; (▲) 40°C; and (X) 30°C





**Figure 4.14** Effect of the initiator concentration of CHPO on the percentage grafting efficiency (30-60°C, MMA monomer concentration 100 phr, reaction time 8 hr) : (◆) 60°C; (■) 50°C; (▲) 40°C; and (X) 30°C

#### 4.2.1.2 Effect of Reaction Temperature

The effect of reaction temperature on the grafted natural rubber were investigated by vary the reaction temperature of 30, 40, 50, and 70°C. The effect of temperature on the grafting characteristics and the molecular weight of graft copolymer were investigated. The condition of graft copolymer were obtained as follows:

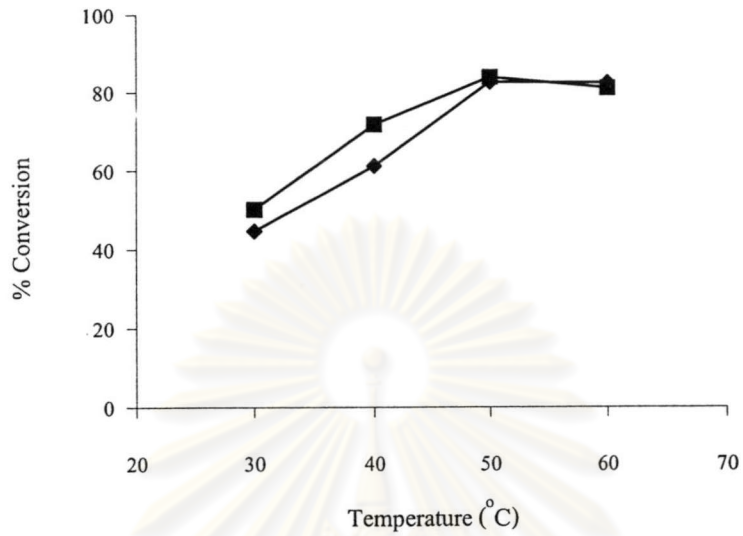
MMA monomer concentration	: 100 phr
Initiator concentration	: 0.5 phr
Reaction temperature	: 30-60°C
Reaction time	: 8 hr

The effects of reaction temperature on the percentage conversion, percentage grafted natural rubber, and percentage grafting efficiency are shown in Table 4.6 and Figures 4.15-4.17. The details of all data and calculation are shown in Appendix A.

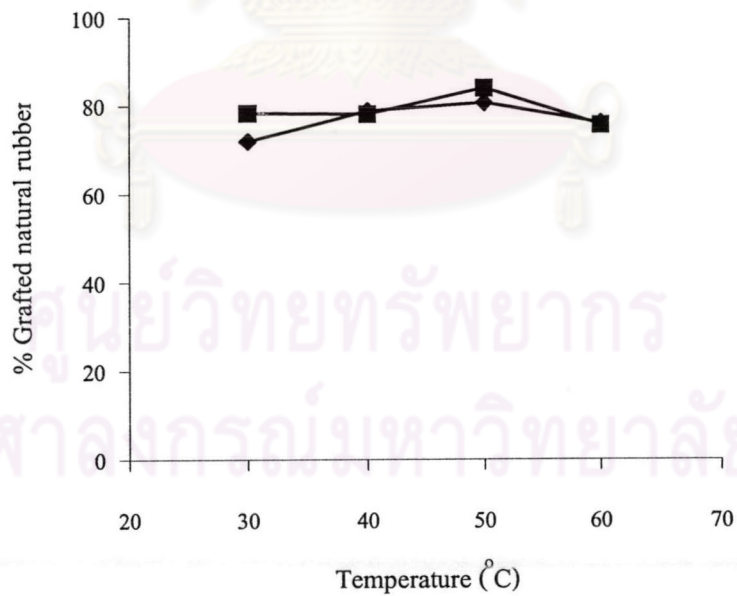
In Figure 4.15, it can be seen that a higher temperature results in high conversion. Decomposition of the initiator (CHPO or TBHPO) increase with an increasing reaction temperature, it causes an increase in both the number of free radicals and the rate of polymerization. The effect of temperature on percentage grafted natural rubber and percentage grafting efficiency from two redox initiators are decreased when the polymerization temperature was higher than 50°C. The initiator decomposition increased with the increasing temperature to give instantaneously abundance of free radicals. The radical underwent either recombination or other side reaction, the initiator efficiency for grafting was thus reduced at higher temperature.

**Table 4.6** Effect of the reaction temperature on the percentage conversion, percentage grafting efficiency and percentage grafted natural rubber at MMA monomer concentration 100 phr, initiator concentration 1.0 phr, and reaction time 8 hr.

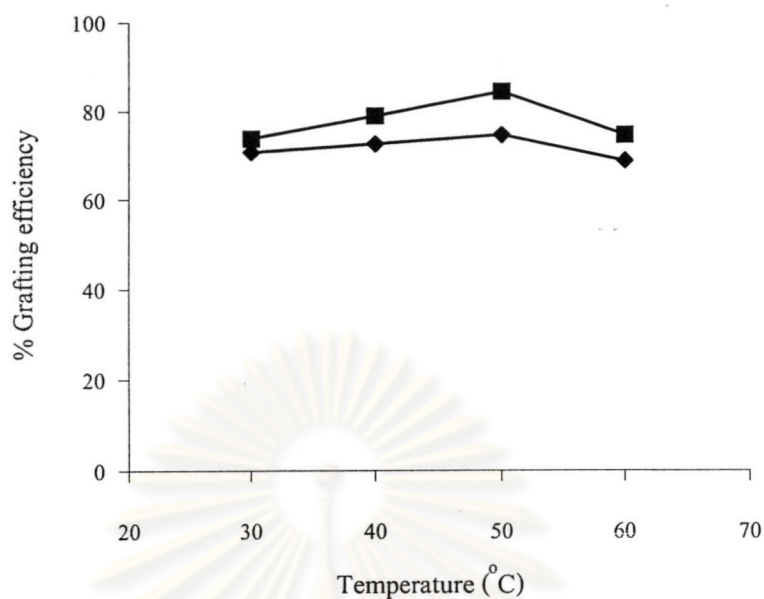
Reaction properties	TBHPO				CHPO			
	Temperature (°C)				Temperature (°C)			
	30	40	50	60	30	40	50	60
Conversion (%)	44.7	61.1	82.5	82.5	50.1	71.7	83.8	81.0
Grafting efficiency (%)	70.7	68.7	74.5	68.6	73.8	78.0	84.4	74.4
Graft properties								
Grafted NR (%)	71.9	81.2	80.5	76.1	73.8	78.0	83.9	75.6
Free NR (%)	14.3	6.8	7.5	9.5	12.9	13.1	8.8	12.6
Free PMMA (%)	13.9	12.1	12.1	14.4	8.9	8.9	7.2	11.6



**Figure 4.15** Effect of reaction temperature on the percentage conversion (30-60°C, MMA 100 phr, reaction time 8 hr) : (◆) TBHPO; and (■) CHPO



**Figure 4.16** Effect of reaction temperature on the percentage grafted natural rubber (30-60°C, MMA monomer concentration 100 phr, reaction time 8 hr) : (◆) TBHPO; and (■) CHPO



**Figure 4.17** Effect of reaction temperature on the percentage grafting efficiency (30-60°C, MMA monomer concentration 100 phr, reaction time 8 hr) : (◆) TBHPO; and (■) CHPO

#### 4.2.1.3 Effect of MMA Monomer Concentration

The natural rubber latex used as the backbone polymer of cis-1,4-polyisoprene was grafted with methyl methacrylate monomer. Rubber particles were swollen with monomer, which was then polymerized onto rubber particles. The effect of monomer concentration on grafted natural rubber were on the percentage of conversion, grafted natural rubber, and grafting efficiency. The monomer concentrations are using in the range of 40-120 phr, based on the dry rubber content. The parameter of graft copolymerization were obtained as follows:

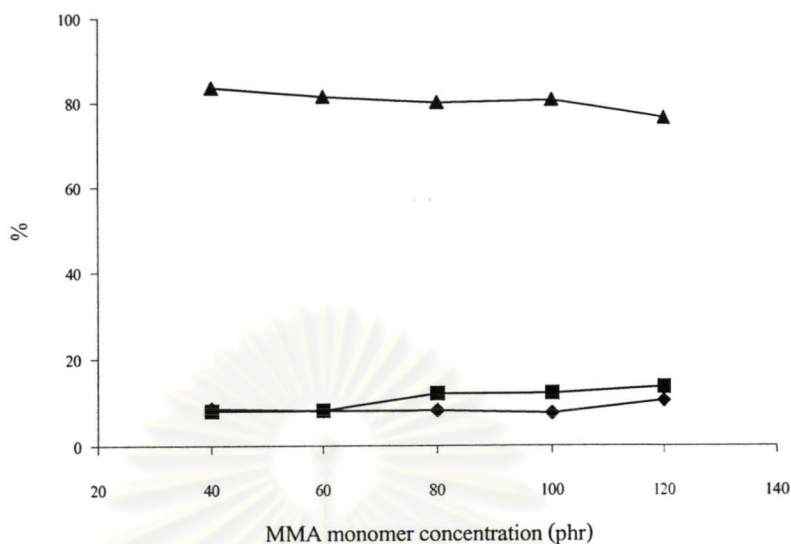
MMA monomer concentration	:	40-120 phr
Initiator concentration	:	0.5 phr
Reaction temperature	:	50°C
Reaction time	:	8 hr

The effect of monomer concentration on the percentage conversion, percentage grafted natural rubber, and percentage grafting efficiency are shown in Table 4.7 and Figure 4.18a-4.19b. The details of all data and calculation are shown in Appendix A.

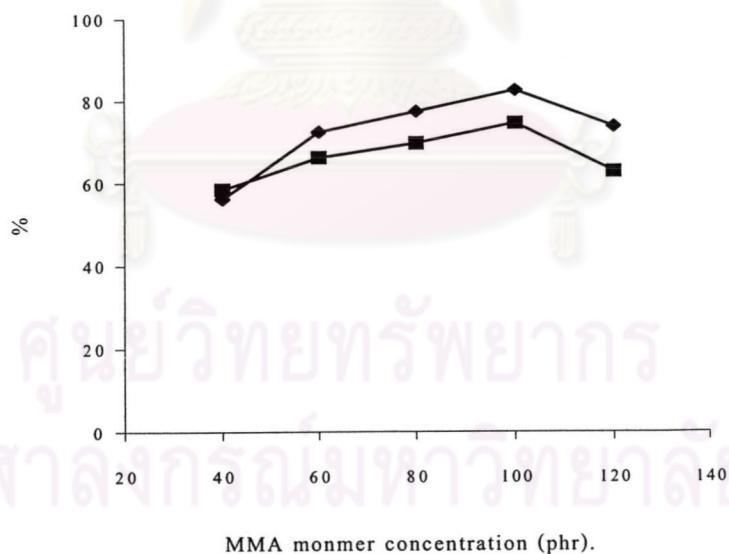
Figures 4.18b and 4.19b show the monomer concentrations increase with the percentage conversion and percentage grafting efficiency. At two redox initiator, the grafting efficiency and percentage grafted natural rubber reach a maximum at the monomer concentration of 100 phr, and thereafter it decreases. At higher monomer concentrations, many reactions, which probably completed with the grafting reaction, take place in the solution. This means that homopolymerization is more pronounced than is graft copolymerization at higher monomer concentration.

**Table 4.7** Effect of the monomer concentration on the percentage conversion, percentage grafting efficiency and percentage graft natural rubber at 50°C, initiator concentration 0.5 phr, and reaction time 8 hr.

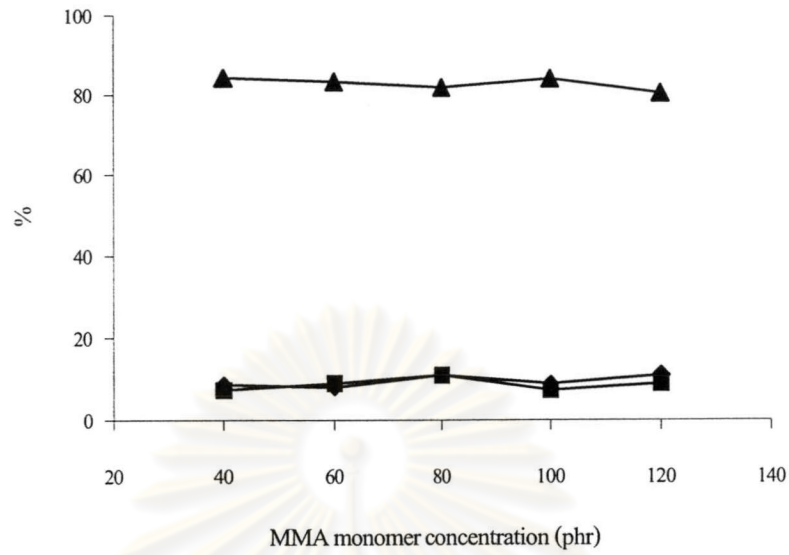
Reaction properties	TBHPO					CHPO				
	MMA monomer Concentration (phr)					MMA monomer Concentration (phr)				
	40	60	80	100	120	40	60	80	100	120
Conversion (%)	56.1	72.4	77.4	82.5	73.7	70.7	69.9	73.8	83.8	71.4
Grafting efficiency (%)	58.4	66.2	69.7	74.5	62.8	67.6	70.3	71.2	84.4	69.9
Graft properties										
Grafted NR (%)	83.5	81.3	80.0	80.5	71.7	84.2	83.2	81.7	83.9	75.8
Free NR (%)	8.5	8.0	8.1	7.5	10.4	8.6	7.9	10.9	8.8	13.2
Free PMMA (%)	8.0	10.6	11.9	12.1	18	7.3	8.9	10.9	7.2	13.8



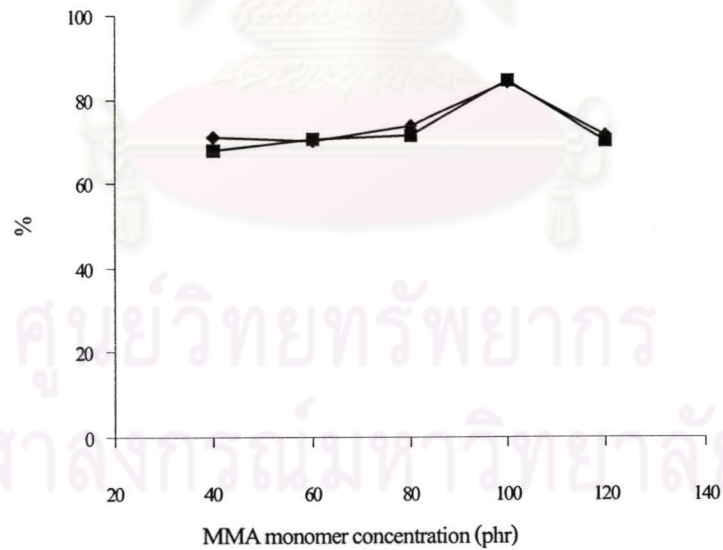
**Figure 4.18a** Effect of the monomer concentration on the percentage free NR (◆), percentage free PMMA (■), and percentage grafted natural rubber (▲) at 50°C, TBHPO 0.5 phr, and reaction time 8 hr



**Figure 4.18b** Effect of monomer concentration concentration on the percentage conversion (◆), and percentage grafting efficiency (■) at 50°C, TBHPO 0.5 phr, and reaction time 8 hr



**Figure 4.19a** Effect of the monomer concentration on the percentage free NR (◆), percentage free PMMA (■), and percentage grafted natural rubber (▲) at 50°C, CHPO 0.5 phr, and reaction time 8 hr



**Figure 4.19b** Effect of monomer concentration concentration on the percentage conversion (◆), and percentage grafting efficiency (■) at 50°C, CHPO 0.5 phr, and reaction time 8 hr

#### 4.2.1.4 Effect of the Reaction Time

The effect of the reaction time on the grafting of methyl methacrylate onto natural rubber by using two redox initiator, CHPO or TBHPO, are shown in Table 4.8. The detail of all data and calculation are shown in Appendix A. The parameters of the graft copolymerization was obtained as follows:

MMA monomer concentration	:	100 phr
Initiator concentration	:	0.5 phr
Reaction temperature	:	50°C
Reaction time	:	4-8 hr

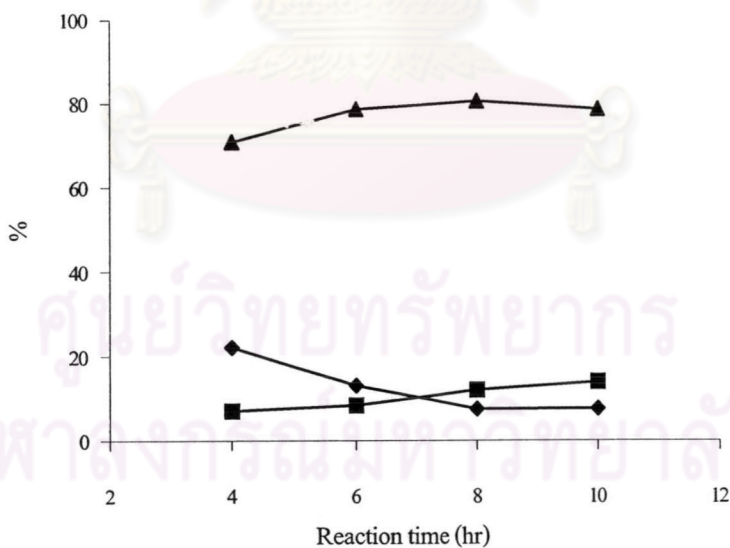
In Figure 4.20b and 4.21b, The percentage conversion, percentage grafting efficiency increase with increasing the reaction time. At the reaction time of 8 hr, its conversion and grafting efficiency reach a maximum, thereafter, the percentage conversion and percentage grafting efficiency decrease. At along reaction time, the PMMA homopolymer is formed more readily than is graft copolymer since there are no new active grafting sites on the rubber particle for more graft copolymerization.

The grafted natural rubber initiated by CHPO at the reaction time of 8 hr, gave the higher percentage grafting efficiency and the lower percentage of free PMMA than the grafted natural rubber initiated by TBHPO. The plausible reasons for the better grafting efficiency of CHPO over that of TBHPO shall be explained latter.

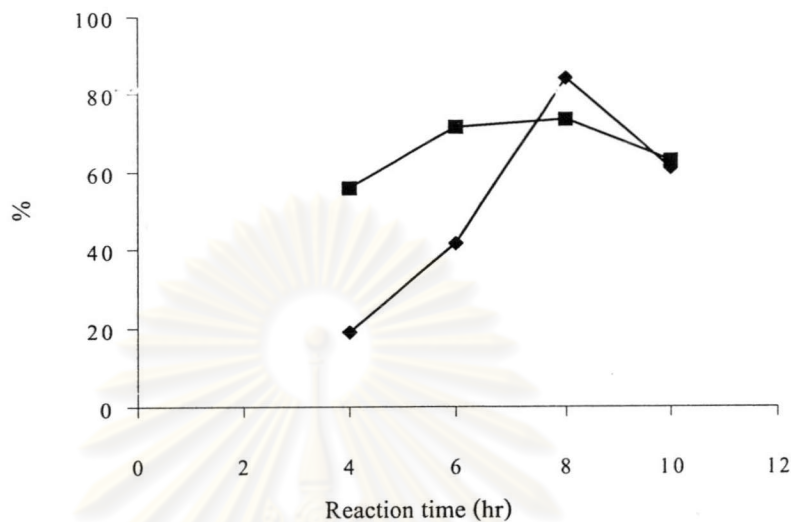


**Table 4.8** Effect of the reaction time on the percentage conversion, percentage grafting efficiency and percentage grafted natural rubber at 50°C, initiator concentration 0.5 phr, and MMA monomer concentration 100 phr.

