Effects of Redox Initiator on Graft Copolymerization of Methyl Methacrylate onto Natural Rubber

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ABSTRACT: Effects of cumene hydroperoxide (CHPO)/ tetraethylene pentamine (TEPA), *tert*-butyl hydroperoxide (TBHPO)/TEPA, and potassium persulfate ($K_2S_2O_8$)/sodium thiosulfate ($Na_2S_2O_3$) redox initiator on methyl methacrylate (MMA) grafted natural rubber by emulsion polymerization were investigated. The optimum reaction condition for each redox initiator on the grafting of natural rubber was studied. The grafted poly(methyl methacrylate) (PMMA) stays on the surface of rubber particles. CHPO dissolves very well in the oil phase and TBHPO dissolves moderately in the oil phase, and $K_2S_2O_8$ /$Na_2S_2O_3$ initiation is water-soluble. Each can interact with TEPA in the aqueous phase. CHPO was found to give a higher grafting efficiency. To promote a greater grafting efficiency and yield a lower homopolymer content of PMMA, vinyl *neo*-decanoate (VneoD) was added. Percentages of grafting of MMA on natural rubber latex initiated by CHPO/TEPA, TBHPO/ TEPA, and $K_2S_2O_8$/$K_2S_2O_3$ of 84.4, 74.5, and 61.1, respectively, were in good agreement with percentages of PMMA in the aqueous phase as 7.2, 12.0, and 17.9 by CHPO, TBHPO, and $K_2S_2O_8$. VneoD produces allylic radicals on polyisoprene chains, favoring the grafting reaction with other vinyl monomers. CHPO/TEPA is thus a better redox system for grafting of MMA monomer on natural rubber latex. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2587–2601, 2006

Key words: rubber; graft copolymers; emulsion polymerization

INTRODUCTION

The chemical modification of natural rubber by grafting with vinyl monomers using various initiator systems has gained considerable importance in modifying the properties of natural rubber. For natural rubber, some research has confirmed that methyl methacrylate (MMA) and styrene are the most suitable monomers for graft polymerization on natural rubber to give a high level of grafting.

Poly(methyl methacrylate) (PMMA) modified natural rubber has been marketed since the mid 1950s under the trade name "Heveaplus," with *tert*-butyl hydroperoxide (TBHPO) as the polymerization initiator.[1] The graft copolymerization of MMA onto natural rubber using V^{5+} as an initiator was investigated by Lenka et al.[2] When the monomer concentration increased, there was an increase in the percentage of grafting in the lower concentration range and thereafter it decreased. A similar trend was found in the initiator effect. They also studied the graft copolymerization of MMA onto creeper natural rubber using potassium peroxydisulfate catalyzed by silver ion.[3] Houston and Romaine[4] studied composite latex particles based on natural rubber latex to yield interpenetrating polymer networks, and semi-interpenetrating polymer networks. MMA has been added to carefully stabilize natural rubber latex and polymerize in situ using an amine-activator initiator, TBHPO. Graft characteristics and solution properties of natural rubber grafted with MMA copolymer in MEK/toluene using benzoyl peroxide as initiator were studied by Enyiegbulam and Aloka.[5] Thiraphattaraphun et al.[6] studied the grafting of MMA monomer onto natural rubber using potassium persulfate as an initiator. The effects of the initiator concentration, reaction temperature, monomer concentration, and reaction time on the monomer conversion and grafting efficiency were investigated. Fukushima et al.[7] studied the graft copolymer of highly deproteinized natural rubber latex (HDPNR) with styrene using TBHPO/tetraethylene pentamine (TEPA) as an organic redox initiator. The difference between the behavior of HDPNR and untreated natural rubber was due to the removal of protein and the naturally occurring antioxidant present in untreated natural rubber latex. Schneider et al.[8] studied the graft copolymerization of natural rubber latex with MMA using TBHPO/TEPA or TBHPO/

dimethylaniline as an initiator. The morphology of the resulting latex interpenetrating network was characterized by transmission electron microscopy and scanning electron microscopy. Different staining methods increase the contrast between the NR phase and the secondary polymers in the composite latex particles. Lee et al.[9] studied the seed emulsion polymerization of natural rubber grafted with PMMA. The formation of graft sites on the polyisoprene backbone was promoted by adding vinyl *neo*-decanoate (VeoD). Two different redox systems, cumene hydroperoxide (CHPO)/TEPA and TBHPO/TEPA, were used to initiate polymerization. CHPO was observed to be more efficient than TBHPO for the grafting of secondary polymers in modified natural rubber; grafting was enhanced considerably in the presence of VneoD. Lehrle and Willis[10] studied the effect of the presence of small quantities of vinyl acetate (VAc) on the efficiency of grafting MMA on natural rubber (NR) molecules in a latex form. Several VAc concentrations have been examined, and the initiator azobis-isobutyronitrile was added to the systems to promote the formation of VAc radicals. There was good evidence of the formation graft copolymer under the conditions used, but it was found that the grafting is not significantly affected by the presence of VAc because the oil-soluble initiator is not accessible to the relatively large amount of VAc. For the present work, we studied the effect of three types of redox initiators namely (CHPO)/TEPA, TBHPO/TEPA, and $K_2S_2O_8/Na_2S_2O_3$ on the grafting extent of MMA on natural rubber. VneoD was added as a grafting promoter and the grafted copolymers were then characterized. The PMMA-grafted NR can be used as compatibilizers for NR-PVC blend or NR-PMMA blend to enhance mechanical properties by increases in interfacial adhesion between the two types of homopolymers.[6]

EXPERIMENTAL

Material properties

The high ammonia natural rubber (HANR) latex was obtained from the Thai Rubber Latex Corp. (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 as follows: Total solid content (TSC), 61.54%; dry solid rubber content, 60.03%; nonrubber solids, 1.50%; ammonia content, 0.70% on total weight, 1.82% on water phase; pH value, 10.92; KOH number, 0.5610; volatile fatty acid number, VFA 0.0194%; mechanical stability time at 55% TSC, 1100 s; specific gravity at 25°C, 0.9411; magnesium content, 23 ppm solid. The rubber phase accounts for approximately 35% w/w of the latex; its presence as particles influences the rubber phase to exhibit asymmetrical distribution of the NR particle sizes ranging from 0.1 to 2.0 μm.

Three initiation systems for emulsion copolymerization were employed as follows: cumene hydroperoxide (CHPO; analytical grade, Fluka, Steinheim, Switzerland)/TEPA (analytical grade, Fluka, Steinheim, Switzerland), TBHPO (analytical grade, Fluka, Steinheim, Switzerland)/TEPA, and potassium persulfate ($K_2S_2O_8$; analytical grade, Fluka, Steinheim, Switzerland)/sodium thiosulfate ($Na_2S_2O_3.5H_2O$; analytical grade, Carlo Erba, Milano, Italy). Sodium dodecylsulfate (analytical grade, Carlo Erba), oleic acid (analytical grade, Merck, Honenbrunn, Germany), methyl methacrylate (MMA), and VneoD (analytical grade, Aldrich, MO), acetone, and acetic acid (Commercial grade, J.P.M and Scientific, Bangkok, Thailand), toluene (analytical grade, Lab Scan Asia, Bangkok, Thailand), methanol (Lab Scan Asia), and $CDCl_3$ ((Lab Scan Asia).

