

# Factorial Experimental Design for Grafting of Vinyl Monomers onto Natural Rubber Latex

W. Arayaprane, <sup>1</sup> G. L. Rempel <sup>2</sup>

<sup>1</sup>Department of Chemical Engineering, Rangsit University, Phatum Thani 12000, Thailand

<sup>2</sup>Department of Chemical Engineering, University of Waterloo, Ontario N2L 3G1, Canada

Received 17 July 2003; accepted 30 December 2003

DOI 10.1002/app.20450

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Graft copolymerization of styrene (St) and methyl methacrylate (MMA) in the presence of natural rubber latex using cumene hydroperoxide/tetraethylenepentamine redox initiator system was prepared at various process variables. The synthesized graft copolymers were purified and then characterized by Fourier transformed infrared spectroscopy analysis. A full 2<sup>4</sup> factorial experimental design was applied to study the effect of various process variables on grafting efficiency. The following four independent variables considered to be mainly affecting the grafting efficiency were reaction temperature, rubber-to-monomer

ratio, St-to-MMA ratio, and initiator amount used in the secondary polymerization. It was shown in this study that the reaction temperature significantly influenced the grafting efficiency, increasing as the temperature was increased. The amount of grafting increased with increasing rubber-to-monomer ratio and St-to-MMA ratio, whereas the amount of grafting decreased with increasing amount of initiator. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 455–463, 2004

**Key words:** factorial experimental design; process variables; grafting efficiency; rubber; latices; graft copolymers

## INTRODUCTION

Graft copolymerization has attracted much attention and is applicable to a new class of specialty polymers with an expanded useful range. Graft copolymers are produced when vinyl monomers are polymerized in the presence of preformed polymer containing double bonds to give chemical bonding to that polymer. The graft copolymerization of vinyl monomer such as styrene and acrylates onto rubber [such as polybutadiene,<sup>1–3</sup> poly(butyl acrylate),<sup>4–5</sup> styrene–butadiene rubber,<sup>6</sup> natural rubber,<sup>7–11</sup> etc.] has been studied extensively. Natural rubber (NR), an unsaturated elastomer having the existence of double bonds in its chains, can be readily grafted with a variety of monomers. An extension of the properties of natural rubber would be possible if one could graft a second polymer within a NR latex particle, using the well-established technique of seeded emulsion polymerization. The graft copolymer of vinyl monomers such as styrene (St) and methyl methacrylate (MMA) onto NR, comprising 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.<sup>12–14</sup>

During the graft copolymerization, the radical formation for initiation reaction can occur either on the natural rubber backbone or on the monomer to be grafted. The radical formation on the monomer results in homopolymerization. Therefore, initiators capable of creating radicals on the NR backbone are preferred. Depending on the initiator systems, the radicals can be created by benzoyl peroxide,<sup>15–16</sup> redox systems,<sup>6–11,17</sup> or photochemical agencies.<sup>18–20</sup> The redox initiation system, consisting of organic hydroperoxide and tetraethylenepentamine (TEPA), offers many advantages because it operates very efficiently at the high pH values normally encountered in NR latex. It is not sensitive to oxygen and works well with the ammonia present.<sup>7,10</sup>

Many authors have noted the influence of various process variables used in seeded emulsion polymerization on grafting reactions, mainly focusing on the grafting of vinyl monomer onto rubber. Cameron and Qureshi<sup>21</sup> studied the grafting reaction of St onto polyisoprene in benzene solution at 60°C. They found that the graft copolymer amount was independent of the initiator (benzoyl peroxide) concentration. Enyiegbulam and Aloka<sup>22</sup> investigated the grafting of MMA onto styrene butadiene rubber (SBR) in methyl ethyl ketone (MEK)/toluene solution initiated by benzoyl peroxide. Grafting efficiency decreased with an increase in the monomer concentration. However, the grafting efficiency was weakly affected by the concentration of benzoyl peroxide initiator. Sundberg et al.<sup>2</sup> investigated the graft polymerization of St onto poly-

Correspondence to: G. L. Rempel.

Contract grant sponsor: Department of Chemical Engineering, Rangsit University.

butadiene latex and found that the grafting efficiency depends on various factors (i.e., monomer/polymer ratio, the amount of initiator, degree of conversion, and concentration of chain transfer agent). Gasperowicz et al.<sup>5</sup> investigated the grafting of St onto poly(butyl acrylate) in emulsion form. The process parameters affecting the grafting efficiency of polystyrene were time, temperature, the concentration of initiator and emulsifier, and the monomer/polymer ratio. The grafting efficiency decreased with increasing reaction time, the monomer/polymer ratio, and emulsifier and initiator concentration. The grafting efficiency was found weakly affected by the temperature of polymerization.

