

Process Variables and Their Effects on Grafting Reactions of Styrene and Methyl Methacrylate onto Natural Rubber

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Received 29 January 2002; accepted 29 August 2002

ABSTRACT: The graft copolymerization of styrene and methyl methacrylate onto natural rubber latex was studied under various reaction conditions using a cumene hydroperoxide redox initiator. The monomer conversion, graft copolymer compositions, and grafting efficiency were determined. The synthesized graft copolymers were purified and then characterized by proton nuclear magnetic resonance (¹H-NMR) analysis and differential scanning calorimetry (DSC). A 2⁶⁻² fractional factorial experimental design was applied to study the main effects on the grafting. The variables investigated in this work were the amount of the initiator and emulsifier, the presence or absence of a chain-transfer agent, the styrene-to-methyl methacrylate ratio, the

monomer-to-rubber ratio, and the reaction temperature. The measured response for the experimental design was the grafting efficiency. The analysis of the results from the design showed the sequence of the main effects on the observed response of the grafting of styrene and methyl methacrylate onto natural rubber, in ascending order. The amount of the chain-transfer agent and the reaction temperature in the range of the test had significant effects and one marginally significant effect was the monomer-to-rubber ratio. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 63–74, 2003

Key words: graft copolymerization; natural rubber modification; styrene; methyl methacrylate

INTRODUCTION

Natural rubber (NR) is a natural biosynthesis polymer having an attractive range of properties, which could be modified to give more desirable properties. The chemical modification of NR by the grafting of vinyl monomers involves the creation of a free radical on the backbone of the rubber, thus having gained significance in modifying the properties of NR. When monomers are polymerized in the presence of a preformed polymer to give chemical bonding to that polymer, the result is graft copolymers. New materials, arising from combining rubber materials with nonrubber polymers, could lead to many technical applications. Grafting reactions often occur during the course of core-shell composite particles' production. The graft copolymers of vinyl monomers such as styrene (ST) and methyl methacrylate (MMA) onto NR, composing the rubbery core, provides resistance to impact, whereas the grafted glassy shell provides rigidity and compatibility to the polymer matrix, which, overall, results in better impact-resistant properties.^{1–5} It was reported that graft copolymers can be used effectively as compatibilizers for polymer blends.^{6,7}

For NR, research has confirmed that MMA and ST are the most suitable monomers when polymerized to give a high level of grafting.⁸ Since NR is obtained from *Hevea brasiliensis* as a latex, the most economical way for the chemical modification of NR is in the latex state. Bloomfield and Swift⁹ studied the graft copolymerization in which NR latex particles were swollen with a monomer, MMA, that was polymerized. In fact, the level of grafting obtained was quite low, but such materials have become commercial materials known as Hevea Plus. A number of reports^{10–13} have appeared on the grafting of vinyl monomers such as MMA or ST onto NR latex particles using an amine-activated hydroperoxide. Hydroperoxides have been found to be particularly susceptible to activation by polyalkylenepolyamines.¹⁴ The redox initiation system consisting of organic hydroperoxide and tetraethylenepentamine was chosen because it operates efficiently at the high pH values normally encountered in NR latex. It is not sensitive to oxygen and works well with ammonia present.

Some articles have dealt with the effects of process conditions on the grafting of vinyl monomers of MMA and/or ST on synthetic rubber latex. Gasperowicz et al.¹⁵ investigated the grafting of ST onto poly(butyl acrylate) in emulsion form. The grafting efficiency was found to decrease with an increasing reaction time, concentration of the initiator, concentration of the emulsifier, and monomer-to-polymer ratio. The same conclusions were also drawn by Xu et al.¹⁶ for the

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Contract grant sponsor: National Science and Technology Development Agency (NSTDA), Thailand.

grafting of ST onto poly(ethyl acrylate) in a seed emulsion process and by Merkel et al.¹⁷ in studying the graft copolymerization of MMA onto polybutadiene latex. Zhao et al.¹⁸ studied the graft copolymerization using styrene–butadiene–rubber (SBR) as the core and ST and MMA as the shell monomers. They gave evidence that the graft copolymerization is a surface-controlled process. Sundberg et al.¹⁹ investigated various factors, that is, the monomer/polymer ratio, amount of the initiator, degree of conversion, and concentration of the chain-transfer agent governing the grafting efficiencies of ST onto polybutadiene latex. The grafting efficiency increased with increasing temperature, whereas it decreased with an increase in the concentration of the chain-transfer agent.

Although much is known about graft copolymerization, the system is a complex one and much remains to be discovered. Some researchers have used statistically based experimental designs to determine the influence of the process conditions on the grafting of maleic anhydride,^{20,21} *p*-phenylene bismaleamic acid,²² or ST²³ onto polypropylene in the solid phase. They developed a methodology based on an experimental design to study the effect of process conditions on grafting. Many process variables are known to affect the grafting reaction. The one-factor-at-a-time technique, varying one factor while keeping the other factors at a constant level, is tedious when a number of factors have to be investigated, whereas statistically based experimental designs provide a more efficient approach to deal with a large number of variables.²⁴ When the effects of such a number of variables on a process are to be studied, evaluation of these variables (to focus on the important ones) is best accomplished using two-level fractional factorial designs. Because this technique is powerful and easy to handle, the fractional factorial design is one of the most commonly used methods to realize the effects of some independent variables that significantly affect the final experimental results.

Investigation of the process variables affecting the grafting reaction is very complicated in view of the great number of process variables involved. The aim of this work was to highlight the effects of process variables on the grafting reaction of ST and MMA onto NR through a statistically based experimental design. The influence of the process variables, including the amount of the initiator, emulsifier, and chain-transfer agent, the reaction temperature, the ST/MMA ratio, and the monomer-to-rubber ratio, were investigated using a two-level fractional factorial design. Statistical analysis was used to study the influence of each process variable irrespective of and in combination with the other process variables on the grafting efficiency during the grafting reaction. This approach is useful for gaining insight into the mechanism of graft copolymerization.

EXPERIMENTAL

Materials

The commercial high-ammonia NR latex containing a 60% dry rubber content (DRC) was the product of N. Y. Rubber Co., Ltd., Bangkok, Thailand, and was used as received. The latex is composed almost entirely of *cis*-polyisoprene. Reagent-grade ST (Aldrich, purity ~99%) and MMA (Aldrich, Milwaukee, WI, purity ~99%) monomers were prepared free of an inhibitor by washing with a 10% sodium hydroxide solution, followed by deionized water and then by distillation under reduced pressure. The chain-transfer agent *n*-dodecyl mercaptan (nDM, Aldrich), the emulsifier sodium dodecylsulfate (SDS, Aldrich, purity ~98%), the stabilizer isopropanol, the buffer potassium hydroxide (KOH, Aldrich), the initiator, the redox initiator system, cumene hydroperoxide (C₉H₁₂O₂, CHPO, Aldrich, purity ~80%), and the activator agent tetraethylenepentamine [HN(CH₂CH₂NHCH₂CH₂NH₂)₂, TEPA, Aldrich] were used as received. Deionized water was used throughout the work.