Preparation of PMMA-grafted natural rubber

Grafted natural rubber using CHPO/TEPA or TBHPO/TEPA initiation

The HANR latex (50 g, DRC 60.04%) was placed in a round-bottomed reactor along with 100 cm^3 of 10 wt % potassium hydroxide solution, and sodium dodecylsulfate (1 phr) as an emulsifier was then added while stirring. The mixture was deoxygenated by passing through the nitrogen gas bubbles for approximately 15 min at room temperature. The stabilizer, oleic acid (10 phr), was added, after 15 min of stirring, the MMA monomer (40, 60, 80, 100, or 120 phr) was then added continuously while stirring for 30 min to allow the latex particles to swell. The mixture was heated up to 30–60°C; the initiator (CHPO or TBHPO) was then added. After 15 min of mixing, the amine activator (10 wt % aqueous solution of TEPA) was added. The bipolar redox initiating system was employed at a ratio of 1 : 1 (based on 0.5–2.0 phr). The reaction was then allowed to proceed for 4–10 h under continuous stirring to complete the polymerization and then the reaction was stopped by adding a few drops of acidified water containing hydrochloric acid.

Grafted natural rubber using $K_2S_2O_8/Na_2S_2O_3$ initiation

The HANR latex (50 g, DRC 60.04%) was placed in a round-bottomed reactor along with 100 cm^3 of 10 wt % potassium hydroxide solution, and sodium dodecylsulfate (1 phr) as an emulsifier was then added while stirring. The mixture was deoxygenated by passing through the nitrogen gas for approximately 15 min at room temperature. The stabilizer, oleic acid (10 phr), was added and the mixture was then heated up to 50–70°C. Potassium persulfate as an initiator was added. After 15 min of mixing, 10 wt % of aqueous

solution of sodium thiosulfate ($Na_2S_2O_3.5H_2O$) was added. The bipolar redox initiating system was employed at a ratio of $K_2S_2O_8/Na_2S_2O_3$ 1 : 0.6 (based on 0.5–2.0 phr). Subsequently, a mixture of MMA and vneoD monomer was added. The reaction was then allowed to proceed for 4–10 h under continuous stirring to complete the polymerization and then the reaction was stopped. The polymer was removed and the unused monomer was extracted by acetone. The dried sheet was then leached with distilled water to remove any water-soluble impurities. The sheet was then thoroughly dried in a vacuum oven (Hotpack 273, PA). Appropriate condition for the graft copolymerization could be obtained through changing the types of initiator (CHPA, TBHPO, or $K_2S_2O_8$), varying the initiator concentration (0.5–2.0 phr based on NR), monomer concentration (40–120 phr based on NR). Reaction temperature (30–60°C) and reaction time (4–10 h).

In addition, the pure NR gel was coagulated by an addition of 2 wt % acetic acid from the HANR latex. The coagulated gel was collected and dried as described in the session of gel content. In the absence of MMA monomer, HANR (100 phr) was polymerized in 0.5 phr CHPO or 0.5 phr TBHPO at 50°C for 8 h, or 1.0 phr $K_2S_2O_8$ at 60°C for 8 h. On the other hand, 100 phr MMA was added to the above condition with three initiating systems. The gel contents of these conditions were determined by gravimetric method to be described in the session of gel content.

Characterization of the PMMA-grafted natural rubber

Conversion

The PMMA-grafted natural rubber latex was cast in an open tray, dried in a vacuum oven at 40°C, leached in distilled water, and dried again in the vacuum oven. The degree of conversion was determined by the percentage increase in weight of PMMA-grafted natural rubber.

Grafting properties

PMMA-grafted natural rubber content and grafting efficiency

The homopolymer and the graft copolymer in the reaction products could be determined by the Soxhlet extraction. The free natural rubber was extracted in a Soxhlet extractor by light petroleum ether for 24 h while free PMMA was extracted by acetone for 24 h.[5] The grafted product containing both the graft copolymer and crosslinked copolymer or gel was determined by the residual weight after the extraction of homopolymer. The data obtained from this step were used to calculate the PMMA-grafted natural rubber.

The weight difference between the initial sample and the extracted samples is the measure of the grafting properties, the grafting efficiency (GE), the percentage of homopolymer, and the percentage of free NR, which were calculated using the following relationships:

Grafting efficiency (%) =

$$\frac{\text{Weight of monomers grafted}}{\text{Weight of monomers polymerized}} \times 100 \quad (1)$$

Homopolymer (%)

$$= \frac{(M_o \times C) - (M_1 - M_2)}{M_o} \times 100 \quad (2)$$

$$\text{Free NR (\%)} = \frac{M_3 - M_4}{M_5} \times 100 \quad (3)$$

where M_o is the mass of monomer (g), C is the conversion of monomer (%), M_1 is the total mass of dry rubber and polymer after extraction and drying (g), M_2 is the mass of dry rubber in the sample, M_3 is the mass of sample after separation of the monomer, homopolymer (g), M_4 is the mass of residue after extraction and drying (g), and M_5 is the total mass of all solids of NR latex and the monomer (g).

Morphology of the PMMA-grafted natural rubber

The grafted natural rubber latex was diluted 400 times with distilled water. In a 2% aqueous solution of OsO_4, 1–2 drops were used to stain the rubber particles in 200 cm^3 of diluted latex for 1 day. A drop of latex was placed on the grid and dried. The morphology of the grafted natural rubber was photographed using transmission electron microscopy (TEM model JEM-200CX) at 120 kV.

Gel content and sol fraction

Gel contents were determined by treating 0.4 g of the graft copolymer or the NR latex with 20 cm^3 toluene, which had been kept without stirring for a week in the dark at ambient temperature. The gel fraction was collected as a bottom fraction obtained by centrifugation at 10,000 rpm for 30 min. The soluble fraction was collected as a sol fraction, which was then precipitated with an excess amount of methanol. The collected gel and sol fractions were dried under reduced pressure at 40°C for a week. The gel content was determined from the mass of the gel and sol fractions.

Average molecular weights of the polymers of the sol fraction

The molecular weight determination was carried out by gel permeation chromatography (GPC, Shimadzu

C-R74 Plus, Tokyo, Japan). The measurements were made using an ultraviolet–visible detector, and a pair of Showa Denko column (Shodex GPC K-806 M; 300 × 8 mm^2, I.D. packing with crosslinked styrene divinylbenzene gel having a number of theoretical plates of 17,000) at 35°C. The HPLC grade chloroform (Lab Scan Asia) was used as an eluent at a flow rate of 1 cm^3 min^{-1}.

The GPC samples were prepared by dissolving the polymer in the sol fraction of the polymer in chloroform, injecting the membrane filtered sample solution of 100 μL into GPC for analysis. The molecular weights of sol fraction were obtained from the calibration lines using polystyrene standard samples (S-66.0) having an M_w range of 2.85×10^4 to 3.16×10^6) supplied by Showa Denko.

Characterization of PMMA-grafted natural rubber

After the solvent extraction of the PMMA-grafted natural rubber, the grafted natural rubber was analyzed for its functional groups by FTIR and NMR techniques.

Fourier transform infrared spectroscopy

Functional groups of the grafted natural rubber were determined by Fourier transform infrared spectrophotometer (Perkin–Elmer model 1760x). The grafted natural rubber samples were dissolved in toluene and cast on the KCl cell for IR investigation. The FTIR peaks for the neat natural rubber and the peaks for the PMMA-grafted NR by three different initiation systems are presented in Figure 1.

Nuclear magnetic resonance spectroscopy (^{1}H NMR and ^{13}C NMR)

The grafted natural rubber was swollen with CDCl$_3$. The ^{1}H NMR and ^{13}C NMR spectra of the solution were operated on the NMR spectrometers (AC-F200, 200 MHz and Advance DPX-400, respectively). The ^{1}H NMR chemical shifts for the PMMA-grafted NR and the ^{13}C NMR chemical shifts are presented in Figures 2 and 3, respectively.

