# Kinetics and Parameters Affecting Degradation of Purified Natural Rubber

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**ABSTRACT:** Purified natural rubber (PNR) was obtained by treatment of high ammonia NR latex with proteinase enzyme for 24 h, followed by double centrifugation. The PNR was later redispersed into latex form with 0.5% (w/v) sodium dodecyl sulfate. The degradation of PNR was performed in latex form by using a combination of the radical initiator potassium persulfate ($K_2S_2O_8$) and propanal. The intrinsic viscosity [$\eta$] of the degraded rubber or liquid rubber that was obtained depended on various parameters such as the initiator concentration, amount of propanal, dry rubber content, reaction time, and temperature. It was found that the [$\eta$] of the rubber can be reduced from 4.31 to 0.19 for the PNR after a 25-h reaction time using 5% dry rubber content PNR latex, 1 part per hundred rubber (phr) of $K_2S_2O_8$, and 32 phr of propanal at 80°C. The kinetics of the degradation reaction were investigated. The highest rate constant found was $11.33 \times 10^{-2}\,\mathrm{s}^{-1}$. The activation energy of the degradation reaction was 76.56 kJ mol$^{-1}$. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3546–3555, 2003

**Key words:** degradation; initiator; kinetics; proteins; rubber

## INTRODUCTION

Natural rubber (NR) 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-polyisoprenic structure with an average molecular weight of about $10^6$. Scientists have long been interested in researching the degradation of NR to prepare low molecular weight or liquid-like NR (LNR). This may be because LNR offers tremendous potential applications such as adhesives, bulk viscosity modifiers, covulcanizing additives, binders, and coatings.[1–5] Liquid rubber is also easy to chemically modify because of its lower molecular weight. The processes that produce degraded rubbers include mechanical, thermal, chemical, and photochemical methods.[6] For the mastication process, chain scission usually induces the formation of radical species; therefore, the recombination reaction can often occur, resulting in the limitation of the degree of degradation reaction. Another drawback is the difficulty in controlling the desired molecular weight of the liquid rubber. Utilization of chemical reagents by thermal reaction or photoreaction seem to offer the potential to control the molecular weight of the degraded rubber under a certain condition. By varying the amount of phenylhydrazine in the system of phenylhydrazine–oxygen developed by French researchers, the desired molecular weight of LNR can be achieved.[7] (This method is accepted and a pilot plant had been set up in the Ivory Coast.) However, the contamination of residual phenylhydrazine on the depolymerized rubber results in dark-brown liquid rubber. It has been reported recently that colorless LNR could be obtained from deproteinized NR by using a radical initiator and a secondary reagent.[8] However, the kinetics of degradation has not been reported. The objective of the present work is the study of the degradation of NR using a chemical process that includes potassium persulfate ($K_2S_2O_8$) as a radical initiator and propanal as a secondary reagent. Parameters affecting the degradation reaction such as the initiator and propanal concentrations, rubber contents, time, and temperature have been investigated. The kinetic rate constant of the degradation of the NR has been evaluated, as has the activation energy of the reaction.

## EXPERIMENTAL

### Materials

High ammonia NR (HANR) latex [dry rubber content, (DRC) = 60%] was purchased from Bangkok Rubber Company, Thailand. Proteinase enzyme (B KP 3939) was supplied by Kao Co. Ltd. Sodium dodecyl sulfate (SDS), anionic surfactant was purchased from Fluka. The reagents used for the degradation reaction, in-
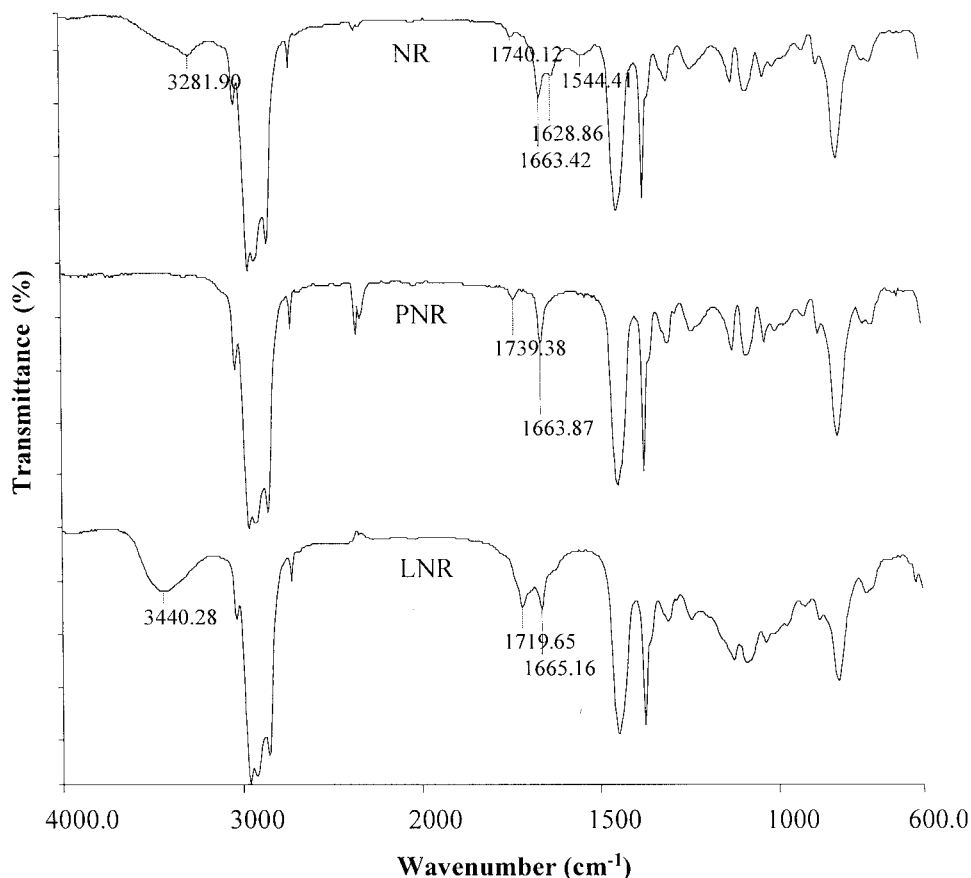
**Figure 1** IR spectra of natural rubber (NR), purified natural rubber (PNR), and liquid natural rubber (LNR).

cluding $K_2S_2O_8$, propanal, and trisodium phosphate (*tert*)dodecahydrate ($Na_3PO_4 \cdot 12H_2O$) were purchased from Fluka.

