

# Noncatalytic Hydrogenation of Natural Rubber Latex

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**ABSTRACT:** Hydrogenation is an important method of chemical modification, which improves the physical, chemical, and thermal properties of diene-based elastomers. Natural rubber latex (NRL) could be hydrogenated to a strictly alternating ethylene-propylene copolymer using diimide generated in an *in situ* system. The diimide generated using the *in situ* technique for hydrogenation of NRL was accomplished by thermolysis of *p*-toluenesulfonyl hydrazide (TSH). A molar ratio of TSH to double bonds equal to 2 : 1 was found to be the optimum ratio to provide a high percentage of hydrogenation. 95% Degree of saturation of

NRL was achieved in *o*-xylene. Hydrogenated products are characterized by FTIR and NMR spectroscopy. The thermal stability of hydrogenated rubber was improved as shown from the results of thermogravimetric analysis. From the differential scanning calorimetry measurement, the glass transition temperature of the hydrogenated product did not appear to change. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2885–2895, 2007

**Key words:** diimide generated; modification; hydrogenation; natural rubber latex

## INTRODUCTION

Natural rubber latex (NRL) obtained from *Hevea brasiliensis* is classified as one of the most important natural resources used industrially because of its excellent elastic property. The nature of the NR hydrocarbon chain is known and accepted as a *cis*-1,4-polyisoprene structure with the chain having possibly oligopeptide and fatty acid ester at the unidentified initiating and chain end respectively.<sup>1</sup> The high resilience, tear resistance, excellent dynamic properties, and fatigue resistance are main advantages of natural rubber believed to result from proteins in the rubber structure.<sup>2</sup> Because of the unsaturation of the carbon-carbon double bond present in the isoprene backbone, natural rubber is degraded when exposed to sunlight, ozone, and oxygen. Chemical modification of NRL has been an active field of research because of the technological importance of the modified products. Hydrogenation is one of the important methods for improving and changing the properties of unsaturated diene-based elastomers toward greater stability against thermal, oxidative, and radiation-induced degradation of the diene polymer.<sup>3</sup> These properties make it available for a wide range of product applications.

Catalytic and noncatalytic hydrogenation of diene containing polymers has been widely studied.<sup>4,5</sup> Classical catalytic hydrogenation, which is the reaction of unsaturated substrates with transition-metal-activated hydrogen, is usually quite expensive.<sup>6</sup> The noncatalytic technique using a hydrogenation reagent has been extensively studied. Diimide has been generated for uses as a hydrogenation agent via oxidation of hydrazine,<sup>7</sup> decarboxylation of potassium azodicarboxylate, photochemical irradiation of 1-thia-3,4-diazolidine-2,5-dione,<sup>8</sup> and from thermolysis of arylsulfonylhydrazide.<sup>9–13</sup> Among these hydrogenation reagents, the thermal decomposition of *p*-toluenesulfonyl hydrazide (*p*-TSH) has been successful. Mango and Lenz<sup>5</sup> reviewed the use of diimide for the hydrogenation of unsaturated polymers. Hahn<sup>10</sup> improved the method for diimide hydrogenation of butadiene and isoprene polymers by the addition of tri-*n*-propyl amine to eliminate side reactions within the butadiene polymer. Phinyocheep et al.<sup>14</sup> studied diimide hydrogenation of a isoprene-styrene diblock copolymer. A solution of 2% (w/v) of polymer in *o*-xylene, 1 : 4 mol ratio between the isoprene double bond and TSH, temperature 135°C, pressure 1 atm under nitrogen gas reaches 98.4% hydrogenation in 4 h. Sammrarn et al.<sup>15</sup> reported 80–85% hydrogenation for a 1% solution (w/v) of polymer in *o*-xylene solvent (100 mL); 1 mol of C=C in rubber per 2 mol of TSH was added in the reaction systems at a temperature of 135°C and a pressure of 1 atm in 8 h.

The objectives of this work were to study the possibility of hydrogenation of NRL by using diimide as an *in situ* reagent, with various rubber concentrations

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([C=C]), diimide concentration, solvent type, type of diimide reagent, and temperature. The reagent used for this study was *p*-toluenesulfonyl hydrazide, which is considered in term of diimide concentration ([*p*-TSH]). Conversion profiles and the effect of impurities on the hydrogenation of NRL are also discussed.

## EXPERIMENTAL

### Material

High ammonia latex rubber was supplied from Thai Latex Rubber (Bangkok, Thailand). Nitrogen gas was obtained from Praxair (Kitchener, Canada). Reagent grade of *o*-xylene was obtained from BDH (Toronto, Canada). Benzene, cyclohexane, hexane, and toluene were purchased from EM Science (Gibsontown, NJ). Tetrahydrofuran (THF) and monochlorobenzene (MCB) were received from Fisher Scientific (Fairlawn, NJ), and all solvents were used as received. *p*-Toluenesulfonyl hydrazide (*p*-TSH), 2,4,6-triisopropylbenzenesulfonyl hydrazide (TPSH), and 2,4,6-trimethylbenzenesulfonyl hydrazide (MSH) were purchased from Aldrich (Steelver, Germany). Ammonium hy-