RESULTS AND DICUSSION

Functional groups in the PMMA-grafted natural rubber by spectroscopy

The functional groups in the PMMA-grafted natural rubber prepared from different redox initiators, CHPO/TEPA, TBHPO/TEPA, and K$_2$S$_2$O$_8$/Na$_2$S$_2$O$_3$ confirmed by FTIR technique in Figure 1, exhibit the characteristic absorption bands of the C—H stretching vibration in aliphatic C—H band at 2975 cm^{-1}, C=C

bending vibration at 842 cm^{-1}, and C—C stretching vibration at 1245 and 1376 cm^{-1}. The new peaks in the spectra of all PMMA grafted natural rubbers by any type of initiator appeared at 1736 and 1153 cm^{-1}, because of the carbonyl groups (C=O stretching) and C—O—C stretching when MMA was grafted on the natural rubber backbone. The PMMA grafted natural rubbers characterized with ^{1}H NMR in Figure 2 by dissolving in CDCl$_3$ exhibited the signal of OCH_3 protons of MMA at about 3.58 ppm, the signal of C=CH_2 protons of isoprene at about 5.1 ppm, and the signal of aliphatic protons of the alkane at about 1–2 ppm. The dissolved PMMA grafted natural rubbers in CDCl$_3$ measured by the ^{13}C NMR in Figure 3 show the signals of C=O of MMA at about 178 ppm, OCH$_3$ of MMA at about 57 ppm, and C=C at about 126 and 136 ppm. This confirms the occurrence of grafting polymerization of MMA onto natural rubber.

PMMA-grafted natural rubber using CHPO or TBHPO initiation

The effect of initiator concentration

According to Table I, when the other reaction parameters were kept constant, the percentage conversion increased as the initiator concentration increased at every temperature investigated. Initially, the increase in initiator concentration produced more graft sites for MMA to graft onto the NR. The percentage grafted natural rubber and percentage grafting efficiency decreased as the initiator concentration increased. The reason is that the homopolymers are formed more readily than the graft copolymer. The grafting efficiency is highest at the initiator concentration of 0.5 phr in the range investigated. When higher concentrations of initiator are used, excessive radicals react with each other, leading to a faster rate of termination or primary termination. Up to 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. For the free NR content at most of the polymerization temperature, a decreasing trend with increasing initiator concentrations was found. Increasing the initiator concentration produced more radicals to initiate and propagate the MMA molecules onto NR molecules. More rubber molecules were used in the reaction and therefore less free NR was left in the reaction mixture. On the other hand, an opposite trend was observed for the free PMMA. Increasing the initiator concentration produced more PMMA content because the higher free radicals at the high concentration of the initiator produced the higher amount of PMMA homopolymer.
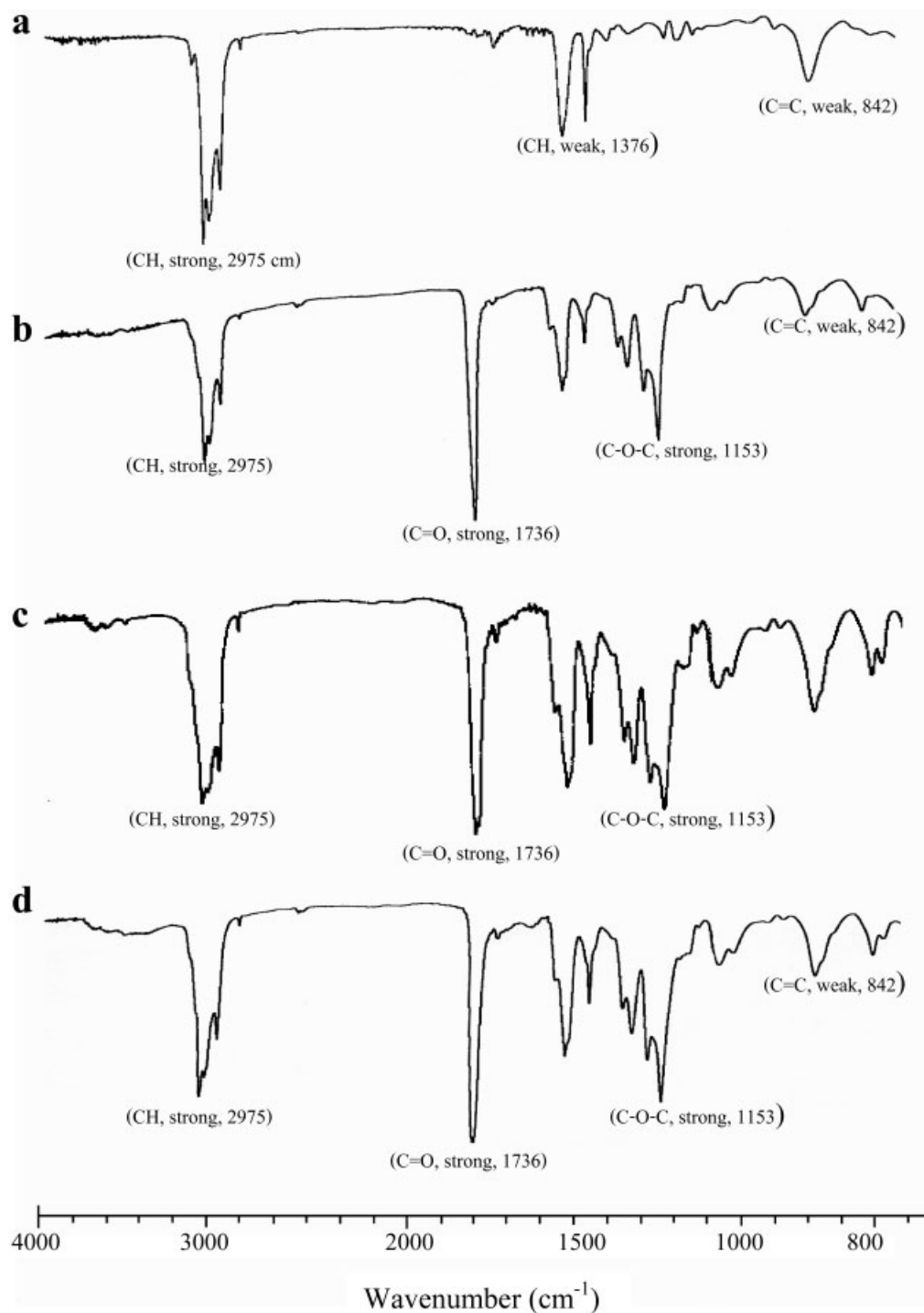
Figure 1 The FTIR spectra of (a) natural rubber, PMMA-grafted natural rubber initiated by (b) CHPO/TEPA, (c) TBHPO/TEPA, and (d) $K_2S_2O_8/Na_2S_2O_3$.