### Preparation of PNR

The PNR was prepared by stirring the HANR latex (30% DRC) with 0.04% (w/v) proteinase enzyme B KP 3939 and 1% (w/v) SDS surfactant at 37°C for 24 h. The NR latex was then centrifuged in an ultracentrifuge (13,000 rpm). The cream fraction was isolated and redispersed in 0.5% (w/v) surfactant. The redispersed latex was recentrifuged and the PNR in the form of a cream fraction was redispersed in 0.5% (w/v) surfactant and kept in latex form with 20% DRC for further reaction.

### Degradation of PNR

The PNR latex was mixed with various amounts of $K_2S_2O_8$, propanal, and $Na_3PO_4$ in a 1-L glass reactor equipped with a condenser and a controlled speed stirrer (400 rpm). The reaction was carried out at 60–80°C over 30 h. The rubber latex was sampled at various reaction times and precipitated in acetone.

The LNR thus obtained was reprecipitated from toluene and methanol. A colorless LNR resulted after drying in a vacuum at 40°C.

### Characterization

The intrinsic viscosities [$\eta$] of NR and its degraded forms were evaluated by using an Ubbelhode viscometer (0.53-mm capillary diameter). The measurement was 0.1–0.2 g/dL of the rubber in toluene solution at 30°C.

Gel permeation chromatography (GPC, Waters 150-CV plus) was used to measure the weight-average molecular weight ($M_w$), number-average molecular weight ($M_n$), and viscosity-average molecular weight ($M_v$) of the degraded rubbers. The GPC system was operated at 30°C using tetrahydrofuran as an eluent and polystyrene for standard calibration. The machine is equipped with a refractive index and capillary viscometer.

The Fourier transform IR (FTIR) spectrum of the rubber was recorded on a Perkin–Elmer System 2000 FTIR spectrophotometer, using film casting directly on an NaCl cell. The ^{1}H-NMR spectrum was recorded on a 300-MHz Bruker AM 300 spectrophotometer.
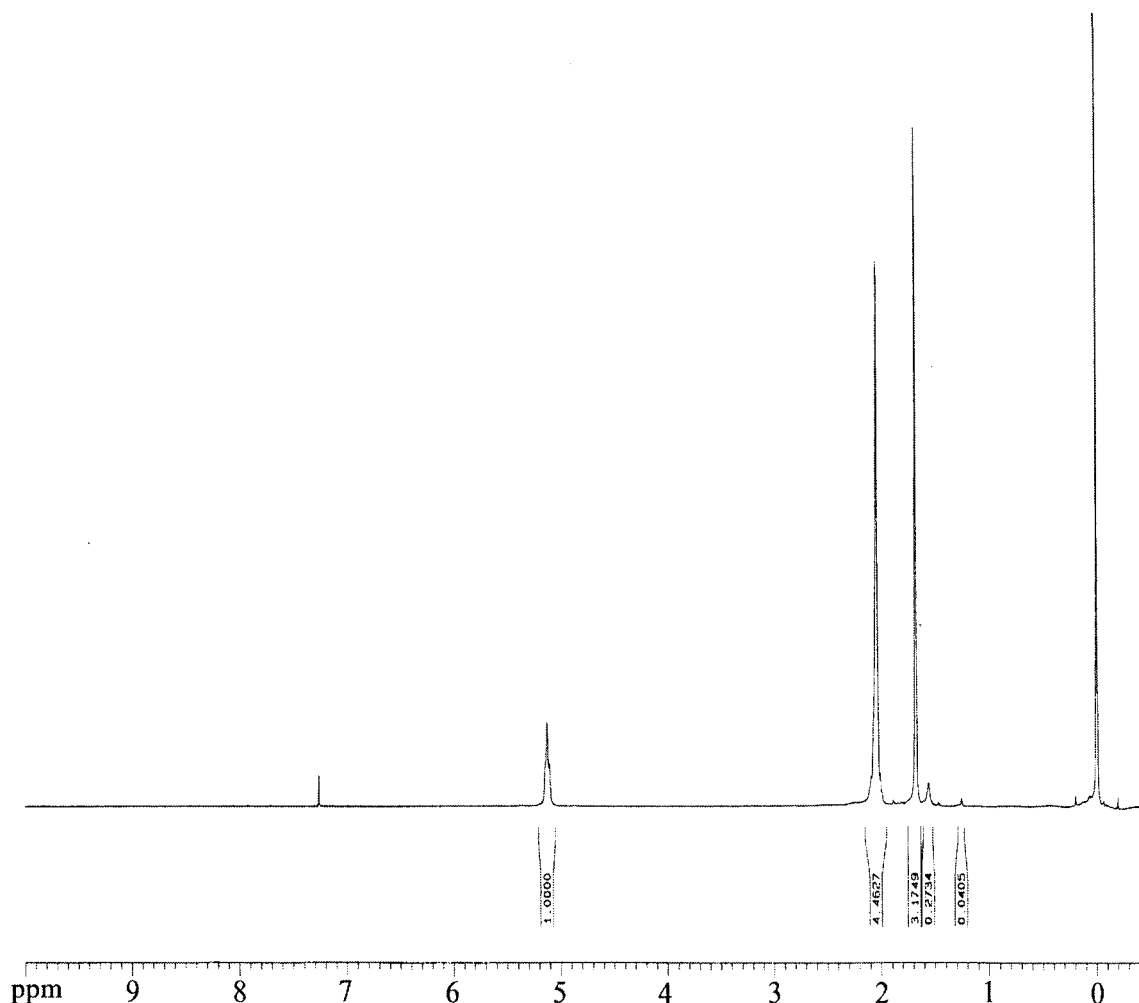
**Figure 2** The $^1$H-NMR spectrum of purified natural rubber (PNR).

## RESULTS AND DISCUSSION

### PNR analysis

The NR obtained from *Hevea brasiliensis* consists of about 3–5% nonrubber constituents.[9] Among these, amino acids or proteins have been identified and it is believed that they are responsible for storage hardening and formation of microgels. Elimination of these constituents might reduce side reactions during chemical modification of the NR. Therefore, purification of the NR was taken into account before further investigation. Utilization of a proteinase enzyme is reported to be an efficient method to eliminate proteins from NR, particularly the one that bonds to the rubber particles.[10–12] In our system, in addition to the utilization of an enzyme, centrifugation was employed twice in order to eliminate other nonrubber components. It was also found that the [$\eta$] was reduced from 5.88 for the original NR to 4.31 for the PNR. The determination of the nitrogen content by micro-Kjeldahl was used to confirm the reduction of proteins in PNR compared to the NR. It was found that the 0.4% nitrogen content of NR was reduced to 0.03% for PNR.