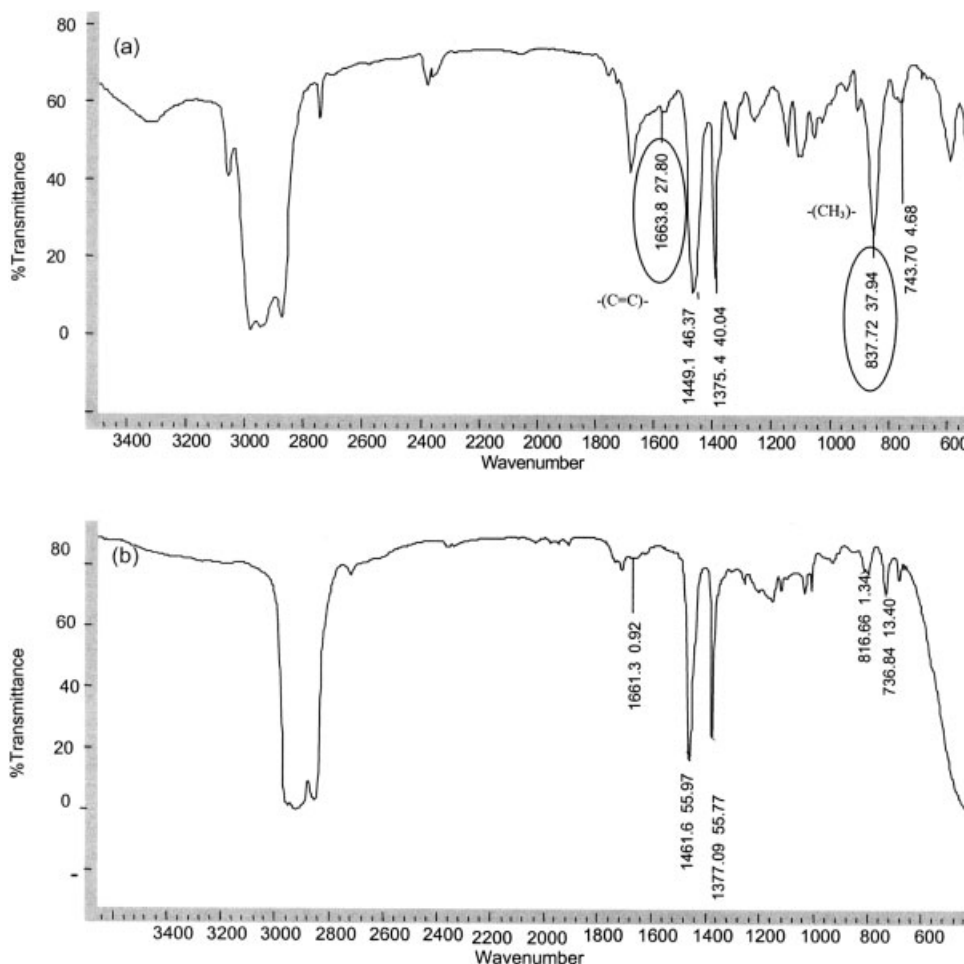
droxide and hydroxylamine were purchased from Fischer Scientific (Fair Lawn, NJ). Hexadecylacrylamide was prepared from the reaction of acryloyl chloride, and hexadecylamine was obtained from Aldrich Chemical Company (Milwaukee, WI). High molecular weight *cis*-1,4-polyisoprene with 97% *cis* configuration (Natsyn) was obtained from Bayer (Sania, Canada).

### Hydrogenation procedure

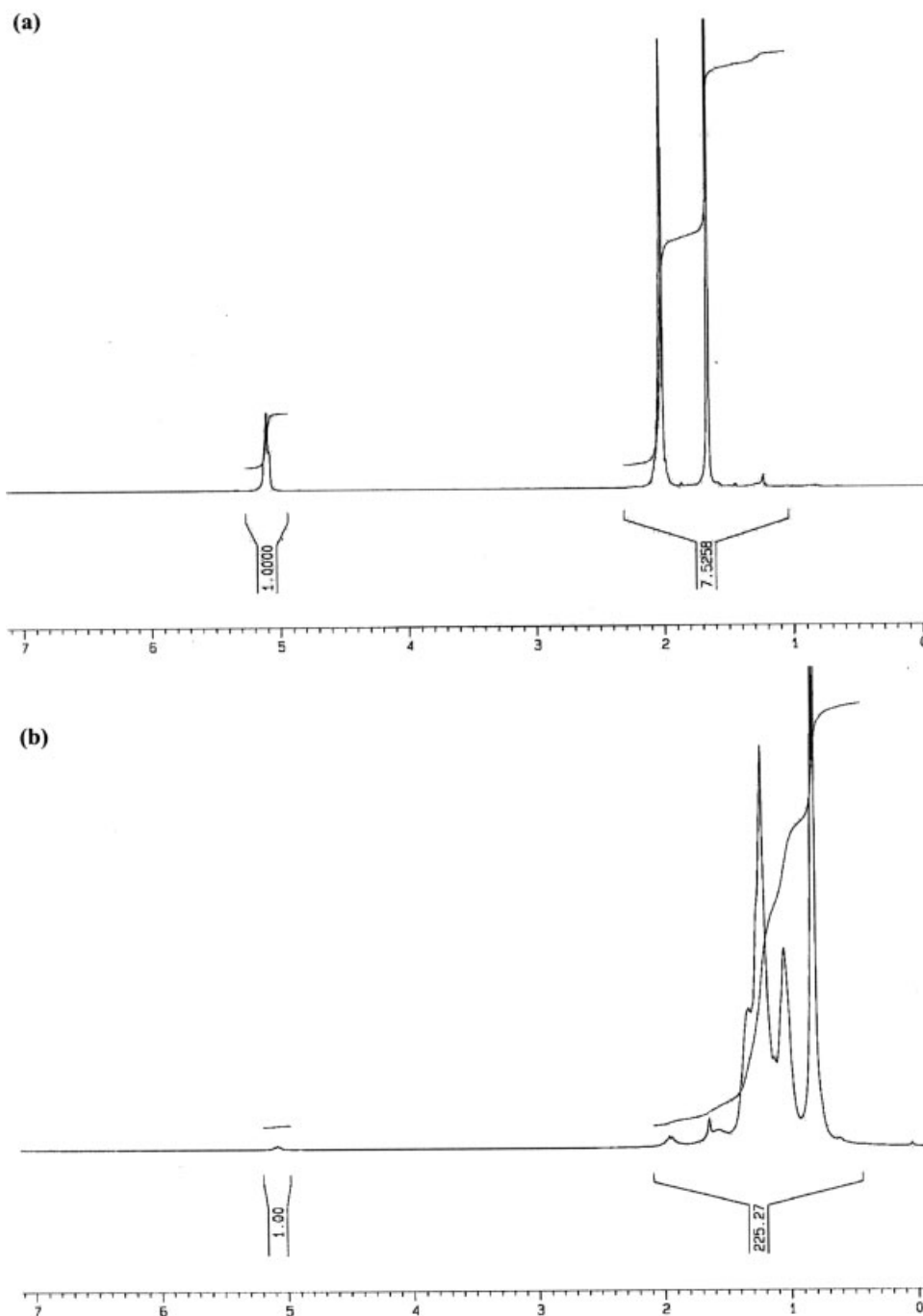
Hydrogenation of the NRL was carried out under nitrogen gas in a 250-mL glass reactor. The solution of NRL in an organic solvent at different concentrations was used with varying amounts of TSH. The solution was refluxed at 135°C for 3 h under nitrogen gas. The product was filtered with filter paper to remove residual TSH, followed by precipitation of the rubber in ethanol, which was then dried under vacuum.

### Characterization

The structure of hydrogenated natural rubber latex (HNRL) was confirmed by FTIR and <sup>1</sup>H-NMR spectroscopy. The samples were prepared by casting a film



**Figure 1** FTIR spectra of (a) NRL and (b) HNRL.



**Figure 2**  $^1\text{H-NMR}$  spectra of (a) NRL and (b) HNRL.

on NaCl plates for a FTIR scan obtained on a BIO-RAD Merlin FTS 3000X (Cambridge, MA) spectrometer.  $^1\text{H-NMR}$  spectra of samples dissolved in  $\text{CDCl}_3$  were obtained using a Bruker 300 MHz spectrometer.