The effect of reaction temperature

The effect of reaction temperature (30, 40, 50, and 70°C) on the PMMA grafted natural rubber was investigated for the grafting characteristics and the molecular weight of PMMA graft NR. The optimum conditions of graft copolymer were obtained as follows: monomer concentration, 100 phr; initiator concentration, 0.5 phr; reaction

temperature, 30–60°C; reaction time, 8 h. In Table I, it can be seen that a higher temperature results in a high conversion. Decomposition of the initiator (CHPO or TBHPO) increases with an increasing reaction temperature; it causes an increase in both the number of free radicals and the rate of polymerization. The percentage grafted natural rubber and percentage grafting efficiency
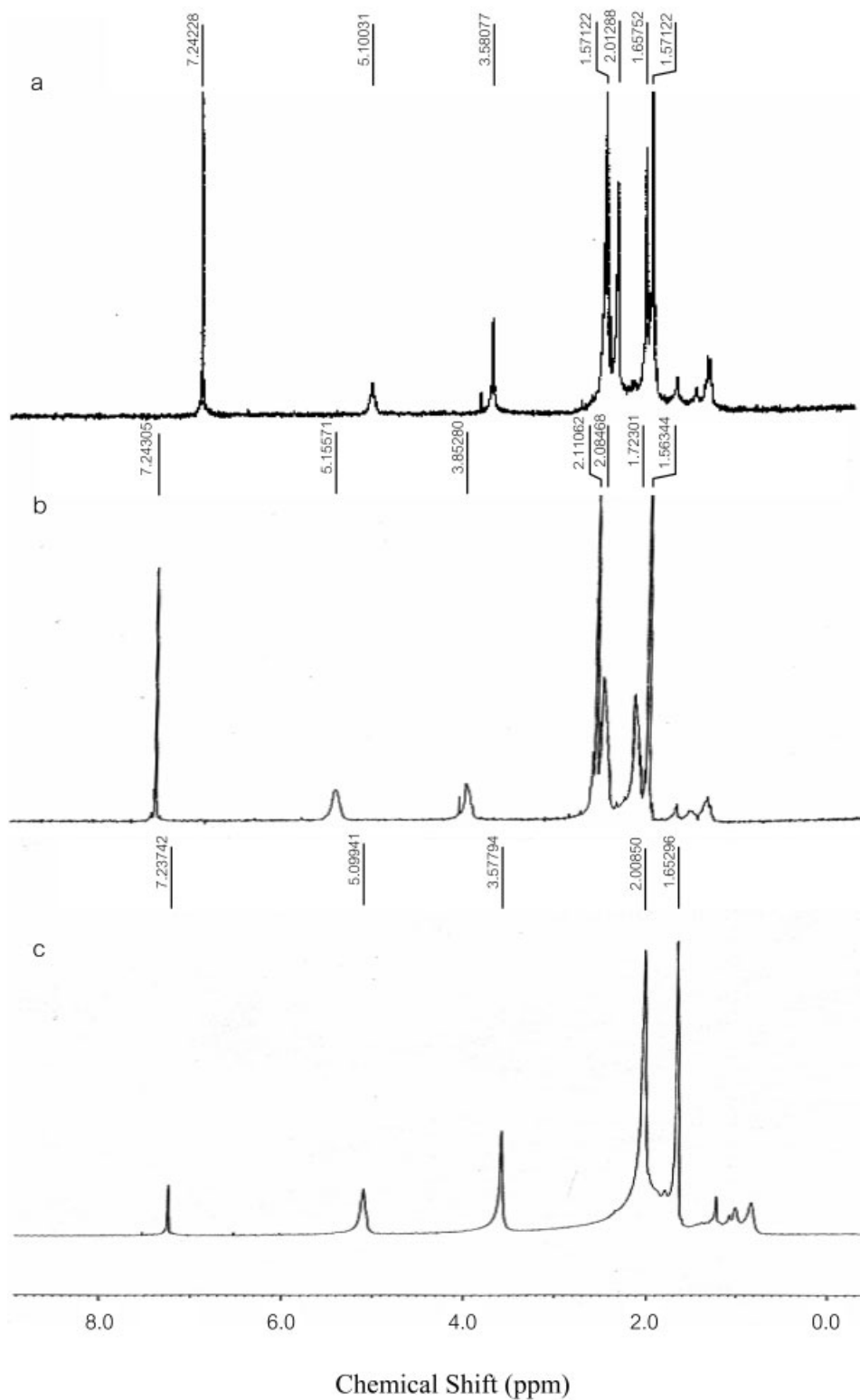
Figure 2 The ^{1}H NMR spectra of PMMA-grafted natural rubber initiated by (a) CHPO/TEPA, (b) TBHPO/TEPA, (c) $K_2S_2O_8/Na_2S_2O_3$.

from two redox initiators decreased when the polymerization temperature was higher than 60°C. The initiator decomposition increased with the increasing temperature to give instantaneously an abundance of free radicals. The radicals underwent either recombination or other side reactions such as chain transfer reaction; the initiator efficiency for grafting was thus reduced at a higher temperature.
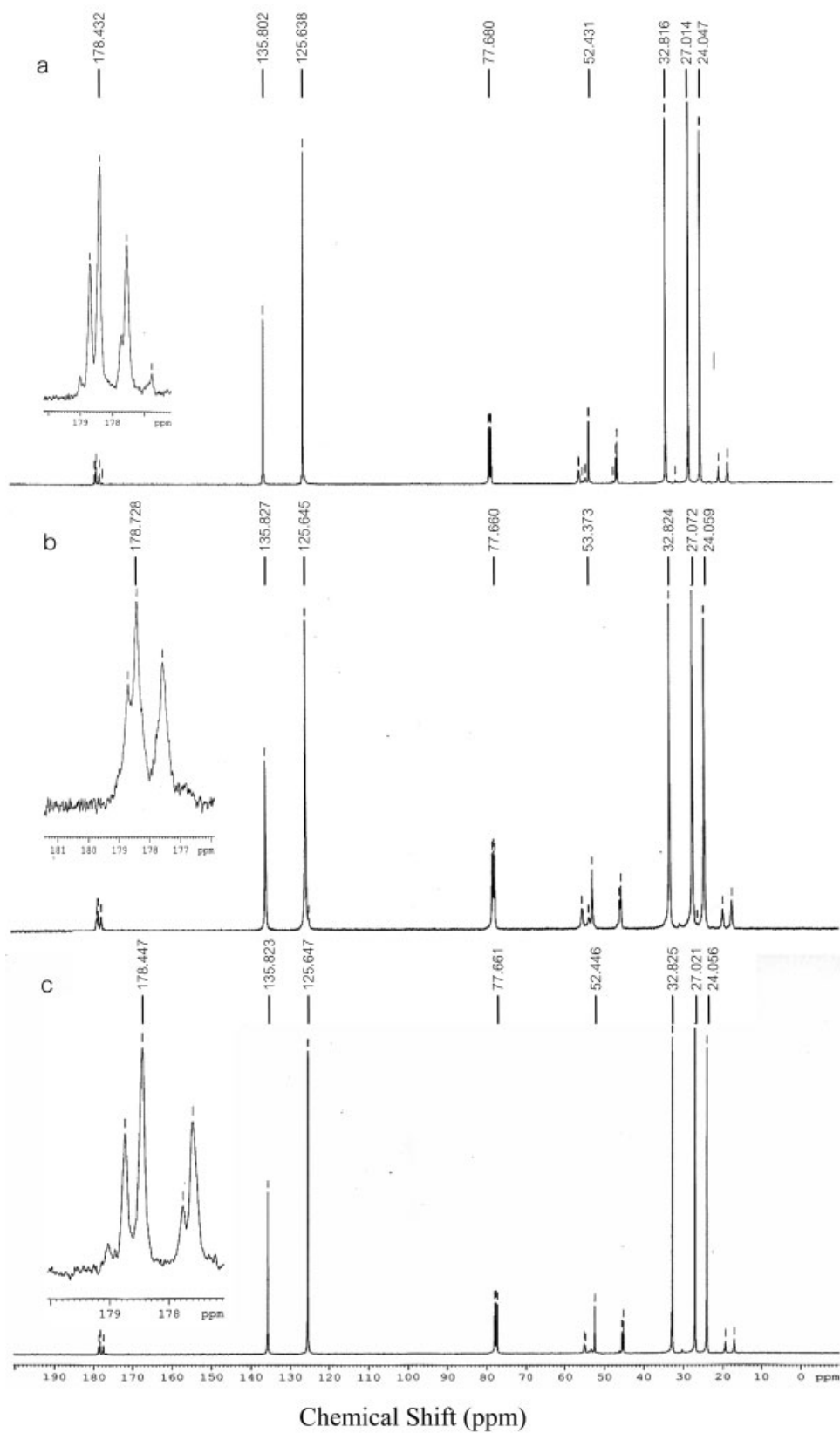
Figure 3 The ^{13}C NMR spectra of PMMA-grafted natural rubber initiated by (a) CHPO/TEPA, (b) TBHPO/TEPA, and (c) $K_2S_2O_8/Na_2S_2O_3$.