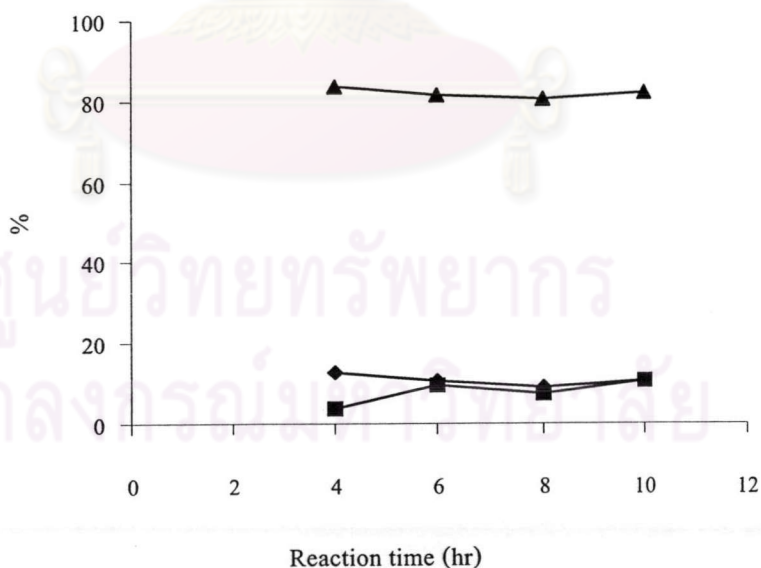
Reaction properties	TBHPO				CHPO			
	Reaction time (hr)				Reaction time (hr)			
	4	6	8	10	4	6	8	10
Conversion (%)	2.4	41.5	82.5	61.0	4.7	39.6	83.8	68.8
Grafting efficiency (%)	11.6	71.4	74.5	63.0	21.9	67.2	84.4	74.0
Graft properties								
Grafted NR (%)	85.8	78.6	80.5	78.6	83.7	81.6	83.9	81.9
Free NR (%)	12.2	13.0	7.5	7.5	12.8	10.5	8.8	10.6
Free PMMA (%)	2.0	8.4	12.1	13.9	3.5	9.3	7.2	10.6



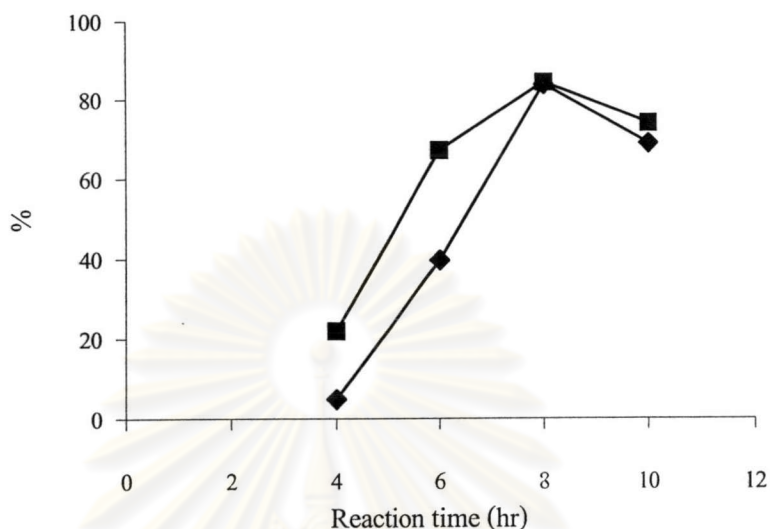
**Figure 4.20a** Effect of the reaction time on the percentage free NR (◆), percentage free PMMA (■), and percentage grafted natural rubber (▲) at 50°C, MMA monomer concentration 100 phr, and TBHPO 0.5 phr



**Figure 4.20b** Effect of reaction time on the percentage conversion NR (◆), and percentage grafting efficiency (■) at 50°C, MMA monomer concentration 100 phr, and TBHPO 0.5 phr



**Figure 4.21a** Effect of the reaction time on the percentage free NR (◆), percentage free PMMA (■), and percentage grafted natural rubber (▲) at 50°C, MMA monomer concentration 100 phr, and CHPO 0.5 phr



**Figure 4.21b** Effect of reaction time on the percentage conversion NR (◆), and percentage grafting efficiency (■) at 50°C, MMA monomer concentration 100 phr, and CHPO 0.5 phr

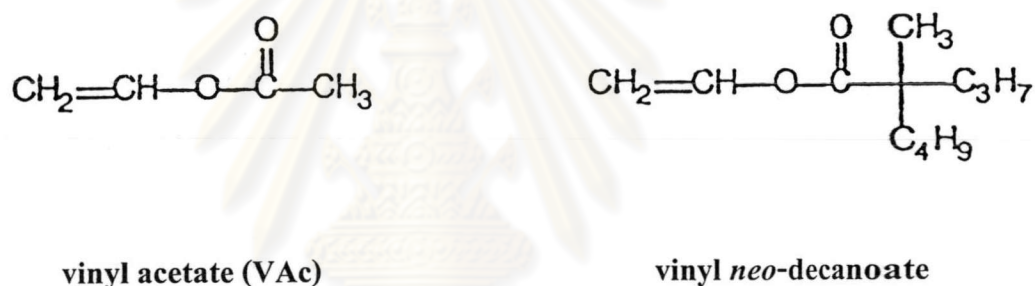
#### 4.2.2 The Preparation of the Grafted Natural Rubber using Potassium Persulfate.

##### 4.2.2.1 Effect of Grafting Promoter

The grafting of second monomer onto polyisoprene may be induced in two ways. The first method is through graft-site initiation, where the initiator derived radicals either add across the double bond or abstract hydrogens from the polyisoprene backbone. The second method is through hydrogen abstraction from polyisoprene by polymeric radicals. Allen et al.[27] found that the rate of polymerization was retarded when vinyl acetate (VAc) was polymerized in the presence of a model compound for a polyisoprenic

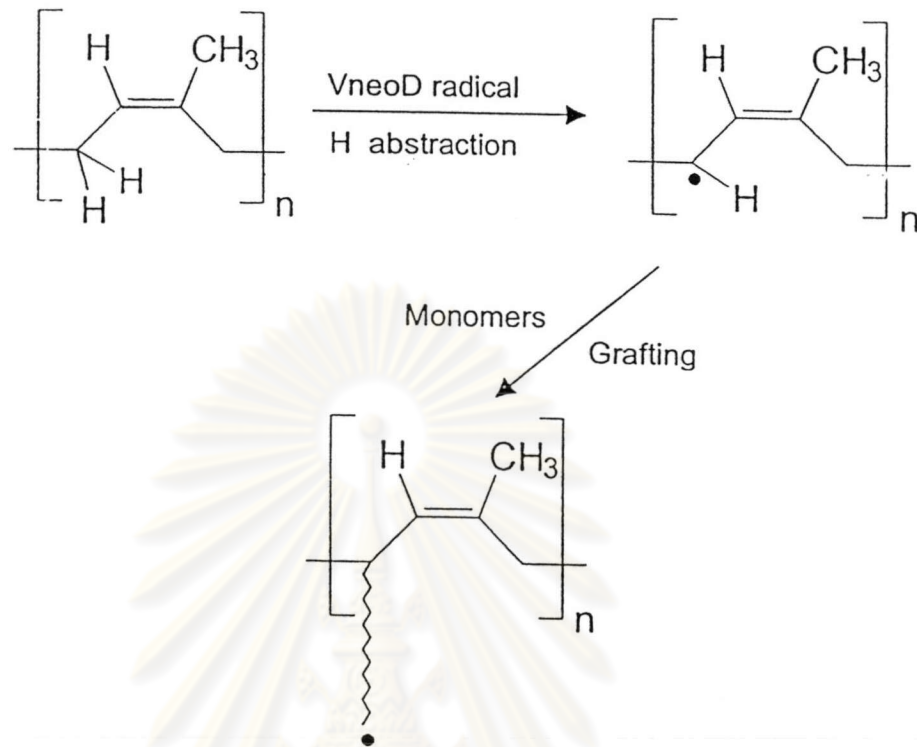
hydrocarbon. In this retardative chain transfer mechanism, a poly(VAc) radical abstracts hydrogen from isopropyl benzene to generate an unreactive allylic-type radical.

Based on these observations, Lehrle and Willis [1] proposed that VAc could facilitate grafting of methyl methacrylate onto natural rubber latex particles in a second-stage (seeded) emulsion polymerization. The results obtained showed less grafting than expected in the presence of VAc, and it was proposed that this could be due to the fact that oil-soluble initiator was not accessible to the high amounts of VAc present in aqueous phase.



**Figure 4.22** Chemical structures of vinyl acetate (VAc) and vinyl *neo*-decanoate

In this study, we used vinyl neodecanoate (VneoD) instead, which is actually a mixture of branch isomers such as vinyl 2-ethyl-2-propylpentanoate as a second monomer for emulsion polymerization, whose structures are shown in Figure 4.22. VneoD is very much less water-soluble than that of VAc and should reside entirely in the particle. VneoD has been observed to abstract hydrogen from polyisoprene and polybutadiene to form an allylic-type radical, which is relatively stable, suggesting that it could facilitate the grafting of other monomers onto natural rubber. The mechanism for this reaction is shown in Figure 4.23.



**Figure 4.23** Reaction scheme for hydrogen abstraction from poly(cis-isoprene) to form graft sites.[28]

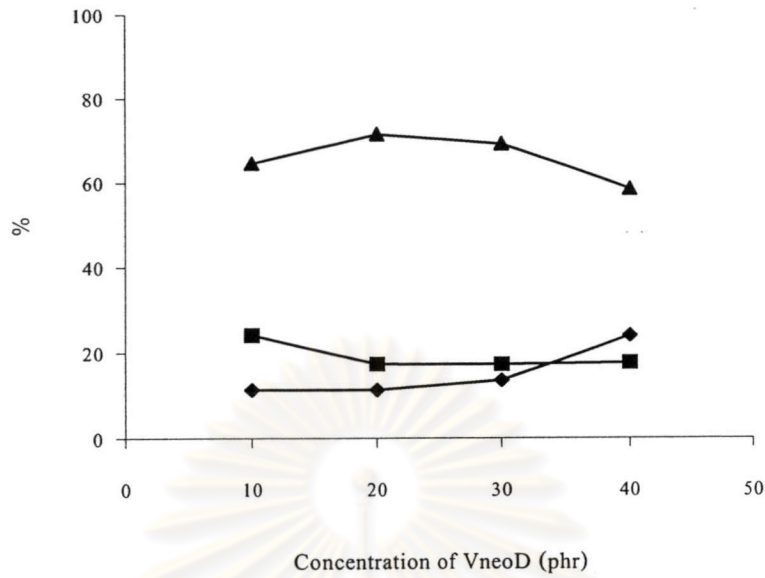
The effect of the grafting reaction agent was investigated by varying the concentration of vinyl neodecanoate (VneoD) as 10, 20, 30 and 40 %weight of methyl methacrylate (MMA). The percentage conversion, percentage grafted natural rubber, and percentage grafting efficiency are shown in Table 4.9 and Figures 4.22a-4.22b. The details of all data and calculation are shown in Appendix A. The parameters of graft copolymerization were obtained as follows:

MMA monomer concentration	:	100 phr
Grafting agent (VneoD)	:	10, 20, 30, 40 %wt of MMA
Initiator concentration	:	1.0 phr
Reaction temperature	:	55°C
Reaction time	:	8 hr

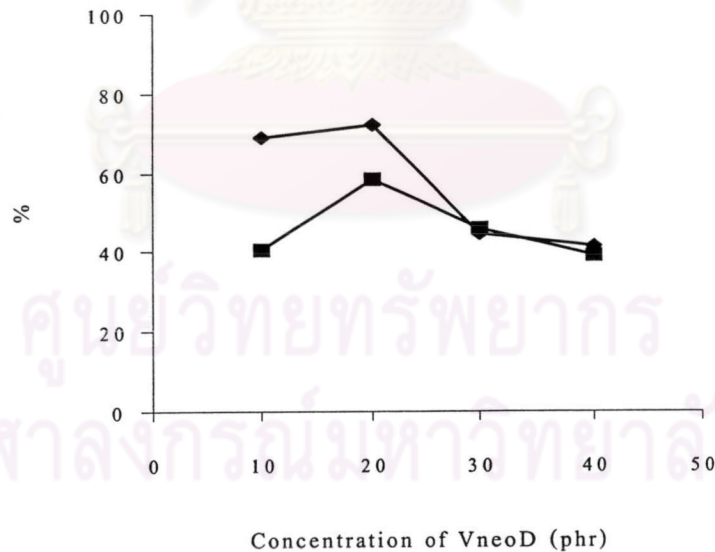
Figures 4.24a and 4.24b show the dependence of the percentage conversion, percentage grafted natural rubber, and percentage grafting efficiency on the concentration of VneoD. Initially, increases in the concentration of VneoD extracted more hydrogen radical from polyisoprene to form an allylic-type radical, which is relatively stable. It could consequently facilitate the grafting of other monomers onto natural rubber. The percentages of conversion and grafting efficiency are at maximum when the concentration of grafting promoting monomer (VneoD) is 20 %wt of methyl methacrylate. We found that conversion and grafting properties are optimal because low percentages of free NR and free PMMA are obtained

**Table 4.9** Effect of the grafting agent on the percentage conversion, percentage grafting efficiency and percentage grafted natural rubber at 55°C, MMA monomer concentration 100 phr,  $K_2S_2O_8$  1.0 phr, and reaction time 8 hr.

Reaction properties	VneoD (%wt of MMA)			
	10	20	30	40
Conversion (%)	68.9	72.2	44.7	41.4
Grafting efficiency (%)	40.6	58.4	46.3	39.5
Graft properties				
Grafted NR (%)	64.6	71.4	69.1	58.4
Free NR (%)	11.3	11.3	13.6	24.0
Free PMMA (%)	24.1	17.3	17.3	17.6



**Figure 4.24a** Effect of grafting agent on percentage free NR (◆), percentage free PMMA (■), and percentage grafted natural rubber (▲) at 55°C,  $K_2S_2O_8$  1.0 phr, MMA monomer concentration 100 phr, and reaction time 8 hr



**Figure 4.24b** Effect of grafting agent on percentage conversion (◆), and percentage grafting efficiency (■) at 55°C,  $K_2S_2O_8$  1.0 phr, MMA monomer concentration 100 phr, and reaction time 8 hr

#### 4.2.2.2 Effect of Initiator Concentration

The effect of initiator concentration at various temperatures on the percentage conversion, percentage grafted natural rubber and percentage grafting efficiency is shown in Tables 4.10-4.11 and Figures 4.25-4.31. The details of all data and calculations are shown in Appendix A. The parameters of graft copolymerization were obtained as follows:

MMA monomer concentration	:	100 phr
Grafting promoter (VneoD)	:	20 %wt of MMA
Initiator concentration	:	0.5-2.0 phr
Reaction temperature	:	50-70°C
Reaction time	:	8 hr

Figures 4.25-4.28 show the effect of initiator concentration on the percentage conversion, percentage grafted natural rubber, and percentage grafting efficiency at different temperatures. In Figure 4.29, the percentage conversion increases as the initiator concentration increases at every temperature investigated. Initially, the increase in the initiator concentration produces more graft sites for methyl methacrylate to graft. Therefore, percentage grafting efficiency, percentage conversion, and percentage grafted natural rubber can, of course, increase. At a higher initiator concentration, an abundance of initiator radical is produced, and excessive radicals react with each other. It can be seen that the maximum percentage conversion, percentage grafted natural rubber, and percentage grafting efficiency is at the initiator concentration of only 1.0 phr and reaction temperature 60°C.

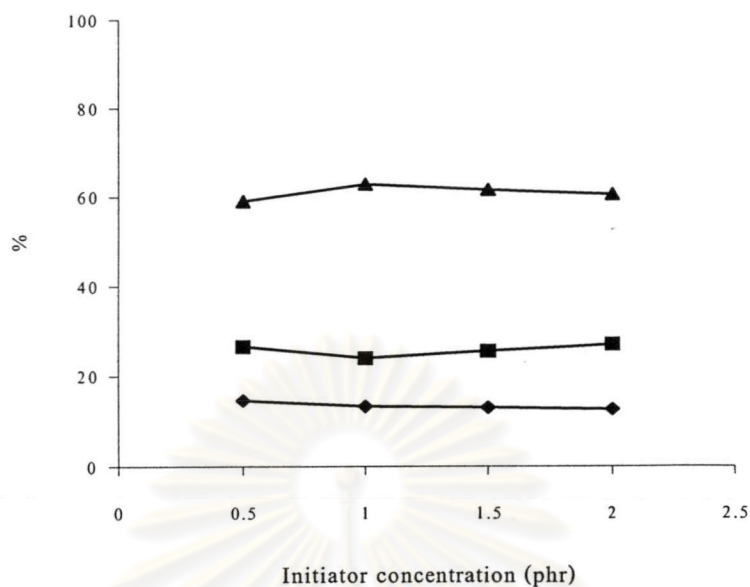


**Table 4.10** Effect of the initiator concentration of  $K_2S_2O_8$  on the percentage conversion, percentage grafting efficiency and percentage grafted natural rubber at 70-60°C, VneoD 20 %wt of MMA, MMA monomer concentration 100 phr, and reaction time 8 hr.