Molecular weight was obtained using a GPC system, which consisted of a Waters 1515 Isocratic HPLC pump and Waters 2414 refractive index detector (RID). Breeze software was used for data collection and processing. A styragel HR 3,4,6 THF column was used for separation. THF at a flow rate of 1 mL/min was used as a mobile phase. The samples of 0.1% w/v

rubber solutions were filtered through a 0.45  $\mu\text{m}$  pore size filter, and then 200  $\mu\text{L}$  of the filtrated samples was injected into the mobile phase. The measurements were carried out at 40°C.

Differential scanning calorimetric (DSC) measurement of the samples was carried out on a TA Instrument DSC Model 2920. The instrument signal is derived from the temperature difference between the sample and the reference. The rubber samples were cooled to 100°C with liquid nitrogen and then heated at a constant rate of 20°C/min to 25°C. The glass tran-

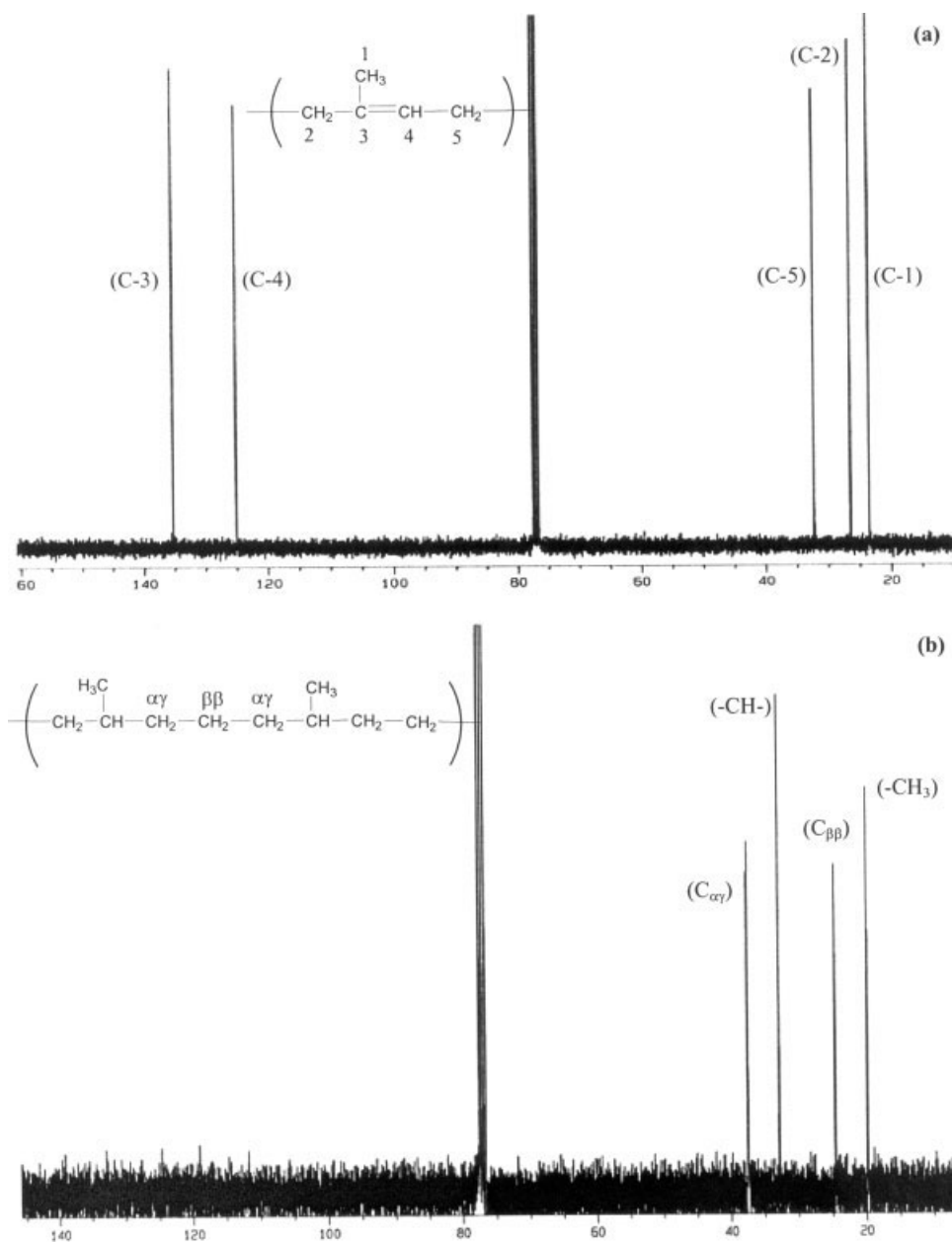


Figure 3  $^{13}\text{C}$ -NMR spectra of (a) NRL and (b) HNRL.

sition temperature ( $T_g$ ) was calculated from the midpoint of the baseline shift of the DSC thermogram.

Thermogravimetric analysis (TGA) of the sample was performed on a PerkinElmer Pyris Diamond TG/DTA. The temperature was raised under a nitrogen atmosphere from room temperature to  $700^\circ\text{C}$  at a constant heating rate of  $10^\circ\text{C}/\text{min}$ . The flow rate of nitrogen gas was  $50\text{ mL}/\text{min}$ . The initial decomposition temperature ( $T_{\text{id}}$ ) and the temperature at the maximum of mass loss rate ( $T_{\text{max}}$ ) were evaluated.