TABLE I
Effects of the Initiator Concentration of TBHPO and CHPO on the Percentage Conversion, the Percentage Grafting Efficiency, and the Percentage of PMMA-Grafted NR at MMA Monomer Concentration 100 phr, and Reaction Time 8 h at 30–60°C

	TBHPO				CHPO			
	Initiator concentration (phr)				Initiator concentration (phr)			
Reaction properties	0.5	1.0	1.5	2.0	0.5	1.0	1.5	2.0
At 60°C								
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
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
At 50°C								
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
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
At 40°C								
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
Grafted NR (%)	81.2	77.8	67.0	62.4	78.0	72.5	71.0	69.4
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
At 30°C								
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
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

Both TBHPO and CHPO were used with TEPA activator. The bipolar redox system was fixed at a ratio of 1 : 1.

The effect of monomer concentration

The natural rubber latex used as the backbone polymer of *cis*-1,4-polyisoprene was grafted with MMA monomer. Rubber particles were swollen with the monomer, which was then polymerized onto rubber particles. The effect of monomer concentration on the percentage of conversion, grafted natural rubber, and grafting efficiency is shown in Table II under the following polymerizing conditions. The monomer concentrations are used in the range of 40–120 phr, based on the dry rubber content. The parameters 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 h. The monomer concentrations increase the percentage conversion and percentage grafting efficiency. The MMA monomer may swell in the NR particles and may be polymerized, and the nonpoly-

TABLE II
Effect of the Monomer Concentration on the Percentage Conversion, the Percentage Grafting Efficiency, and the Percentage of PMMA-Grafted NR at 50°C, Initiator Concentration 0.5 phr, and Reaction Time 8 h

	TBHPO					CHPO				
	Monomer concentration (phr)					Monomer concentration (phr)				
Reaction properties	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
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	11.98	12.1	18	7.3	8.9	10.9	7.2	13.8

TABLE III
Effect of the Reaction Time on the Percentage Conversion, the Percentage Grafting Efficiency, and the Percentage of PMMA-Grafted NR at 50°C, Initiator Concentration 0.5 phr, and MMA Monomer Concentration 100 phr

Reaction Properties	TBHPO				CHPO			
	Reaction time (h)				Reaction time (h)			
	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
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

merized MMA amount cannot be just extracted by acetone. For the two redox initiators, the grafting efficiency reached a maximum at a monomer concentration of 100 phr, and thereafter it decreased. Percentage of free NR decreased steadily and then increased when the monomer concentration was 120 phr. On the other hand, the percentage grafted NR decreased steadily while the percentage free PMMA increased. At higher monomer concentrations, many side reactions, which probably competed with the grafting reaction, take place in the aqueous phase, such as chain transfer to monomer. This means that homopolymerization is more pronounced than graft copolymerization at higher monomer concentration. In addition, the influence of CHPO on graft copolymerization of MMA and NR is higher than that of TBHPO. We anticipated that TBHPO is rather bulky and its steric hindrance effects toward initiator dissociation are higher. More discussion shall be presented in locus of polymerization.

The effect of the reaction time

The effects of the reaction time on the grafting of MMA onto natural rubber by using two redox initiators, CHPO or TBHPO, are shown in Table III. The parameters for the graft copolymerization were as follows: MMA monomer concentration, 100 phr; initiator concentration, 0.5 phr; reaction temperature, 50°C; reaction time, 4–10 h. According to Table III, the percentage conversion, and percentage grafting efficiency increase with increasing the reaction time. At a reaction time of 8 h, its conversion and grafting efficiency reached a maximum, thereafter, the percentage conversion and percentage grafting efficiency decreased. Basically, conversion of MMA monomer to graft onto the NR molecules should increase with increasing the reaction time or at least having a constant conversion. We observed that the longer reaction time decreased the conversion, grafting efficiency, percentage grafted NR, and percentage free NR but increased the free PMMA. With a long reaction time, the free PMMA is formed more readily than is the

graft copolymer, since there might have only a few new active grafting sites available on the rubber particle for higher graft copolymerization. Radical recombination at the longer reaction time could be another reason for the low conversion and low grafting to give the shorter soluble chains. Chain scission to give the shorter soluble chains or chain transfer to initiator could be the additional possible cause for this case. The grafted natural rubber initiated by CHPO at a reaction time of 8 h gives a higher percentage grafting efficiency and a lower percentage of free PMMA than the PMMA grafted natural rubber initiated by TBHPO. The plausible reasons for the better grafting efficiency of CHPO over that of TBHPO are explained in the locus of polymerization.

PMMA-grafted natural rubber using potassium persulfate/sodium thiosulfate initiation

The effect of grafting promoter

The grafting of a second monomer onto polyisoprene may be induced in two ways. The first method is through a graft-site initiation, where the initiator derived radicals either add across the double bond or abstract hydrogen atoms from the polyisoprene backbone. The second method is through a hydrogen abstraction from polyisoprene by polymeric radicals as shown in Figure 4. Allen et al.[11] found that the rate of polymerization was retarded when VAc was polymerized in the presence of a model compound for a polyisoprenic hydrocarbon. In this retardative chain transfer mechanism, poly(VAc) radical abstracts the hydrogen atoms from isopropyl group to generate an unreactive allylic-type radical. Lehrle and Willis[10] proposed that VAc could facilitate grafting of MMA 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 this result could be due to the fact that an oil-soluble initiator was not accessible to the high amounts of VAc present in aqueous phase.