The effects of process variables on the grafting is very complicated to investigate, in view of the great number of variables involved, some of which are type and concentration of initiator, monomer concentration, rubber latex concentration, reaction time, and reaction temperature. In the present article, the graft copolymerization using NR as the core and St and MMA as the shell monomers in the seeded emulsion process was carried out through a factorial experimental design, in which four variables with high (+) and low (-) levels were varied. The effects of temperature, rubber-to-monomer ratio, St-to-MMA ratio, and initiator amount used in the secondary polymerization on the grafting efficiency were investigated.

## EXPERIMENTAL

### Materials

NR latex used was 60% dry rubber content (DRC), commercial high-ammonia NR latex (from Excel Rubber Public Co., Songla, Thailand). Reagent grade St (Aldrich, Milwaukee, WI; purity ~ 99%) and MMA (Aldrich, purity ~ 99%) monomer were destabilized in the conventional way by washing with a 10% aqueous solution of NaOH and then with deionized water until neutral. It was then stored in a refrigerator until required. The emulsifier sodium dodecyl sulfate (SDS; Aldrich, purity ~ 98%), the stabilizer isopropanol, the buffer potassium hydroxide (KOH; Aldrich), the initiators, redox initiator system, cumene hydroperoxide (C<sub>9</sub>H<sub>12</sub>O<sub>2</sub>, CHPO; Aldrich, purity ~ 80%), and the activator agent TEPA [HN(CH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>; Aldrich], were used as received. Deionized water was used throughout the work.

### Preparation of grafted natural rubber

The graft copolymerization reaction was carried out in a 1000-mL four-necked, round-bottomed flask equipped with stirrer, thermometer, reflux condenser, and gas inlet tube. NR latex weighing 100 g was charged into the flask, containing 300 g of deionized

water, 1.8 g of isopropanol as a stabilizer, and 0.9 g of SDS as an emulsifier. Then, the mixture was deoxygenated by bubbling nitrogen for at least 30 min through the diluted, but still stable, latex. If necessary, aqueous solution of KOH was added to maintain the pH of the latex above 10. The nitrogen flow rate was then reduced to a low level before the addition of the monomer mixture. The monomer mixture was fed to the reactor and the TEPA as an activator agent was then added. The NR seed latex was swollen with the monomer mixture for 1 h at reaction temperature before adding the initiator. The redox initiation system, consisting of cumene hydroperoxide and TEPA in a ratio of 1 : 1, was used. The polymerization reaction was performed at a stirring speed of 300 rpm and at the desired low temperature of 50°C and the desired high temperature of 70°C for 8 h. The polymerization was stopped by adding phenol. The posttreatment included the coagulation of polymer latex and the washing by deionized water. The gross polymers were recovered and dried to constant mass in a vacuum oven at 40°C to a constant weight.

Ungrafted NR was washed out in a Soxhlet extractor by using 60–80°C boiling point petroleum ether for 24 h. The extracted sample as such for the second extraction with a MEK/acetone (50 : 50 v/v) mixture for 24 h after extracting with petroleum ether was used for extracting free copolymers. The grafting efficiency was determined gravimetrically by using the relationship:

Grafting efficiency (GE, %)

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

The presence of functional groups of the graft copolymers was verified by a Mattson 1000 FTIR spectrometer. The sample (1 mg) was dispersed in dry KBr (250 mg), and the mixture was ground to fine particles in a mortar and then pressed to form moisture-free disks.

The morphology was examined by 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 OsO<sub>4</sub> solution was added and allowed to stain the rubber in the graft copolymers overnight.

Process variables were varied according for a full 2<sup>4</sup> factorial design used to study the effects of reaction temperature (TEMP), rubber-to-monomers ratio (R/M), St-to-MMA ratio (St/MMA), and initiator amount (INI) on grafting efficiency (GE). The coding of the experimental levels is shown in Table I. The low level is coded as -1, whereas the high level of each independent variable is coded as +1. The experiments (a total of 16 runs) are listed in Table II by using the

TABLE I  
Low and High Levels of Factors for Factorial Designed Experiments

Factors	Name	Amount (Low = -1)	Amount (High = +1)
TEMP	Reaction temperature	50°C	70°C
R/M	Rubber/monomer ratio	1.0	1.5
ST/MMA	Styrene/methyl methacrylate	0.33	1.0
INI	Cumene hydroperoxide	1 phr <sup>a</sup>	2 phr

<sup>a</sup> Parts per hundred parts rubber by mass.

coding scheme shown in Table I. The grafting efficiency was analyzed by using analysis of variance (ANOVA). The *F* test was used to evaluate if a variable has a significant effect ( $F > 6.61$ ).