Preparation of grafted NR

The graft polymerizations were carried out using a 300-mL Parr reactor, equipped with a condenser. NR latex and an aqueous solution of the additive were charged to the reactor and the dissolved oxygen present in the ingredients was removed by purging nitrogen gas for at least 30 min through the mixture, providing a still-stable latex. If necessary, a buffer was added to maintain the pH of the system at 10. The monomer mixture with mercaptan was fed to the reactor and TEPA was then added. The NR seed latex was swollen with the monomer mixture for 1 h at the reaction temperature before adding the redox initiator. The polymerization reaction was performed at a stirring speed of 200 rpm at the desired temperature for 8 h. The polymerization was maintained at a constant temperature for all polymerization runs. The posttreatment included the coagulation of the polymer latex and washing with deionized water. The gross polymers were recovered and dried to a constant mass in a vacuum oven at 40°C. The recipes and variable design factors for the graft copolymerization are shown in Tables I and II, respectively.

The conversions of monomers were determined by gravimetry. The gross polymers were resolved into graft copolymers, free NR, and free copolymers by Soxhlet extraction. A 60–80°C boiling point petroleum ether and a methyl ethyl ketone (MEK)/acetone (50:50 v/v) mixture were used for extracting the free rubber and free copolymers [polystyrene (PST)/MMA] for 24 h, respectively. The weight difference between the initial sample and the extracted samples is the measure of the graft copolymers (GNR), the free copoly-

TABLE I
Standard Recipes Used for Graft Copolymerization

Ingredients	Quantities
NR (60% DRC)	50 g
Water	70 g
Isopropanol	3 g
Potassium hydroxide	0.12 g
CHPO (CHPO:TEPA = 1:1)	Variable
SDS	Variable
nDM	Variable
ST/MMA	Variable

mers (FP), and the grafting efficiency (GE) and was calculated using the following relationships:

GE (%)

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

$$\text{GNR (\%)} = \frac{\text{weight of graft copolymers}}{\text{weight of the gross polymers}} \times 100 \quad (2)$$

$$\text{FP (\%)} = \frac{\text{weight of free copolymers}}{\text{weight of the gross polymers}} \times 100 \quad (3)$$

The monomer conversion is defined as the weight of the monomer polymerized (grafted and free) divided by the initial weight of the monomers.

¹H-NMR spectra were obtained on a Bruker AC 250-MHz NMR spectrometer, which was found to combine accuracy and reproducibility (± 2 wt %) with an ease of analysis. Analyses were carried out using a 5–10% (w/v) solution in deuterated chloroform (CDCl₃). The peaks at 5.15 ppm are assigned to the olefinic protons content in the NR. The signals at 6.5–7.5 ppm are attributed to the phenyl group of PST. The peaks observed at 3.7 ppm are attributed to the methoxy group of poly(methyl methacrylate) (PMMA). From the different signal areas, the amount of ST per proton (ST), the amount of isoprene per proton (NR), and the amount of MMA per proton (MMA) were calculated using the following equations:

$$\text{ST} = \frac{A_{\delta=7.5-6.5}}{5} \quad (4)$$

$$\text{MMA} = \frac{A_{\delta=3.7}}{3} \quad (5)$$

$$\text{NR} = \frac{A_{\delta=5.1}}{1} \quad (6)$$

The fractions of ST ($F_{\text{ST-g}}$) and MMA ($F_{\text{MMA-g}}$) in the graft copolymers were calculated by the following equations:

$$F_{\text{ST-g}} = \text{ST} / (\text{ST} + \text{MMA}) \quad (7)$$

$$F_{\text{MMA-g}} = \text{MMA} / (\text{ST} + \text{MMA}) \quad (8)$$

Thermal characterization of the graft copolymers was carried out using a Perkin–Elmer DSC-4 differential scanning calorimeter with a Perkin–Elmer thermal analysis data station Model TADS-101. A 10-mg sample was placed in the DSC sample pan, and the heating rate was 10°C min⁻¹. The sample was quenched to -150°C, heated to 200°C and kept at this temperature for 2 min, quenched again to -150°C, followed by heating to 200°C to remove the heat history, and the second heating scan was recorded. The temperature at the inflection point was taken to be the glass transition temperature (T_g).

The morphology of the copolymers was examined using a JEM-200CX transmission electron microscope (TEM) at 120 kV. The grafted latex was diluted 400 times with deionized water to a concentration of 0.025 % wt. To this solution, 1 mL of a 2% aqueous OsO₄ solution was added and allowed to stain the NR in the graft copolymers overnight.

Experimental designs

The large number of independent variables involved in the graft copolymerization processes led to a thorough experimental study. The grafting efficiency was determined gravimetrically, with the responses or dependent variables to be measured for each run. In this work, six process variables, which are expected to

TABLE II
Graft Copolymerization Experiments: Low and High Level of Design Factors

Factors	Name	Amount (low = -1)	Amount (high = +1)
[INT]	Cumene hydroperoxide	1 phr	2 phr
TEMP	Reaction temperature	50°C	70°C
[EMUL]	Sodium dodecylsulfate	1 phr	2 phr
[CTA]	<i>n</i> -Dodecyl mercaptan	0 phr	0.5 phr
ST/MMA	Styrene/methyl methacrylate	0.75	1.0
M/R	Monomer/rubber ratio	1.0	1.25

TABLE III
Design Factor Levels for Factorial-designed Experiments

Experiment	Design factor					
	INT	TEMP	EMUL	CTA	ST/MMA	M/R
GNR01	-1	-1	-1	-1	-1	-1
GNR02	+1	-1	-1	-1	+1	-1
GNR03	-1	+1	-1	-1	+1	+1
GNR04	+1	+1	-1	-1	-1	+1
GNR05	-1	-1	+1	-1	+1	+1
GNR06	+1	-1	+1	-1	-1	+1
GNR07	-1	+1	+1	-1	-1	-1
GNR08	+1	+1	+1	-1	+1	-1
GNR09	-1	-1	-1	+1	-1	+1
GNR10	+1	-1	-1	+1	+1	+1
GNR11	-1	+1	-1	+1	+1	-1
GNR12	+1	+1	-1	+1	-1	-1
GNR13	-1	-1	+1	+1	+1	-1
GNR14	+1	-1	+1	+1	-1	-1
GNR15	-1	+1	+1	+1	-1	+1
GNR16	+1	+1	+1	+1	+1	+1