VneoD is relatively hydrophobic when compared with VAc because of the presence of the *neo*-decane
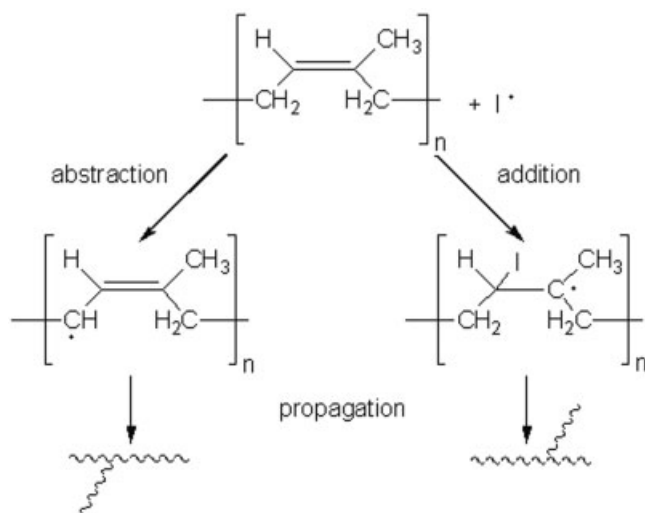
Figure 4 Abstraction and addition reactions that can lead to grafting to polydiene system. I, initiating alkyloxyl radical.

group instead of the methyl group at one chain end as shown in Figure 5. The effect of the grafting promoter was investigated by varying the concentrations of VneoD as 10, 20, 30, and 40 wt % of MMA. The parameters of graft copolymerization were obtained as follows: MMA monomer concentration, 100 phr; VneoD of 10, 20, 30, 40 wt % of MMA; initiator concentration, 1.0 phr; reaction temperature, 55°C; reaction time, 8 h. Table IV shows the dependence of the
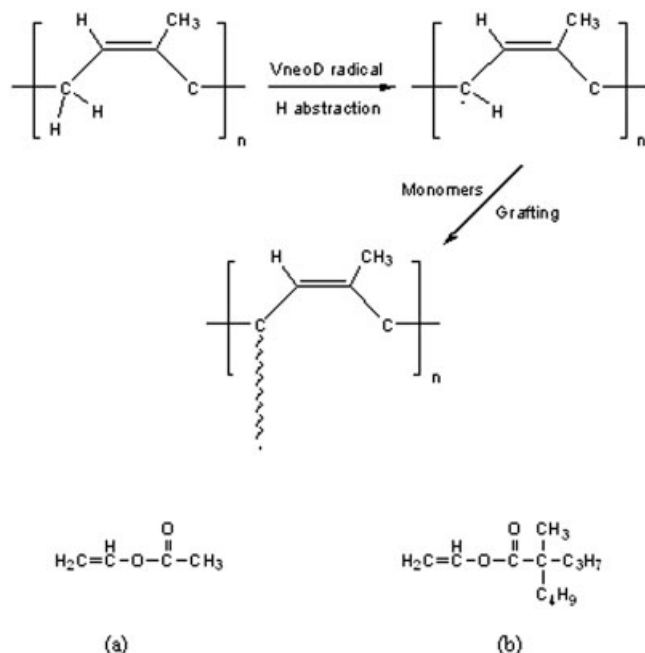

Figure 5 Reaction scheme of hydrogen abstraction from poly(*cis*-isoprene) to form grafting sites and the monomer structures of (a) VAc and (b) VneoD.

TABLE IV
Effect of the Grafting Agent on the Percentage Conversion, the Percentage Grafting Efficiency, and the Percentage of PMMA-Grafted NR at 55°C, MMA Monomer Concentration 100 phr, $K_2S_2O_8$ 1.0 phr, and Reaction Time 8 h

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
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

percentage conversion, the percentage of grafted natural rubber, and the percentage grafting efficiency on the concentration of VneoD. Initially, increases in the concentration of VneoD extracted more hydrogen radical from polyisoprene to form allylic-type radicals, which are 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 MMA. We found that conversion and grafting properties are optimal because low percentages of free NR and free PMMA are obtained. When increasing the grafting promoter beyond 20% of MMA monomer, the concentration of the grafted MMA monomer was unfortunately decreased accordingly. The allylic-type radicals were thus abundance and the propagation of the VneoD radicals to abstract the hydrogen radicals from the NR backbone was obstructed. The drastic decreases in conversion, grafting efficiency, and grafted NR were thus evitable.

The effects of initiator concentration on polymerization temperature

The effects of initiator concentration at various temperatures on the percentage conversion, percentage grafted natural rubber, and percentage grafting efficiency as shown in Table V gave the following condition: 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 h.

The percentage conversion increased as the initiator concentration increases at every temperature investigated. Initially, the increase in the initiator concentration produced more graft sites for MMA. Therefore, the percentage grafting efficiency, the percentage conversion, and the percentage of grafted natural rubber can, of course, increase. At a higher initiator concentration, an abundance of initiator radical was produced, and excessive radicals either reacted with each

TABLE V
Effects of the Initiator Concentration of $K_2S_2O_8$ on the Percentage Conversion, the Percentage Grafting Efficiency, and the Percentage of the PMMA-Grafted NR at 50–70°C, VneoD 20 wt % of MMA, MMA Monomer Concentration 100 phr, and Reaction Time 8 h

Reaction Properties	Initiator concentration (at 70°C)				Initiator concentration (at 60°C)				Initiator concentration (at 55°C)				Initiator concentration (at 50°C)			
	0.5	1.0	1.5	2.0	0.5	1.0	1.5	2.0	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	63.5	72.2	73.2	72.3	43.3	49.0	67.0	71.1
Grafting efficiency (%)	39.5	47.5	43.7	40.9	48.9	61.1	61.1	48.8	42.5	58.4	41.8	37.4	39.5	46.5	43.0	43.9
Grafted NR (%)	59.0	62.9	61.6	60.5	65.1	70.8	67.4	62.6	60.9	71.4	61.6	58.4	69.7	68.8	63.9	65.2
Free NR (%)	14.5	13.2	13.0	12.6	13.3	11.4	11.0	14.4	17.0	11.3	14.1	15.7	12.1	13.0	13.3	11.6
Free PMMA (%)	26.5	23.9	25.5	27.0	21.7	17.8	21.6	23.0	22.2	17.3	24.3	26.0	18.2	18.2	22.8	23.2

other or produced more homopolymer of PMMA. Increasing the reaction temperature is to increase the decomposition rate of the initiator; it gives an increased number of free radicals, and therefore promotes the higher rates of polymerization and the higher conversion. At higher reaction temperatures, the lower percentage of grafting efficiency and grafted NR were observed with greater amounts of free PMMA. Besides, chain scission could occur at the higher reaction temperature to initiator, monomer, or solvent to lower the grafting content. It can be seen that the optimum percentage conversion, the percentage of grafted natural rubber, and the percentage grafting efficiency is at the initiator concentration of only 1.0 phr and reaction temperature 60°C as already shown in Table V. In addition, the $K_2S_2O_8$ itself can act as a thermal induced initiator at 70°C because it produced the highest conversion with lower grafting efficiency and highest free PMMA.

The effect of MMA monomer concentration in the presence of VneoD

The effect of MMA monomer concentration on the extent of grafting was investigated by changing the monomer concentration within a range of 40–120 phr. The parameters of graft copolymerization were ob-

tained 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 h.

We can see from Table VI that as the monomer concentration increases, increases in the percentage conversion, the percentage of grafted natural rubber, and the percentage grating efficiency are found. It reached a maximum value at the monomer concentration of 100 phr, and thereafter it decreased. At a higher monomer concentration, competition reactions to the grafting probably take place in solution, i.e., homopolymerization is more favored at higher monomer concentrations, i.e., homopolymerization takes place at the expense of graft copolymerization. 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.