## RESULTS AND DISCUSSION

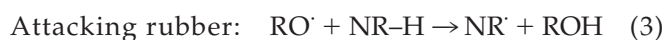
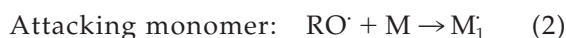
### Mechanism of grafting

In the preparation of the grafted NR particles, initiation of polymerization is due to free radicals produced by the interaction of cumene hydroperoxide dissolved in the monomer swollen rubber particles and TEPA in the aqueous phase of the latex. With such a hydrophobic-hydrophilic catalyst combination, it is probable that the cumene hydroperoxides decompose to yield alkoxy radicals (RO<sup>•</sup>) formed at the particle-water interface, which might interact with the monomer or the rubber molecule producing a macroradical that initiates grafting. The alkoxy radicals can not only add to double bonds or abstract  $\alpha$ -methylene hydrogen atoms to produce polyisoprenyl radicals, which initiate monomers to form the graft copolymers, but also to initiate monomers to form polymeric radicals, which combine with polyisoprenyl radicals to terminate or

transfer to NR to form graft copolymers. Some of the free polymer radicals still terminate to form free copolymers.

The following reaction scheme is proposed for the graft copolymerization of vinyl monomers onto NR by the free-radical method:

Initiation



Propagation

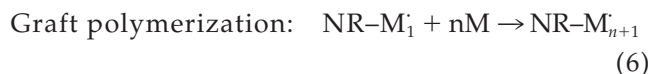
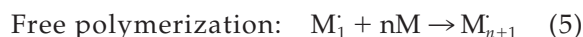


TABLE II  
2<sup>4</sup> Design Levels and Grafting Efficiency Obtained in the Present Work

Run	Design factor				Grafting efficiency (%)
	[TEMP]	[R/M]	[ST/MMA]	[INI]	
GNR01	-1	-1	-1	-1	31.81
GNR02	+1	-1	-1	-1	42.29
GNR03	-1	+1	-1	-1	57.75
GNR04	+1	+1	-1	-1	61.53
GNR05	-1	-1	+1	-1	59.67
GNR06	+1	-1	+1	-1	66.22
GNR07	-1	+1	+1	-1	59.15
GNR08	+1	+1	+1	-1	72.19
GNR09	-1	-1	-1	+1	34.85
GNR 10	+1	-1	-1	+1	54.03
GNR 11	-1	+1	-1	+1	37.89
GNR 12	+1	+1	-1	+1	55.16
GNR 13	-1	-1	+1	+1	28.69
GNR 14	+1	-1	+1	+1	51.21
GNR 15	-1	+1	+1	+1	30.58
GNR 16	+1	+1	+1	+1	75.79

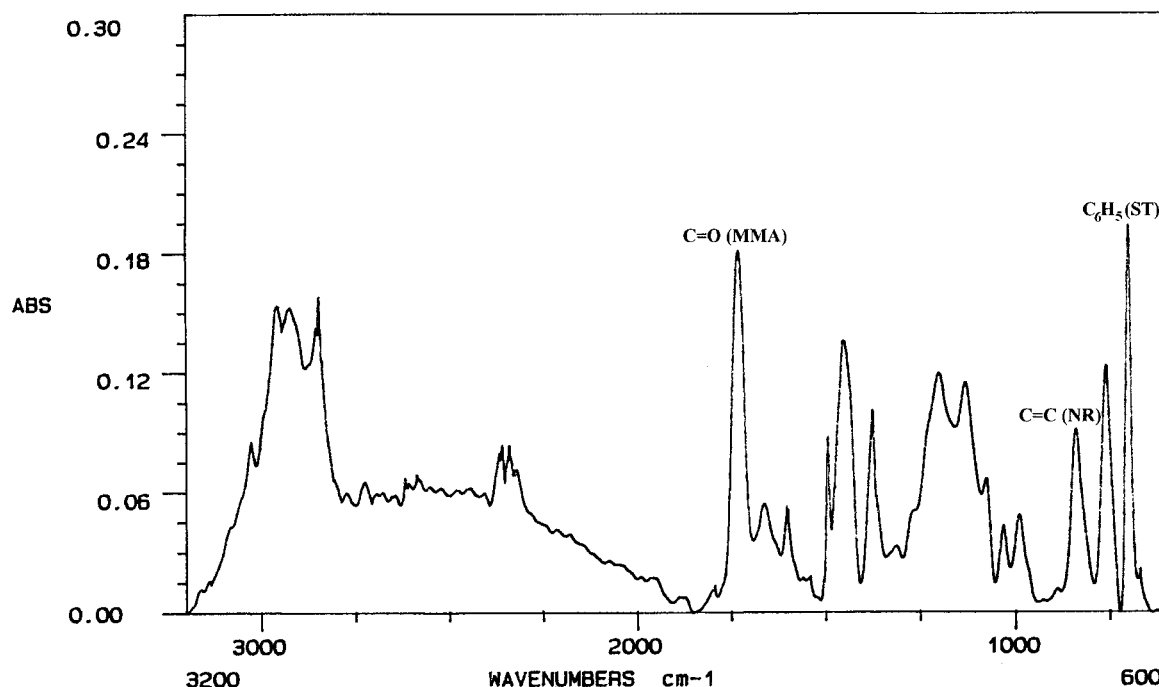
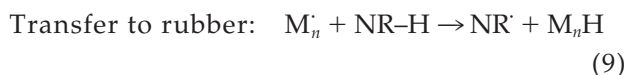
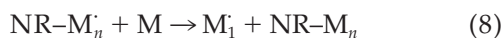


Figure 1 FTIR spectrum of graft copolymers.