The chemical structure of the PNR was analyzed by IR spectroscopy and $^1$H-NMR. The IR spectrum of NR in Figure 1 indicates the appearance of characteristic amide bands at 3282 (N—H stretching), 1629 (amide I vibration), and 1544 cm$^{-1}$ (amide II vibration), which can be attributed to the signals of proteins.[13] These signals are not found in the spectrum of PNR in Figure 1. This evidence can be qualitatively used to confirm that the proteins in the NR were eliminated. The $^1$H-NMR spectrum of the PNR in Figure 2 shows the presence of a proton signal adjacent to C=C at 5.13 ppm and a methyl group signal adjacent to the C=C of the 1,4-cis structure at 1.67 ppm. The methylene proton signal of the saturated hydrocarbon was found at 2.03 ppm. These results reveal that the *cis*-1,4-polyisoprenic structure was not destroyed by the enzymatic treatment process.

### Degradation reaction

Generally, polyisoprenic rubber (synthetic or natural) is prone to systematic degradation at a high tempera-
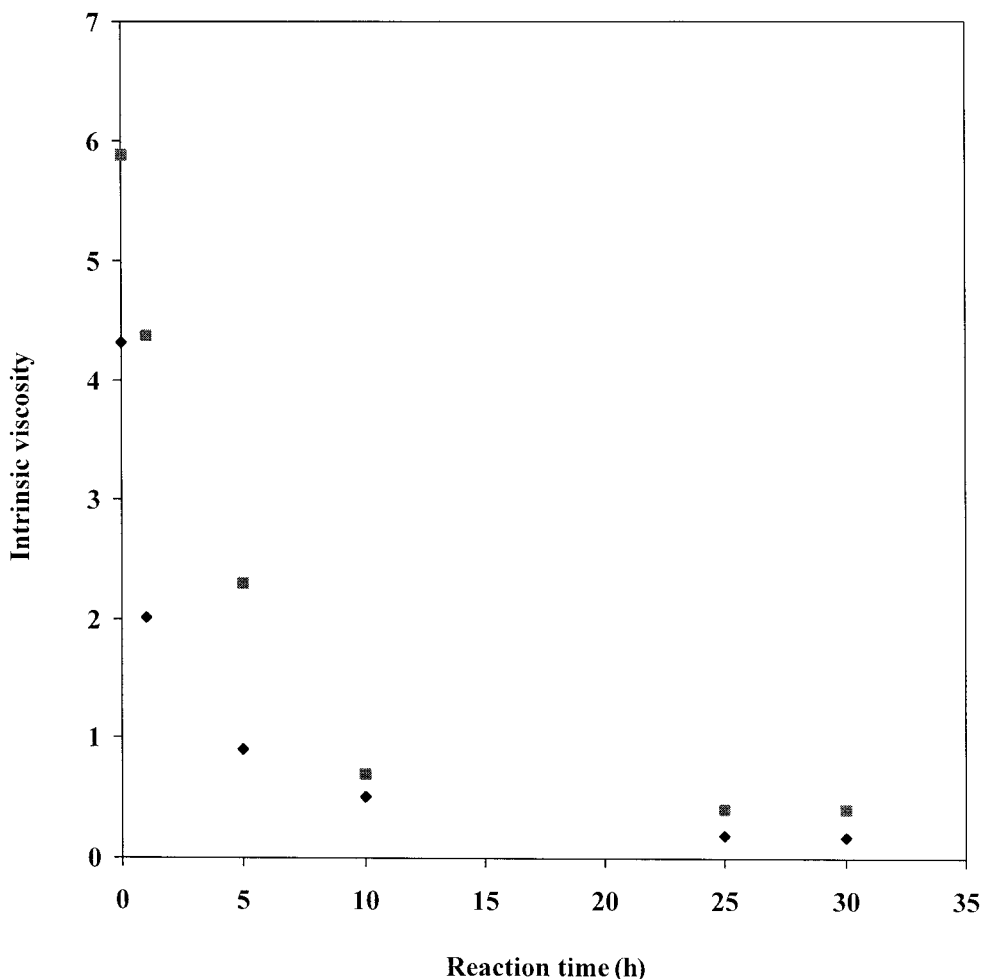
**Figure 3** Plots of the intrinsic viscosity $[\eta]$ of LNR prepared from 1 phr of $K_2S_2O_8$, 32 phr of propanal, and 0.34 phr of $Na_3PO_4$ at various reaction times with ($\blacklozenge$) 5% DRC PNR latex or ($\blacksquare$) 5% DRC NR latex.

ture ($>100°C$) in the presence of oxygen.[14,15] However, it is difficult to control the molecular weight of the degraded rubber and gels often occur. It has been widely reported that a high temperature can cause the formation of radical species on the polymeric chain; thus, in the presence of oxygen, hydroperoxide is formed as the primary oxidation product. The decomposition of the hydroperoxide will later lead to chain rupture. In our work, $K_2S_2O_8$ was employed as a principal reagent to induce radical species before the intervention of oxygen, similar to other oxidative degradation systems. Treatment of 5% DRC PNR latex with 1 part per hundred rubber (phr) of $K_2S_2O_8$ and 0.34 phr of $Na_3PO_4$ was carried out at 70°C. It was found that, without the addition of propanal, the molecular weight of PNR was decreased but gel formation was detected after a 2-h reaction time. It can be postulated that the added radical initiator may play a role in inducing active radicals on the rubber chain, leading to chain degradation, including the formation of new macroradicals. These radicals might be able to react with each other to form crosslinked products.