The effect of reaction time in the presence of VneoD

The effect of reaction time on the grafting of MMA onto natural rubber is shown in Table VII. The parameters of graft copolymerization were obtained as follows: MMA monomer concentration, 100 phr; grafting promoter (VneoD), 20 wt % of MMA; initiator concen-

TABLE VI
Effect of the MMA Monomer Concentration on the Percentage Conversion, the Percentage Grafting Efficiency, and the Percentage of PMMA-Grafted NR, at 20 wt % VneoD Based on MMA at 60°C, $K_2S_2O_8$ 1.0 phr, and Reaction Time 8 h

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
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

TABLE VII
Effect of the Reaction Time on the Percentage Conversion, the Percentage Grafting Efficiency, and the Percentage of PMMA-grafted NR 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 (h)			
	4	6	8	10
Conversion (%)	70.9	81.8	85.1	84.7
Grafting efficiency (%)	46.6	55.4	61.1	51.8
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

TABLE VIII
Effect of Redox Initiator Systems on Percentage Conversion, the Grafting Efficiency, and the Percentage of PMMA-Grafted NR 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
Grafted NR (%)	83.9	80.5	70.8
Free NR (%)	8.8	7.5	11.4
Free PMMA (%)	7.2	12.0	17.8

tration, 1.0 phr; reaction temperature, 60°C; reaction time, 4–8 h. As the reaction time increases, increases in the percentage conversion and the percentage of grafted natural rubber are found. At a reaction time of 8 h, it reaches a maximum percentage conversion, percentage of grafted natural rubber, and percentage grafting efficiency, beyond this time they decreases significantly. We also observed that PMMA homopolymer is formed more pronouncedly than the PMMA-grafted NR.

Comparison of the redox initiator types on grafting of natural rubber

Three initiation systems, CHPO/TEPA, TBHPO/TEPA, and $K_2S_2O_8/Na_2S_2O_3$, were used for grafting polymerization with HANR latex, which optimum conditions are shown in Table VIII. It can be seen that CHPO/TEPA gave the highest grafting efficiency, percentage of grafted natural rubber, and percentage conversion. The CHPO was thus more effective than TBHPO or $K_2S_2O_8$ for grafting MMA onto natural rubber. Because the partitioning ability of the initiator between monomer-swollen NR and the aqueous phase is quite different, the graft property is indeed affected. It is expected that the radical concentration from CHPO/TEPA on the natural rubber particles would be higher than those of TBHPO and $K_2S_2O_8$, since TBHPO/TEPA is soluble in both the organic and aqueous phase, while $K_2S_2O_8/NaS_2O_3$ is only soluble in the aqueous phase. The abstraction pathway may be facilitated through the stability of resulting allylic radicals. It could have a very slow re-initiation rate coefficient with other monomers. The addition pathway is anticipated to be the major route for propagation.

Locus of polymerization

In the grafting reaction of MMA 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:

(a) Partition of the initiator between the monomer-swollen natural rubber and the aqueous phase is quite different for each initiator.
(b) Partition nucleation in the aqueous phase could take place.

As mentioned earlier, the three initiator systems were used differently in polarity. The oil soluble initiator, CHPO or TBHPO, was employed with the amine (TEPA). The rate of producing primary radicals (k_d) of CHPO, 1.7×10^{-6} s^{-1} in benzene at 130°C, is higher than the k_d of TBHPO, 3×10^{-7} s^{-1} in benzene at 130°C.[12] Consequently, CHPO generates more radicals than TBHPO. The hydroperoxide radical from CHPO or TBHPO partitions strongly into the organic phase or the rubber surface whereas the amine (TEPA) prefers to remain in the aqueous phase, initiating the graft polymerization at the rubber/water interface to result in the higher PMMA graft NR.[4] The location of the CHPO/TEPA or TBHPO/TEPA is shown in Figure 6.[13]

As mentioned earlier, 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.[14] 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 inactive towards the monomer, which now act as radical terminators. The second is the abstraction mechanism, in which VneoD radical abstracts hydrogen from the allylic position on polyisoprene backbone as shown in Figure 6.

Characterization of grafted natural rubber

Grafted natural rubber morphology

Figure 7 shows TEM micrographs of the grafted natural particles from different redox initiator systems.
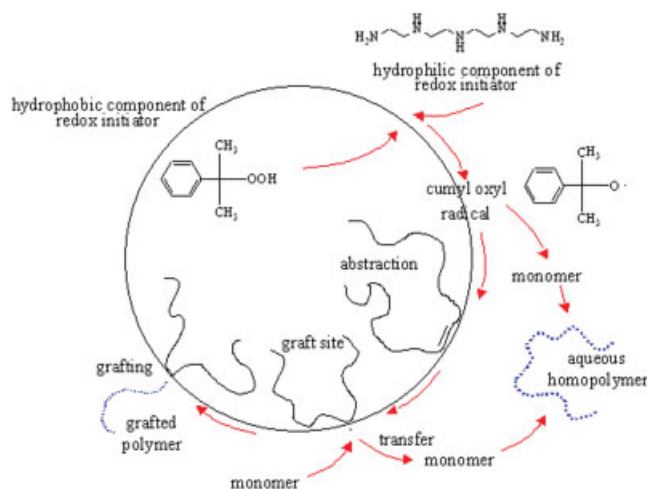

Figure 6 Possible reaction sites in the modified natural rubber latex in the bipolar redox initiation systems. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
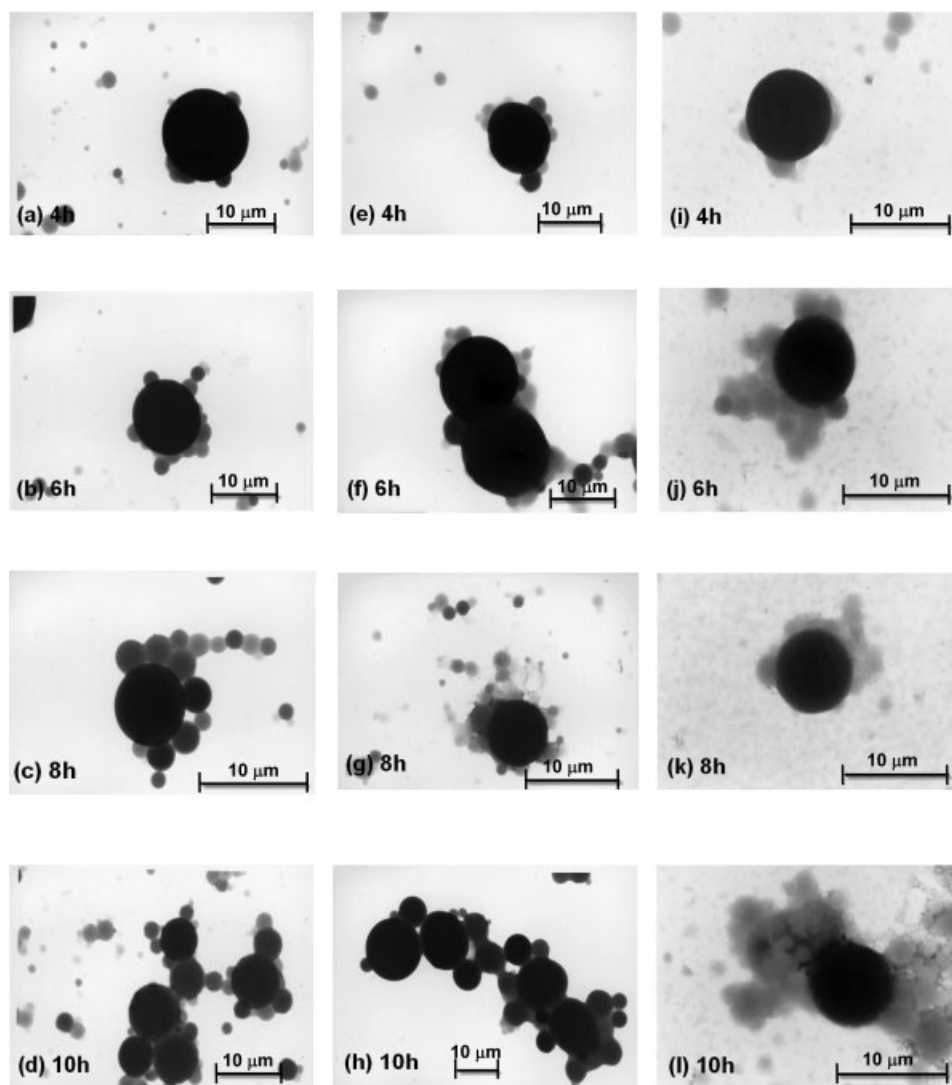
Figure 7 Transmission electron micrographs of the grafted natural rubber latex under various reaction time: (a)–(d) MMA 100 phr by TBHPO 0.5 phr at 50°C; (e)–(h) by CHPO 0.5 phr at 50°C; (i)–(l) $K_2S_2O_8$ 1.0 phr, VneoD 20 wt % of MMA and 100 phr MMA at 60°C; all of them are polymerized for 4, 6, 8, and 10 h.