Chain-transfer to macromolecules



Termination



where RO is the alkoxy radical; M is the vinyl monomer;  $M_n'$  is polymeric radical; NR-H is natural rubber; H is the  $\alpha$ -methylene hydrogen atom; NR is the polyisoprenyl radical; and NR- $M_n'$  is the growing graft copolymer radical chain.

To determine the presence of the graft copolymers, the products were extracted by petroleum ether and a mixture of acetone and MEK, respectively. After the solvent extraction, the graft copolymers were analyzed by FTIR. Figure 1 shows the FTIR spectrum for

the residue (the graft copolymers). There are several characteristic peaks attributed to  $R_2C=CHR$  of isoprene, C=O stretching of ester groups of MMA, and the monosubstituted benzene ring of St at wavenumbers of 837, 1732, and 698  $\text{cm}^{-1}$ , respectively. This is evidence that the graft copolymers were formed during the grafting of St and MMA onto NR latex.

### Kinetics

For graft copolymerization of St and MMA on NR, monomer conversion as a function of reaction time was investigated. Conversion is defined as the fraction of monomer at time  $t$ , which has been converted to polymer. For all 16 experiments, the shape of conversion versus time curves was identical and the rate of polymerization was similar. As shown in Figure 2(a, b), the percentage of conversion of St and MMA monomers increased greatly up to 120 min, after which it was constant.

The grafting efficiency of St and MMA on NR as a function of conversion was observed. Figure 3(a, b) shows the plots of grafting efficiency versus conversion, which had a similar trend for all 16 experiments. The grafting efficiency first increased gradually up to 70% conversion and then steeply increased. This suggests that the conversion at the beginning increased rapidly because most of the St and MMA monomers were polymerized in the aqueous phase to form new polymeric radicals until the monomers were almost occupied and reached

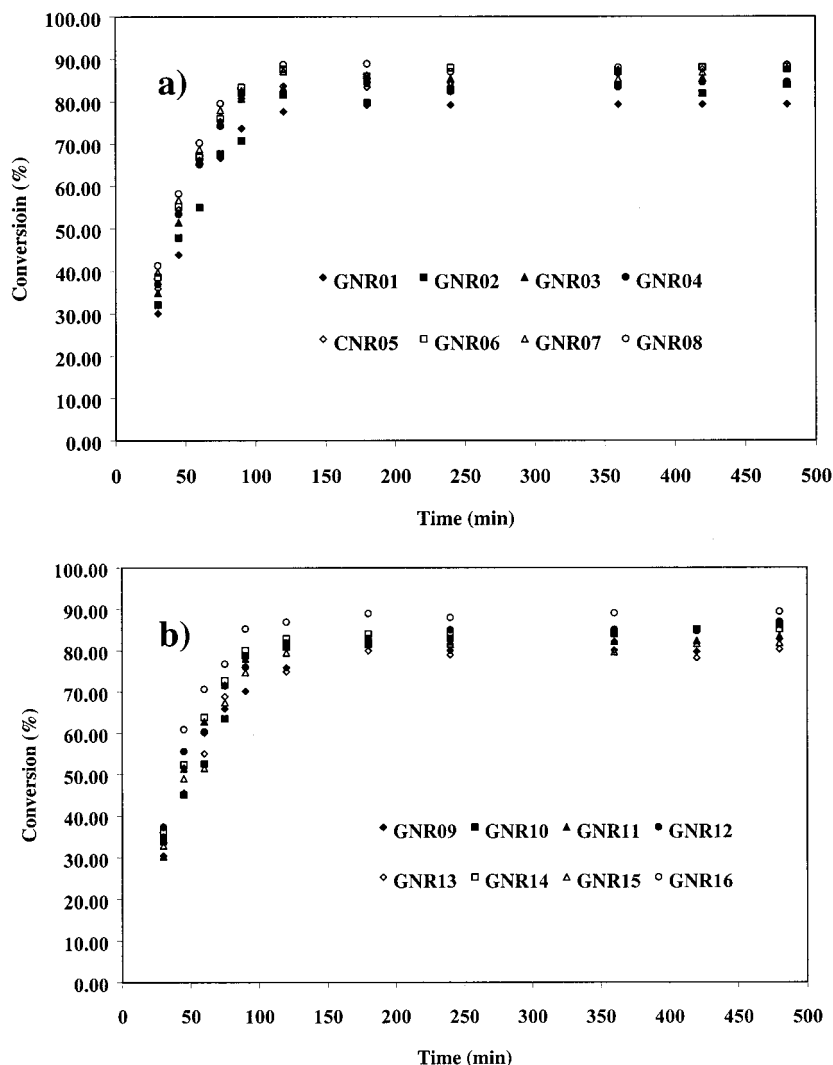


Figure 2 Conversion versus time profiles: (a) low-level initiator amount and (b) high-level initiator amount.