## RESULTS AND DISCUSSION

The final degree of hydrogenation of NRL was confirmed by FTIR spectroscopy and  $^1\text{H}$ -NMR spectro-

scopic analysis. Figures 1(a) and 1(b) show the FTIR spectra of NRL and HNRL. The most apparent change at  $1663$  and  $863\text{ cm}^{-1}$  are a reduction in intensity of the peaks due to  $\text{C}=\text{C}$  stretching and olefinic  $\text{C}-\text{H}$  bending, as the extent of hydrogenation of  $\text{C}=\text{C}$  increased. The other peaks that appear in the HNRL spectra are caused from TSH left in the solution. The  $^1\text{H}$ -NMR spectra of NRL and HNRL are shown in Figures 2(a) and 2(b). The  $^1\text{H}$ -NMR spectra of NRL shows signals at  $1.75$ ,  $2.12$ , and  $5.25\text{ ppm}$ , which are attributed to  $-\text{CH}_3$ ,  $-\text{CH}_2-$ , and olefinic protons, respectively. After hydrogenation, the peak at  $5.25\text{ ppm}$  drastically decreases and new peaks appear at  $0.8$  and  $1.2\text{ ppm}$ , attributed to  $-\text{CH}_3$ ,  $-\text{CH}_2-$ , and  $-\text{CH}$  of the hydrogenated polymer. Confirmation was

**TABLE I**  
Results from 2<sup>3</sup> Factorial Design Experiment for NRL Hydrogenation

Run	Temp (°C)	[ <i>p</i> -TSH] (mM)	[C=C] (mM)	Degree of hydrogenation (%)
1	125	64	88	65.5
2	145	64	88	78.5
3	125	180	88	83.5
4	145	180	88	90.0
5	125	64	256	50.2
6	145	64	256	56.1
7	125	180	256	67.4
8	145	180	256	72.4
9	125	64	88	63.5
10	145	64	88	80.2
11	125	180	88	81.5
12	145	180	88	88.9
13	125	64	256	50.1
14	145	64	256	54.1
15	125	180	256	69.4
16	145	180	256	71.6

Solvent = *o*-xylene, time = 4 h.

obtained from <sup>13</sup>C-NMR spectrum as shown in Figures 3(a) and 3(b). The polymer product is a strictly alternating copolymer of ethylene propylene. The peak areas at 135.4 and 125.2 ppm decrease with an increase in the reduction of the olefinic carbons and four new peaks appear at 37.8, 33.1, 24.8, and 20.0 ppm, which are attributed to C<sub>α</sub>, —CH, C<sub>β</sub>, and —CH<sub>3</sub> carbons, respectively. The addition of *p*-TSH into the rubber may cause the *cis*–*trans* isomerization within the rubber chain. Schulz et al.<sup>6</sup> reported that *cis*–*trans* isomerization possibly occurred for hydrogenation of unsaturated hydrocarbon polymer, using *p*-toluenesulphonyl hydrazide (*p*-TSH). From the FTIR and NMR spectra, there is no indication of any substitution on the main chain.

### Two-level factorial design experiments

Factorial designs are generally used for experimental systems involving several factors to study the main effects and joint effects of factors on the response.<sup>16</sup>

Two-level factorial design experiments are widely used to screen the influence of each reaction factor. In this work, the principal factors, which had an effect on the degree of hydrogenation were [*p*-TSH], [C=C], and temperature. When a two-level factorial design was applied to calculate the effect of parameters in the experiment, the levels of factors may be arbitrarily called “low (–1)” and “high (+1).” The range of [*p*-TSH], [C=C], and temperature were 88–256 mM, 64–180 mM, and 125–145°C, respectively. In Table I, the results for the factorial design experiments are presented. Yate’s algorithm was applied to investigate the main effects and interaction effects on the degree of hydrogenation.<sup>17</sup> Tables II and III represent the results of a Yate’s algorithm calculation and the calculation of effects and standard error of a 2<sup>3</sup> factorial experiment. The results in Table III indicated that [*p*-TSH], [C=C], and temperature had a profound influence on the degree of hydrogenation; while, [*p*-TSH] and temperature had a positive effect, which implies that the degree of hydrogenation increased with an increase in the [*p*-TSH] and temperature. In contrast, [C=C] showed a large negative effect on the degree of hydrogenation. The binary interactions and three-factor interactions were not highly significant in this system.

### Univariate experiments

The statistical experiments described earlier provide only information on the significance and interaction of the factors. To determine how each variable affects the hydrogenation degree, the univariate experiments of the parameters were carried out individually to determine their influence on the degree of hydrogenation as shown in Figures 4–6. The univariate experimental data are presented in Table IV.

### Effect of TSH concentration

TSH is one of the most popular reagents for releasing a diimide (N<sub>2</sub>H<sub>2</sub>) intermediate under a thermal decomposition reaction.<sup>18</sup> As described in the literature,

**TABLE II**  
Yate’s Algorithm Calculation of the 2<sup>3</sup> Factorial Experiment

Exp	Temp (°C)	[ <i>p</i> -TSH] (mM)	[C=C] (mM)	Average degree of hydrogenation (%)	(1)	(2)	(3)	Divisor	Estimate	Identification
1	–1	–1	–1	64.5	143.825	315.740	561.465	8	70.183	Average
2	1	–1	–1	79.3	171.915	245.725	30.335	4	7.584	Temp
3	–1	1	–1	82.5	105.295	21.820	63.225	4	15.806	[ <i>p</i> -TSH]
4	1	1	–1	89.5	140.430	8.515	–9.205	4	–2.301	[Temp]*[ <i>p</i> -TSH]
5	–1	–1	1	50.2	14.825	28.090	–70.015	4	–17.504	[C=C]
6	1	–1	1	55.1	6.995	35.135	–13.305	4	–3.326	[Temp]*[C=C]
7	–1	1	1	68.4	4.945	–7.830	7.045	4	1.761	[ <i>p</i> -TSH]*[C=C]
8	1	1	1	72.0	3.570	–1.375	6.455	4	1.614	[Temp]*[C=C]*[ <i>p</i> -TSH]

**TABLE III**  
The Calculation of Effects and Standard Errors for 2<sup>3</sup> Factorial Design Experiment

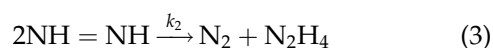
Effect	Estimate ± standard error
Average	70.18 ± 0.29
Main effects	
[N <sub>2</sub> H <sub>4</sub> ]	7.58 ± 0.57
[H <sub>2</sub> O <sub>2</sub> ]	15.81 ± 0.57
[C=C]	-17.50 ± 0.57
Two-factor interaction	
[N <sub>2</sub> H <sub>4</sub> ]*[H <sub>2</sub> O <sub>2</sub> ]	-2.30 ± 0.57
[N <sub>2</sub> H <sub>4</sub> ]*[C=C]	-3.33 ± 0.57
[H <sub>2</sub> O <sub>2</sub> ]*[C=C]	1.76 ± 0.57
Three-factor interaction	
[H <sub>2</sub> O <sub>2</sub> ]*[C=C]*[N <sub>2</sub> H <sub>4</sub> ]	1.61 ± 0.57

the diimide could undergo reaction as shown in eqs. (1)–(3)