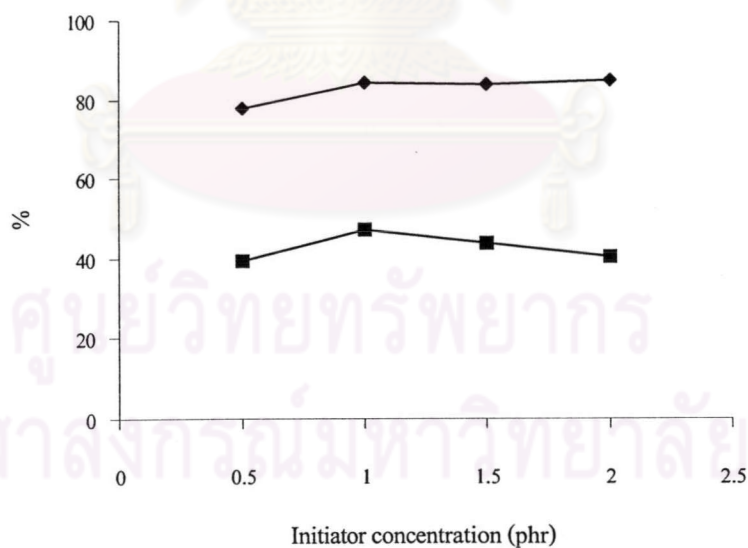
Reaction properties	70°C				60°C			
	Initiator concentration (phr)				Initiator concentration (phr)			
	0.5	1.0	1.5	2.0	0.5	1.0	1.5	2.0
Conversion (%)	78.0	84.4	83.7	84.5	74.5	85.1	84.2	82.1
Grafting efficiency (%)	39.5	47.5	43.7	40.9	48.9	61.1	61.1	48.8
Graft properties								
Grafted NR (%)	59.0	62.9	61.6	60.5	65.1	70.8	67.4	62.6
Free NR (%)	14.5	13.2	13.0	12.6	13.3	11.4	11.0	14.4
Free PMMA (%)	26.5	23.9	25.5	27.0	21.7	17.8	21.6	23.0

**Table 4.11** Effect of the initiator concentration of  $K_2S_2O_8$  on the percentage conversion, percentage grafting efficiency and percentage grafted natural rubber at 55-50°C, VneoD 20 %wt of MMA, MMA monomer concentration 100 phr, and reaction time 8 hr.

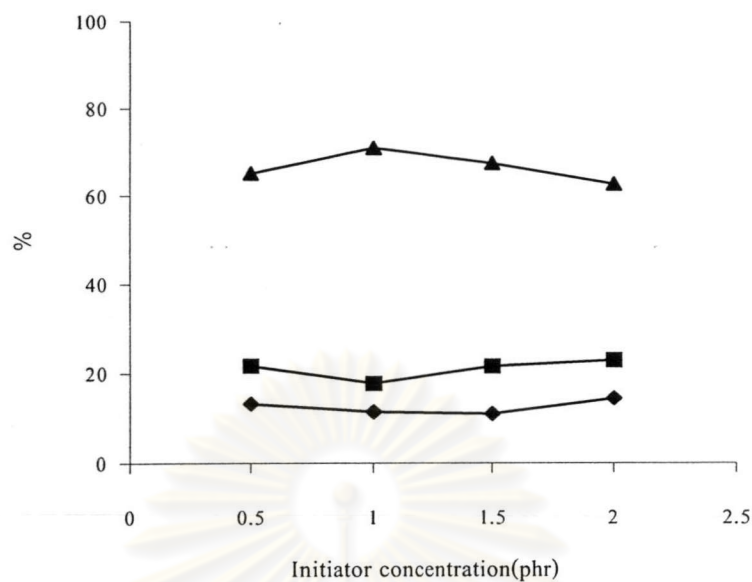
Reaction properties	55°C				50°C			
	Initiator concentration (phr)				Initiator concentration (phr)			
	0.5	1.0	1.5	2.0	0.5	1.0	1.5	2.0
Conversion (%)	63.5	72.2	73.2	72.3	43.3	49.0	67.0	71.1
Grafting efficiency (%)	42.5	58.4	41.8	37.4	39.5	46.5	43.0	43.9
Graft properties								
Grafted NR (%)	60.9	71.4	61.6	58.4	69.7	68.8	63.9	65.2
Free NR (%)	17.0	11.3	14.1	15.7	12.1	13.0	13.3	11.6
Free PMMA (%)	22.2	17.3	24.3	26.0	18.2	18.2	22.8	23.2



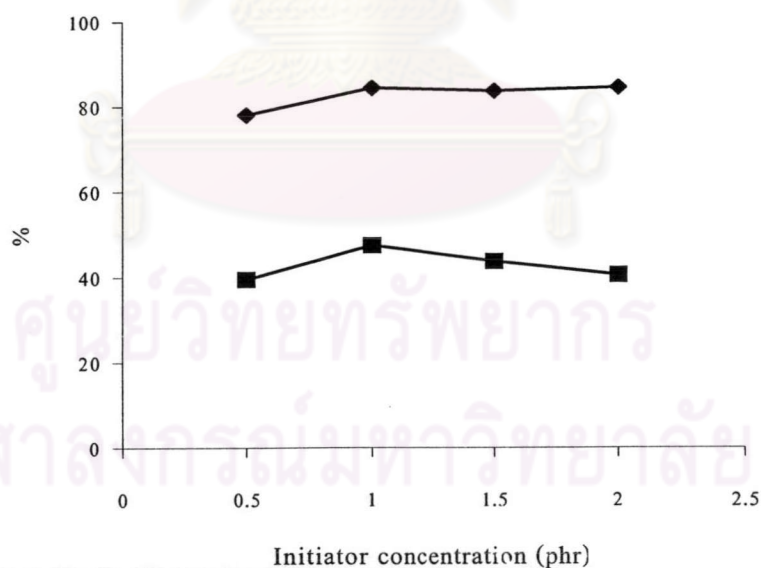
**Figure 4.25a** Effect of initiator concentration of  $K_2S_2O_8$  on the percentage free NR (◆), percentage free PMMA (■), and percentage grafted natural rubber (▲) at  $70^\circ C$ , VneoD 20 %wt of MMA, MMA monomer concentration 100 phr, and reaction time 8 hr



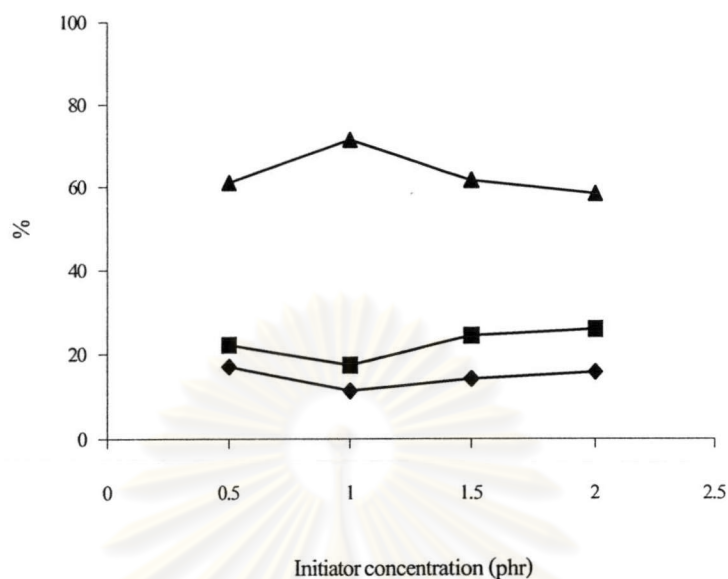
**Figure 4.25b** Effect of initiator concentration of  $K_2S_2O_8$  on the percentage conversion (◆), and percentage grafting efficiency (■) at  $70^\circ C$ , VneoD 20%wt of MMA, MMA monomer concentration 100 phr, and reaction time 8 hr.



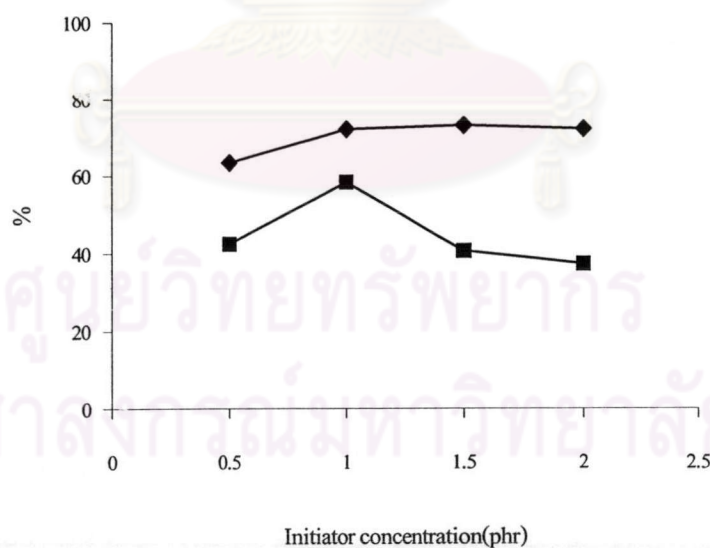
**Figure 4.26a** Effect of initiator concentration of  $K_2S_2O_8$  on the percentage free NR ( $\blacklozenge$ ), percentage free PMMA ( $\blacksquare$ ), and percentage grafted natural rubber ( $\blacktriangle$ ) at  $60^\circ\text{C}$ , VneoD 20 %wt of MMA, MMA monomer concentration 100 phr, and reaction time 8 hr



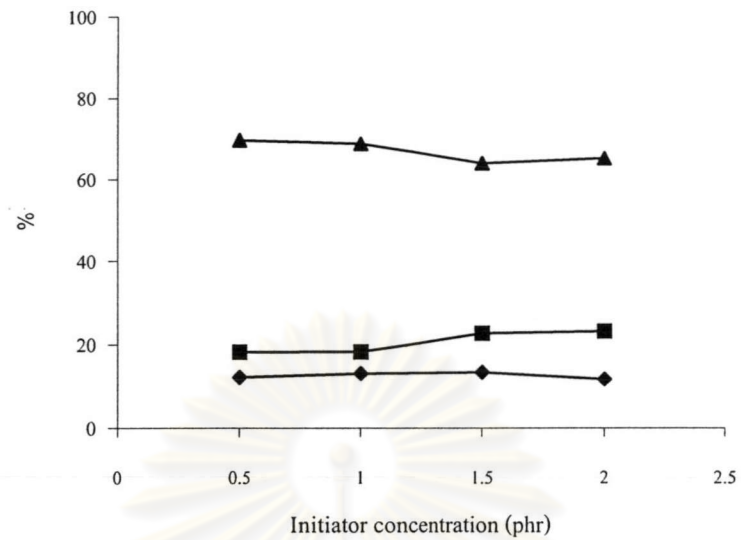
**Figure 4.26b** Effect of initiator concentration of  $K_2S_2O_8$  on the percentage conversion ( $\blacklozenge$ ), and percentage grafting efficiency ( $\blacksquare$ ) at  $60^\circ\text{C}$ , VneoD 20%wt of MMA, MMA monomer concentration 100 phr, and reaction time 8 hr.



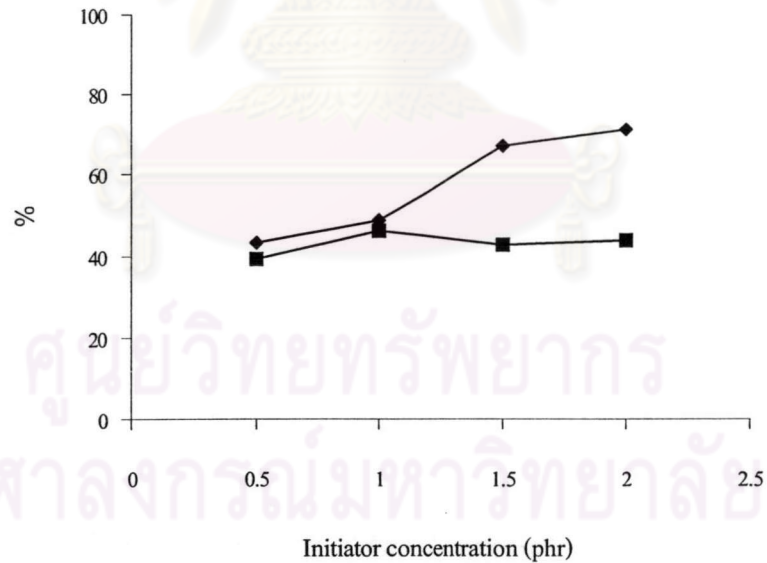
**Figure 4.27a** Effect of initiator concentration of  $K_2S_2O_8$  on the percentage free NR (◆), percentage free PMMA (■), and percentage grafted natural rubber (▲) at 55°C, VneoD 20 %wt of MMA, MMA monomer concentration 100 phr, and reaction time 8 hr



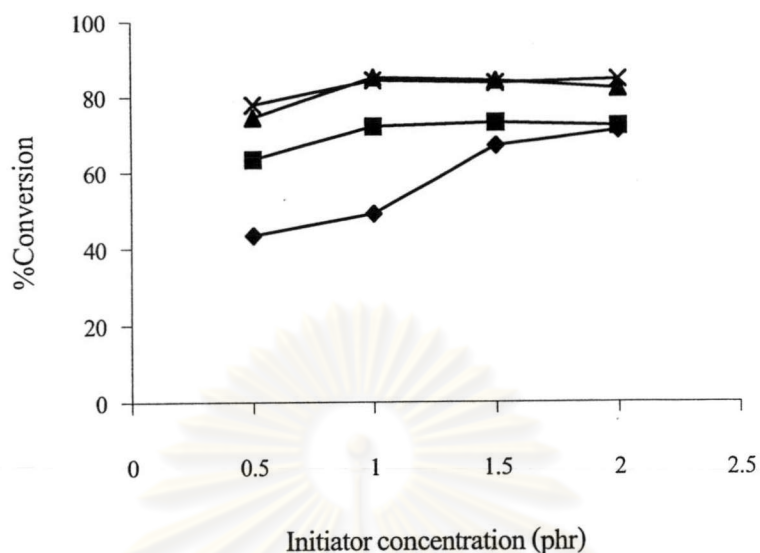
**Figure 4.27b** Effect of initiator concentration of  $K_2S_2O_8$  on the percentage conversion (◆), and percentage grafting efficiency (■) at 55°C, VneoD 20%wt of MMA, MMA monomer concentration 100 phr, and reaction time 8 hr.



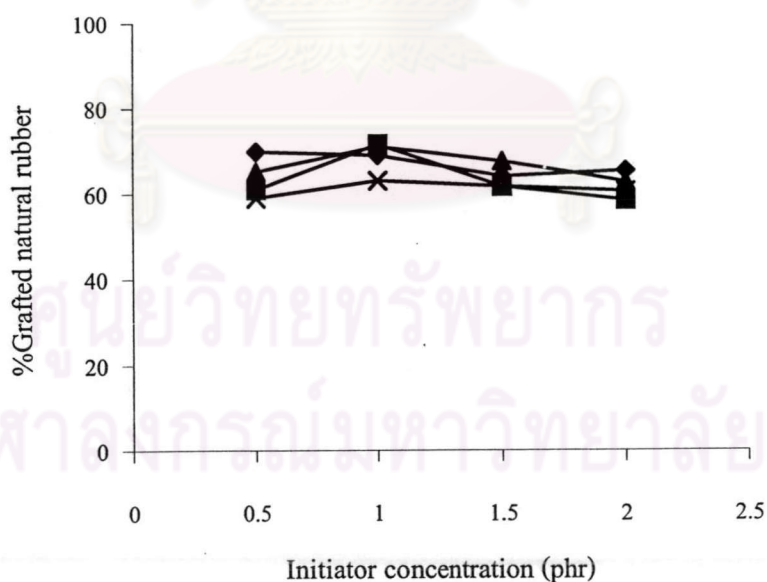
**Figure 4.28a** Effect of initiator concentration of  $K_2S_2O_8$  on the percentage free NR (◆), percentage free PMMA (■), and percentage grafted natural rubber (▲) at  $50^\circ C$ , VneoD 20 %wt of MMA, MMA monomer concentration 100 phr, and reaction time 8 hr



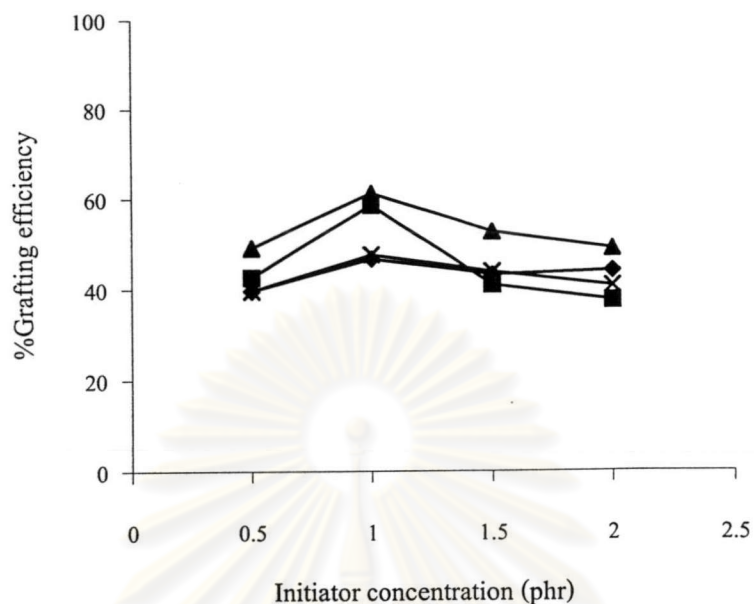
**Figure 4.28b** Effect of initiator concentration of  $K_2S_2O_8$  on the percentage conversion (◆), and percentage grafting efficiency (■) at  $50^\circ C$ , VneoD 20%wt of MMA, MMA monomer concentration 100 phr, and reaction time 8 hr



**Figure 4.29** Effect of initiator concentration of  $K_2S_2O_8$  on the percentage conversion (50-70°C, VneoD 20 %wt of MMA, MMA monomer concentration 100 phr, reaction time 8 hr) : (◆) 50°C; (■) 55°C; (▲) 60°C; and (X) 70°C



**Figure 4.30** Effect of initiator concentration of  $K_2S_2O_8$  on the percentage grafted natural rubber (50-70°C, VneoD 20 %wt of MMA, MMA monomer concentration 100 phr, reaction time 8 hr) : (◆) 50°C; (■) 55°C; (▲) 60°C; and (X) 70°C



**Figure 4.31** Effect of initiator concentration of  $K_2S_2O_8$  on the percentage grafting efficiency (50-70°C, VneoD 20 %wt of MMA, MMA monomer concentration 100 phr, reaction time 8 hr) : (◆) 50°C; (■) 55°C; (▲) 60°C; and (X) 70°C

#### 4.2.2.3 Effect of Reaction Temperature

The effect of reaction temperature on the percentage conversion, percentage grafted natural rubber, and percentage grafting efficiency are shown in Table 4.12 and Figures 4.32a-4.32b. The details of all data and calculations are shown in Appendix A. The parameters of graft copolymerization were obtained as follows:

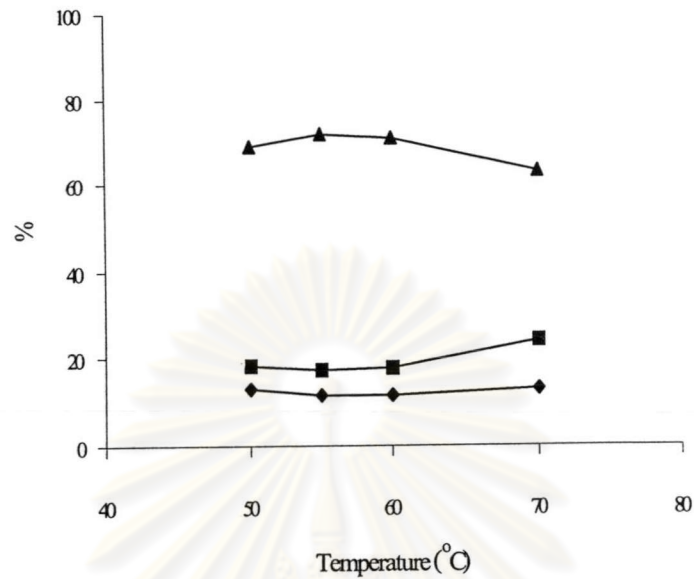
MMA monomer concentration	:	100 phr
Grafting promoter (VneoD)	:	20 %wt of MMA
Initiator concentration	:	1.0 phr
Reaction temperature	:	50-70°C
Reaction time	:	8 hr

In Figures 4.32a and 4.32b, it can be seen that a higher polymerization temperature results in a higher conversion. By increasing the temperature, decomposition of the initiator increases, it gives an increased number of free radicals, and therefore the higher rates of polymerization. The effects of reaction temperature on percentage grafting efficiency and grafted natural rubber are found decreasing when the polymerization temperature is higher than 60 °C.