maximum conversion at the particular time. Then, the new growing polymer chains were chemically bonded to the surface of the NR particles, thus forming graft copolymers, leading to a sudden increase in GE at high conversion. Similar behavior of graft copolymerization of St and MMA onto polybutadiene was observed by Aerdts et al.<sup>3</sup>

### The influence of process variables

Because a factorial design was used to organize the experiments, analysis of the results is facilitated with ANOVA. The values obtained for grafting efficiency for the 16 experiments of the  $2^4$  factorial design is shown in column 5 of Table II. From these results, the highest grafting efficiency was (75.79%), obtained in the experiment GNR16. To ensure that the assumptions of normality and constant variance were met, the response variable, grafting efficiency, was calculated. The importance of these effects may be confirmed

with the ANOVA. The total sum of squares ( $SS_{\text{total}}$ ) is calculated as

$$SS_{\text{total}} = \sum_{i=1}^n y_i^2 - (\sum_{i=1}^n y_i)/n$$

where  $y_i$  is the response, and  $n$  is the number of experiments. The sum of squares (SS) for any main and interaction effect is  $SS_{\text{effect}} = 2^{k-2}(\text{effect})^2$ , where  $k$  is known as the number of effects. The error sum of square ( $SS_{\text{error}}$ ) is a result of the differences between the total sum of square and the sum over all the  $SS_{\text{main effect}}$  and  $SS_{\text{interaction effect}}$ . The degrees of freedom for the main effects are the total number of levels less one. The main effect has  $(2 - 1)$  degrees of freedom, whereas the interaction effect has  $(2 - 1)(2 - 1)$  degrees of freedom. Therefore, there are 16 (the total number of experiments) - 10 (the sum over all the

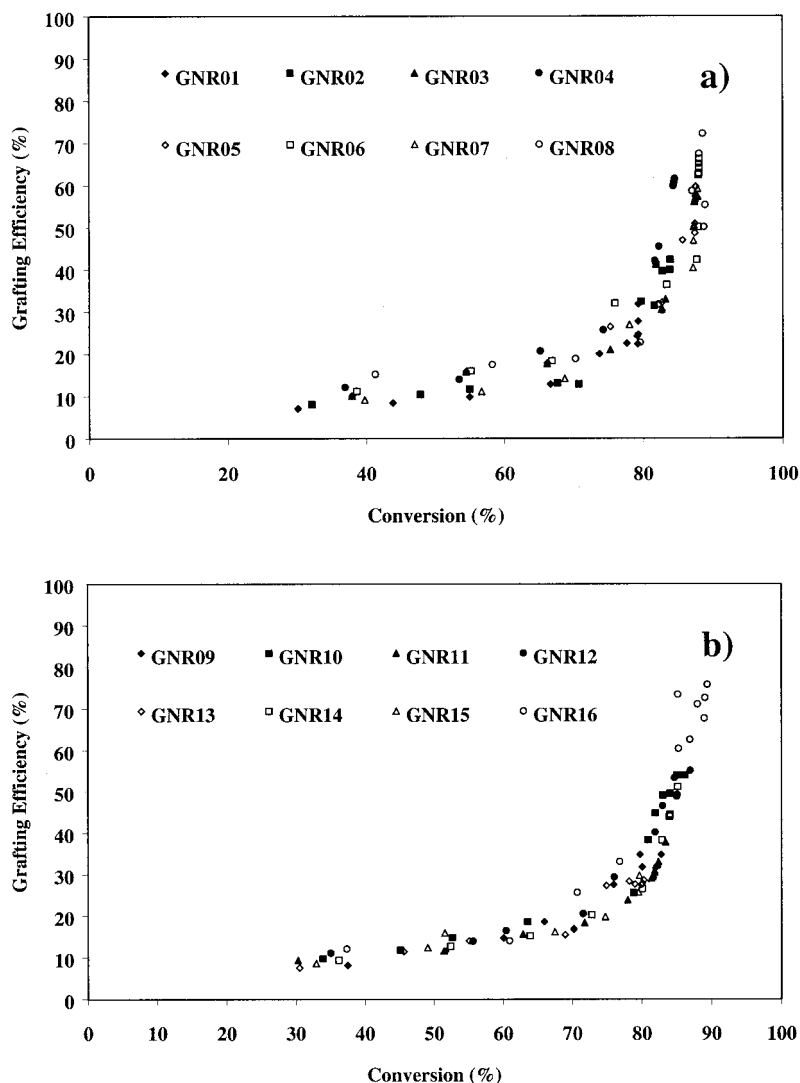


Figure 3 Grafting efficiency as a function of conversion: (a) low-level initiator amount and (b) high-level initiator amount.