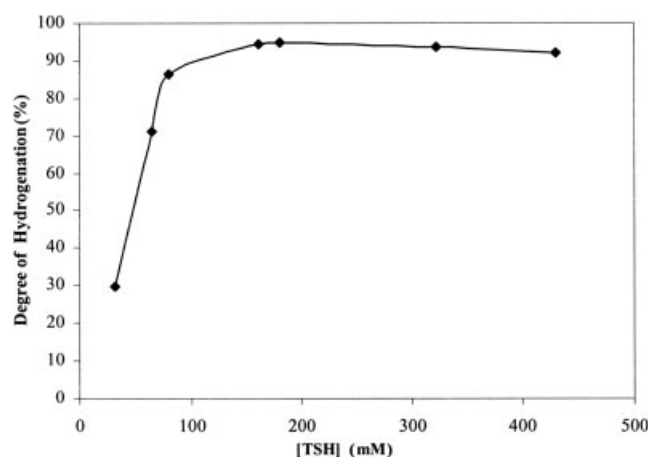
*p*-Toluene sulphonyl hydrazide



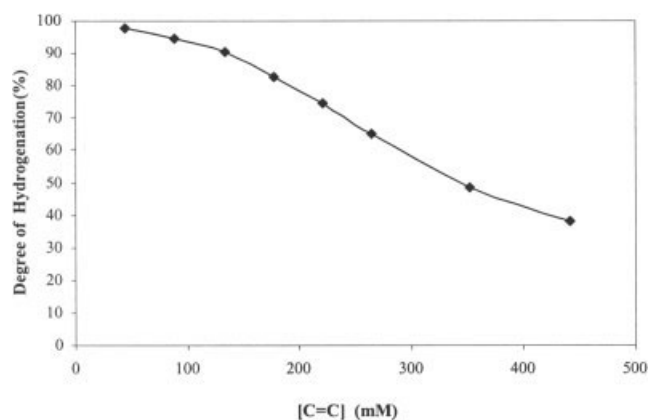
Double bonds (—C=C—) + Diimide (N<sub>2</sub>H<sub>2</sub>)



TSH was only slightly soluble in *o*-xylene at room temperature, but it could be totally dissolved on heating. As the reaction proceeded, the reaction mixture changed from colorless to deep yellow with release of the diimide molecule [eq. (1)]. The diimide then underwent hydrogen addition in the polymer structure [eq. (2)]. To investigate the effect of TSH concentration on the degree of hydrogenation, the TSH concentration was varied over the range of 32–430 mM.

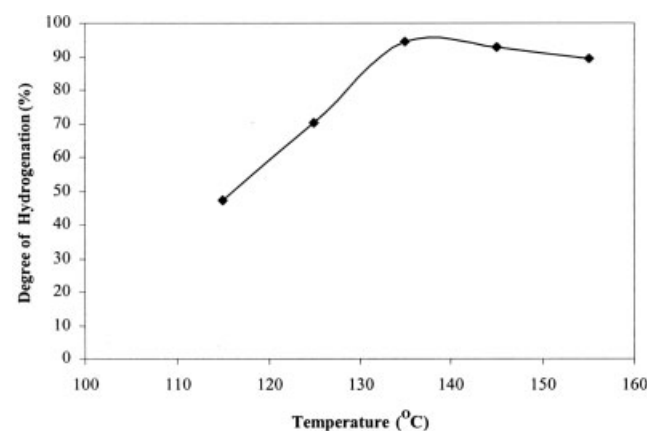


**Figure 4** Effect of *p*-TSH concentration on hydrogenation. [C=C] = 88 mM, *T* = 135°C in *o*-xylene, time = 4 h.



**Figure 5** Effect of rubber concentration on hydrogenation [*p*-TSH] = 161 mM, *T* = 135°C in *o*-xylene, time = 4 h.

The condition was 88 mM rubber concentration in *o*-xylene at 135°C. Theoretically, a 1:1 TSH to C=C molar ratio should give complete hydrogenation. Harwood et al.<sup>19</sup> reported that ~5 mol of hydrazide per mole of butadiene or isoprene unit are required for complete hydrogenation. Sammrn et al.<sup>15</sup> showed that 2 mol of *p*-TSH per mole of double bond in NR was required to achieve 85% hydrogenation in 8 h. The result of this experiment for NRL is given in Figure 4. It was found that the degree of hydrogenation was low at a low level of *p*-TSH concentration. However, 161 mM of *p*-TSH concentration (the mole ratio of C=C : TSH = 1 : 1.8) was used to attain 95% hydrogenation. As expected, the degree of hydrogenation increases as the TSH concentration increases. Mango and Lenz<sup>5</sup> reported that the rate of hydrogenation depends on the microstructure of the polyisoprene segments. They found that the vinyl segments were hydrogenated at a greater rate than either the *cis* or *trans* 1,4 units ( $k_{\text{vinyl}} > k_{\text{cis}} - k_{\text{trans}}$ ).



**Figure 6** Effect of temperature on hydrogenation [*p*-TSH] = 161 mM, [C=C] = 88 mM, in *o*-xylene, time = 4 h.

TABLE IV  
Univariate Data of NRL Hydrogenation

Run	Temp (°C)	[ <i>p</i> -TSH] (mM)	[C=C] (mM)	Degree of hydrogenation (%)
1	135	32	88	29.6
2	135	64	88	71.0
3	135	81	88	94.4
4	135	161	88	94.1
5	135	161	88	94.2
6	135	161	88	94.4
7	135	180	88	94.7
8	135	180	88	94.6
9	135	322	88	93.6
10	135	430	88	91.9
11	135	161	44	97.8
12	135	161	88	94.7
13	135	161	88	94.7
14	135	161	132	90.5
15	135	161	176	82.8
16	135	161	221	74.5
17	135	161	265	65.0
18	135	161	353	48.6
19	135	161	441	38.0
20	115	161	88	47.3
21	125	161	88	70.0
22	135	161	88	94.6
23	145	161	88	92.8
24	155	161	88	89.3

Solvent = *o*-xylene, time = 4 h.

The rate of disproportionation ( $k_2$ ) was reported to be faster than that for the reaction between diimide and double bonds of the diene polymers ( $k_1$ ); that is,  $k_2 > k_1$ <sup>10</sup>. At a TSH concentration equal to 161 mM, the ratio of the substrate and diimide concentration appears to be high enough to prevent disproportionation of the latter [eq. (3)] becoming an unduly wasteful side reaction.<sup>19</sup>

#### Effect of rubber concentration

To investigate the effect of rubber concentration on the degree of hydrogenation, the rubber concentration was varied over the range 44–441 mM. The [*p*-TSH] concentration was 161 mM in *o*-xylene at 135°C. Figure 5 shows an increase in the rubber concentration caused a reduction in the degree of hydrogenation. It is likely that the active diimide species from TSH was not adequate for carbon–carbon double bonds in the system, and thus, the degree of hydrogenation declined with increasing rubber concentration. Since rubber solution at high rubber concentration was more viscous than that at low rubber concentration, it was possible that for the high rubber concentration system, it was difficult for the diimide to diffuse and react with C=C in the rubber structure, and thus, the degree of hydrogenation was decreased. Moreover, impurities such as lipid and water in NRL might cause a reduction in the hydro-

genation level. In contrast to the present results, Nang et al.<sup>20</sup> reported that rate of hydrogenation increased with increasing rubber concentration.