have an effect on the grafting efficiency, were considered. These variables include the concentrations of the initiator, emulsifier, and chain-transfer agent, the reaction temperature, the ST/MMA ratio, and the monomer-to-rubber ratio. The effects are complex and may include many interactions. When using a two-level fractional factorial design, the number of experiments can be reduced without loss of information about the main effects. However, some information about interaction effects will be lost. In this case, a two-level fractional factorial design was chosen since the higher-order interactions were expected to be negligible. Process variables were varied according a 2_{IV}^{6-2} design, resolution $R = (IV)$. For each process variable, a “- level” and a “+ level” were chosen in the range to be studied (Table II). The low level, coded as -1, and the high level of each design factor, coded as +1, were also defined for each independent variable. The independent variables are listed in the first column of Table II and represent the amount of the initiator (INT), emulsifier (EMUL), and chain-transfer agent (CTA), ST-to-MMA ratio (ST/MMA), monomer-to-rubber ratio (M/R), and reaction temperature (TEMP). The experiments (a total of 16 runs) are listed in Table III using the coding scheme shown in Table II.

The grafting efficiency was analyzed using analysis of variance (ANOVA). To ensure that the assumptions of normality and constant variance were met, the response variable (grafting efficiency) was calculated. The F test was used to evaluate if a variable had a significant effect ($F > 18.5$). The data processing and calculations were carried out using Statistica (Version 5) programs.

RESULTS AND DISCUSSION

The effect of the process variables on the total conversion, as well as the contents of the components of the

gross polymers, such as free rubber, free copolymers, and graft copolymers, and the grafting efficiency are presented in Table IV. From these results, it can be seen that the grafting efficiency ranges from 43.6 to 85.4%, graft copolymers from 55.1 to 76.5%, free copolymers from 6.0 to 27.1%, and free rubber from 8.4 to 26.1%, depending on the process condition, which will be subsequently discussed in detail.

Rate of polymerization

For the graft copolymerization process in which the redox initiator couple, CHPO/TEPA, is used, most of the free radicals are produced at the monomer-swollen particle/water interface, since the peroxide is soluble in the organic phase, whereas the activator TEPA is water-soluble. CHPOs in a dilute aqueous solution decompose to yield alkoxy radicals. The alkoxy radicals quite likely interact with the monomer or the rubber molecule, producing macroradicals which initiate grafting. During the formation of the graft copolymers, the surface of the latex particles became the loci of polymerization. It is possible that the backbone in the NR, being more active, becomes the site of graft copolymerization. The alkoxy radicals not only attack the backbone to produce polyisoprene radicals, which initiate monomers to form the graft copolymers, but also initiate monomers to form free polymer radicals, which combine with polyisoprene radicals to terminate or transfer to NR to form graft copolymers. Also, some of the free polymer radicals still terminate to form free copolymers on the surfaces of the latex particles. The growing polymer chains, grafted or ungrafted, will be terminated by recombination with another macroradical, chain transfer, or disproportionation.

For graft copolymerization of ST and MMA on NR, monomer conversion as a function of reaction time

TABLE IV
Effect of Process Variables on Monomer Conversion and Grafting Properties

Experiment	Monomer conversion (%)	Free rubber (%)	Free copolymers (%)	Graft copolymers (%)	Grafting efficiency (%)
GNR01	90.0	26.1	18.8	55.1	53.5
GNR02	92.6	22.1	12.1	65.8	70.5
GNR03	92.2	13.1	17.9	69.1	62.8
GNR04	93.5	13.6	9.9	76.5	79.5
GNR05	91.6	14.7	24.0	61.3	49.8
GNR06	93.5	15.1	26.7	58.2	44.7
GNR07	91.5	24.1	14.6	61.3	64.0
GNR08	93.3	20.1	6.0	73.9	85.4
GNR09	92.8	13.4	27.1	59.5	43.6
GNR10	93.9	10.0	25.7	64.2	46.9
GNR11	91.9	18.2	17.1	64.7	58.1
GNR12	92.8	18.8	18.7	62.5	54.5
GNR13	91.5	20.0	17.5	62.5	56.9
GNR14	93.1	20.5	21.8	57.7	47.0
GNR15	91.7	11.8	26.2	62.1	45.3
GNR16	93.6	8.4	23.3	68.4	51.9

Reaction time, 8 h.

was investigated. Figure 1(a,b) shows the monomer conversion versus time profiles for all 16 experiments from the 2_{IV}^{6-2} fractional factorial design. When using fractional design, more than one variable is changed

per experiment and the conversion versus the time profiles for the 2_{IV}^{6-2} design are grouped according to the chain-transfer agent amount at each of the two temperature levels used. For all 16 experiments, the shape of conversion versus time curves were identical and the rates of polymerization were similar. The polymerization rates were extremely rapid during the initial period (<180 min) before reaching a plateau level (Fig. 1). This is shown by the rapid increase of monomer conversion. After the first 2–3 h, conversion of the vinyl monomer in the reactor was high and remained constant. Although a slight difference among the limiting conversions reached was observed (probably within experimental error), under no circumstances, did the conversion levels approach 95%.

Figure 1(a) shows conversion versus time profiles for the low level amount of the chain-transfer agent at a low-level temperature (close signs) and a high-level temperature (open signs), respectively. It can be seen that it takes much longer to reach a limiting conversion using the low-level temperature when compared with the high-level temperature, since the rate of the redox reaction usually follows a Arrhenius-type relationship and, consequently, the radical decomposition rates increase with increasing temperature.^{25–27}

Figure 1(a,b) shows conversion versus time profiles for the experiments using a low-level and a high-level amount of the chain-transfer agent, respectively. When the chain-transfer agent was added, the amount of the chain-transfer agent further influenced the rate of polymerization. As the chain-transfer agent was added, the rate of the chain-transfer reaction of free radicals to the chain-transfer agent increases, which results in a decrease of macroradical formation, thereby decreasing the graft and free copolymerization.