number of main and interaction effects)  $- 1 = 5$  degrees of freedom for error. If we divide each of the sum of squares by the corresponding number of degrees of freedom, we obtain the mean squares (MS) for the effect, the interaction, and error. According to  $F$  statistics for testing the significance of main and interaction effects, the  $F$  test is calculated by dividing the mean squares for each effect by the mean squares for error. The 95% confidence interval ( $F_{1,5} = 6.61$ ) provides a test to decide whether the variance due to an observed response is significant or not. If the  $F$  test is smaller than 6.61, the variance due to the observed response is not significant. If the observed  $F$  test is larger than 6.61, the observed response is probably significant. Results for main effects and two-factor interactions are identified in Table III, showing the  $F$  test of effects of the process variables on grafting efficiency. 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 (-). In this design, one significant effect with respect to grafting efficiency was TEMP. All interactions could be eliminated because of no significance (seen in Table III).

To facilitate understanding of such behavior, the effect of each independent variable will be discussed separately. Table IV shows the mean grafting efficiency of grafting of St and MMA onto NR as a response to the four variables investigated.

The reaction temperature was the independent variable that had a positive effect on grafting efficiency (Table III). The mean grafting efficiency increased from 42.55 to 59.80 when the temperature was increased from 50 to 70°C, respectively (Table IV). According to the Arrhenius relation, the grafting efficiency increased with increasing temperature; this was due to the rate of decomposition of the initiator, which depended on the temperature. On the other hand,

**TABLE III**  
**Results for Main Effects and Two-Factor Interactions for Observed Response and the Analysis of Variance**

Effect name	Effect	SS	df	MS	F <sup>a</sup>	Significance
Mean	51.18	—	—	—	—	—
TEMP	17.25	1190.77	1.00	1190.77	14.62	Yes
R/M	10.16	412.80	1.00	412.80	5.06	No
ST/MMA	8.52	290.62	1.00	290.62	3.56	No
INI	-10.30	424.46	1.00	424.46	5.21	No
TEMP by R/M	2.57	26.44	1.00	26.44	0.32	No
TEMP by ST/MMA	4.58	83.77	1.00	83.77	1.03	No
TEMP by INI	8.79	309.14	1.00	309.14	3.79	No
R/M by ST/MMA	-2.18	18.99	1.00	18.99	0.23	No
R/M by INI	-2.50	24.98	1.00	24.98	0.31	No
ST/MMA by INI	-7.44	221.34	1.00	221.34	2.72	No
Error	—	407.50	5.00	81.50	—	—
Total SS	—	3410.81	15.00	—	—	—

$R^2 = 0.88053$ , Reaction time = 8 h.

<sup>a</sup>  $F_{1,5} = 6.61$  with  $\alpha = 0.05$ . If  $F < 6.61$ , then the variable is not significant.

higher temperature may reduce the viscosity of the system and increase the mobility of the molecular chains to facilitate the grafting reaction. Furthermore, Sundberg et al.<sup>2</sup> states that the major influence of temperature was that the actual concentration of monomer in the particle can be very low at higher temperatures.

The mean grafting efficiency increased from 42.10 to 56.26 when the rubber-to-monomer ratio was increased from 1 to 1.5, respectively (Table IV). The grafting efficiency increased with increasing R/M ratio. This means that the graft reaction occurred mainly on the surface of the seed latex particles. Therefore, with increasing NR content in the system, the contact area between monomer and NR increased. As a result, the grafting efficiency increased with increasing R/M ratio. A similar observation was made by Merkel et al.<sup>1</sup> in the case of grafting of MMA onto polybutadiene.

The positive effect of St/MMA ratio on grafting efficiency was shown in Table IV. The mean grafting