#### Effect of reaction temperature

Experiments were carried out from 115 to 155°C with a TSH concentration of 161 mM and rubber concentration of 88 mM in *o*-xylene. The results obtained are shown in Figure 6. It was found that an increase in temperature increases the degree of hydrogenation until the temperature is over 135°C, at which point the degree of hydrogenation decreased. An increase in temperature also increases the rate of decomposition of diimide, which relates to the need for an increasing amount of diimide in the system. At high temperature, the rate of disproportionation ( $k_2$ ) was faster than that of the reaction between diimide and double bonds of diene polymers ( $k_1$ ).<sup>10</sup> It was believed that the diimide species were suddenly degraded at high temperature ( $k_2$  increase), so the degree of hydrogenation decreased.

#### Effect of parameters

The effect of solvent and other impurities in the latex component, which was believed to decrease the degree of hydrogenation, were also investigated.

*Effect of solvent types.* The specific choice of solvent for a given polymer is dependent upon the ease of product isolation, and it was most convenient to use the lowest boiling point solvent consistent with dissolving all component of the reaction system.<sup>19</sup> A series of experiments were undertaken using different solvents for the NRL hydrogenation at a base condition of [*p*-TSH] = 161 mM, [C=C] = 88 mM, and 135°C. The effect of solvent type on the hydrogenation of NRL is shown in Table V. NRL dissolved better in a polar solvent than in a nonpolar solvent, in contrast to TSH, which was more soluble in a nonpolar solvent. The result shows *o*-xylene was the best solvent for the hydrogenation of NRL, using TSH diimide generated *in situ*. It is likely that TSH dissolves in *o*-xylene to a

TABLE V  
Effect of Solvent on the NRL Hydrogenation

Exp	Solvent	% Hydrogenation
25	Tetrahydrofuran	62.3
26	Monochlorobenzene	82.9
27	Toluene	84.6
28	Benzene	89.0
29	<i>o</i> -Xylene	95.2
30	Cyclohexane	79.9
31	Hexane	77.1

Condition: [*p*-TSH] = 161 mM, [C=C] = 88 mM,  $T = 135^\circ\text{C}$ , time = 4 h.

**TABLE VI**  
Effect of Source of Diimide on the NRL Hydrogenation

Exp	Source of diimide	% Hydrogenation
32	TSH	70.9
33	MSH	75.0
34	TPSH	84.4

Condition:  $[p\text{-TSH}] = 88 \text{ mM}$ ,  $[\text{C}=\text{C}] = 64 \text{ mM}$ ,  $T = 135^\circ\text{C}$  in *o*-xylene, time = 4 h.

greater extent than other solvents and easily produces diimide, which reacts with carbon-carbon double bonds to achieve a higher degree of hydrogenation.

*Effect of type of diimide source.* A series of experiments were undertaken using different diimide sources for NRL hydrogenation at a base condition of  $[\text{diimide}] = 64 \text{ mM}$ ,  $[\text{C}=\text{C}] = 88 \text{ mM}$ , and  $35^\circ\text{C}$ . The effect of the diimide source type on hydrogenation of NRL is summarized in Table VI. TPSH and MSH were also found to be a source of diimide for hydrogenation of NRL. Cusack et al.<sup>9</sup> found that the thermal decomposition rate of TPSH is 380 times that of TSH. The MSH thermal decomposition rate is 24 times that of TSH. Under these conditions, TPSH is the best diimide source for NRL hydrogenation due to its decomposition rate, and the diimide species is a more stable system than is the production of TSH or MSH.

*Effect of impurities.* The effect of impurities was suspected to reduce the hydrogenation rate for hydrogenation of NRL when using an osmium hydrogenation catalyst. To study the effect of impurity on the degree of hydrogenation of NRL from the diimide *in situ* reagent method, the hydrogenation of deproteinized NRL was examined. The deproteinized rubber was prepared according to the literature method.<sup>21</sup> The experiments were carried out at  $[p\text{-TSH}]$  of 161 mM,  $[\text{C}=\text{C}]$  of 88 mM, and  $135^\circ\text{C}$  in *o*-xylene. Table VII shows the effect of nitrogen content in the rubber. The degree of hydrogenation of deproteinized NRL was at the same level as that for NRL. It was established that the protein content in the rubber does not cause a decrease in activity of the diimide reagent for the latex system. It is possible that the nitrogen group in protein cannot coordinate with the active species or prohibit diimide generation. To clarify this idea for the

**TABLE VII**  
Effect of Nitrogen Content on Degree of Hydrogenation of NRL

Exp	Rubber type	% Nitrogen content	% Hydrogenation
35	NRL	0.20	94.5
36	DPNRL	0.02	90.5

Condition:  $[p\text{-TSH}] = 161 \text{ mM}$ ,  $[\text{C}=\text{C}] = 88 \text{ mM}$ ,  $T = 135^\circ\text{C}$ , time = 4 h, in *o*-xylene. NRL, natural rubber latex; DPNRL, deproteinized natural rubber latex.