The degradation reaction of the PNR was then performed by the addition of 32 phr of propanal into 5% DRC of PNR latex in the presence of 1 phr of $K_2S_2O_8$ and 0.34 phr of $Na_3PO_4$ at 70°C. The same condition was also investigated with unpurified NR latex. It was found that the $[\eta]$ values of both cases were exponentially reduced according to the increased reaction time (Fig. 3). It can be postulated that the radical species induced by $K_2S_2O_8$ should lead to chain degradation, forming new macroradicals. These radicals were then consumed by the propanal, resulting in the prevention of the recombination reaction. The proposed mechanism is shown in Figure 4. The effect of the amount of propanal on the degradation is presented in a later section. The decrease of the $[\eta]$ of the PNR shown in Figure 3 seems to be better than the NR. This may be due to the presence of nonrubber constituents, which act as antioxidants, or the presence of microgels, which retard the oxidative degradation in the system. The kinetic rate constants of the PNR and NR are investigated in a later section. The resulting degraded or LNR from PNR is a colorless product and the one
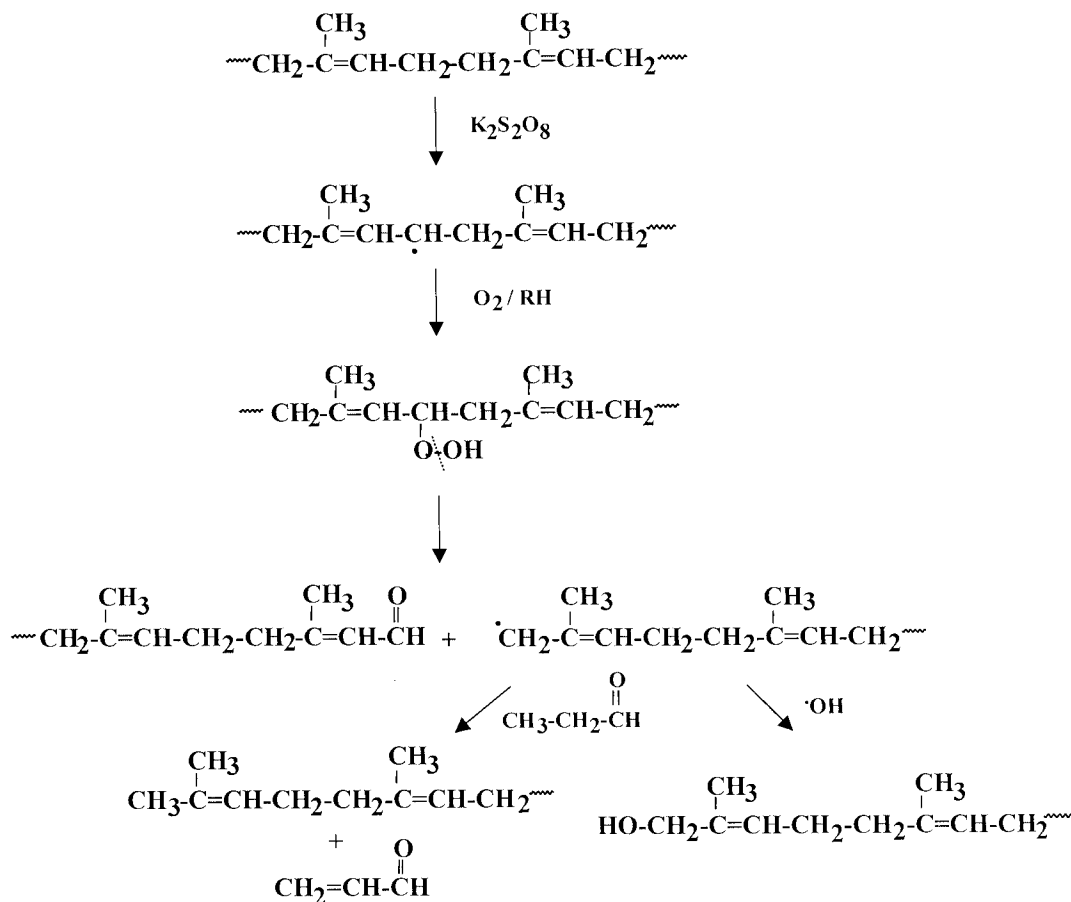
$$
\begin{array}{cc}
\text{CH}_3 & \text{CH}_3 \\
| & | \\
\text{\textasciitilde CH}_2\text{-C=CH-CH}_2\text{-CH}_2\text{-C=CH-CH}_2\text{\textasciitilde}
\end{array}
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$\downarrow \quad K_2S_2O_8$

$$
\begin{array}{cc}
\text{CH}_3 & \text{CH}_3 \\
| & | \\
\text{\textasciitilde CH}_2\text{-C=CH-}\overset{\bullet}{\text{CH}}\text{-CH}_2\text{-C=CH-CH}_2\text{\textasciitilde}
\end{array}
$$

$\downarrow \quad O_2 / RH$

$$
\begin{array}{cc}
\text{CH}_3 & \text{CH}_3 \\
| & | \\
\text{\textasciitilde CH}_2\text{-C=CH-CH-CH}_2\text{-C=CH-CH}_2\text{\textasciitilde} \\
| \\
\text{O}\cdot\text{OH}
\end{array}
$$

$\downarrow$

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\begin{array}{cc}
\text{CH}_3 \quad\quad \text{CH}_3 \quad \text{O} & \quad\quad \text{CH}_3 \quad\quad\quad \text{CH}_3 \\
| \quad\quad\quad | \quad\quad || & \quad\quad | \quad\quad\quad\quad | \\
\text{\textasciitilde CH}_2\text{-C=CH-CH}_2\text{-CH}_2\text{-C=CH-CH} \;+\; {}^{\bullet}\text{CH}_2\text{-C=CH-CH}_2\text{-CH}_2\text{-C=CH-CH}_2\text{\textasciitilde}
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\text{CH}_3\text{-C=CH-CH}_2\text{-CH}_2\text{-C=CH-CH}_2\text{\textasciitilde} & \text{HO-CH}_2\text{-C=CH-CH}_2\text{-CH}_2\text{-C=CH-CH}_2\text{\textasciitilde} \\
+ \\
\overset{\text{O}}{\overset{||}{\text{CH}_2\text{=CH-CH}}}
\end{array}
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**Figure 4** The proposed mechanism of the degradation reaction of natural rubber in the presence of $K_2S_2O_8$ and propanal.

from NR is a brown color. The color might come from the presence of carotenoid pigments or oxidation of nonrubber constituents in the NR. The $[\eta]$ values at a 25-h reaction time of the LNR from PNR and NR were 0.19 and 0.41, respectively. No significant difference of the $[\eta]$ at a 30-h reaction time was found in these cases, compared to a 25-h reaction time.

In our system, $Na_3PO_4$ was used as a reagent to control the pH. It was reported that at a pH lower than 8.5, the decomposition of $K_2S_2O_8$ was less efficient.[17] We used 0.34 phr of $Na_3PO_4$ and it made the degradation condition pH about 10.

The $^1$H-NMR spectrum of the LNR is the same as that of the PNR starting material. There are characteristic peaks of proton and methyl proton adjacent to the unsaturated unit at 5.13 and 1.67 ppm, respectively. The methylene proton of the saturated hydrocarbon is found at 2.03 ppm. The *cis*-1,4-polyisoprenic structure is still unchanged.