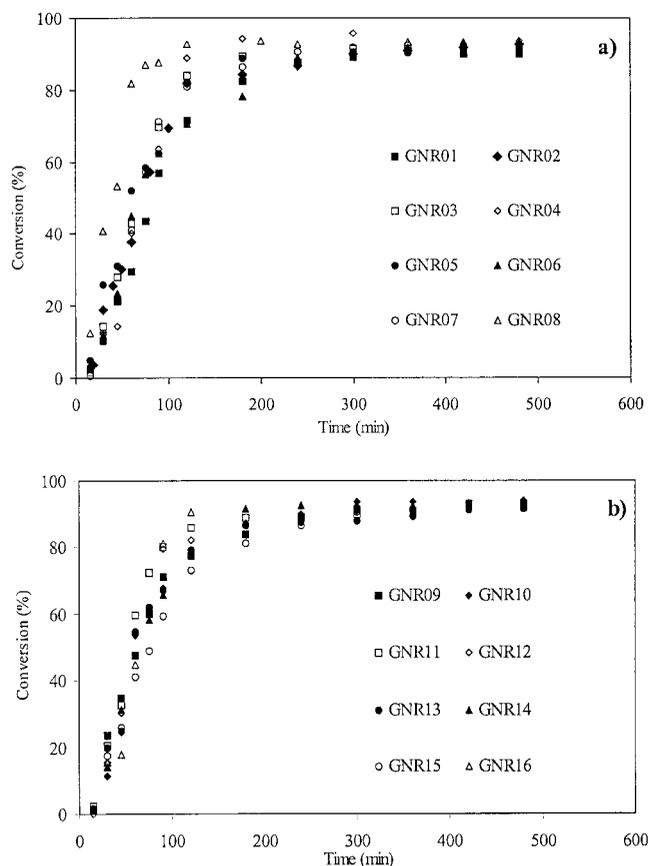


Figure 1 Conversion versus time profiles at (closed signs) low-level temperature and (open signs) high-level temperature: (a) low-level CTA; (b) high-level CTA.

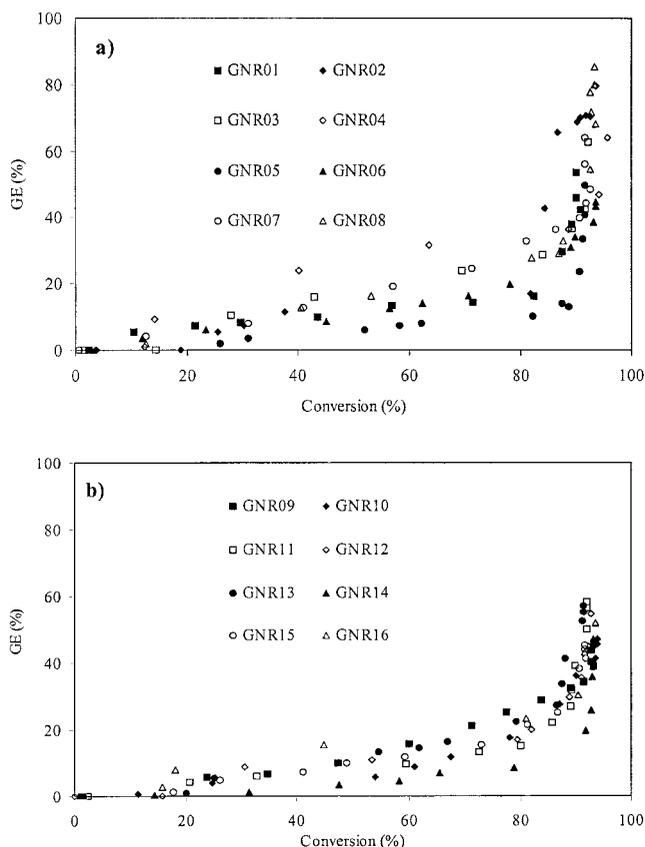


Figure 2 Grafting efficiency as a function of conversion at (closed signs) low-level temperature and (open signs) high-level temperature: (a) low-level CTA; (b) high-level CTA.

Figure 2(a,b) shows the plots of the grafting efficiency (GE) versus conversion, which had a similar trend for all 16 experiments. At the beginning (conversion < 10%), no graft copolymerization was observed. As the polymerization proceeds, the grafting efficiency increased gradually over the range of conversion of 10–80% and then steeply increased at high conversion (>80%). Figure 3 shows that the percentage of ST and MMA in the free copolymers decreased dramatically with the conversion. In the early stage of polymerization (10–80% conversion), the larger percentage of the second-stage copolymers (60% of the ST/MMA copolymers) is located in a new crop of particles. At conversions of 85% and higher, however, this percentage decreases drastically. At the end of polymerization (90% conversion), only 10% of the ST/MMA copolymers is in new particles. A sudden increase in the percentage of the graft copolymers with high conversion can be explained by the growth of seed particles that takes place by encapsulation of the copolymer chain initiated in the aqueous phase at the surface of the seed particle. Thus, the free copolymers become grafted chains at high conversion. Aerdts et al.²⁸ found similar results when they studied the graft copolymerization of ST and MMA onto polybutadiene.

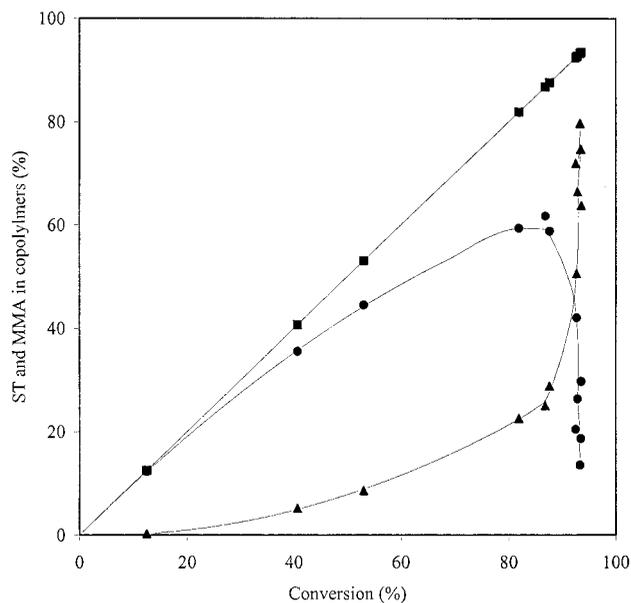


Figure 3 Variation of percentage of ST and MMA with conversion: (▲) in graft copolymers; (●) in free copolymers; (■) in gross polymers for GNR08.