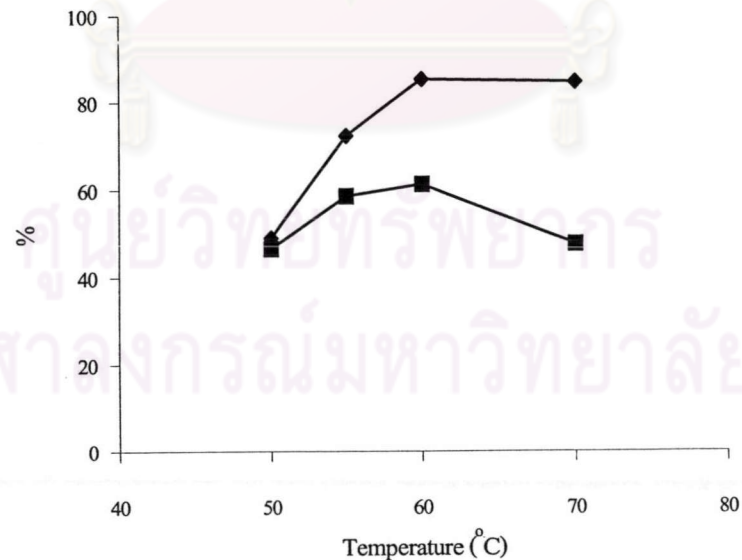
**Table 4.12** Effect of the reaction temperature on the percentage conversion, percentage grafting efficiency and percentage grafted natural rubber at VneoD 20 %wt of MMA,  $K_2S_2O_8$  1.0 phr, MMA monomer concentration 100 phr, and reaction temperature 8 hr.

Reaction properties	Temperature (°C)			
	50	55	60	70
Conversion (%)	49.0	72.2	85.1	84.4
Grafting efficiency (%)	46.5	58.4	61.1	47.5
Graft properties				
Grafted NR (%)	68.8	71.4	70.8	62.8
Free NR (%)	13.0	11.3	11.4	13.2
Free PMMA (%)	18.2	17.3	17.8	23.9





**Figure 4.32a** Effect of reaction temperature on the percentage free NR (◆), percentage free PMMA (■), and percentage grafted natural rubber (▲) at  $K_2S_2O_8$  1.0 phr, VneoD 20 %wt of MMA, MMA monomer concentration 100 phr, and reaction time 8 hr



**Figure 4.32b** Effect of reaction temperature on the percentage conversion (◆), and percentage grafting efficiency (■) at  $K_2S_2O_8$  1.0 phr, VneoD 20 %wt of MMA, MMA monomer concentration 100 phr, and reaction time 8 hr

#### 4.2.2.3 Effect of MMA monomer Concentration

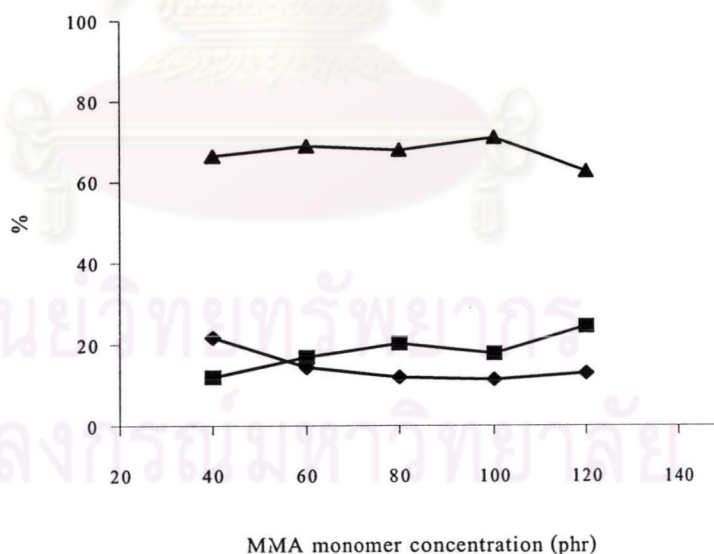
The effect of MMA monomer concentration on the extent of grafting was investigated by changing the monomer concentration within the range of 40-120 phr. The detail of all data and calculations are shown in Appendix A. The parameters of graft copolymerization were obtained as follows:

MMA monomer concentration	:	40-120 phr
Grafting promoter (VneoD)	:	20 %wt of MMA
Initiator concentration	:	1.0 phr
Reaction temperature	:	60°C
Reaction time	:	8 hr

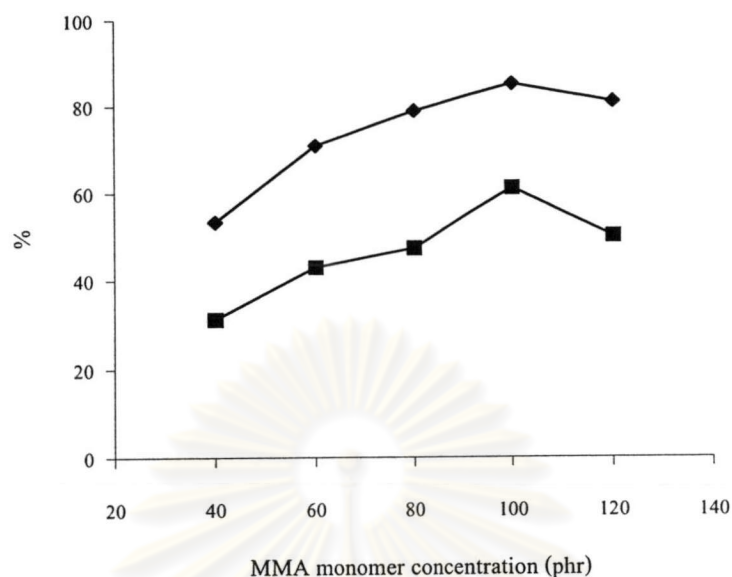
From Figures 4.33a-4.33b, it can be seen that as the monomer concentration increases, increases in the percentage conversion, percentage grafted natural rubber, and percentage grafting efficiency are found. It reaches a maximum value at the monomer concentration of 100 phr, and thereafter it decreases. At a higher monomer concentration, reactions competitive to the grafting probably take place in solution, i.e., homopolymerization is more favored at higher monomer concentrations. On the other hand, the rate of monomer diffusion is bound to be progressively affected by the polymer deposition, which of course, grows most rapidly when high concentrations of monomer are used.

**Table 4.13** Effect of the MMA monomer concentration on the percentage conversion, percentage grafting efficiency and percentage grafted natural rubber at 60° C,  $K_2S_2O_8$  1.0 phr, and reaction time 8 hr.

Reaction properties	MMA monomer concentration(phr)				
	40	60	80	100	120
Conversion (%)	53.3	70.8	78.8	85.1	80.9
Grafting efficiency (%)	31.2	42.9	47.3	61.1	50.1
Graft properties					
Grafted NR (%)	66.3	68.7	67.8	70.8	62.6
Free NR (%)	21.7	14.4	12.0	11.4	13.0
Free PMMA (%)	12.0	16.9	20.3	17.8	24.5



**Figure 4.33a** Effect of MMA monomer concentration on percentage free NR (◆), percentage free PMMA (■), and percentage grafted natural rubber (▲) at  $K_2S_2O_8$  1.0 phr, 60°C, VneoD 20 %wt of MMA, and reaction time 8 hr



**Figure 4.33b** Effect of MMA monomer concentration on percentage conversion (◆), and percentage grafting efficiency (■) at  $K_2S_2O_8$  1.0 phr,  $60^\circ\text{C}$ , VneoD 20 %wt of MMA, and reaction time 8 hr

#### 4.2.2.4 Effect of Reaction Time

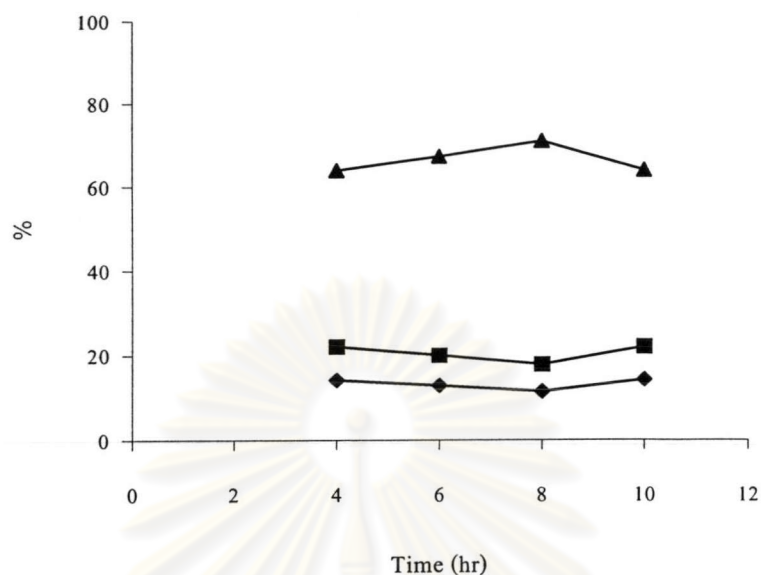
The effect of reaction time on the grafting of methyl methacrylate onto natural rubber is shown in Table 4.14 and Figures 4.34a-4.34b. The details of all data and calculations are shown in Appendix A. The parameters of graft copolymerization were obtained as follows:

MMA monomer concentration	:	100 phr
Grafting promoter (VneoD)	:	20 %wt of MMA
Initiator concentration	:	1.0 phr
Reaction temperature	:	$60^\circ\text{C}$
Reaction time	:	4 – 8 hr

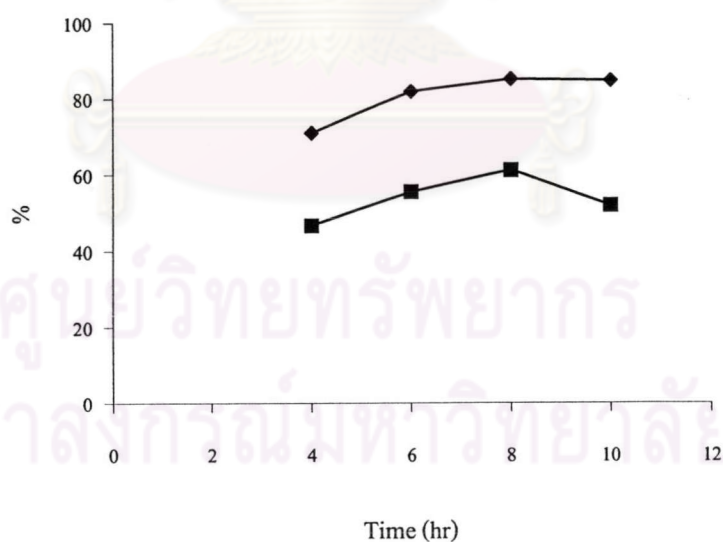
From Figures 4.34a and 4.34b, it can be seen that as the reaction time increases, there are increases in the percentage conversion, and percentage grafted natural rubber. At the reaction time of 8 hr, it reaches a maximum percentage conversion, percentage grafted natural rubber, and percentage grafting efficiency, thereafter they both slightly decrease. Through many experiences, we can conclude that PMMA homopolymer is formed more readily than the grafting to get the graft copolymer.

**Table 4.14** Effect of the reaction time on the percentage conversion, percentage grafting efficiency and percentage grafted natural rubber at 60° C,  $K_2S_2O_8$  1.0 phr, VneoD 20 %wt of MMA, and MMA monomer concentration 100 phr.

Reaction properties	Reaction time (hr)			
	4	6	8	10
Conversion (%)	70.9	81.8	85.1	84.7
Grafting efficiency (%)	46.6	55.4	61.1	51.8
Graft properties				
Grafted NR (%)	63.8	67.2	70.8	63.8
Free NR (%)	14.2	12.8	11.4	14.2
Free PMMA (%)	22.0	20.0	17.8	22.0



**Figure 4.34a** Effect of reaction time on percentage free NR (◆), percentage free PMMA (■), and percentage grafted natural rubber (▲) at 60°C,  $K_2S_2O_8$  1.0 phr, VneoD 20 % wt of MMA, and MMA monomer concentration 100 phr



**Figure 4.34b** Effect of reaction time on percentage conversion (◆), and percentage grafting efficiency (■) at 60°C,  $K_2S_2O_8$  1.0 phr, VneoD 20 %wt of MMA, and MMA monomer concentration 100 phr

Up to this stage, the optimum condition for the preparation of grafted natural rubber is found as follows:

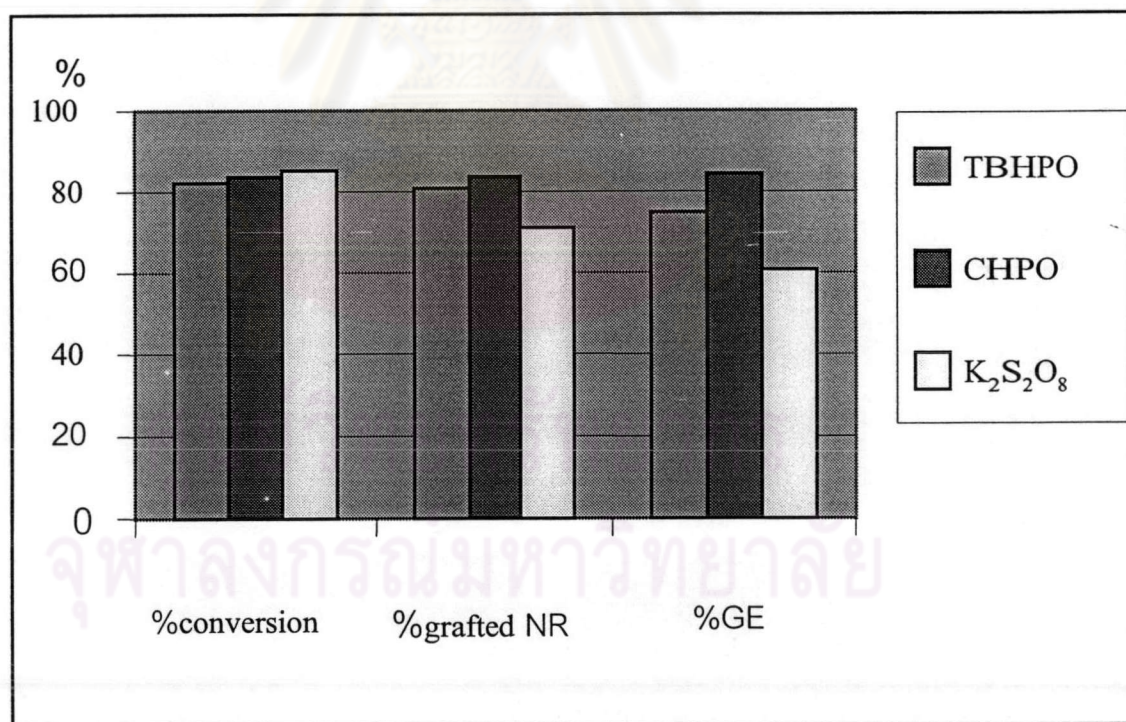
- a.) The concentration of CHPO 0.5 phr, the rubber content 100 phr, the reaction temperature 50°C, the monomer content 100 phr, and reaction time 8 hr.
- b.) The concentration of TBHPO 0.5 phr, the rubber content 100 phr, the reaction temperature 50°C, the monomer content 100 phr, and reaction time 8 hr.
- c.) The concentration of  $K_2S_2O_8$  1.0 phr, the rubber content 100 phr, monomer ratio (VneoD : MMA) 20:80, MMA monomer concentration 100 phr, the reaction temperature 60°C, and reaction time 8 hr.

#### 4.2.2 Types of Redox Initiator on Grafting of Natural Rubber

Graft copolymerizations of methyl methacrylate onto natural rubber particles were prepared. Three initiation systems, CHPO/TEPA, TBHPO/TEPA, and  $K_2S_2O_8/Na_2S_2O_3$ , were used. The optimum conditions, as just concluded above, for the preparation of the grafted natural rubber by the initiation system are shown in Table 4.15 and Figure 4.35.

**Table 4.15** Effect of redox initiator systems on percentage grafting efficiency, percentage grafted natural rubber, and percentage grafting efficiency at the optimum condition.

Reaction properties	CHPO	TBHPO	$K_2S_2O_8$
Conversion(%)	83.8	82.5	85.1
Grafting efficiency (%)	84.4	74.5	61.1
Graft properties			
Grafted NR (%)	83.9	80.5	70.8
Free NR (%)	8.8	7.5	11.4
Free PMMA (%)	7.2	12.0	17.8



**Figure 4.35** Effect of types of redox initiator on percentage conversion, percentage grafted natural rubber, and percentage grafting efficiency at the optimum condition.

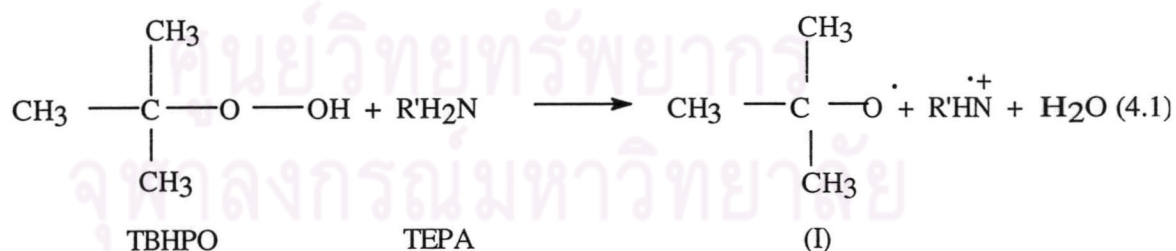


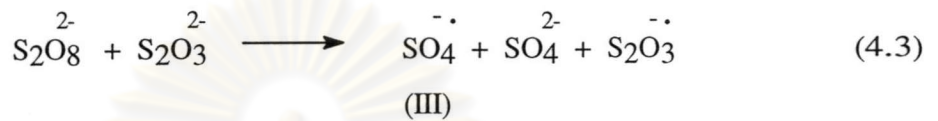
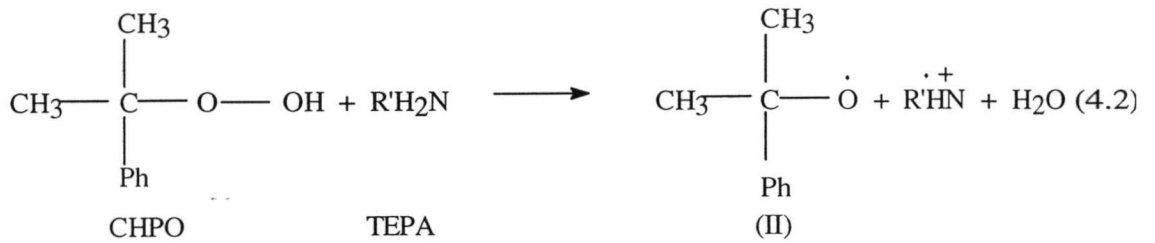
From Figure 4.35, it can be seen that CHPO gave a highest grafting efficiency, percentage grafted natural rubber, and percentage conversion. The CHPO was observed to be more effective than TBHPO and  $K_2S_2O_8$  for grafting methyl methacrylate onto natural rubber. Because the partitioning ability of the initiator between monomer-swollen NR and aqueous phase is quite different, the graft property is indeed affected. It is expected that the radical concentration from CHPO on the natural rubber particles would be higher than those of TBHPO and  $K_2S_2O_8$ , since TBHPO is soluble in both organic and aqueous phase, and  $K_2S_2O_8$  is only soluble in aqueous phase.