The IR spectrum of LNR in Figure 1 shows that after degradation, additional peaks of carbonyl compounds compared to the PNR were found at 1720 cm$^{-1}$. These peaks may come from the oxidative degradation of PNR as reported in the literature.[16] A hydroxyl signal was also found at 3440 cm$^{-1}$ in the IR spectrum of LNR, which might come from the addition of the hydroxyl radical generated during the reaction (see Fig. 4).

## Parameters affecting degradation reaction

The degradation of PNR using various amounts of $K_2S_2O_8$ (1, 2, and 3 phr) at 70°C was studied and the results are shown in Figure 5. Generally, a higher amount of radical initiators results in a better degradation process. However, when the radical initiators are too high, this may result in a high amount of radical polymeric species being formed, which may lead to the increase of the possibility of a chain recombination reaction. It was found that using 2 phr of $K_2S_2O_8$ gave the lowest $[\eta]$ of 0.27 after 10 h, whereas 1 and 3 phr gave 0.51 and 0.36, respectively. The $[\eta]$ values of the LNR were 0.19, 0.18, and 0.21 after 25 h of reaction using 1, 2, and 3 phr of the initiators, respectively (see Table I).

By varying the amount of propanal as 16, 32, and 64 phr for the system of 1 phr of $K_2S_2O_8$ and 0.34 phr of $Na_3PO_4$, it was found that after 10 h of reaction at 70°C, the $[\eta]$ of the degraded rubbers were 0.79, 0.51, and 0.52, respectively. The results of a 25-h reaction
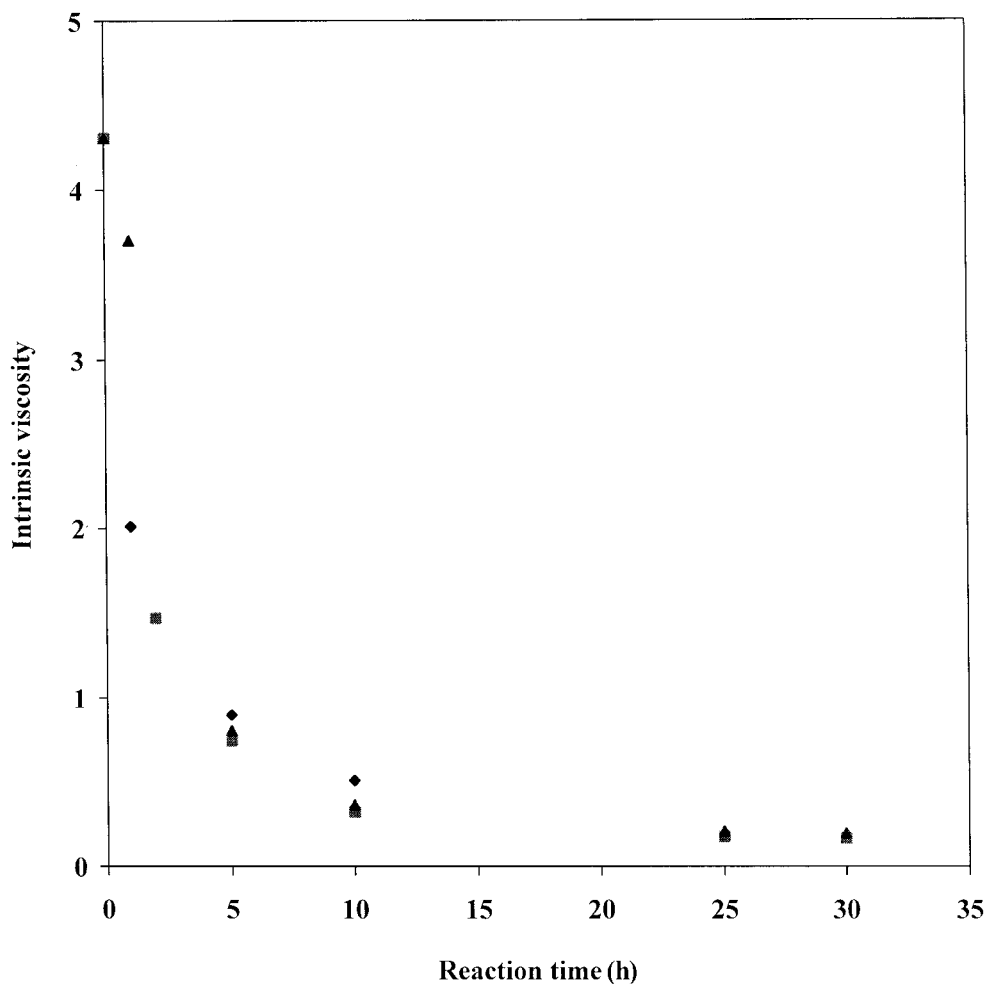
**Figure 5** Plots of the intrinsic viscosity [$\eta$] of LNR prepared from 5% DRC PNR latex, 32 phr of propanal, and 0.34 phr of Na$_3$PO$_4$ at various reaction times with ($\blacklozenge$) 1 phr of K$_2$S$_2$O$_8$, ($\blacksquare$) 2 phr of K$_2$S$_2$O$_8$, and ($\blacktriangle$) 3 phr of K$_2$S$_2$O$_8$.

time are shown in Table I. These results confirmed that the propanal plays some role in the oxidative degradation reaction. It can be postulated that as the degradation was proceeding, the propanal might help in capturing the new macroradicals generated from the reaction, inhibiting the recombination reaction (Fig. 4). However, an excess amount of propanal (64 phr) may not be necessary because of self aldol condensation

can occur rather than the reaction with the rubber chain.

The reaction temperature has an influence on the efficiency of the initiation and degradation process. Figure 6 shows the results of degradation systems using 5% DRC PNR latex, 1 phr of K$_2$S$_2$O$_8$, 32 phr of propanal, and 0.34 phr of Na$_3$PO$_4$ carried out at 60, 70, and 80°C. It was found that after 25 h, the [$\eta$] values at

**TABLE I**
**Results of Intrinsic Viscosity ([$\eta$]) and Kinetic Rate Constant ($k$) Obtained from Degradation of PNR Latex at 70°C**