The morphology of NR and the grafted NR is shown in Figure 4. The darker areas represent the NR core regions, while the lighter areas show PST/MMA film

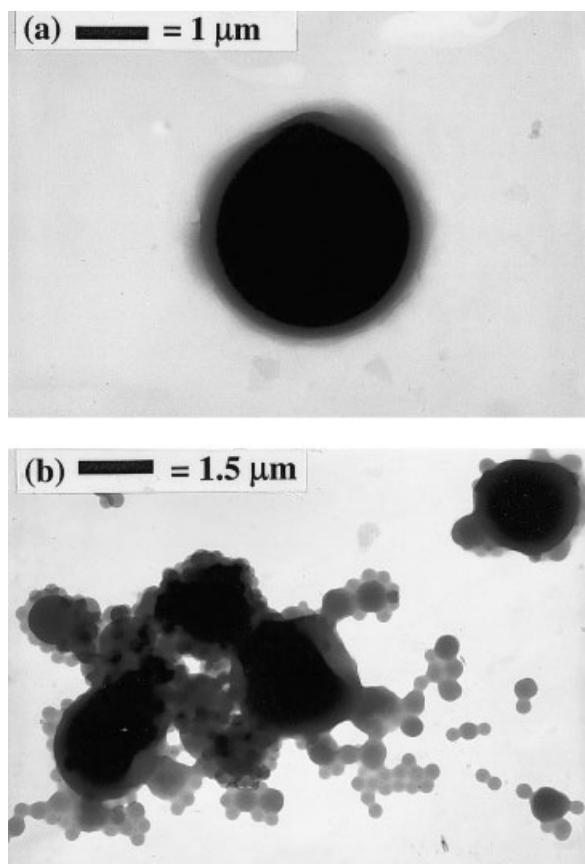


Figure 4 Transmission electron micrographs of (a) NR ($\times 45,000$) and (b) GNR08 for reaction time 8 h ($\times 30,000$).

as the shell. Figure 4(a) shows that the NR latex particle is spherical in nature with a smooth surface. The NR latex particles coated with ST and MMA revealed irregular shapes, indicating that the PST/MMA is distributed continuously on the surface [Fig. 4(b)]. This phenomenon is probably due to phase separation, that is, the rubber polymer is immiscible with PST/MMA. The solubility parameters for PST and PMMA are 9.1 and 9.2 $(\text{cal}/\text{cc})^{1/2}$, respectively, while that for NR is 8.0 $(\text{cal}/\text{cc})^{1/2}$. Phase separation in the particle could be due to the immiscibility of the polymer pair (the difference in solubility parameters between the core and shell material is large, about 1 $(\text{cal}/\text{cc})^{1/2}$) capture of the aqueous-formed primary particle onto the existing surface cannot be disregarded. Furthermore, it was demonstrated that grafting of the second-stage polymer onto the core particle produces heterogeneous structures (core-shell structures), which are formed by phase separation of incompatible polymers during polymerization. Most of the MMA and ST polymerized in the aqueous phase form secondary particles, which are flocculated with the NR seed particles and then overcoat the periphery of the rubbery core surface with glassy shell copolymers. According to the mechanism forwarded by Dimonie et al.,²⁹ second-stage polymerization takes place both in monomer-swollen seed particles and in particles newly nucleated in the aqueous phase. Hence, the original seed particles would grow by polymerization within the seed and/or by flocculation with new chains generated in the aqueous phase.

Graft copolymer compositions

When graft copolymerization of two monomers that are assumed to differ only in their reactivity ratios is achieved by a batch process, it is well known that a continuous drift in the graft copolymer compositions occurs from the beginning to the end of the polymerization process. The $^1\text{H-NMR}$ results were used to calculate the graft copolymer compositions. The $^1\text{H-NMR}$ spectrum of the graft copolymers is shown in Figure 5. The results of the graft copolymer compositions are given in Table V. It can be seen that the level of ST in the graft copolymers is higher than that of MMA.

The nature of the monomer is a very important factor in determining the reactivity of the polymeric radical. Aerdts et al.²⁸ reported a large difference in the reactivity ratios, namely, $r_{\text{MMA}} = 0.19 \pm 0.05$ and $r_{\text{ST}} = 0.73 \pm 0.05$ at 323 K. A rule of thumb has been proposed: The most reactive monomers give the least reactive polymeric radicals and the least reactive monomers yield the most reactive polymeric radicals.^{30–33} Thus, the reactivity of ST and MMA is in the following order: $\text{ST} > \text{MMA}$, and the reactivity of the polymeric radicals formed from these monomers is in

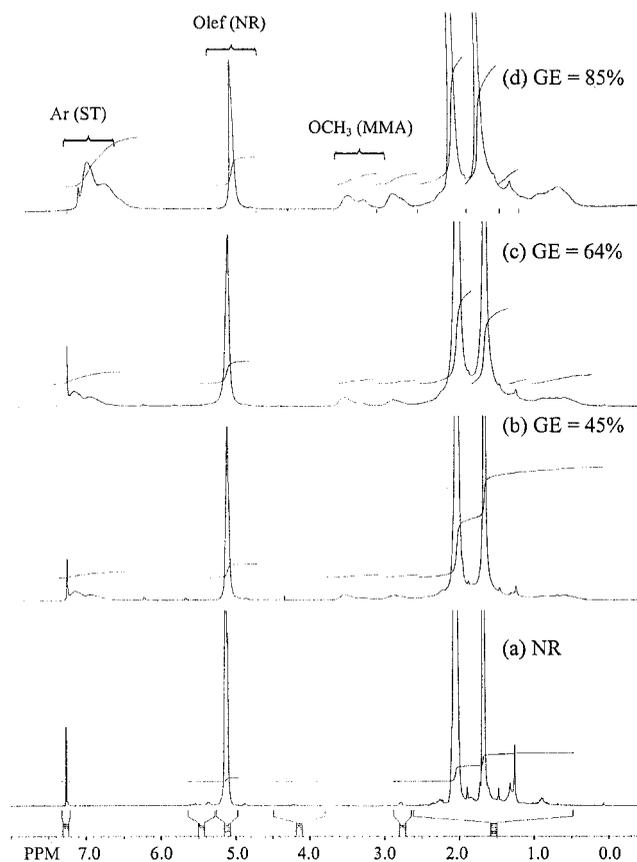


Figure 5 $^1\text{H-NMR}$ spectra, 250 MHz, of (a) NR, (b) GNR15, (c) GNR07, and (d) GNR08. Ar (ST) represents the resonance of the aromatic protons of the ST unit, Olef (NR) represents the resonance of the olefinic protons of the NR unit, and OCH_3 (MMA) represents the resonance of the methoxy protons.

the reverse order (via the rule thumb of Mayo): polystyryl radical $<$ PMMA radical.