### 4.2.3 Mechanism of Grafting

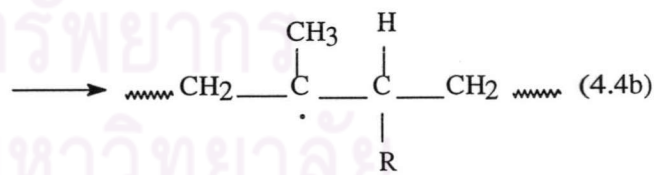
The three initiation systems, CHPO/TEPA, TBHPO/TEPA, and  $K_2S_2O_8/Na_2S_2O_3$ , were used to initiate the graft copolymerizations of methyl methacrylate onto natural rubber particle. The following plausible explanation is suggested for the grafting process:

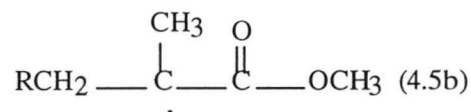
#### a.) Initiation:





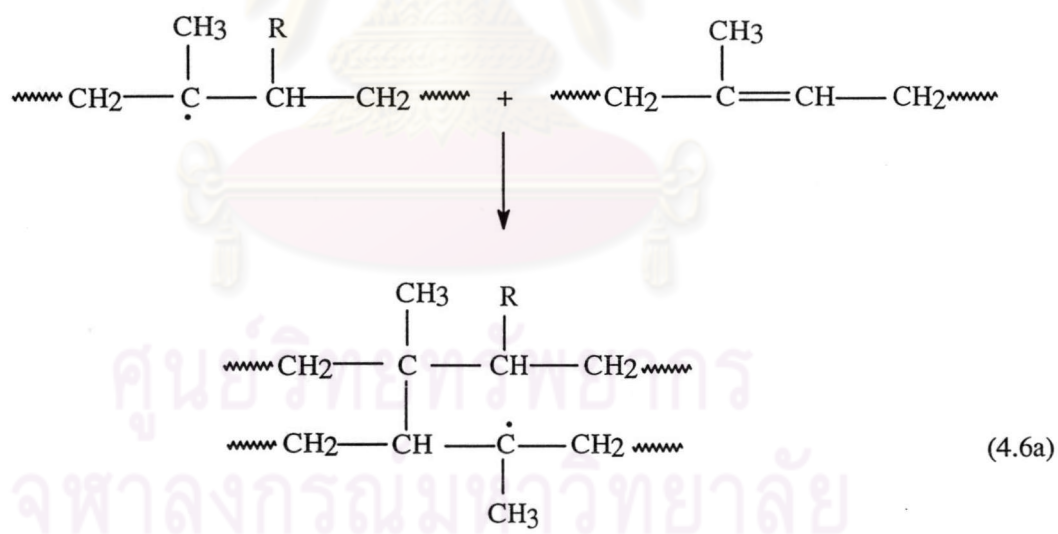
The three redox initiators could decompose to yield the radicals, as shown in reaction numbers 4.1-4.3. The free initiator radicals (I, II, and III are represented as R' in the proceeding reaction) may promote grafting in two different ways. The pre-existing polymer was a backbone, which can readily undergo addition (through residual double bonds) or abstraction (of labile hydrogen) to form a grafting site.

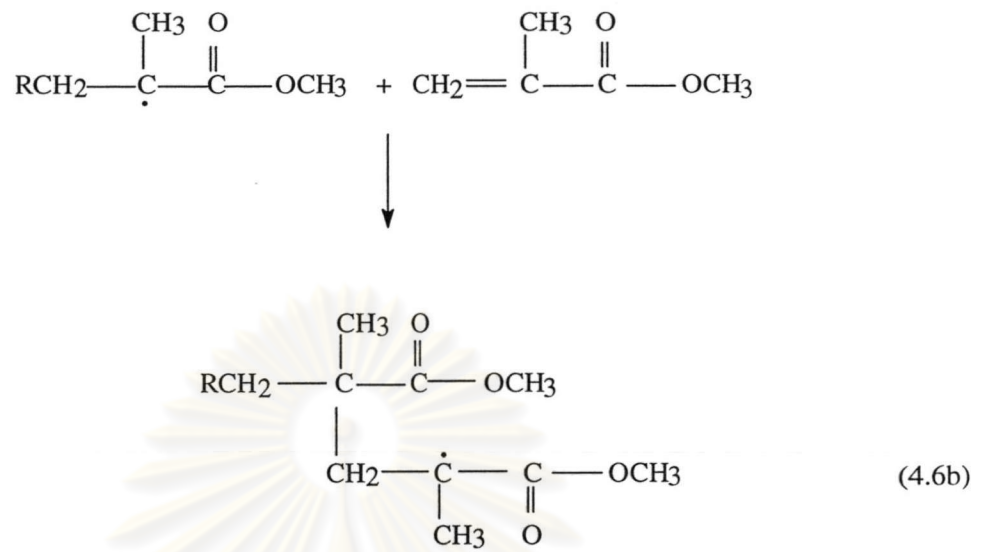




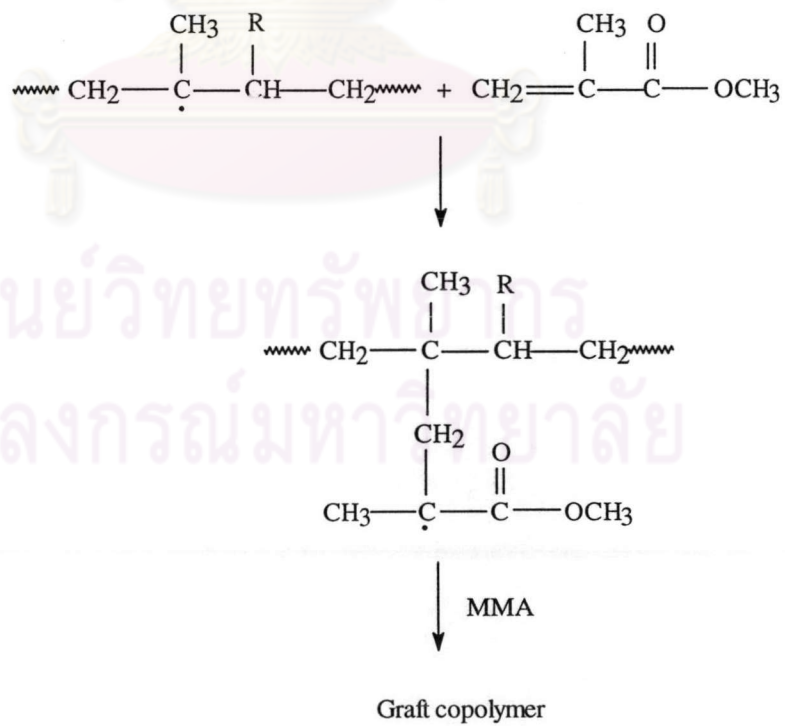
**b.) Propagation:**

**i.) Polymerization of Monomer Itself**



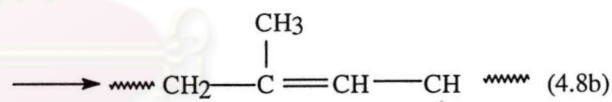
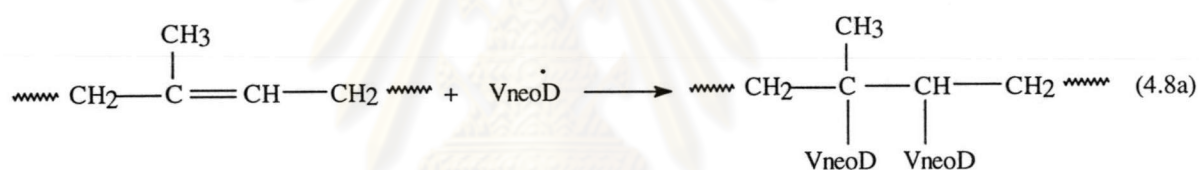


## ii.) Free Radical Grafting of MMA Monomer onto Natural Rubber

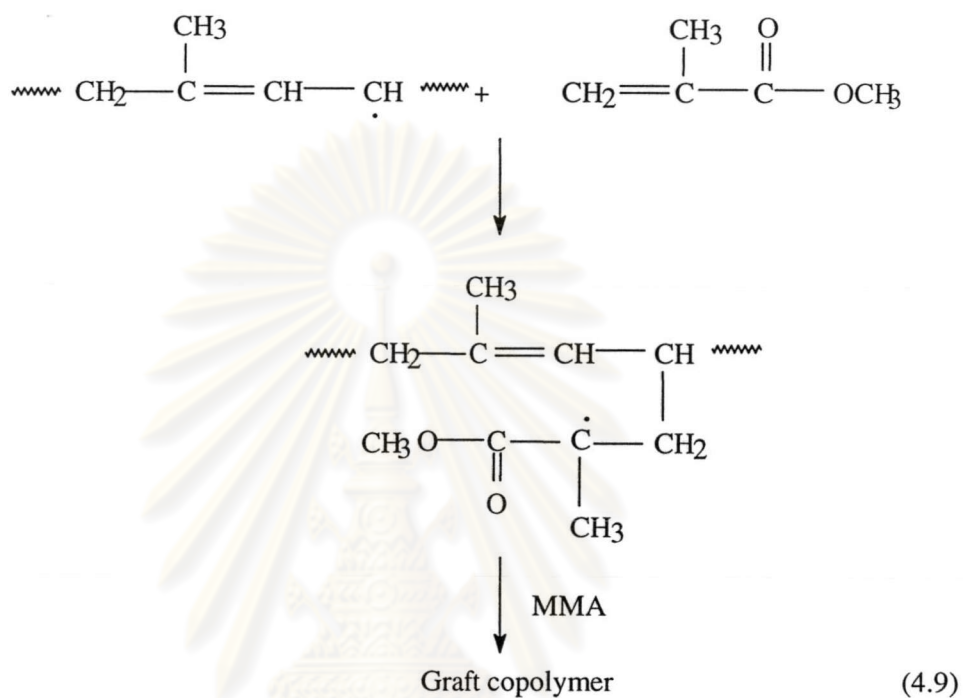


The abstraction pathway may be facilitated through the stability of resulting allylic radical. It could have a very slow re-initiation rate coefficient with other monomers. The addition pathway is the major route for propagation.

As mentioned above, the initiation of graft copolymerization by  $K_2S_2O_8/Na_2S_2O_3$  took place in the presence of VneoD as the grafting promoter. Monterio et al. [29] proposed that the first step of the reaction is that the VneoD radicals add across the double bond on the polyisoprene to form radicals that are unreactive towards the monomer, which now act as radical terminators. The second is the abstraction mechanism, in which VneoD radicals abstract hydrogen from the allylic position on polyisoprene backbone.

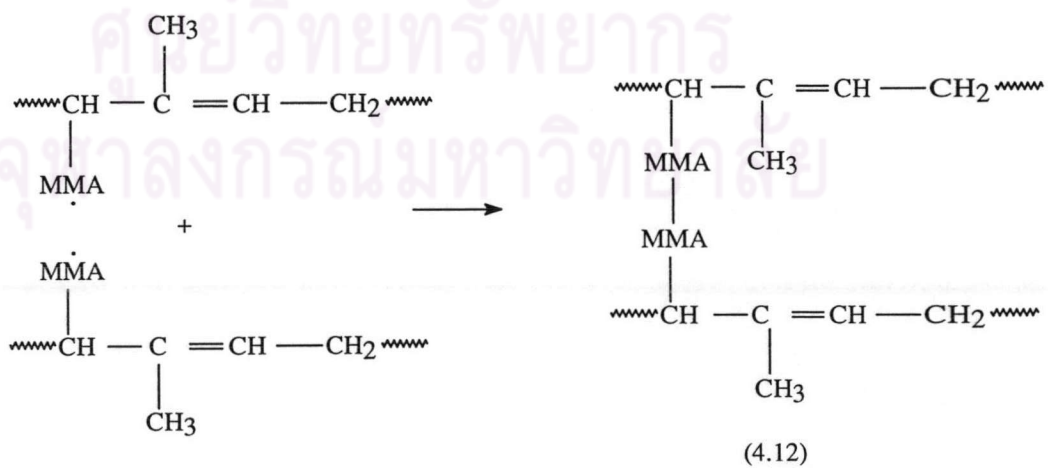
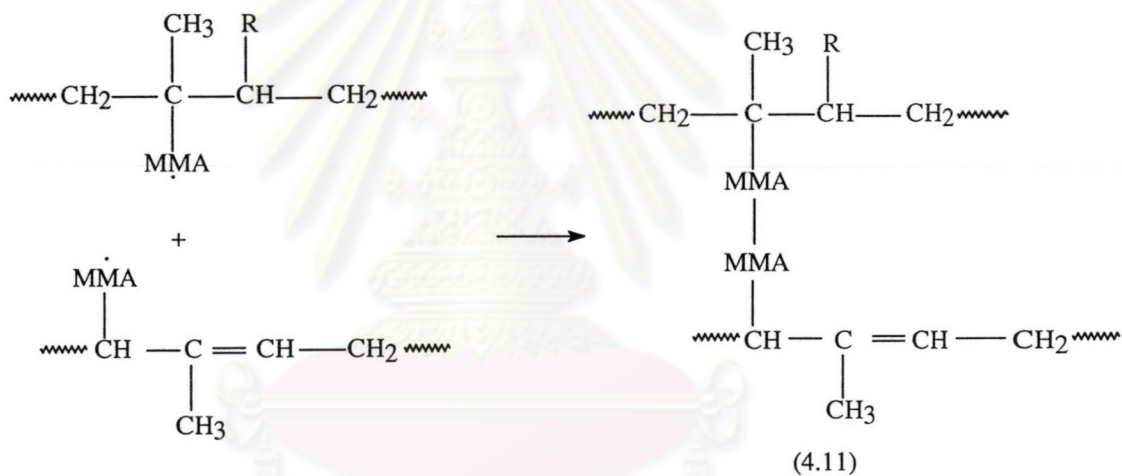
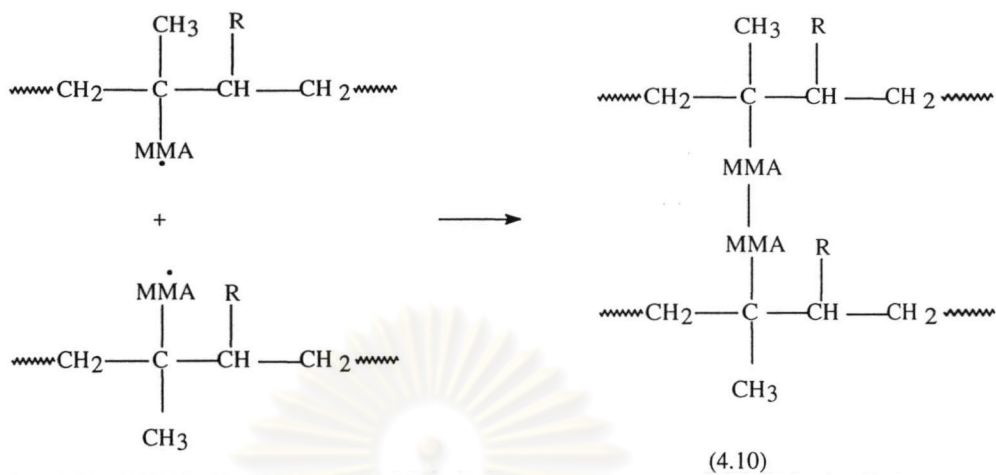


The allylic radical is slow to propagate with the unreactive VneoD, and thus providing more frequencies for MMA monomer to graft onto the natural rubber.



### c.) Termination

The macroradicals may follow two competing pathways. They can either initiate the grafting of monomer or branching or crosslinking. In this study, the grafted natural rubbers were not all soluble in  $\text{CHCl}_3$  or toluene and gel formation was found. The crosslinking can be possible occurred by recombination of two macroradicals.



### 4.3 Characterization of Grafted Natural Rubber

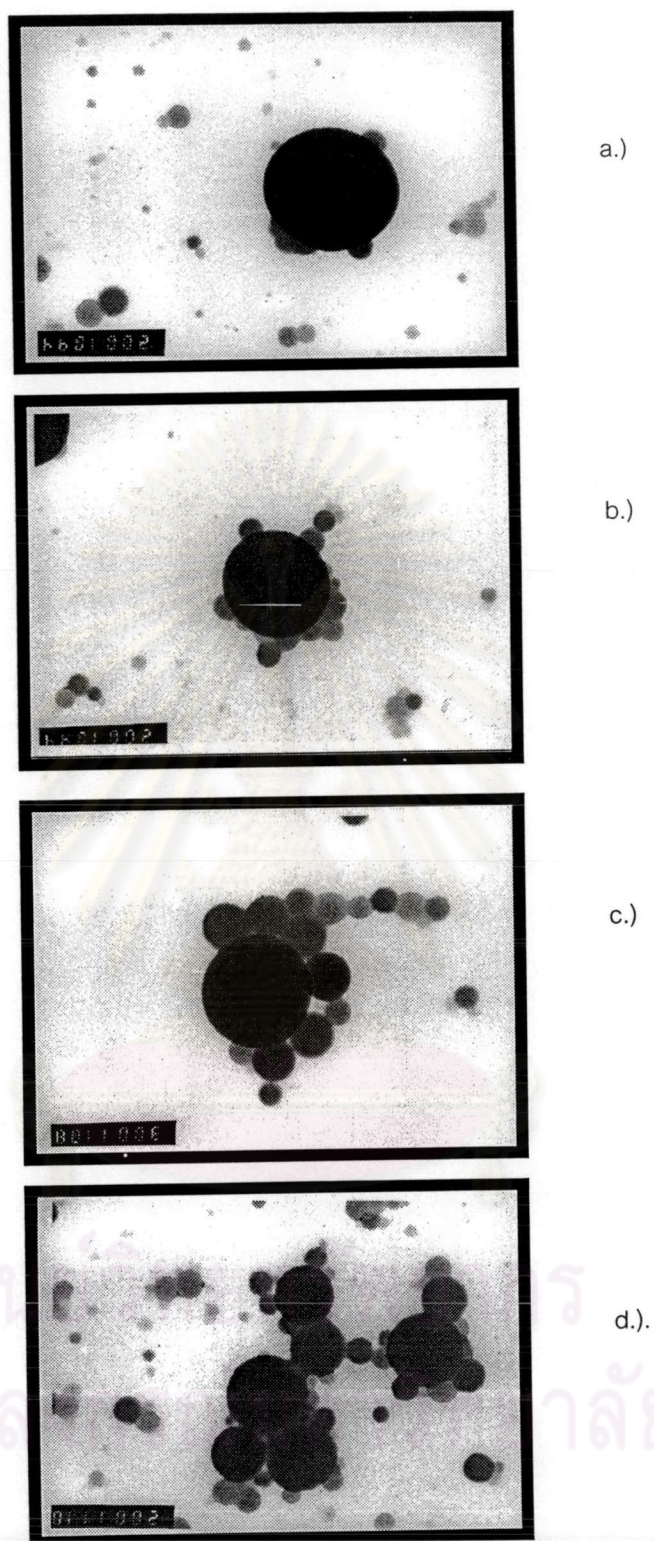
#### 4.3.1 Grafted Natural Rubber Morphology

In the graft copolymerization of methyl methacrylate onto natural rubber latex with different initiator systems, we used three different redox initiator systems, CHPO/TEPA, TBHPO/TEPA, and  $K_2S_2O_8/Na_2S_2O_3$ . The grafting reaction occurred largely on the surface of rubber particle.