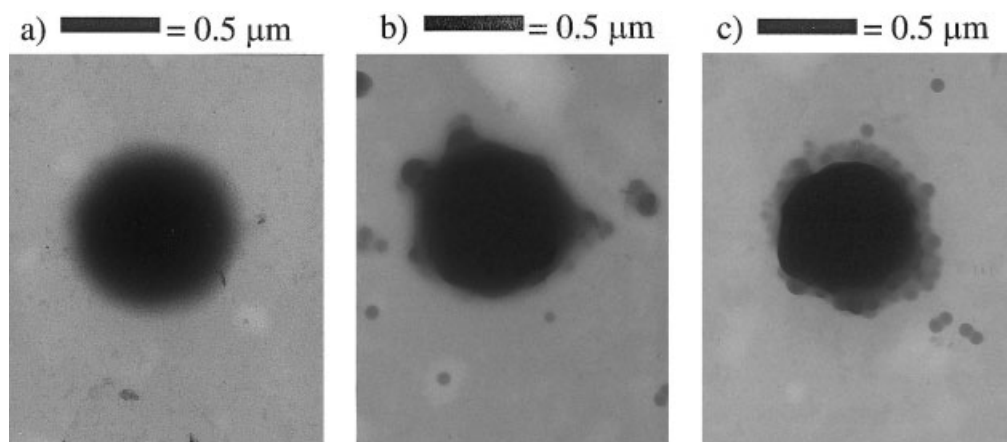
efficiency increased from 46.91 to 55.44 when the St/MMA ratio was increased from 0.33 to 1, respectively (Table IV). This indicates that when the amount of St in the monomer mixture was increased, a more favorable condition resulted to produce graft copolymers rather than free copolymers. Thus, St was grafted and left a substantial amount of MMA in the water and polymer phase. Huang and Sundberg<sup>23-26</sup> have suggested that the amount of material, which may be grafted, depended upon the identity of the monomer as well as initiator. It can be concluded that higher grafting efficiency was achieved at a high level of St/MMA ratio.

The effect of the initiator amount on grafting in Table IV showed that the mean grafting efficiency decreased from 56.33 to 46.02 when the amount of initiator was increased from 1.0 to 2.0 phr, respectively. The increase in the amount of initiator caused an increase in rate of radical entry. This can be explained by the fact that the radicals transfer to either rubber or monomer, producing macroradicals. As the

**TABLE IV**  
**The Effect of Process Variables on Mean Grafting Efficiency**

Statistical experimental design	Mean	-95% Confidence limit	95% Confidence limit
TEMP			
-1	42.55	34.34	50.75
+1	59.80	51.60	68.01
R/M			
-1	42.10	37.89	54.30
+1	56.26	48.05	64.46
ST/MMA			
-1	46.91	38.71	55.12
+1	55.44	47.23	63.64
INI			
-1	56.33	48.12	64.53
+1	46.02	37.82	54.23

Note. SE for mean = 3.19.



**Figure 4** Transmission electron micrographs of polymers: (a) natural rubber; (b) 30.58% GE; (c) 72.19% GE ( $\times 30,000$ ).

initiator concentration was increased, it was probable that the rate of chain transfer for the monomeric radicals to the NR backbone was less than the rate of termination of monomeric radicals, thus accounting for the reduced grafting efficiency with increased initiator amount. Therefore, more copolymers were produced than graft copolymers. To study the grafting reaction of St onto polyisoprene, Cameron and Qureshi<sup>21</sup> found that the graft copolymer amount was independent of the initiator concentration. There is confusion on the effect of initiator amount because some workers claim that grafting efficiency decreased with increasing initiator amount,<sup>1,5</sup> while other claims that grafting efficiency increased with increasing initiator amount.<sup>6</sup>

In a previous article,<sup>27</sup> it was shown that an increase of initiator amount caused a slight increment in the grafting efficiency, in contrast to current work, which showed that the grafting efficiency decreased with increasing the amount of initiator. For this work, the monomer used was without purification by vacuum distillation. The reason for different effects on grafting efficiency between this work and the previous one seemed to be confusing, but the fact was that high-purity monomer was used to avoid interference with the redox properties of the initiator system. It is possible that the rate of decomposition of hydroperoxide was affected by some of the impurities contained in monomers. It can be explained that when the low-purity monomer was used, the grafting efficiency obtained was lower than the experimental data of the previous work.<sup>27</sup> However, the cost of monomer purification must be considered. The lower cost, in this case, would likely outweigh the monomer purification.

#### Effect of grafting efficiency on particle morphology

The grafted NR particles consisting of a polyisoprene core and compatibilizing St and MMA shell were prepared by emulsion polymerization. The particle mor-

phology is shown in Figure 4. The darker areas represent the NR core regions, while the lighter areas are copolymer film as shell. The surface of the NR latex particle is smooth [Fig. 4(a)]. The morphology of the core-shell formation of grafted NR latex is shown in Figure 4(b, c). The presence of nodules on the surface of the graft copolymers may be due to the growing macroradical chains, which are grafted onto the surface of the NR particle and continue to propagate to form the shell layer. On the other hand, most of the MMA and St polymerized in the aqueous phase to form secondary particles, which then flocculated with the NR seed particles and overcoated the periphery of the rubbery core surface with a glassy shell copolymers. At the low-grafting efficiency [Fig. 4(b)], the NR seed particle is a compact packing of copolymer particles. When the grafting efficiency increased, the copolymer particles enhanced the encapsulation of the core and then fused to give a shell layer [Fig. 4(c)]. Figure 4 clearly shows that increasing the grafting efficiency gives thicker copolymer shells around the NR cores. The NR seed particles have the complete closed shell at a high level of grafting efficiency.