Regardless of the origin of the radical site on the backbone polymer, the ability of this site to participate in a grafting reaction is dependent on its reactivity. If the radical site on the backbone polymer is much more stable than is the polymeric radical generated from the monomer, then the monomer does not readily add onto the backbone polymer and this radical is not effective as a grafting site. Thus, it is important to distinguish between the reactivity of all the radical species relative to their tendency to react with the monomer. For the polyisoprene molecule, the two methylene groups in the isoprene residue are not equivalent and it seems likely that the attack occurs preferentially at carbon 4, so that the methyl group exerts the greatest stabilizing influence on the resulting allylic radical.³⁴

In the grafting system, the attack of the alkoxy radical on *cis*-polyisoprene most likely occurred by chain transfer to form the polyisoprenyl radical. The reactivity of the polystyryl radical is about the same as that of the polyisoprenyl radical (both are stabi-

TABLE V
Graft Copolymer Compositions

Experiment	ST (%wt)	Isoprene (%wt)	MMA (%wt)	F_{ST-g}	F_{MMA-g}	GE (%)
GNR01	10.6	81.5	7.9	0.563	0.437	53.5
GNR02	16.4	77.4	6.2	0.718	0.282	70.5
GNR03	14.2	77.1	8.7	0.613	0.387	62.8
GNR04	15.3	77.2	7.6	0.723	0.277	79.5
GNR05	15.4	79.2	5.4	0.733	0.267	49.8
GNR06	12.9	79.8	7.3	0.629	0.371	44.7
GNR07	15.3	77.9	6.8	0.686	0.314	64.0
GNR08	14.9	73.0	12.1	0.541	0.459	85.4
GNR09	9.2	85.4	5.4	0.620	0.380	43.6
GNR10	13.0	82.5	4.5	0.734	0.266	46.9
GNR11	10.5	79.0	10.5	0.519	0.481	58.1
GNR12	12.6	79.1	8.3	0.592	0.408	54.5
GNR13	10.7	82.8	6.5	0.610	0.390	56.9
GNR14	9.0	84.8	6.2	0.583	0.417	47.0
GNR15	13.0	82.7	4.3	0.744	0.256	45.3
GNR16	13.0	78.6	8.4	0.599	0.401	51.9

Reaction time, 8 h.

lized by resonance). In addition, the ST monomer is one of the most active of the vinyl monomers, and in spite of the low reactivity of the polyisoprenyl radical, the ST monomer can still be grafted onto it. However, MMA is quite an inactive monomer compared to ST. Conversely, the PMMA radical is a very active polymeric radical compared to the polystyryl radical. Therefore, the polyisoprenyl radical could not compete with the more active PMMA radical. The chemical nature of isoprene is similar to ST; this leads to the assumption that the grafting can take place due to the abstraction of a hydrogen atom from the polymer backbone.

Influence of process variables

Process variables including the amount of the initiator, emulsifier, and chain-transfer agent, reaction temper-

ature, ST/MMA ratio, and monomer-to-rubber ratio were investigated. The grafting efficiency was analyzed using analysis of variance. To ensure that the assumptions of normality and constant variance were met, the response variable, the grafting efficiency, was calculated. The 95% confidence interval ($F_{1,2} = 18.5$) provides a test to decide whether the variance due to an observed response is significant or not. If the F test is smaller than 18.5, the variance due to the observed response is not significant. If the observed F test is larger than 18.5, the observed response is probably significant. Results for the main effects and two-factor interactions are identified in Table VI, showing the F test of effects of the process variables on the grafting efficiency. In this design, two significant effects with respect to the grafting efficiency were CTA and TEMP and one marginally significant effect was the mono-

TABLE VI
Results of Main Effects and Two-factor Interactions for Observed Response and the Analysis of Variance of % GE

Effect name	GE (%)	SS	df	MS	F^a	Significance
Mean	57.14					
INT	5.81	134.90	1.00	134.90	8.80	No
TEMP	11.07	490.60	1.00	490.60	32.00	Yes
EMUL	-3.03	36.65	1.00	36.65	2.39	No
CTA	-13.25	702.19	1.00	702.19	45.81	Yes
ST/MMA	6.26	156.65	1.00	156.65	10.22	No
M/R	-8.18	267.61	1.00	267.61	17.46	? ^b
INT by TEMP	4.46	79.63	1.00	79.63	5.20	No
INT by EMUL	-2.55	25.91	1.00	25.91	1.69	No
INT by CTA	-6.73	181.08	1.00	181.08	11.81	No
INT by ST/MMA	0.98	3.83	1.00	3.82	0.25	No
INT by M/R	-0.43	0.73	1.00	0.72	0.05	No
TEMP by CTA	-7.24	209.86	1.00	209.86	13.69	No
TEMP by M/R	2.54	25.80	1.00	25.80	1.68	No
Error		30.66	2.00	15.33		
Total SS	2346.09	15.00				

$R^2 = 0.98693$. Reaction time, 8 h.

^a $F(1,2) = 18.5$ with $\alpha = 0.05$. If $F < 18.5$, then the variable is not significant.

^b This variable is marginally significant.