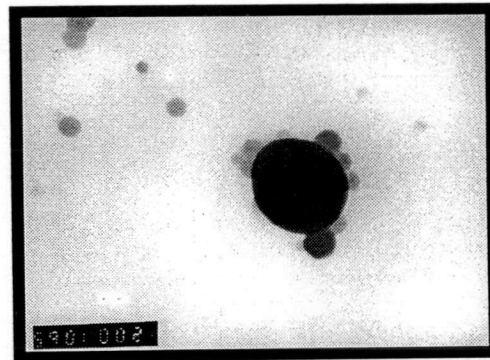
Figures 4.36-4.38 show TEM micrographs of the grafted natural particles from different redox initiator systems. The surface morphology of the grafted rubber was studied by  $OsO_4$  staining. The rubber particles are dark and the lighter color of the outer layer is composed of many clusters of PMMA particles. The grafting between the plastic (PMMA) and elastomer (natural rubber) components leads to the compatibility of two domains, resulting in a favorable state of the dispersion and some possibly chemical bonds linking the two phases together. The morphology of the particle during the period of polymerization, the thickness of graft copolymer (the outer layer) on the surface of seed particles increased with the increasing the reaction time.

The initiator type influences on the morphology of the graft copolymer. From Figures 4.47c, 4.48c, and 4.49c, the surfaces of the grafted natural rubber particles initiated by CHPO and TBHPO have the presence of nodules of MMA monomer on the surfaces of the natural rubber particles. It is due to the growing macroradical chains, which are generated onto the surface of natural rubber particle and continued to propagate to form the outer layer. On the other hand, the surface of grafted natural rubber particle initiated from  $K_2S_2O_8$  and VneoD used as the grafting promoter is smooth. Most of MMA monomers are polymerized in the microdomain at the surface layer of natural rubber particle. Because the physical partitioning of the initiator

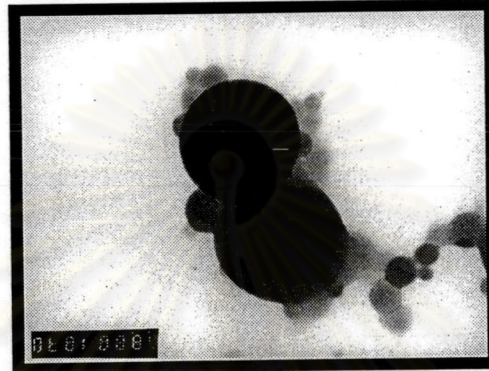




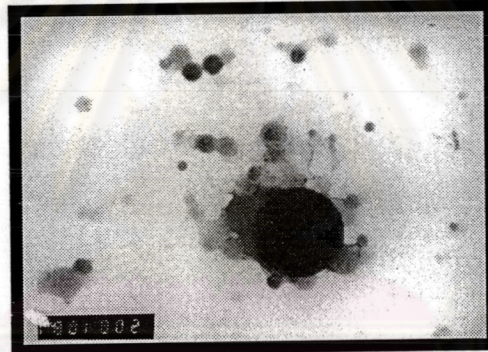
**Figure 4.36** Transmission electron micrographs of grafted natural rubber latex; MMA 100 phr; TBHPO 0.5 phr; 50°C. a.) 4 hr (x 30,000), b.) 6 hr (x30,000), c.) 8 hr (x45,000 ), and d.) 10 hr (x30,000)



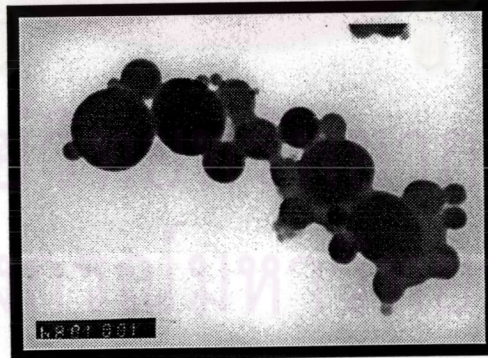
a.)



b.)

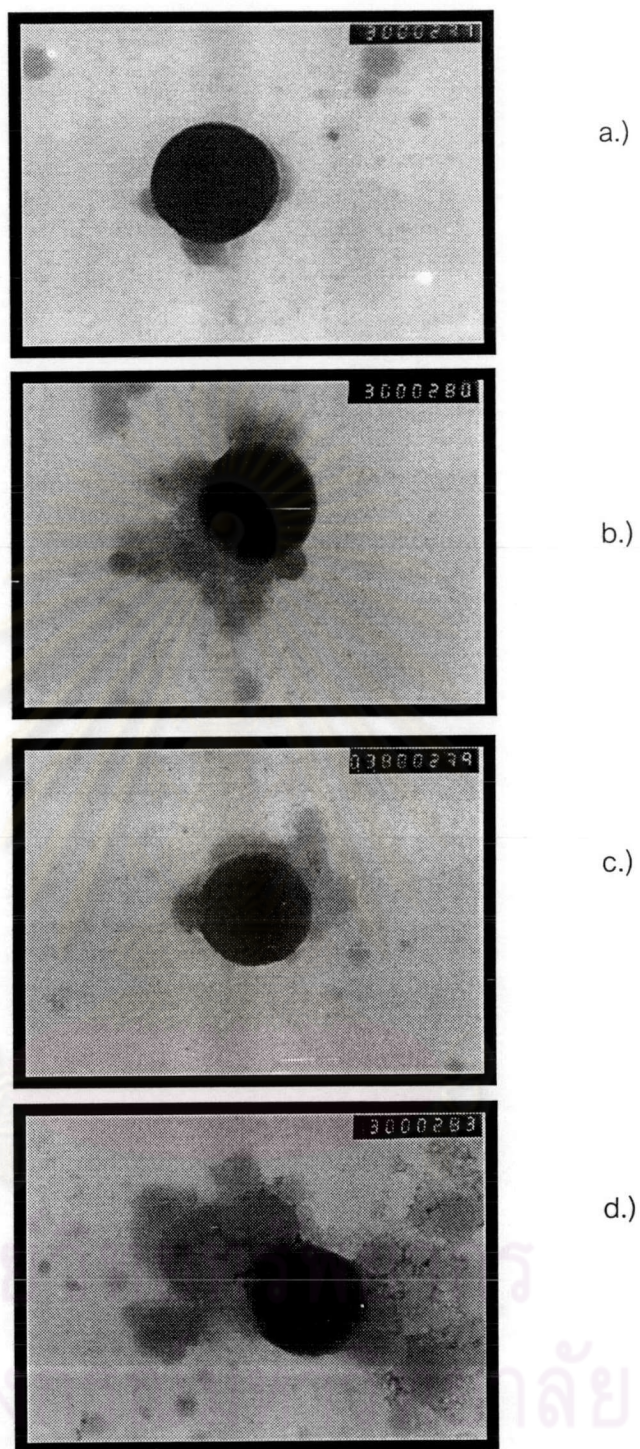


c.)



d.)

**Figure 4.37** Transmission electron micrographs of grafted natural rubber latex; MMA 100 phr; CHPO 0.5 phr; 50°C. a.) 4 hr (x 30,000), b.) 6 hr (x30,000), c.) 8 hr (x45,000 ), and d.) 10 hr (x16,500)



**Figure 4.38** Transmission electron micrographs of grafted natural rubber latex; 60°C;  $K_2S_2O_8$  1.0 phr; VneoD 20 %wt of MMA; and monomer concentration 100 phr  
a.) 4 hr (x 45,000), b.) 6 hr (x45,000), c.) 8 hr (x45,000 ), and d.) 10 hr (x45,000)

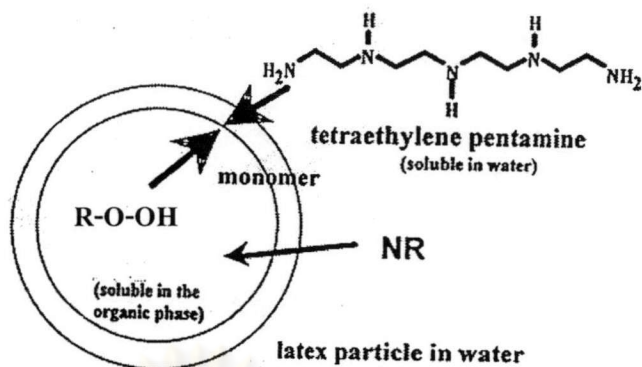
radicals between the polymer (NR) and aqueous phase may contribute a significant difference to the surface morphology.

#### 4.5.2.1 Locus of Polymerization

In the grafting reaction of methyl methacrylate onto natural rubber with different initiator systems, the locus of polymerization is very important. The different initiators initiate the grafting polymerization via two loci in the mixture:

- Partition of the initiator between the monomer-swollen natural rubber and the aqueous phase is quite different by each initiator.
- Partition nucleation in the aqueous phase could take place.

The three initiator systems were used. The oil soluble initiator, CHPO or TBHPO, was employed with the amine (TEPA). The rate of producing primary radicals ( $k_d$ ) of CHPO,  $1.7 \times 10^{-6} \text{ (s}^{-1}\text{)}$  in benzene at  $130^\circ\text{C}$ , is higher than the  $k_d$  of TBHPO,  $3 \times 10^{-7} \text{ (s}^{-1}\text{)}$  in benzene at  $130^\circ\text{C}$ . [30] Consequently, CHPO generates more radicals than those of TBHPO. The hydroperoxide radical from CHPO or TBHPO partitions strongly into the organic phase or the rubber surface, whereas the amine (TEPA) prefers to remaining in the aqueous phase, initiating the polymerization at the rubber/water interface. [19] The location of the CHPO/TEPA or TBHPO/TEPA is shown in Figure 4.46.



**Figure 4.46** Site of reaction in modified natural rubber latex in the bipolar redox initiation systems.[22]

Now, TBHPO is soluble in both organic and aqueous phases. On other hand, CHPO is insoluble in aqueous phase due to its high hydrophobicity. The partitioning of CHPO or TBHPO between monomer-swollen natural rubber and aqueous phase will be significantly different. It has been expected that the radical concentration generated from CHPO in natural rubber particles would be higher than THBPO because TBHPO is soluble in both organic and aqueous phase. The higher concentration of peroxide radicals in natural rubber particle, the more crosslinking and/or grafting is induced by both monomeric and polymeric radicals.

$K_2S_2O_8$  is a water-soluble initiator, the  $K_2S_2O_8$  generates its radicals in the aqueous phase with  $Na_2S_2O_3$ . Although it can diffuse near the rubber particles, the grafting reaction takes place sluggishly. Thus for the persulfate system, the concentrations of radical were relatively lower in the natural rubber particles to result in a lower grafting yield.

To conclude, the partitions of CHPO, TBHPO, and  $K_2S_2O_8$  between the monomer-swollen natural rubber and the aqueous phase are quite different. Such difference yields the different percentages of grafting efficiency.

It is well known that the graft copolymerization yield both graft copolymer and homopolymer. In this study, the homopolymers could be poly(methyl methacrylate) and ungrafted natural rubber. The nature of the monomer is a very important factor in producing the desirable extent of graft copolymer. Methyl methacrylate monomer has the highest water solubility,  $650 \text{ mmolL}^{-1}$ . [26] Therefore, the poly(methyl methacrylate) nucleation in the aqueous phase take place quite easily, especially when the hydrophilic  $\text{K}_2\text{S}_2\text{O}_8$  initiator is used, wherein a significant number of radicals in the aqueous phase is generated. Because of the different locus of polymerization, a decrease of grafting in the modified natural rubber phase is resulted in when  $\text{K}_2\text{S}_2\text{O}_8/\text{Na}_2\text{S}_2\text{O}_3$  is used. On the other hand, the hydrophobic nature of CHPO initiator prefers to residing on the natural rubber particles rather than in aqueous phase. In other words, more grafting copolymerization and grafted rubber are found (see Table 4.15)

#### 4.3.2 Effect of $\bar{M}_w$ , $\bar{M}_n$ , and Polydispersity of the Grafted Natural Rubber.

Analysis of averaged molecular weights and distribution of the graft copolymer was determined by Gel-Permeation Chromatography (GPC), using chloroform (HPLC grade) as an eluent. The  $\bar{M}_w$ ,  $\bar{M}_n$  and polydispersity ( $\bar{M}_w/\bar{M}_n$ ) of the grafted natural rubber were analyzed by comparing with the standard calibration curves of polystyrene standard having a  $\bar{M}_w$  range of  $2.85 \times 10^4 - 3.16 \times 10^6$

The weight average molecular weight ( $\bar{M}_w$ ) is related to the weight of the individual molecular as represented by the Equation 4.13.

$$\bar{M}_w = \frac{\sum(M_i W_i)}{\sum W_i} \quad (4.13)$$

Where  $M_i$  = Molecular weight of the polymer of fraction  $i$

$W_i$  = Weight of the polymer in fraction  $i$

And  $i$  = Fraction number (from 1 to  $x$ )

The number averaged molecular weight ( $\bar{M}_n$ ) is dependent on the number of molecules having each discrete and is represented by Equation 4.14.

$$\bar{M}_n = \frac{\sum W_i}{\sum N_i} \quad (4.14)$$

Where  $N_i$  = the number of molecules in fraction  $i$

The  $\bar{M}_w$  and  $\bar{M}_n$  values may be used to provide an index for the range of molecular weight distribution as follows:

$$\bar{M}_w/\bar{M}_n = d \quad (4.15)$$

Where  $d$  = polydispersity index

Table 4.16 shows the gel content, weight averaged molecular weight ( $\bar{M}_w$ ), number averaged molecular weight ( $\bar{M}_n$ ), and polydispersity ( $\bar{M}_w/\bar{M}_n$ ) for natural rubber coagulated from the natural rubber latex, the latex was stirred at 50°C with CHPO or TBHPO 0.5 phr for 8 hr, at 60°C with  $K_2S_2O_8$  1.0 phr for 8 hr in the absence of methyl methacrylate monomer, respectively.

**Table 4.16** The gel content,  $\bar{M}_w$ ,  $\bar{M}_n$ , and  $\bar{M}_w/\bar{M}_n$  at various initiators and concentration. (in absence of methyl methacrylate monomer)

	Gel content	$\bar{M}_n/10^5$	$\bar{M}_w/10^5$	$\bar{M}_w/\bar{M}_n$
NR	50.8	3.5	12.1	3.5
<sup>a</sup> NR/CHPO	65.1	1.0	3.6	3.5
<sup>a</sup> NR/TBHPO	66.4	0.9	3.8	4.4
<sup>b</sup> NR/K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	35.6	0.8	2.1	2.7

<sup>a</sup>Polymerization was carried out at CHPO 0.5 phr or TBHPO 0.5 phr; rubber content 100 phr; 50 °C; and time 8 hr.

<sup>b</sup>Polymerization was carried out at K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> 1.0 phr; rubber content 100 phr; 60 °C; and time 8 hr.

From Table 4.16, it is evident from a comparison of the untreated natural rubber with the natural rubber stirred with different redox initiators, CHPO/TEPA, TBHPO/TEPA, and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, in the absence of methyl methacrylate. The value of  $\bar{M}_w$  and  $\bar{M}_n$  were reduced by stirring with redox initiators. The decreased in  $\bar{M}_w$  indicated that the mainly high molecular weight fractions of rubber to form the low molecular weight fractions. To prepare the graft copolymer a high yield, the degradation of rubber has to be minimized.[12] The chain scission of natural rubber molecules will result in the formation of unstable molecules, which can react together via graft copolymerization, and will lead to increase in molecular weight of rubber molecule. The gel contents of natural rubber stirred with CHPO and TBHPO were increased comparing with the untreated natural rubber but the gel content of the natural rubber stirred with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was reduced.



**Table 4.17** The gel content,  $\bar{M}_n$ ,  $\bar{M}_w$ , and  $\bar{M}_w/\bar{M}_n$  from the optimum condition at different redox initiators.

Initiator	Gel content	$\bar{M}_n/10^5$	$\bar{M}_w/10^5$	$\bar{M}_w/\bar{M}_n$
<sup>a</sup> NR/CHPO	65.1	1.0	3.6	3.5
<sup>a</sup> NR/TBHPO	66.4	0.9	3.8	4.4
<sup>a</sup> NR/K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	35.6	0.8	2.1	2.7
<sup>b</sup> NR/CHPO	74.5	3.0	4.9	1.6
<sup>b</sup> NR/TBHPO	72.5	1.6	4.0	2.4
<sup>b</sup> NR/K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	42.2	1.0	2.9	2.9

<sup>a</sup> All are in the absence of MMA monomer.

<sup>b</sup> All are in the presence of MMA monomer.

Table 4.17 shows the amounts of the gel content, weight average molecular weight ( $\bar{M}_w$ ), number average molecular weight ( $\bar{M}_n$ ), and polydispersity ( $\bar{M}_w/\bar{M}_n$ ) of grafted natural rubber from CHPO/TEPA, TBHPO/TEPA, and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> at the optimum condition. The gel content,  $\bar{M}_w$ , and  $\bar{M}_n$  were increased in the presence of MMA monomer when compared with those without the MMA monomer. The gel content and  $\bar{M}_w$  of grafted natural rubber were at maxima using the redox initiator of CHPO/TEPA. The lower  $\bar{M}_w$  of grafted natural rubber initiated by K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, is found because K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> degrades natural rubber. These results demonstrate that the CHPO/TEPA initiation system was justified to be the most appropriate radical initiator for the graft copolymerization of methyl methacrylate onto natural rubber.