**TABLE VIII**  
Effect of Impurity on Hydrogenation of Synthetic *cis*-1,4-Polyisoprene

Exp	Substance	% Hydrogenation
37	–	41.0
38	Hexylamine	45.3
39	Hexadecylamide	70.3
40	Ammonium hydroxide	75.0

Condition:  $[p\text{-TSH}] = 161 \text{ mM}$ ,  $[\text{C}=\text{C}] = 88 \text{ mM}$ , impurity 0.25% by weight,  $T = 135^\circ\text{C}$  in *o*-xylene.

effect of the impurity, an experiment was set up using *cis*-1,4-polyisoprene (CPIP) as an analogue of NRL in terms of rubber microstructure. Hexylamine and hexadecylamide, which have nitrogen functional groups similar to those in proteins, were added to the CPIP hydrogenation system to test whether the effect would be similar to the protein effect on degree of NRL hydrogenation. The effect of high ammonia content in latex was also investigated to see whether it had an influence on the degree of hydrogenation. Table VIII shows the effect of nitrogen containing additives in the rubber. The reaction conditions were:  $[\text{C}=\text{C}] = 88 \text{ mM}$ ,  $[p\text{-TSH}] = 161 \text{ mM}$  at  $T = 135^\circ\text{C}$  in *o*-xylene. It was found that all compounds with nitrogen functional groups increase the degree of hydrogenation for hydrogenation of CPIP. It was believed that the nitrogen group could provide base in the reaction, which reacts with *p*-toluenesulfonic acid in the system. The *p*-toluenesulfonic acid was produced from thermal decomposition as shown in eq. (1). In addition, addition of base species into the system may increase the reaction rate by assisting in the deprotonation of TSH. One such attempt to hydrogenate polyisoprene with TSH in the presence of an amine base (pyridine) has been reported. Addition of tertiary amine, tri-*n*-propyl amine was believed to result in protonation of amine instead of the olefin, which should greatly decrease the propensity of the *p*-toluenesulfonate anion (which is excellent nucleophile) in attacking the polymer backbone.<sup>5</sup>

*Effect of water content in natural rubber latex.* High ammonia NRL contains 40% water by weight. The rubber particles disperse in water to form an emulsion. Water

**TABLE IX**  
Effect of Dry Rubber Content on the Rate of NRL Hydrogenation

Exp	DRC (%)	% Hydrogenation
41	60	94.7
42	50	93.5
43	40	92.5
44	30	91.8

Condition:  $[p\text{-TSH}] = 161 \text{ mM}$ ,  $[\text{C}=\text{C}] = 88 \text{ mM}$ ,  $T = 135^\circ\text{C}$  in *o*-xylene.



**TABLE X**  
Molecular Weight and Molecular Weight Distribution of Natural Rubber and Hydrogenated Natural Rubber

Sample	% Hydrogenation	$M_n$ ( $10^{-5}$ Da)	$M_w$ ( $10^{-6}$ Da)	$M_w/M_n$
NRL	–	4.12	1.09	2.65
HNRTSH <sup>a</sup>	52.5	3.20	0.81	2.54
	95.7	3.10	0.81	2.61

Condition:  $[C=C] = 81$  mM,  $[p\text{-TSH}] = 161$  mM at 1 bar of  $P_{N_2}$  and  $135^\circ\text{C}$  for 4 h in glass reactor.

<sup>a</sup> HNR from noncatalytic hydrogenation.

present in the latex may also possibly reduce the degree of hydrogenation of NRL when using diimide generated *in situ*. Experiments were carried out in which various amounts of water were present in the NRL in terms of percentage dry rubber content (DRC) at the base condition  $[p\text{-TSH}] = 161$  mM,  $[C=C] = 88$  mM, and  $135^\circ\text{C}$ . Percentage DRC is defined as the percent of dry rubber content in the natural rubber latex. The range of DRC in this study was between 30 and 60% by weight, corresponding to 70–40% water by weight, respectively. The effect of water content within the NRL on the degree of hydrogenation is summarized in Table IX. It was found that the degree of hydrogenation was not significantly decreased with an increase in the amount of water (decrease %DRC).

#### Molecular weight of hydrogenated natural rubber

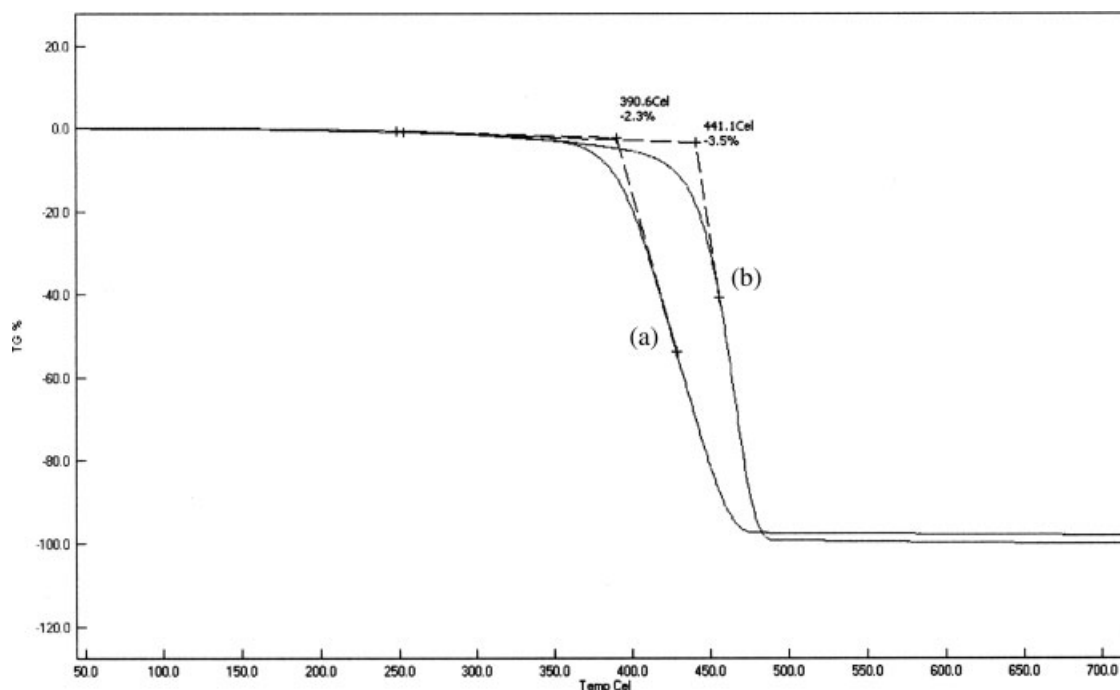
Molecular weight and molecular weight distribution are fundamental characteristics of a polymer material.

Gel-permeation chromatography (GPC) is a useful separation method for polymers and provides a measure of relative molecular weight.<sup>22</sup> Generally, rubber from *Hevea brasiliensis* has a high molecular weight with a broad molecular weight distribution. It also has been confirmed to have a bimodal distribution as seen from GPC analysis.<sup>23</sup> The molecular weight and molecular weight distribution of NRL and HNRL are presented in Table X.