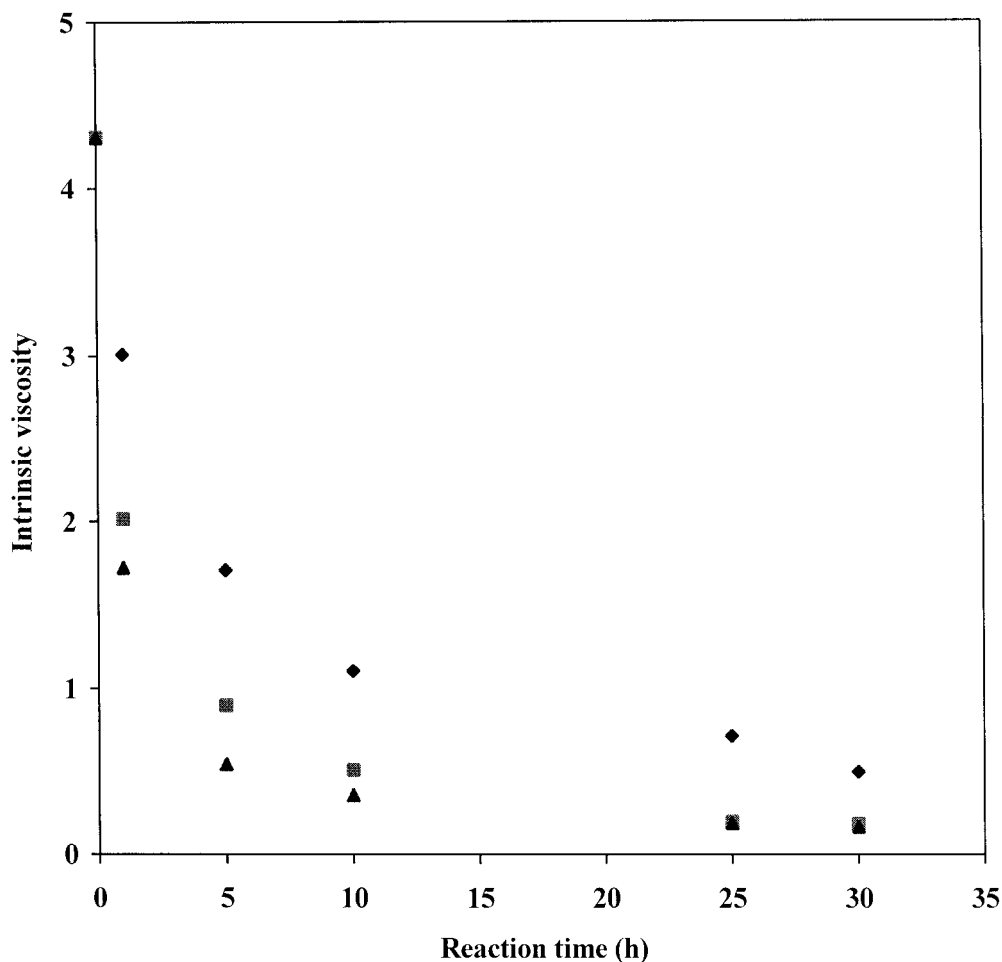| Samples | K$_2$S$_2$O$_8$ (phr) | | | | Propanal (phr) | | DRC (%) | [$\eta$] after 25 h | $k \times 10^{-2}$ (s$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| LNR 1 | 1 | — | — | — | 32 | — | 5 | 0.19 | 7.34 |
| LNR 2 | — | 2 | — | — | 32 | — | 5 | 0.18 | 8.10 |
| LNR 3 | — | — | 3 | — | 32 | — | 5 | 0.21 | 7.01 |
| LNR 4 | 1 | — | — | 16 | — | — | 5 | 0.36 | 4.07 |
| LNR 5 | 1 | — | — | — | 32 | — | 5 | 0.19 | 7.34 |
| LNR 6 | 1 | — | — | — | — | 64 | 5 | 0.20 | 7.11 |

DRC, dry rubber content.

**Figure 6** Plots of the intrinsic viscosity [$\eta$] of LNR prepared from 5% DRC PNR latex, 1 phr of $K_2S_2O_8$, 32 phr of propanal, and 0.34 phr of $Na_3PO_4$ and various reaction times at ($\blacklozenge$) 60, ($\blacksquare$) 70, and ($\blacktriangle$) 80 °C.

60, 70, and 80°C were 0.71, 0.19, and 0.19, respectively, as shown in Table II. It seems that the higher temperature resulted in better lowering of the [$\eta$] (i.e., a lower molecular weight can be obtained). This may be due to the increased temperature that results in increasing the formation of radicals on the molecular chain, leading to an increases in the rate of the degradation reaction as evaluated in the next section. However, if the reaction was

carried out by using higher amount of initiator (2 phr), the [$\eta$] values after 25 h at 60, 70, and 80°C were 0.42, 0.18, and 0.27, respectively. At the higher temperature, the rate of formation of the active radicals was increased, as was the rate of recombination of the macroradicals. Therefore, the [$\eta$] at 80°C was higher than at 70°C.

The rubber concentration used for the degradation reaction also affects the decrease of the molecular

**TABLE II**
**Results of Intrinsic Viscosity ([$\eta$]) and Kinetic Rate Constant ($k$) Obtained from**
**Degradation of PNR Latex at 60, 70, and 80°C**

| Samples | $K_2S_2O_8$ (phr) | Propanal (phr) | DRC (%) | Temperature (°C) | | | [$\eta$] after 25 h | $k \times 10^{-2}$ (s$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| LNR 7 | 1 | — | 32 | 5 | 60 | — | — | 0.71 | 2.38 |
| LNR 8 | 1 | — | 32 | 5 | — | 70 | — | 0.19 | 7.34 |
| LNR 9 | 1 | — | 32 | 5 | — | — | 80 | 0.19 | 11.33 |
| LNR 10 | — | 2 | 32 | 5 | 60 | — | — | 0.42 | 3.61 |
| LNR 11 | — | 2 | 32 | 5 | — | 70 | — | 0.18 | 8.10 |
| LNR 12 | — | 2 | 32 | 5 | — | — | 80 | 0.27 | 5.49 |

DRC, dry rubber content.