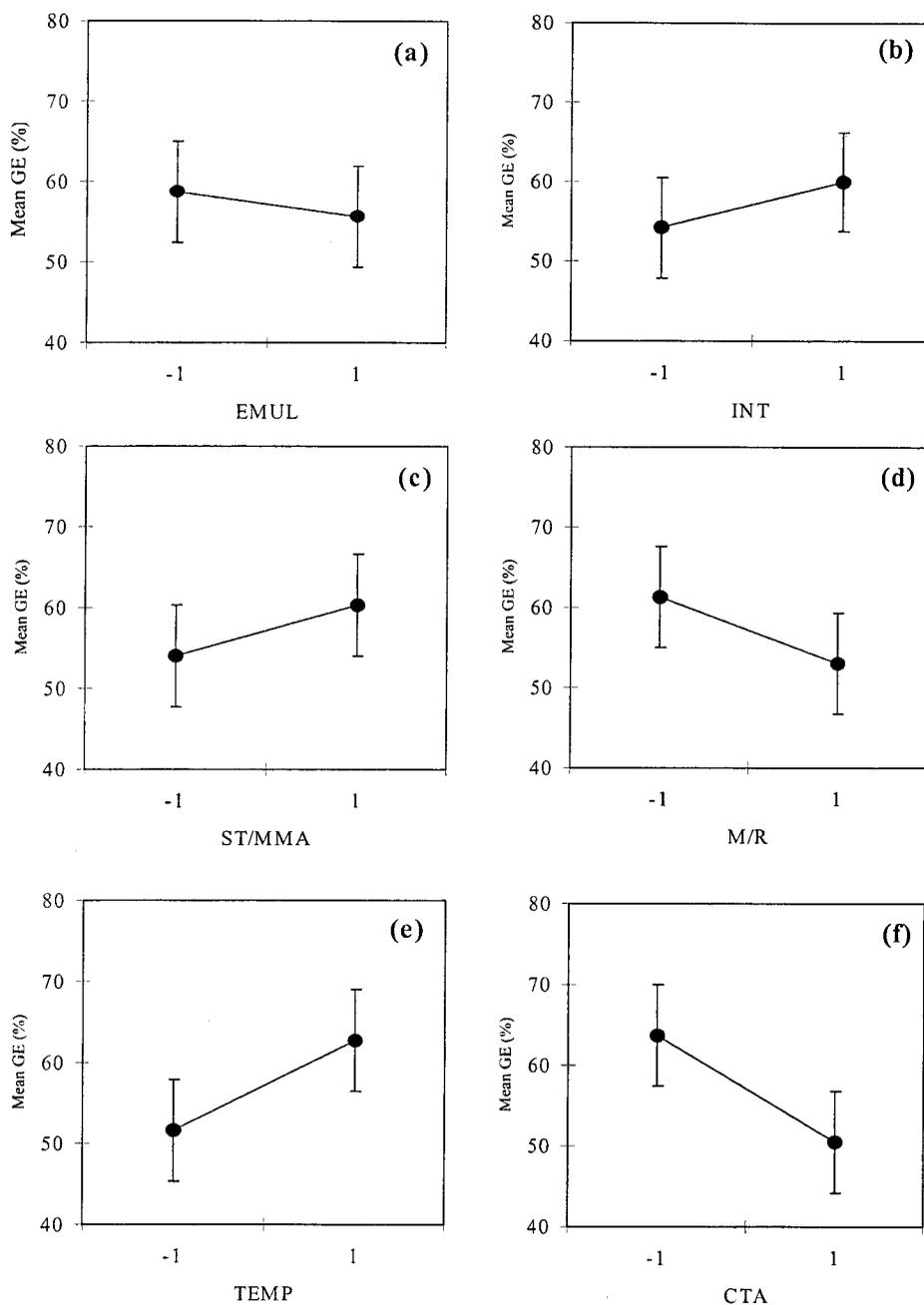


Figure 6 Effect of process variables on the mean grafting efficiency.

mer-to-rubber ratio. All interactions could be eliminated because of no significance (see in Table VI).

According to the definition, the main effect of the controlled independent variable is the mean of the difference between the values at the high level (+) and the values at low level (-). Figure 6 shows the mean grafting efficiency of the grafting of ST and MMA onto NR as a response to the six variables investigated.

The emulsifier has a little effect on the grafting efficiency when the amount of the emulsifier changes from a low level to a high level [Fig. 6(a)]. The emulsifier, added in the second-stage emulsion polymerization, was effective in stabilizing the particles. The emulsifier concentration on the seed particle surface

has little effect on the grafting efficiency in the absence of coagulation or renucleation of particles. At a high level of an emulsifier concentration, the grafting efficiency slightly decreased, due to the occurrence of second nucleation. This indicates that, under such conditions, more free micelles exist in the water phase; these could be initiated to form a new crop of particles, so there would be less monomer left for grafting. Bloomfield and Swift⁹ reported that an excess of an emulsifier can lead to the formation of particles composed entirely of the second polymers, which is usually an undesirable situation.

The effect of the amount of the initiator on grafting is shown in Figure 6(b), which indicates that the graft-

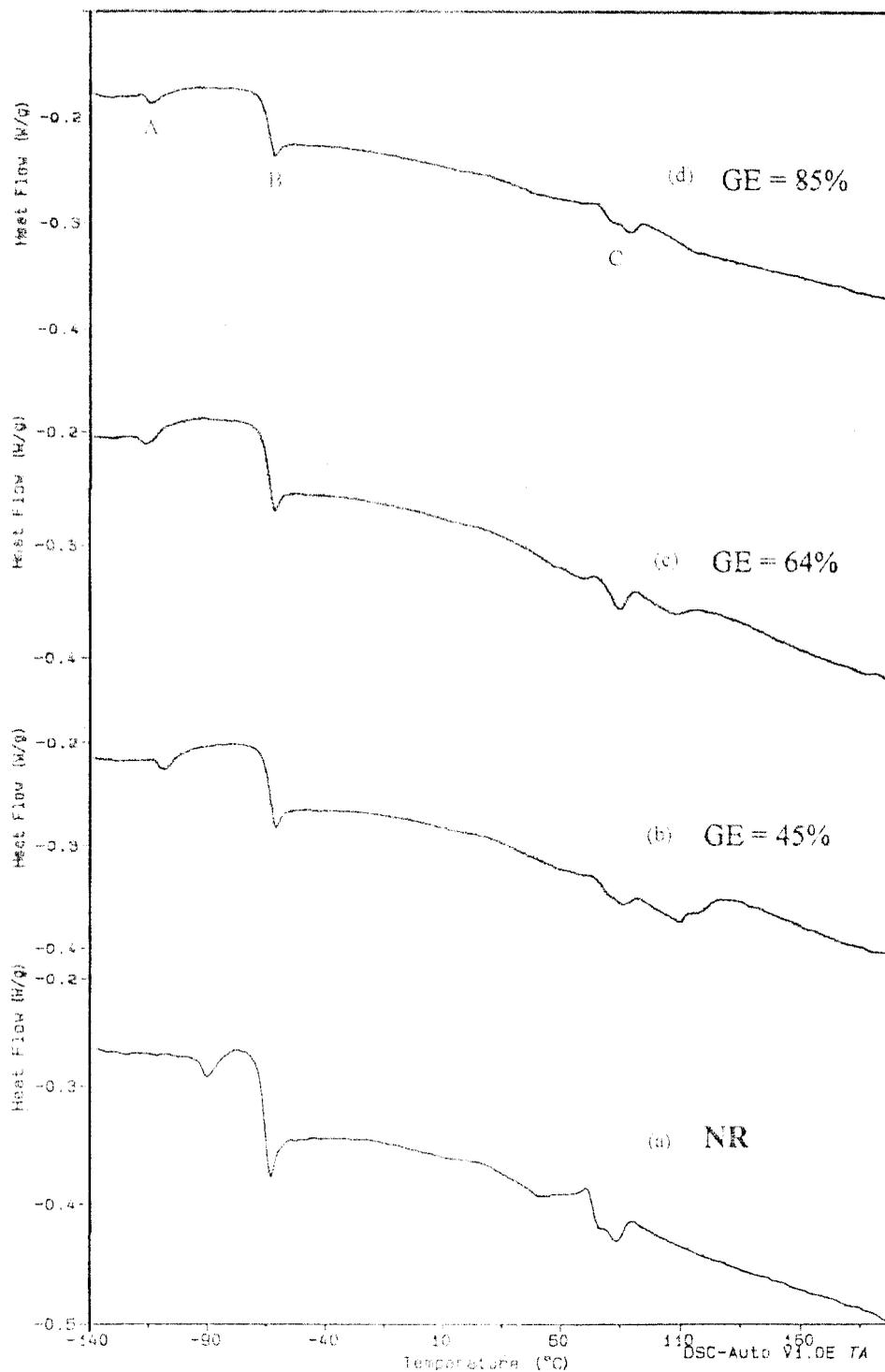


Figure 7 DSC curves for (a) NR, (b) GNR15, (c) GNR07, and (d) GNR08.

ing efficiency increases slightly with an increasing amount of the initiator. The increase in the amount of the initiator causes an increase in the rate of radical entry. This can be explained by the fact that the radicals transfer to either rubber or monomer, producing macroradicals, resulting in an increase in grafting. As the initiator concentration is increased, it is probable that the number of grafting sites increase while more free copolymers are also produced; therefore, the

overall amount of the graft copolymers increased slightly. Zhao et al.¹⁸ observed similar results for the graft copolymerization of ST and MMA onto SBR latex particles in the core-shell emulsion process. Some workers¹⁵⁻¹⁷ claimed that the graft efficiency decreases with an increasing initiator concentration, so there is still confusion on this matter.