The MW of HNR prepared by diimide generated *in situ* ( $MW = 0.81 \times 10^6$ ) was lower than that of NR ( $MW = 1.09 \times 10^6$ ). The reason for decrease in MW of HNR was due to the high reaction temperature and long reaction time. Thermal degradation of *p*-TSH was believed to cause the decrease in molecular weight after hydrogenation via side reaction. The molecular weight changed slightly after hydrogenation for homogeneous catalytic and diimide hydrogenation. Even homogeneous catalytic hydrogenation, at a higher temperature ( $150^\circ\text{C}$ ) and a shorter reaction time than used for diimide hydrogenation, led to a significant decrease in molecular weight of the hydrogenated rubber.<sup>24</sup> Nang et al.<sup>20</sup> also reported that MW of hydrogenated *cis*-1,4-polyisoprene decreased after hydrogenation via diimide generated *in situ*.

#### Thermal properties of hydrogenated natural rubber

Thermal analysis is used to investigate the physical properties of substrates as a function of temperature. These experiments are carried out using a DSC and a TGA to find the glass transition temperature ( $T_g$ ) and



**Figure 7** DSC thermograms of hydrogenated natural rubber: (a) 50.8%, (b) 95.7%.

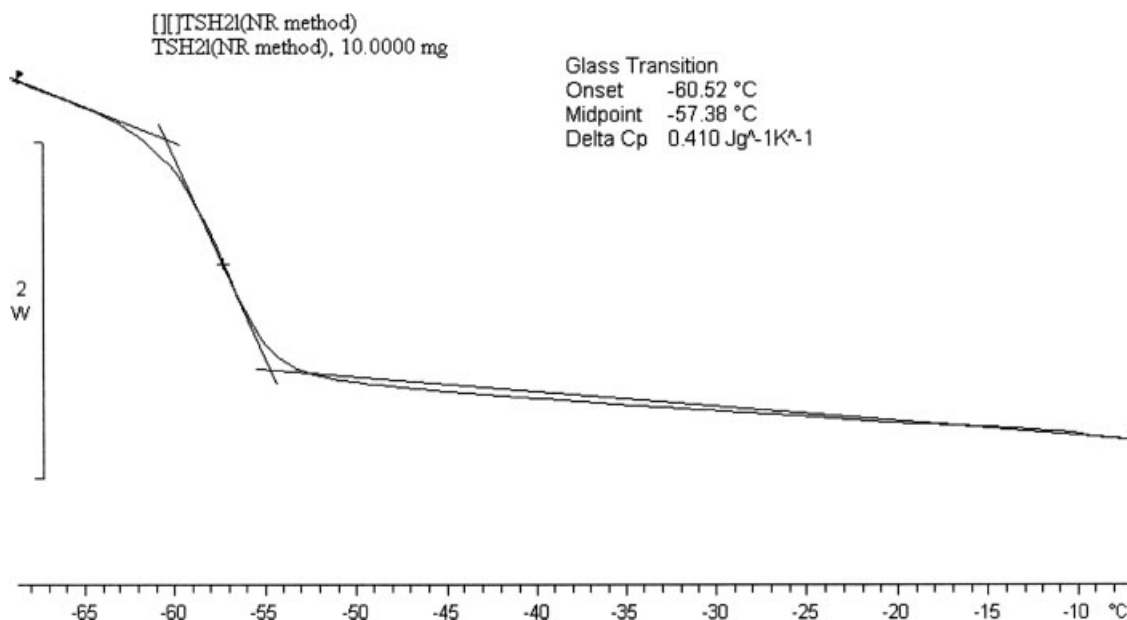


Figure 8 DSC thermograms of hydrogenated natural rubber.

decomposition temperature, respectively. The results of the decomposition temperature and  $T_g$  of HNR are shown in Figures 7 and 8 and Table XI.

Thermogravimetric analyses of NRL, HNRL, and an ethylene-propylene copolymer (EPDM) were conducted under a nitrogen atmosphere. The TG curves for HNRL samples compared with NRL are shown in Figure 7. It can be seen that the polymer degradation is an overall one-step reaction because the TG curve of the samples provide smooth weight loss curves. The initial decomposition temperature ( $T_{id}$ ) was determined from the intersection of two tangents at the onset of the decomposition temperature. The maximum decomposition temperature ( $T_{max}$ ) of each sample was obtained from the peak maxima of the derivative of the TG curves. The results in Table XI show that the hydrogenation can improve the thermal stability of NR by converting the weak  $\pi$  bond within NRL to the stronger C–H  $\sigma$  bond. On comparison with standard EPDM, it was found that  $T_{id}$  and  $T_{max}$  of the completely hydrogenated NR were close to

those of EPDM. It can be concluded that the structure of HNR provides a facile entry and alternative method to alternating ethylene-propylene copolymers.

The glass transition temperature,  $T_g$ , is one of the most important parameters for characterization of polymer structure. The  $T_g$  is a transition related to the motion in the amorphous sections of polymer. It is determined from the midpoint of the baseline shift of the DSC thermogram. The DSC thermogram of the HNR sample is presented in Figure 8. The DSC thermogram of the HNR sample indicates a one step baseline shift. This suggests that the HNR sample has a single glass transition temperature. This also suggests that no side reactions occurred during the hydrogenation process. In addition, the glass transition temperature of HNR was slightly increased with an increase in the level of hydrogenation. The standard EPDM (ethylene/propylene = 50/50, diene = 9.5%) having the higher  $T_g$  ( $-44.6^\circ\text{C}$ ) shows a higher degree of crystallization within the polymer structure compared with that of HNR. It can be concluded that the hydrogenation does not affect the glass transition temperature of NR; consequently, the HNR product still is a highly rubbery. A similar observation was also made by Singha et al. for HNR obtained using the  $\text{RhCl}(\text{PPh}_3)_3$  catalytic hydrogenation system.<sup>3</sup>

TABLE XI  
Analysis of Glass Transition Temperature and Decomposition Temperature of Rubber Samples

Rubber	% Hydrogenation	$T_g$ ( $^\circ\text{C}$ )	$T_{id}$ ( $^\circ\text{C}$ )	$T_{max}$ ( $^\circ\text{C}$ )
EPDM <sup>a</sup>	–	–48.4	452.7	470.7
NRL	–	–64.0	357.2	380.9
HNRL	50.8	–60.5	390.6	422.3
HNRL	95.7	–58.4	441.5	469.1

<sup>a</sup> The ethylene-propylene copolymer (EPDM) has the ratio of ethylene/propylene as 70/30 and 11.5% of diene content.

## CONCLUSIONS

The noncatalytic diimide hydrogenation of NRL with diimide generated *in situ* by thermolysis of *p*-toluene sulfonylhydrazide (TSH) is a useful method for hydrogenation of NRL. A ratio 2 mol of TSH/1 mol of

C=C provided >90% hydrogenation. The effect of impurities present in the latex and water were not significant. The diimide hydrogenation method provides a viable process to improve the thermal stability of NRL without affecting its glass transition temperature.

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