**TABLE III**
**Results of Intrinsic Viscosity ($[\eta]$), Viscosity-Average Molecular Weight ($M_v$), Weight-Average Molecular Weight ($M_w$), and Number-Average Molecular Weight ($M_n$) of Degraded Rubbers**

| Samples | $[\eta]^a$ | $M_v \ (\times 10^4)^b$ | $M_w \ (\times 10^4)^b$ | $M_n \ (\times 10^4)^b$ |
|---------|-----------|-----------|-----------|-----------|
| 1 | 0.20 | 2.12 | 5.52 | 0.32 |
| 2 | 0.21 | 2.41 | 6.82 | 1.95 |
| 3 | 0.24 | 3.37 | 8.15 | 2.79 |
| 4 | 0.35 | 4.01 | 9.62 | 1.61 |
| 5 | 0.55 | 7.01 | 11.60 | 2.09 |
| 6 | 0.83 | 13.05 | 22.21 | 3.03 |
| 7 | 1.14 | 16.48 | 29.61 | 2.21 |
| 8 | 1.36 | 20.42 | 33.39 | 5.46 |

[a] Measured by viscometer
[b] Measured by gel permeation chromatography.

weight of the PNR. Increasing the DRC may result in an increase of the possibility of chain recombination of polymeric radical species, which are generated during the degradation. It was not surprising to find therefore that the $[\eta]$ values were 0.18, 0.23, and 0.42 for 5, 10, and 15% DRC PNR latexes, respectively, with 2 phr of

$K_2S_2O_8$, 32 phr of propanal, and 0.34 phr of $Na_3PO_4$ and carried out at 70°C for 25 h.

## Kinetics of NR degradation

For the investigation of the kinetics of degradation of the PNR, the Mark–Houwink relationship in eq. (1) was employed. The $K$ and $a$ values were evaluated by using eight samples of different molecular weights of LNR that were prepared. The $[\eta]$ was achieved with a viscometer and the $M_v$, $M_w$, and $M_n$ were measured by GPC. The results are shown in Table III. The $K$ and $a$ values of the Mark–Houwink equation were evaluated from the plot of the $\ln[\eta]$ and $\ln M_v$ ($K = 3.46 \times 10^{-5}$, $a = 0.863$). These values are similar to the work reported by Sanchez.[18] These $K$ and $a$ values were further used for transformation of the $[\eta]$ of other samples into $M_v$

$$[\eta] = KM_v^a \tag{1}$$

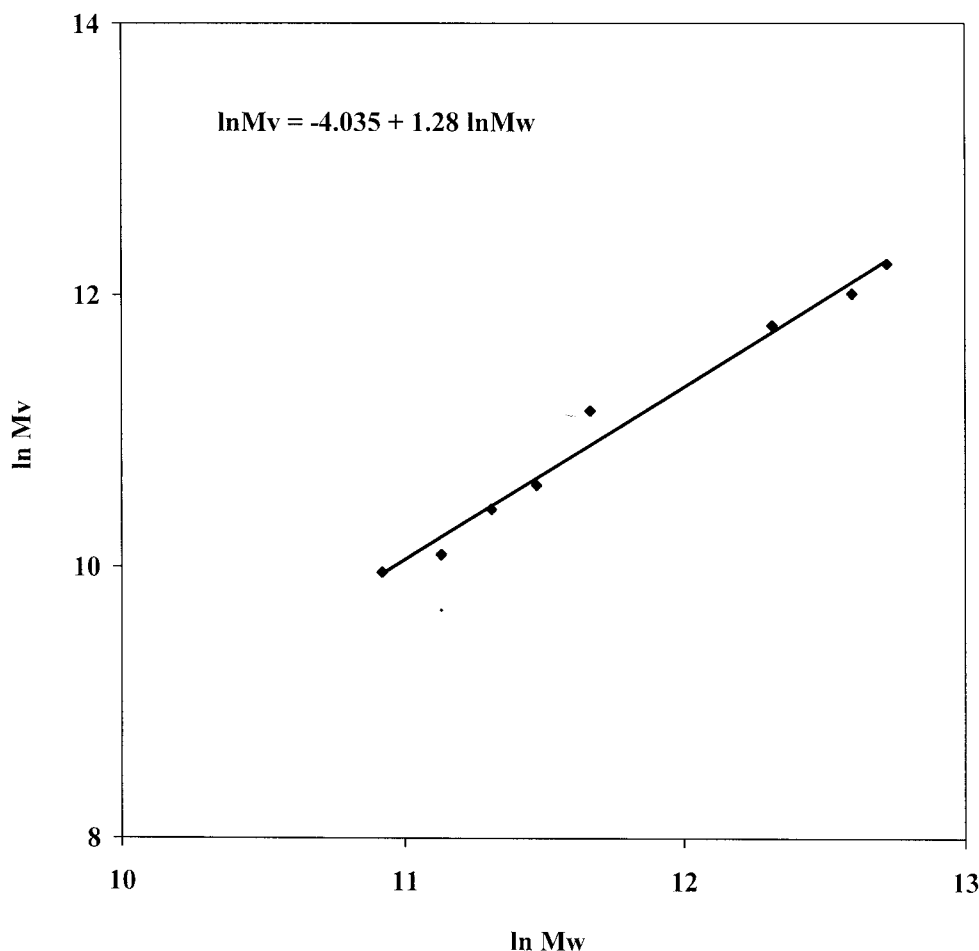The $M_v$ can also be expressed as in eq. (2). It has been reported in the literature that the $M_v$ and $M_w$ values



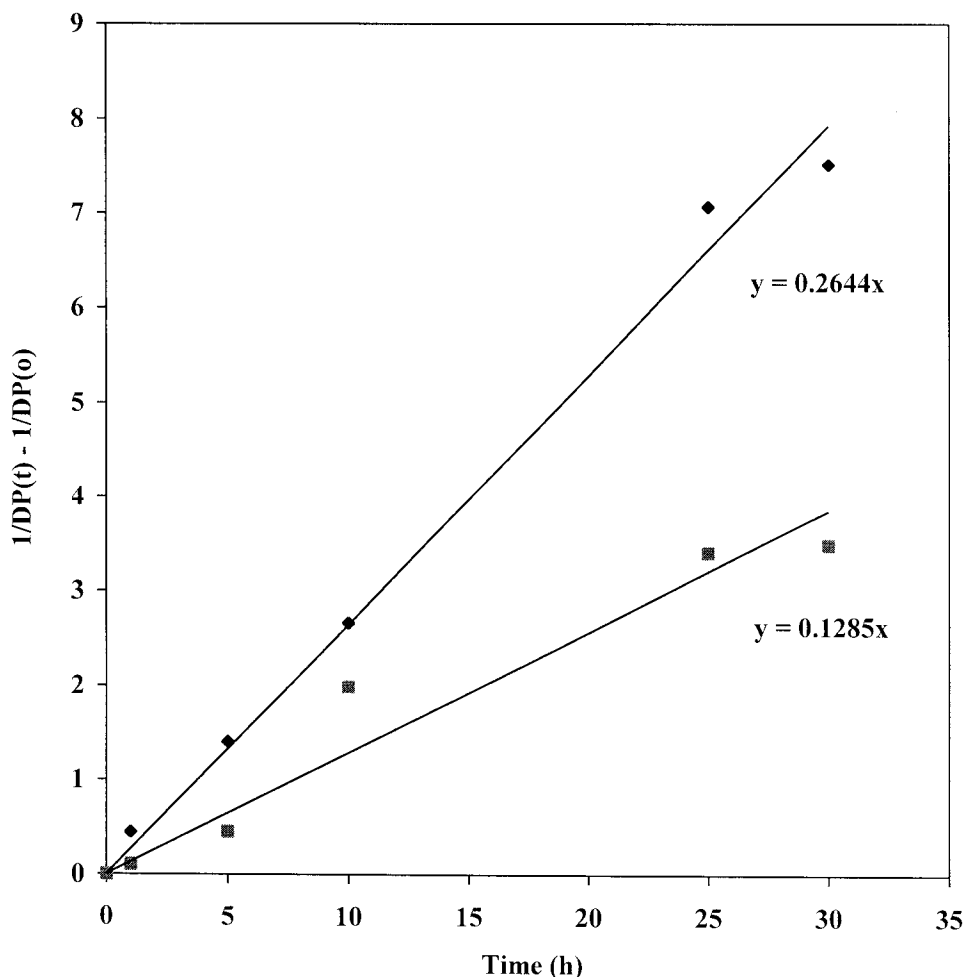**Figure 7** Plots of $\ln M_v$ and $\ln M_w$ of LNR.