When the ST/MMA ratio was increased, the grafting efficiency increased [Fig. 6(c)]. This indicates that when

the amount of ST in the monomer mixture was increased a more favorable condition resulted to produce graft copolymers rather than free copolymers. ST is grafted more easily than is MMA because of resonance stabilization. Thus, ST was grafted and left a substantial amount of MMA in the water and the polymer phase. It can be concluded that a high grafting efficiency was achieved at a high level of ST/MMA. Huang and Sundberg^{30–33} suggested that the amount of graft copolymers depends upon the identity of the monomer.

The graft efficiency decreases with an increasing monomer-to-rubber ratio [Fig. 6(d)]. The polymerization occurs mainly in the shell of the particles. When the monomer-to-rubber ratio increases, the contact area between the monomer and NR decreases gradually. As grafting proceeds and a certain shell thickness of the grafted material is reached, grafting decreases due to the reduced availability of the polymer backbone. Therefore, more free copolymers are produced than are graft copolymers. Also, systems with a higher monomer-to-rubber ratio have a lower surface area at the reaction site, and the rate of free copolymer termination is more favored than is the rate of transfer of the polymeric radical to NR, thus accounting for the reduced grafting efficiency with an increase in the monomer-to-rubber ratio. This experiment was performed to confirm that the grafting occurs mainly on the surface of the seed latex particles, but not inside the particles. Similar results were observed by Xu et al.,¹⁶ Merkel et al.,¹⁷ and Zhao et al.¹⁸

The polymerization temperature had a positive effect on the grafting efficiency [Fig. 6(e)]. The grafting efficiency increased with an increasing temperature; this is due to the swellability of rubber, the solubility of the monomer and its high diffusion rate, and the rate of decomposition of the initiator, which depends on the temperature. On the other hand, higher temperature may reduce the viscosity of the system and increase the mobility of the molecular chains to facilitate the grafting reaction.

Statistical analysis of the data (*F* test in Table VI) showed that CTA had the strongest effect on the grafting efficiency. The grafting efficiency decreased when the chain-transfer agent was added [Fig. 6(f)]. Addition of the chain-transfer agent would affect mainly the transfer reactions altering the graft chains. This can be explained on the basis that the radicals of a graft chain or polymer backbone are most likely to transfer to the chain-transfer agent. This implies that the presence of the chain-transfer agent in the reaction mixture hinders the propagation of the chains. Thus, the grafting efficiency decreased in the presence of a chain-transfer agent. Similar observations have been published for the grafting of ST onto polybutadiene latex particles.¹⁹

Glass transition temperatures

To investigate the structure of the graft copolymers, DSC was used to explore the macromolecule chains' motion. Figure 7 shows DSC curves of graft copolymers with different levels of grafting efficiency as well as that of NR. For NR (curve a), three peaks were observed. The most intense peak (B peak) at -65°C is attributed to the glass transition temperature (T_g). The secondary transition temperature, the A peak, at about -88°C corresponds to the motion of short sections of the main chain or of the side chain and the C peak is observed at 73°C due to the motion of the low molecular weight components of rubber with a broad molecular weight distribution. From the DSC curves (curve b–d) of the graft copolymers with different grafting efficiencies, the secondary transition temperatures shift toward the lower-temperature side with increasing grafting efficiency.

T_g is affected by the size of the side groups and the mobility of the chain. Any factor disturbing the closest packing of the main chain will lower the T_g ; any factor stiffening or increasing the interaction between chains will increase the T_g . This behavior was not observed in the DSC results (Table VII). The majority of these graft copolymers have relatively few graft chains, insufficient to affect the free volume available to the backbone. The T_g of the backbone of the graft copolymers is the same as that of the unmodified rubber. However, from Table VII, several interesting observations indicate the lowering of the secondary transition temperature of the graft copolymers. It also can be seen that the area at the secondary transition temperature decreases at a high grafting efficiency, reflecting the extent of the mobility of the number of chain segments at that temperature. The secondary transitions are seen to be related to the grafting side chains, that is, the secondary transition peak decreased in intensity and area with an increasing grafting efficiency. The difference in values of the second transition temperature for graft copolymers is due to the amount of the side chains attached to NR.

CONCLUSIONS

For graft copolymerization of ST and MMA onto NR latex using a redox initiator system, a 2_{IV}^{6-2} experimental design was found to be a very useful tool to study the influence of the process conditions on the grafting efficiency. The following two independent variables were considered to have a significant effect on the grafting efficiency: the amount of the chain-transfer agent and the reaction temperature. The addition of the chain-transfer agent significantly affected the grafting efficiency by acting as radical scavengers. The increase in the grafting efficiency with an increasing temperature resulted from the rate of thermal decomposition of the initiator. The grafting efficiency de-

TABLE VII
Transition Temperatures of Graft Copolymers

Experiment	GE (%)	Transition temperature (°C)		
		T_g (B peak)	Second transition temperature (A peak)	Second transition temperature (C peak)
NR	—	-65.1	-88.0	73.4
GNR02	70.5	-65.4	-113.7	79.5
GNR03	62.7	-65.9	-102.0	76.3
GNR06	44.7	-65.3	-104.7	78.3
GNR07	64.0	-65.4	-112.9	78.4
GNR08	85.4	-66.6	-113.3	73.8
GNR09	43.6	-65.1	-113.0	76.6
GNR11	58.1	-65.4	-112.1	72.2
GNR12	54.5	-65.6	-102.1	73.1
GNR13	56.9	-65.2	-105.6	74.1
GNR15	45.3	-64.9	-106.0	74.2
GNR16	51.9	-65.7	-108.5	73.3

creased with an increasing monomer-to-rubber ratio. This suggests that the grafting reactions occur mainly on the surface of the seed latex particles. The grafting efficiency slightly increased with an increasing ST-to-MMA ratio over the range investigated. In addition, the graft efficiency decreased with an increasing initiator concentration. The amount of the emulsifier did not appear to influence the grafting, but served to enhance the particle stability. Characterization of the graft copolymers by $^1\text{H-NMR}$ and DSC provided the evidence for the grafting on the NR backbone.

Financial support of this research by the National Science and Technology Development Agency (NSTDA), Thailand, is gratefully acknowledged by the authors.

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