### 4.3.3 Effect of glass transition of the grafted natural rubber.

In this study, the glass transition temperature ( $T_g$ ) was measured by differential scanning calorimetry (DSC). Figures 4.40-4.33 show the DSC thermograms of the natural rubber and grafted natural rubber. The DSC thermograms were measured at the temperature range from  $-100$  to  $100^\circ\text{C}$ .

From DSC thermograms of the natural rubber and graft copolymers with different initiation systems have the deflection between  $-63$  to  $-65^\circ\text{C}$ . There is no shift in the glass transition temperature of the natural rubber in all graft copolymers. The  $T_g$  is affected by size and mobility of chains. The majority of these polymers has a relatively few grafted chains, insufficient to affect the free volume available to the backbone, and the  $T_g$  of the backbone. The  $T_g$  of the backbone will initially be the same as for the natural rubber.

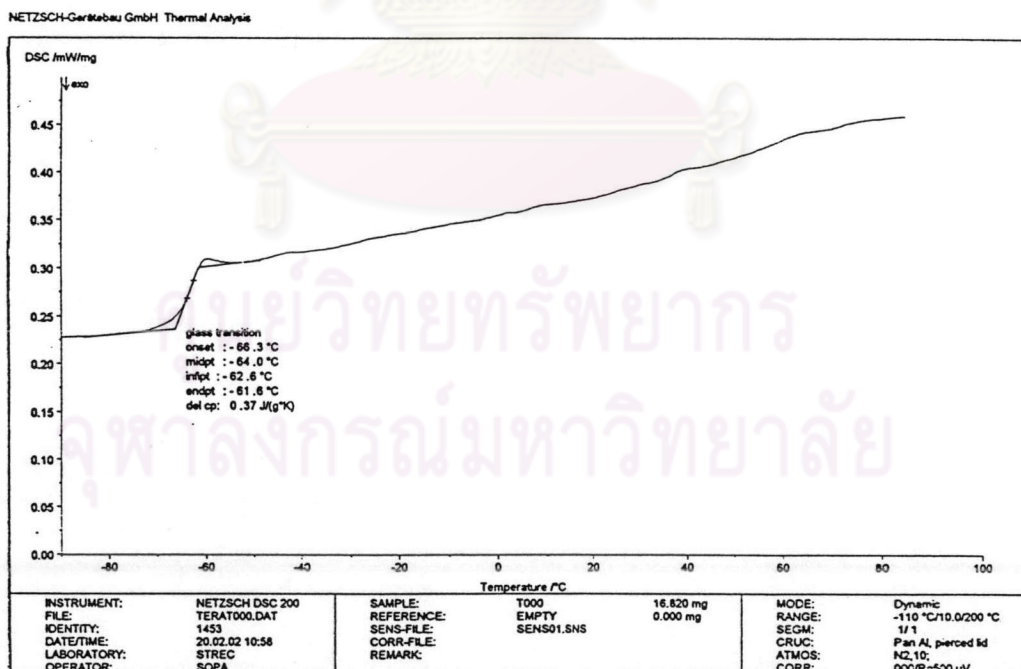


Figure 4.40 DSC thermogram of natural rubber.

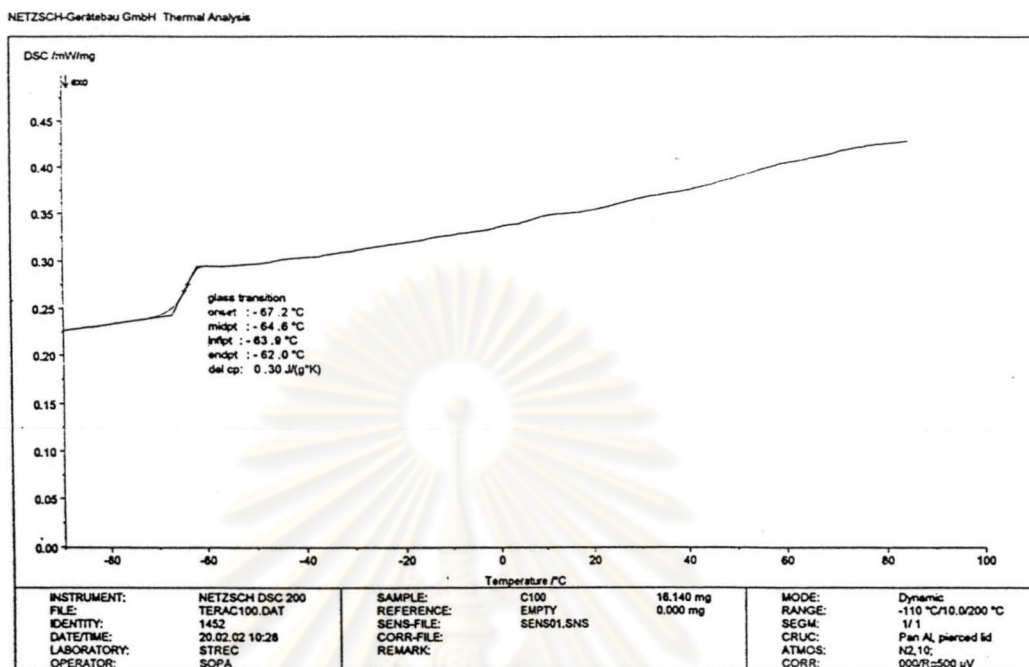


Figure 4.41 DSC thermogram of grafted natural rubber from CHPO initiation.

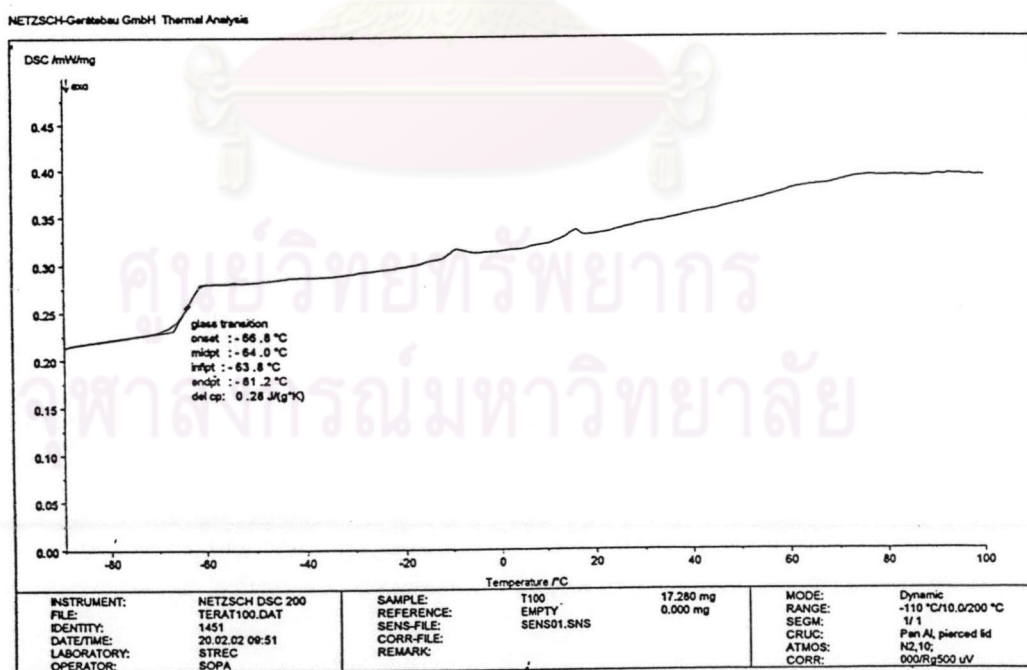


Figure 4.42 DSC thermogram of grafted natural rubber from TBHPO initiation.

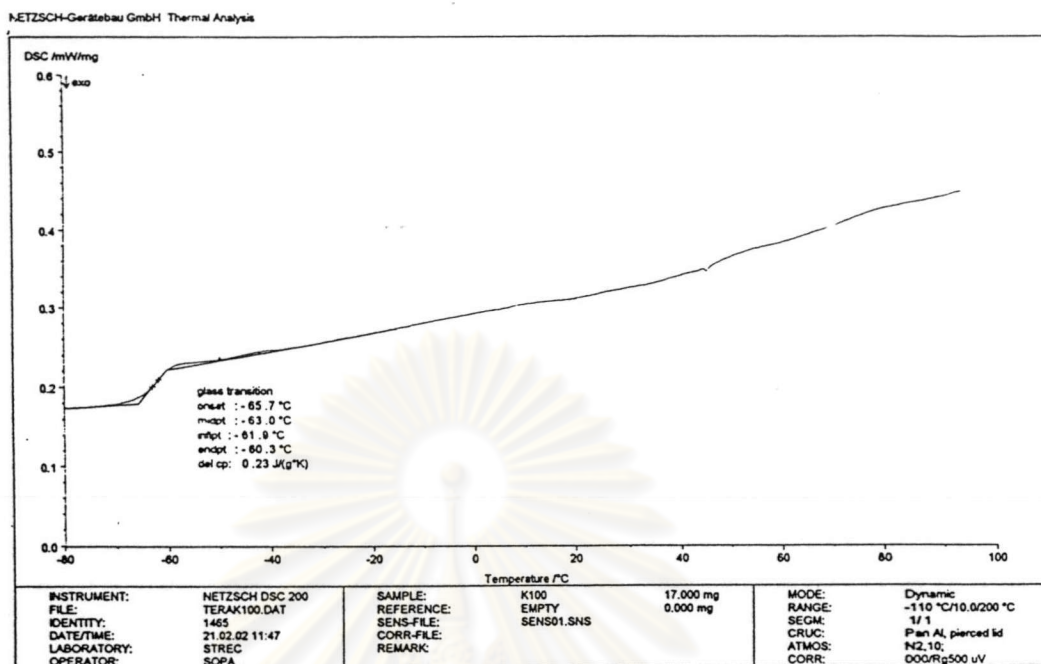


Figure 4.43 DSC thermogram of grafted natural rubber from  $K_2S_2O_8$  initiation.

#### 4.3.4 Functional Groups in the Grafted Natural Rubber

The modified natural rubber by graft copolymerization with methyl methacrylate monomer was characterized by FT-IR and NMR. FT-IR and NMR are used to study functional groups in the grafted natural rubber.

##### a.) Characterization by FT-IR

The grafted natural rubbers were prepared from different redox initiators, CHPO/TEPA, TBHPO/TEPA, and  $K_2S_2O_8/Na_2S_2O_3$ . The functional groups in the grafted natural rubber were confirmed by FT-IR technique. Figures 4.44-4.47 show the infrared spectra for natural rubber and grafted natural rubber. The assignments of IR

absorption peak are given in Table 4.18. The FT-IR spectra of natural rubber exhibited the characteristic absorption bands of the C-H stretching vibration in aliphatic C-H band at  $2975\text{ cm}^{-1}$ , the C=C bending vibration at  $842\text{ cm}^{-1}$  and the C-C stretching vibration at  $1245\text{ cm}^{-1}$ . The new peaks in the spectra of grafted natural rubber appeared at  $1736$  and  $1153\text{ cm}^{-1}$ , due to the carbonyl groups (C=O stretching) when methyl methacrylate was grafted on the natural rubber backbone. This confirms the occurrence of grafting reaction.

**Table 4.18** The important characteristic peaks for the FT-IR spectra of the grafted natural rubber

Natural Rubber	Grafted Natural Rubber			Assignment of functional group
	CHPO	TBHO	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	
Wave number (cm <sup>-1</sup> )	Wave number (cm <sup>-1</sup> )	Wave number (cm <sup>-1</sup> )	Wave number (cm <sup>-1</sup> )	
842	842	842	842	C=C bending, weak
1245	1245	1245	1245	C-C stretching, weak
2975	2975	2975	2975	C-H stretching, strong
-	1153	1153	1153	C-O-C stretching, strong
-	1736	1736	1736	C=O stretching, strong

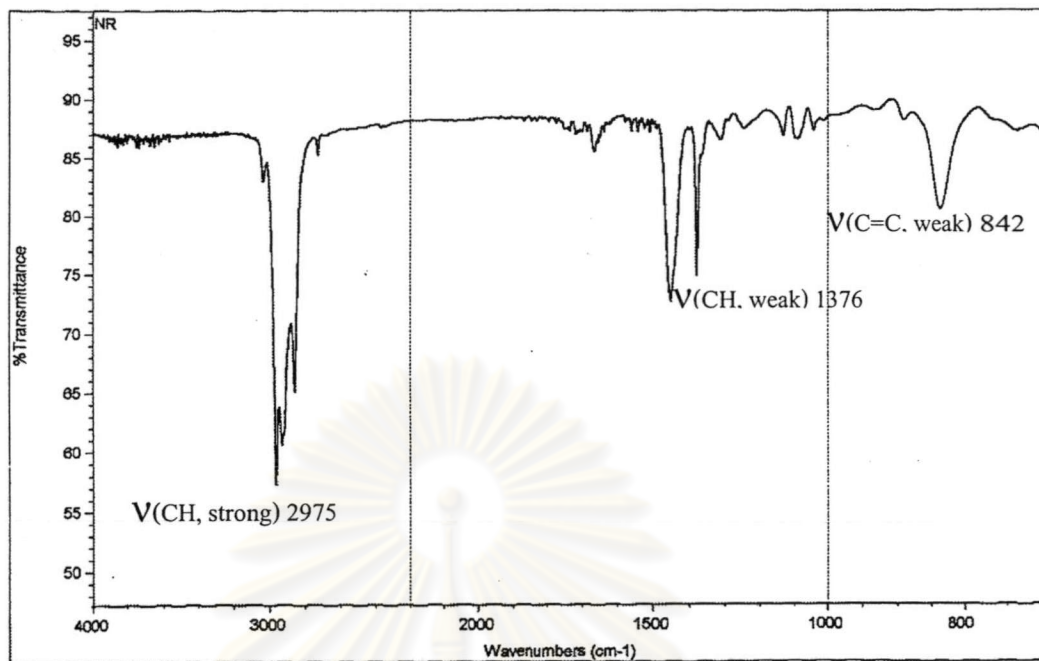


Figure 4.44 The FT-IR spectrum of natural rubber.

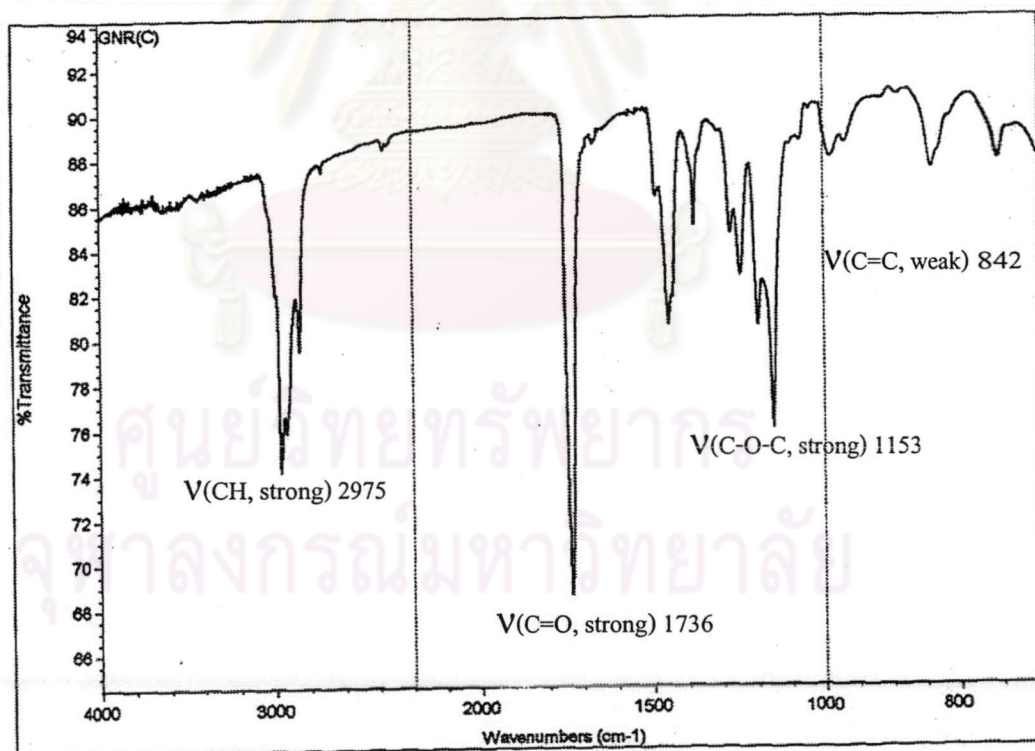


Figure 4.45 The FT-IR spectrum of grafted natural rubber initiation by CHPO.

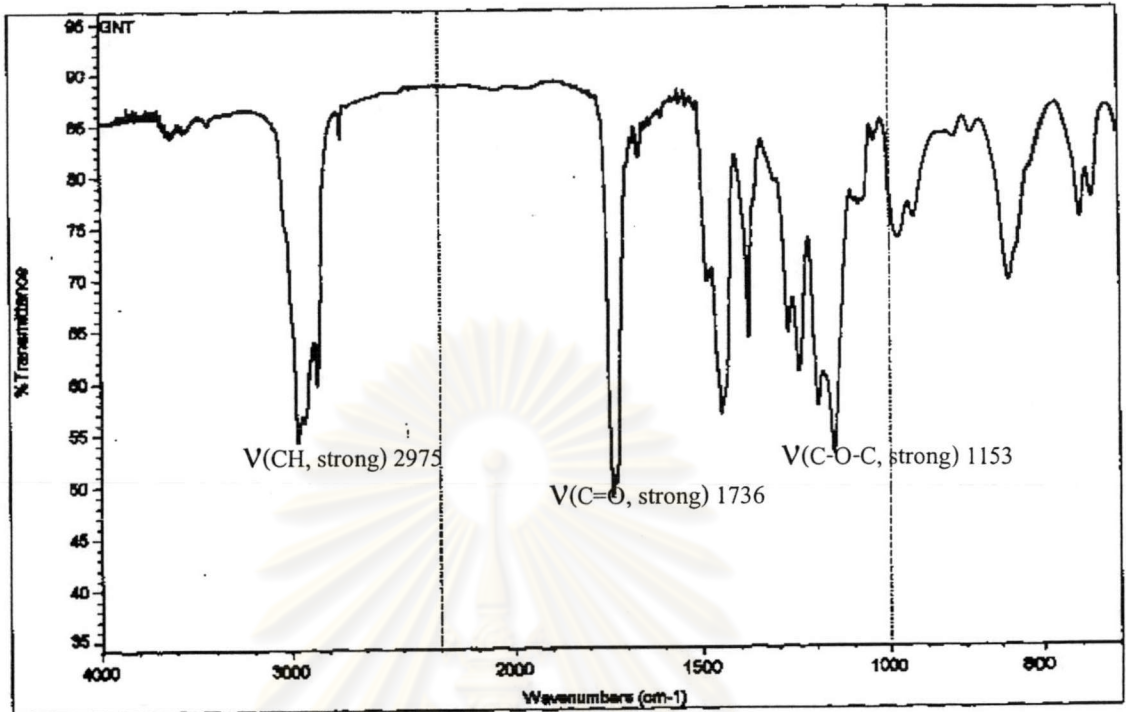


Figure 4.46 The FT-IR spectrum of grafted natural rubber initiation by TBHPO.