#### CONCLUSION

A 2<sup>4</sup> experimental design was used to study the effect of the process variables on grafting efficiency for graft polymerizing St and MMA onto NR latex by using redox initiator system. The conversion increased rapidly at the beginning to reach a plateau level. The grafting efficiency increased gradually and then steeply increased at high conversion. A wide range of grafting efficiency is achievable by varying the reaction conditions. The experimental design was shown to be adequate in conducting the graft copolymerization, as it allowed analysis of the results for the two levels of variables proposed. Reaction temperature was considered to have a significant effect on the



grafting efficiency. The increase in grafting efficiency with increasing temperature resulted in the higher chain mobility afforded by lower viscosity of the reaction medium at a high temperature level. The grafting efficiency increased with increasing rubber-to-monomer ratio. This suggests that the periphery of the latex particle was the site of the grafting reaction. The grafting efficiency slightly increased with increasing St-to-MMA ratio over the range investigated. In addition, the grafting efficiency decreased with increasing initiator concentration. Characterization of the graft copolymers by FTIR and TEM indicates the occurrence of grafting on the rubber backbone in the core-shell latex particles. Furthermore, it was confirmed that the graft copolymerization is a surface-controlled process.

Financial support for the research from the Department of Chemical Engineering, Rangsit University is gratefully acknowledged.

## References

- Merkel, M. P.; Dimonie, V. L.; El-Aasser, M. S.; Vanderhoff, J. W. *J Polym Sci, Part A: Polym Chem* 1987, 25, 1755.
- Sundberg, D. C.; Arndt, J.; Tang, M.-Y. *J Dispers Sci Technol* 1984, 5, 433.
- Aerdts, A. M.; de Krey, J. E. D.; Kurja, J.; German, A. L. *Polymer* 1994, 35, 1636.
- Min, T. I.; Klein, A.; El-Aasser, M. S.; Vanderhoff, J. W. *J Polym Sci, Polym Chem Ed* 1983, 21, 2845.
- Gasparowicz, A.; Kolendowicz, M.; Skowronski, T. *Polymer* 1982, 23, 839.
- Zhao, J.; Yuan, H.; Pan, Z. *J Appl Polym Sci* 1994, 53, 1447.
- Hourston, D. J.; Romaine, J. *J Appl Polym Sci* 1990, 39, 1587.
- Fukushima, Y.; Kawahara, S.; Tanaka, Y. *J Rubber Res* 1998, 1, 154.
- Arayaprane, W.; Prasassarakich, P.; Rempel, G. L. *J Appl Polym Sci* 2002, 83, 2993.
- Schneider, M.; Pith, T.; Lambla, M. *J Appl Polym Sci* 1996, 62, 273.
- Schneider, M.; Pith, T.; Lambla, M. *Polym Adv Technol* 1995, 6, 326.
- Asaletha, R.; Groeninckx, G.; Kumaran, M. G.; Thomas, S. *J Appl Polym Sci* 1998, 69, 2673.
- Oommen, Z.; Thomas, S. *J Appl Polym Sci* 1997, 65, 1245.
- Oommen, Z.; Groeninckx, G.; Thomas, S. J.; *Polym Sci, Part B: Polym Phys* 2000, 38, 525.
- Elliott, D. J.; Watson, W. F. *Trans Inst Rubber Ind* 1959, 35, 63.
- Allen, P. W.; Merrett, F. M. *J Polym Sci* 1956, 22, 193.
- Daniels, E. S.; Dimonie, V. L.; El-Aasser, M. S.; Vanderhoff, J. W. *J Appl Polym Sci* 1990, 41, 2463.
- Cooper, W.; Vaughan, G.; Miller, S.; Fielden, M. *J Polym Sci* 1959, 34, 651.
- Cooper, W.; Vaughan, G. *J Polym Sci* 1959, 37, 241.
- Cooper, W.; Sewell, P. R.; Vaughan, G. *J Polym Sci* 1959, 41, 167.
- Cameron, G. G.; Quereshi, M. Y. *J Polym Sci, Polym Chem Ed* 1980, 18, 2143.
- Enyiegbulam, M. E.; Aloka, I. U. *J Appl Polym Sci* 1992, 44, 1841.
- Huang, N. J.; Sundberg, D. C. *J Polym Sci, Part A: Polym Chem* 1995, 33, 2533.
- Huang, N. J.; Sundberg, D. C. *J Polym Sci, Part A: Polym Chem* 1995, 33, 2551.
- Huang, N. J.; Sundberg, D. C. *J Polym Sci, Part A: Polym Chem* 1995, 33, 2571.
- Huang, N. J.; Sundberg, D. C. *J Polym Sci, Part A: Polym Chem* 1995, 33, 2587.
- Arayaprane, W.; Prasassarakich, P.; Rempel, G. L. *J Appl Polym Sci* to appear.