**Figure 8** Plots of $1/DP_{(t)} - 1/DP_{(0)}$ versus the time of LNR prepared from 1 phr of $K_2S_2O_8$, 32 phr of propanal, and 0.34 phr of $Na_3PO_4$ at various reaction times with ($\blacklozenge$) 5% DRC PNR latex or ($\blacksquare$) 5% DRC NR latex.

are related to some extent.[19–21] For $a = 1$, $M_v$ is identical to $M_w$, as shown in eq. (3).

$$M_v = \left(\frac{\Sigma\ NiMi^{1+a}}{\Sigma\ NiMi}\right)^{1/a} \qquad (2)$$

if $a = 1$,

$$M_v = \frac{\Sigma\ NiMi^2}{\Sigma\ NiMi} = M_w \qquad (3)$$

By using the experimental results for $M_v$ and $M_w$ in Table III, it was found that plots of $\ln M_v$ and $\ln M_w$ (Fig. 7) show a straight line with a slope and an intercept equal to 1.28 and −4.035, respectively. The relationship of $M_v$ and $M_w$ can be converted in the form of eq. (4), and it is then used as a calibration curve for liquid rubbers at various conditions under study.

$$M_v = 1.77 \times 10^{-2} M_w^{1.28} \qquad (4)$$

The values of the weight-average degree of polymerization ($DP_w$) and number-average degree of polymerization ($DP_w$) were estimated from the values of $M_w$ and $M_n$ determined by GPC (see Table III). The plots of $DP_w$ versus $DP_n$ gave a straight line of the slope value of 6.27. The relationship of $DP_w$ and $DP_n$ is then expressed as in eq. (5).

$$DP_n = 6.27\ DP_n \qquad (5)$$

If the chain degradation occurred in a random scission manner, the degree of degradation is defined as the fraction of bonds broken ($\alpha$) as described in the literature.[22–24] In the degradation of a high molecular weight polymer, if every interunit bond in every molecule is equally liable to break, the $\alpha$ can be derived as in eq. (6).

$$\alpha = \frac{1}{DP_{n(t)}} - \frac{1}{DP_{n(0)}} = kt \qquad (6)$$

The kinetic rate constant ($k$) of NR degradation can be calculated where $DP_{n(0)}$ and $DP_{n(t)}$ are the $DP_n$ values at the initial time ($t = 0$) and time $t$, respectively.

By using eqs. (1), (4), and (5), the values of $[\eta]$ obtained from various conditions can be transformed into the values of $DP_n$. Therefore, the $k$ value of the degradation reaction can be evaluated from the slope of the plot of $1/DP_{n(t)} - 1/DP_{n(0)}$ at various reaction times. Figure 8 shows the plots of $1/DP_{n(t)} - 1/DP_{n(0)}$ versus the time of the degradation of PNR and NR using 5% DRC latex, 1 phr of $K_2S_2O_8$, 32 phr of propanal, and 0.34 phr of $Na_3PO_4$ at 70°C. The $k$ values of the degradation of PNR and unpurified NR were found to be (7.34 and 3.57) $\times$ $10^{-2}$ s$^{-1}$, respectively. These results showed that, in the same chemical degradation method, the PNR presented a higher rate constant than the NR. The rate constant of various degradation conditions such as the different amounts of initiator, the propanal, and temperature were also evaluated and presented in Tables I and II. It was clear that the rate of degradation of PNR at 60°C is slower than the reaction at 70 or 80°C (Table II).

To evaluate the activation energy of the degradation reaction, the kinetics of degradation of PNR at 60, 70, and 80°C using 5% DRC PNR latex, 1 phr of $K_2S_2O_8$, 32 phr of propanal, and 0.34 phr of $Na_3PO_4$ were investigated. The $k$ values of the reactions at 60, 70, and 80°C were found to be (2.38, 7.34, and 11.33) $\times$ $10^{-2}$ s$^{-1}$, respectively. The highest rate constant is found at 80°C. The activation energy for cleavage of a carbon—carbon single bond of a rubber molecule was calculated from the Arrhenius equation.[25] The plot of ln $k$ versus the reciprocal of a different temperature gave an activation energy value of 76.56 kJ mol$^{-1}$. This value is actually less than the activation energy (108.0 kJ mol$^{-1}$) needed to break down the isoprene unit of NR carried in cyclohexane at 60–100°C.[26] This result showed that the chemical degradation of PNR in this work is much faster than the thermal degradation of NR.

## CONCLUSIONS

There were better degradation results for NR, which was purified by the elimination of proteins, than the unpurified NR. This may be due to the presence of nonrubber constituents, which act as antioxidants, or the presence of microgels, which retard the oxidative degradation in the system. It was found that the radical initiator $K_2S_2O_8$, propanal, and the temperature played important roles in the degradation reaction. The kinetic rate constants at different conditions of degradation of PNR were measured. The highest kinetic rate constant was found to be 11.33 $\times$ $10^{-2}$ s$^{-1}$. By using 5% DRC PNR latex with 1 phr of $K_2S_2O_8$, 32 phr of propanal, and 0.34 phr of $Na_3PO_4$, the activation energy for oxidative degradation was found to be 76.56 kJ mol$^{-1}$.

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