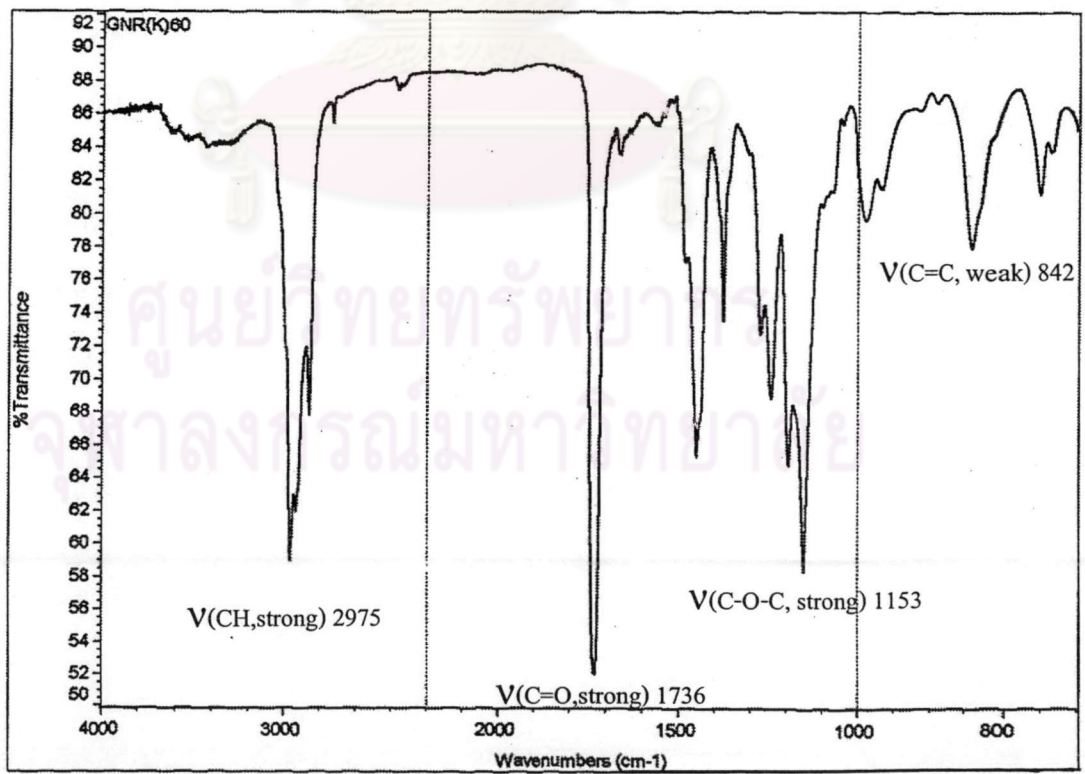


Figure 4.47 The FT-IR spectrum of grafted natural rubber initiated by  $K_2S_2O_8$ .

### b.) Characterization by $^1\text{H-NMR}$

The grafted copolymers of grafted natural rubber were characterized by NMR. The grafted natural rubber samples were dissolved with  $\text{CDCl}_3$ . Figures 4.48-4.50 show the  $^1\text{H-NMR}$  spectra of grafted natural rubber. The assignment is given in Table 4.19. The  $^1\text{H-NMR}$  spectra of grafted natural rubber exhibited the signal of  $\text{OCH}_3$  protons of methyl methacrylate at about 3.6 ppm, the signal of  $\text{C}=\text{CH}$  proton of isoprene at about 5.1 ppm, and the signal of aliphatic protons of alkane at about 1-2 ppm.

**Table 4.19** The important signal for the NMR spectra of the grafted natural rubber.

Initiators	Chemical shift (ppm.)	Assignment
CHPO	3.58	$-\text{OCH}_3$
	5.10	$\text{C}=\text{CH}_2$
TBHPO	3.65	$-\text{OCH}_3$
	5.15	$\text{C}=\text{CH}_2$
$\text{K}_2\text{S}_2\text{O}_8$	3.57	$-\text{OCH}_3$
	5.09	$\text{C}=\text{CH}_2$



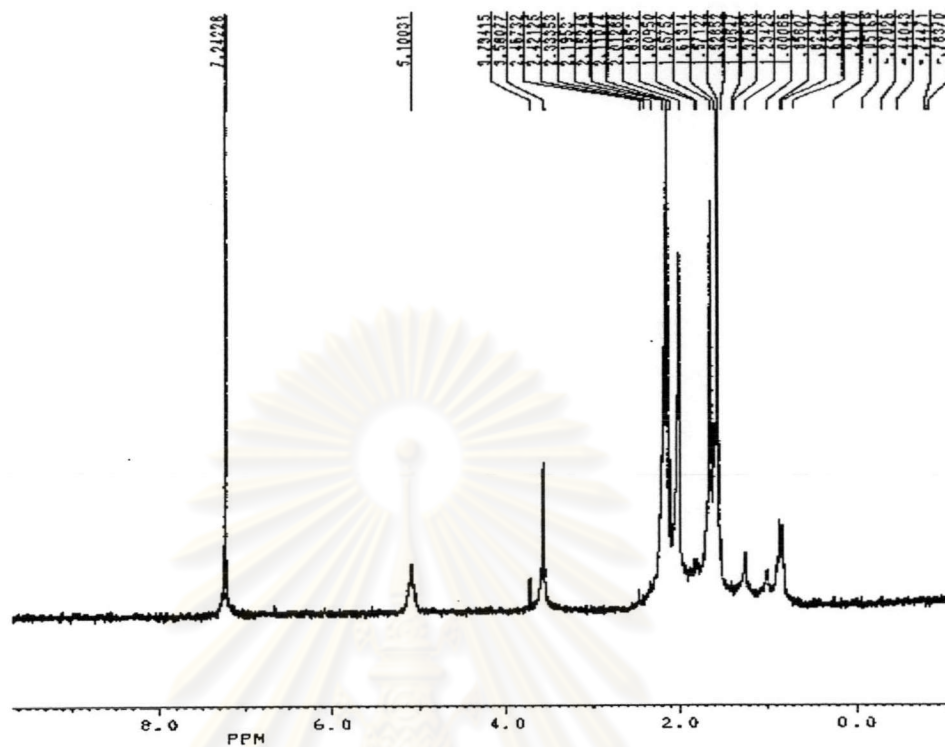


Figure 4.48 The  $^1\text{H}$ -NMR spectrum of grafted natural rubber initiated by CHPO.

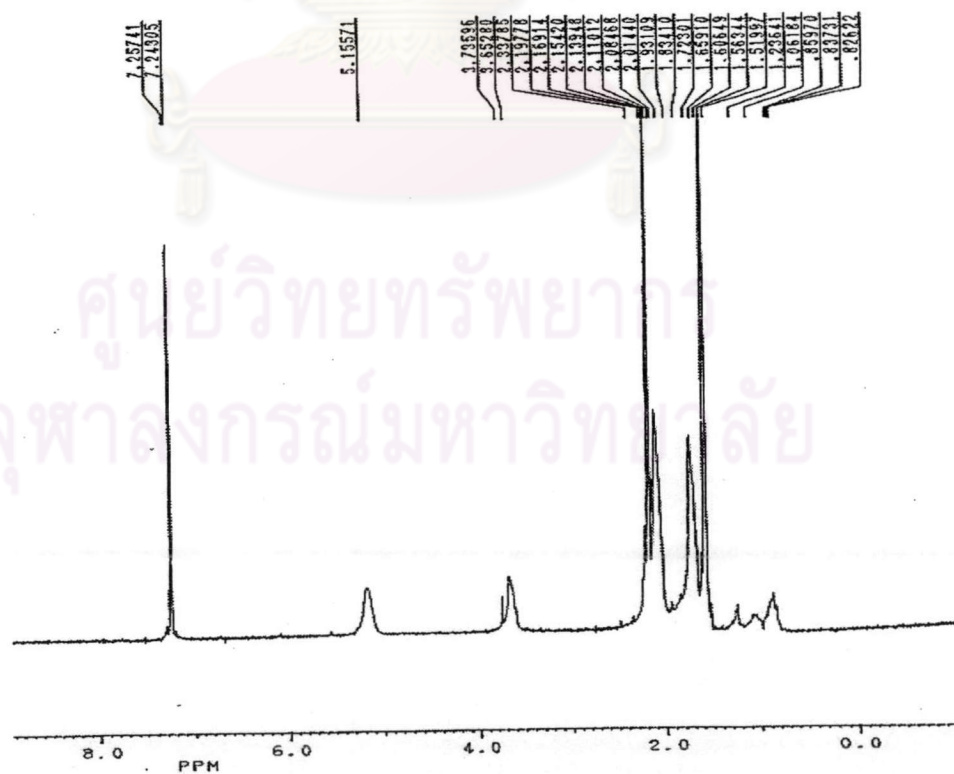


Figure 4.49 The  $^1\text{H}$ -NMR spectrum of grafted natural rubber initiated by TBHPO.

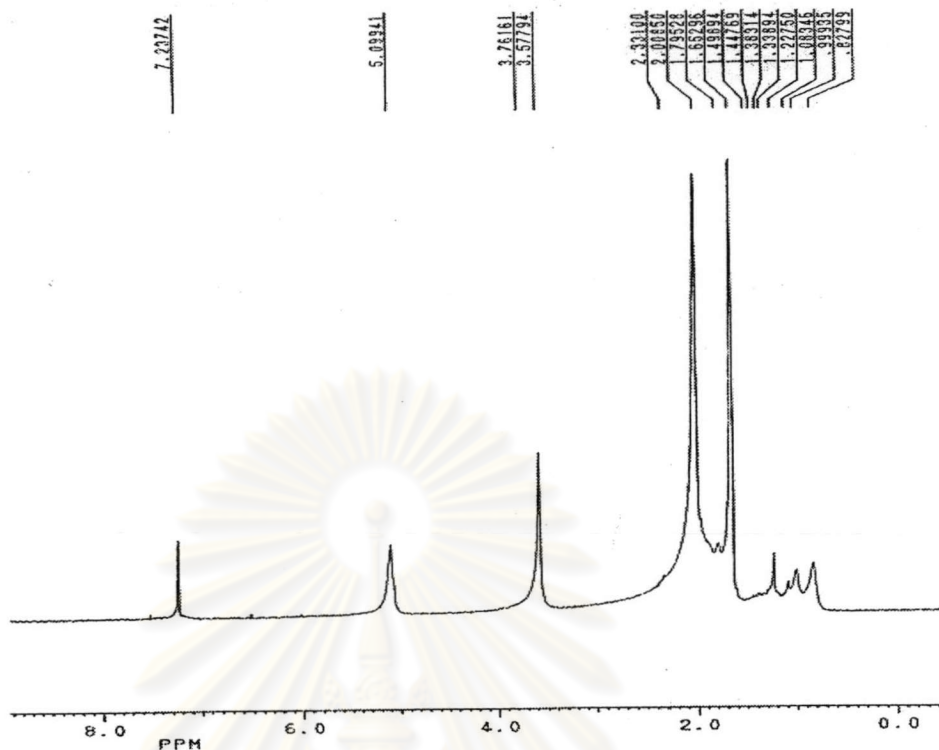


Figure 4.50 The  $^1\text{H}$ -NMR spectrum of spectra natural rubber initiated by  $\text{K}_2\text{S}_2\text{O}_8$ .

### c.) $^{13}\text{C}$ -NMR Characterization

The graft copolymer composition was determined by  $^{13}\text{C}$ -NMR. The grafted natural rubbers were dissolved with  $\text{CDCl}_3$ . The  $^{13}\text{C}$ -NMR spectra of grafted natural rubber are shown in Figures 4.51-4.53. The  $^{13}\text{C}$ -NMR spectra of grafted natural rubber show the signal of  $\text{C}=\text{O}$  of MMA at about 178 ppm, the signal of  $\text{OCH}_3$  of MMA at about 57 ppm, and the signals of  $\text{C}=\text{C}$  at about 126 and 136 ppm. This confirms the occurrence of grafting polymerization of MMA onto natural rubber.

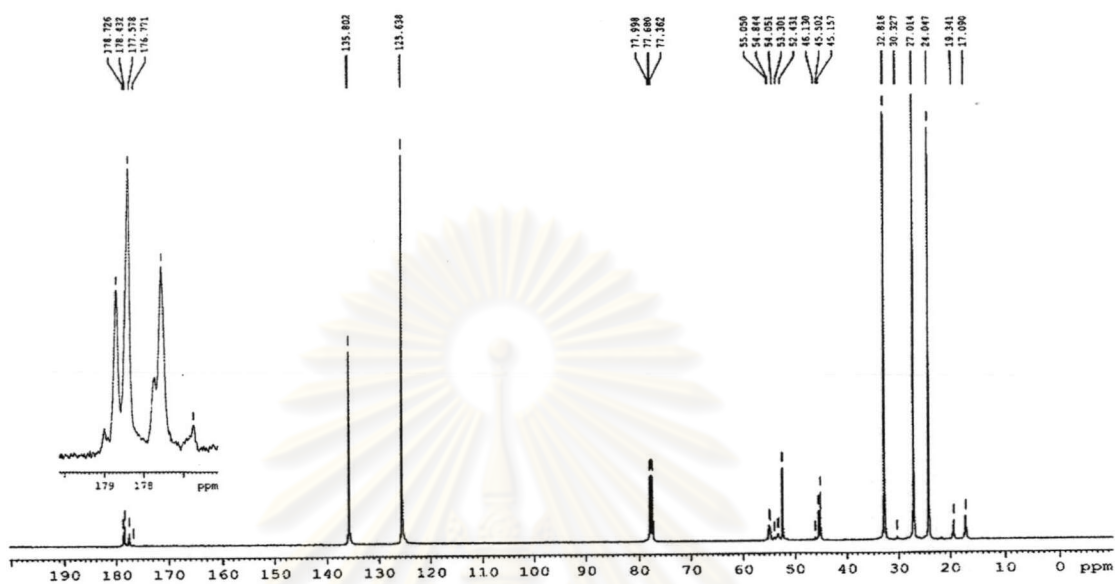


Figure 4.51 The  $^{13}\text{C}$ -NMR spectrum of grafted natural rubber initiated by CHPO.

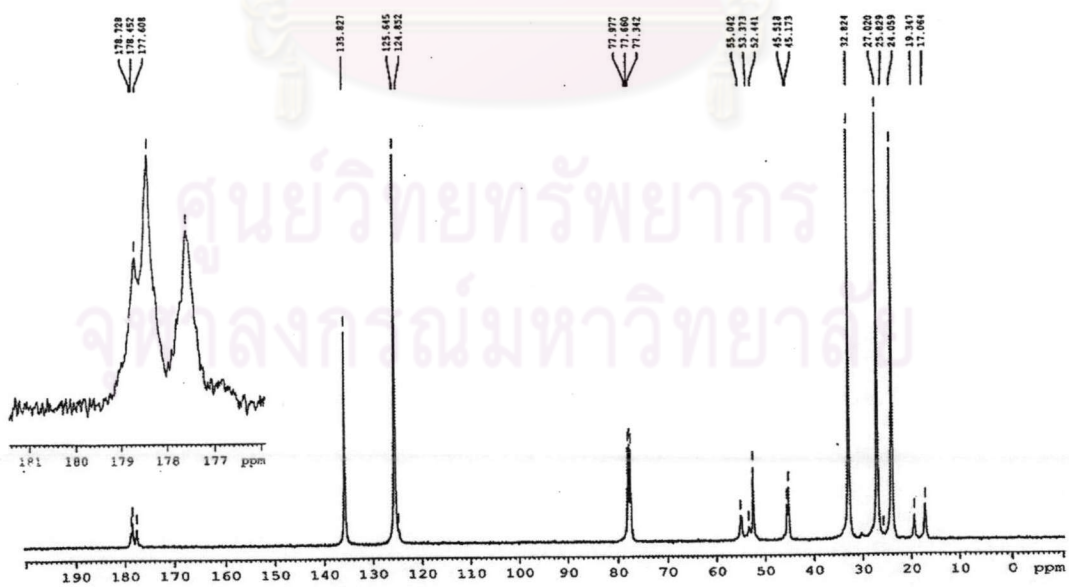


Figure 4.52 The  $^{13}\text{C}$ -NMR spectrum of grafted natural rubber initiated by TBHPO.

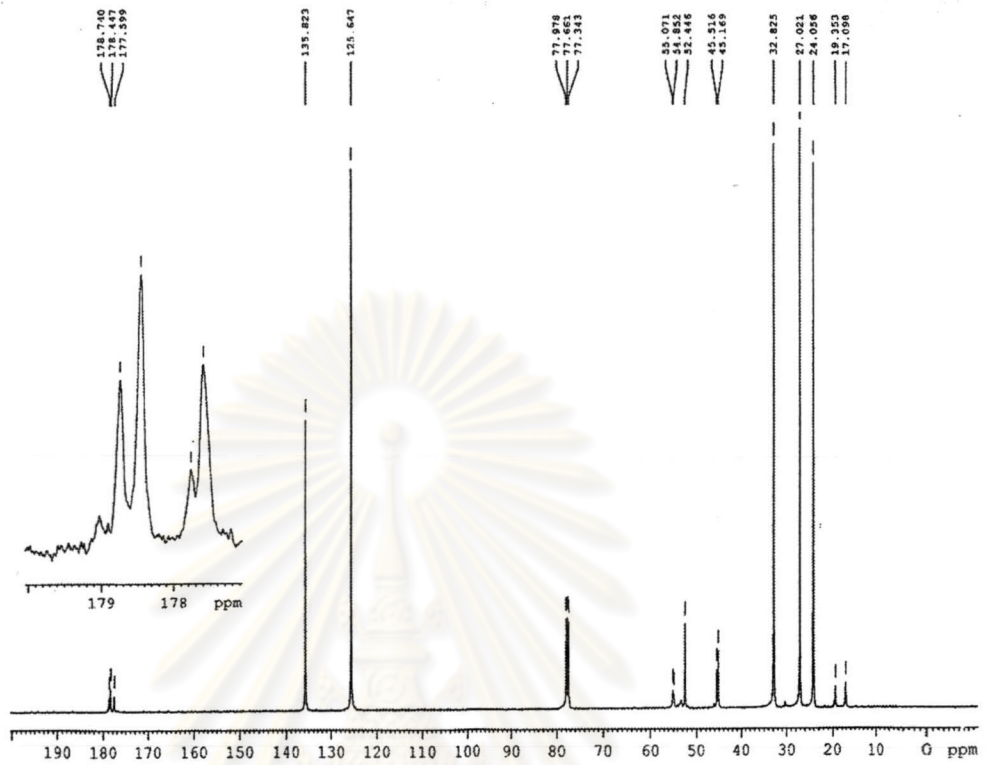


Figure 4.53 The  $^{13}\text{C}$ -NMR spectrum of grafted natural rubber initiated by  $\text{K}_2\text{S}_2\text{O}_8$ .

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