The surface morphology of the grafted rubber was studied by OsO_4 staining at the carbon–carbon double bonds of the NR to increase contrast and gradation of the NR particles. 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 compatibility of the two domains, resulting in a favorable state of the dispersion and some possible chemical bonds linking the two phases together. The morphology of the particles during the period of polymerization and the thickness of the graft copolymer (the outer layer) on the surface of seed particles increased with the increasing the reaction time as shown in Figure 7.

The initiator type influences on the morphology of the graft copolymer. In Figure 7 (all micrographs at the left and center columns), the surfaces of the grafted natural rubber particles initiated by CHPO and TBHPO exhibit the presence of nodules of many MMA particles on the surface of the natural rubber particles. This is due to the growing macroradical chains, which were generated onto the surface of natural rubber particles, continuing to propagate to form the outer layer. The grafting reaction occurred largely on the surface of the rubber particles. On the other hand, the photographs at the right column illustrating the surface of grafted natural rubber particles initiated with $K_2S_2O_8/Na_2S_2O_3$ and VneoD used as the grafting promoter are smooth. Most of MMA monomers are polymerized on the microdomain at the surface layer of natural rubber particles because the physical partitioning of the initiator radicals between the polymers (NR) and aqueous phase may contribute a significant difference to the surface morphology.

TABLE IX
The Gel Content, M_w, M_n, and M_w/M_n at Various Initiators and Concentrations

Type of product	Gel content	M_n (10^5)	Sol fraction ($M_w \times 10^5$)	M_w/M_n
NR	50.8	3.5	12.1	3.5
NR/CHPO[a]	65.1	1.0	3.6	3.5
NR/TBHPO[a]	66.4	0.9	3.8	4.4
NR/$K_2S_2O_8$[b]	35.6	0.8	2.1	2.7
NR/CHPO[c]	74.5	3.0	4.9	1.6
NR/TBHPO[c]	72.5	1.6	4.0	2.4
NR/$K_2S_2O_8$[c]	42.2	1.0	2.9	2.9

[a] Polymerization was carried out at CHPO 0.5 phr or TBHPO 0.5 phr; rubber content 100 phr; 50°C; and time 8 h in the absence of MMA.
[b] Polymerization was carried out at $K_2S_2O_8$ 1.0 phr; rubber content 100 phr; 60°, and time 8 h in the absence of MMA.
[c] All are in the presence of MMA monomer (100 phr) at the above optimum condition.

Averaged molecular weights of the uncrosslinked polymer in the sol fraction

The weight-averaged molecular weight (M_w) is related to the weight of the individual molecules as represented by the eq. (4), where M_i is the molecular weight of the polymer of fraction i, W_i is the weight of the polymer in fraction i, and i is the fraction number (from 1 to x)

$$M_w = \Sigma \ (M_iW_i)/\Sigma W_i \qquad (4)$$

The number-averaged molecular weight (M_n) is dependent on the number of molecules and is represented by eq. (5), where N_i is the number of molecules in fraction i.

$$M_n = \Sigma \ W_i/\Sigma N_i \qquad (5)$$

The M_w and M_n values may be used to provide an index for the range of molecular weight distribution or polydispersity index, d, as shown in eq. (6):

$$M_w/M_n = d \qquad (6)$$

Table IX shows the gel content, weight averaged molecular weight (M_w), number averaged molecular weight (M_n), and polydispersity (M_w/M_n) for the uncrosslinked polymers in the sol fraction. The gel fractions of the NR without MMA grafting monomer in the presence of CHPO/TEPA or TBHPO/TEPA of 65.1 and 66.4%, respectively, were anticipated to be the crosslinked NR itself. With the presence of $K_2S_2O_8$/$Na_2S_2O_3$ initiation, chain session or chain degradation could possibly take place. The gel fraction of the HANR latex as the aggregate of phospholipids is in a micellar form (a natural surfactant). When the hydrophobic initiator (CHPO/TEPA or TBHPO/

TEPA) was added, the aggregate state was disturbed slightly because of the same hydrophobic nature and some polymerization could take place to increase the gel content. In contrast, the presence of relative polar initiator such as $K_2S_2O_8$/$Na_2S_2O_3$ disturbed significantly the aggregate form to result in the lower gel content. The $K_2S_2O_8$/$Na_2S_2O_3$ initiating system is thus considered as the chain session initiator for NR. When the grafting MMA was added and polymerized in the presence of the three initiating systems, the gel contents of the three systems increased with the least increase found in the $K_2S_2O_8$/$Na_2S_2O_3$ initiating system.

When the three initiating systems were added into the reaction mixture and polymerized as scheduled, the uncrosslinked polymer (NR) in the sol fraction could polymerize to be crosslinked polymers, which could not be dissolved in either toluene or chloroform for the molecular weight determination and was separated out from the soluble fraction. In addition, chain session or degradation of the polymer in the sol fraction to give the lower molecular weight may take place.[7] Chain scission of any molecule results in the formation of unstable molecules, which cannot polymerize. The uncrosslinked polymers in the sol fraction gave the lower M_n and M_w values than those before the polymerization. Only the nondegraded portion in the sol fraction can polymerize. The uncrosslinked polymers produced by the CHPO/PETA initiation in the sol fraction produced the higher M_w (4.9×10^5) and the narrower polydispersity index (1.6) than the other two initiation systems. The correlation between the gel fraction and the sol fraction cannot be made.

CONCLUSIONS

The graft polymerization of the MMA monomer onto NR particles was confirmed spectroscopically by spectra and functional groups. The graft copolymerization of MMA onto natural rubber prepared by emulsion polymerization by three different redox initiator systems, CHPO/TEPA, TBHPO/TEPA, and potassium persulfate ($K_2S_2O_8$)/$Na_2S_2O_3$, were used to initiate the graft copolymerization. The influential factors of the initiator concentration, reaction temperature, monomer concentration, grafting agent (for $K_2S_2O_8$), and reaction time were investigated to compare the initiation efficiency. The $K_2S_2O_8$/$Na_2S_2O_3$ was used with VneoD as a grafting promoter to enhance the grafting of MMA onto the natural rubber latex. The VneoD with an appropriate concentration (20 wt % of MMA) has been anticipated to extract hydrogen atom from polyisoprene to form an allylic-type radical, which is relatively stable and can facilitate the grafting of MMA onto natural rubber. The graft copolymer initiated with CHPO/TEPA gave the highest percentage grafting efficiency and percentage of grafted natural rub-

ber, i.e., the more hydrophobic initiator (CHPO) was more efficient than those of TBHPO and $K_2S_2O_8$ for grafting a relatively polar monomer onto natural rubber. The $K_2S_2O_8/Na_2S_2O_3$ initiating system reduces significantly the amounts of gel fraction and the polymer molecular weights in the sol fraction.

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