

## BROMINATION OF NATURAL RUBBER WITH *N*-BROMOSUCCINIMIDE

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### ABSTRACT

The mechanism of bromination of natural rubber (NR) was studied by solution-state <sup>1</sup>H-NMR spectroscopy. The bromination of NR was carried out at 20–50 °C with *N*-bromosuccinimide as the brominating agent, and the kinetic study of bromination was conducted under nitrogen atmosphere at 30–50 °C for various reaction times. The influence of bromine atom substituent on the bromination rate constant (*k*) also was investigated. Bromine atom content was found to be dependent upon the reaction time, indicating first-order kinetics. The activation energy of bromination of NR, calculated from the reaction rate constants, was 19.3, 5.5, and 5.8 kJ mol<sup>-1</sup> for bromine atom linked to carbon atom with methylene proton and methylene protons, respectively. [doi:10.5254/rct.21.78980]

### INTRODUCTION

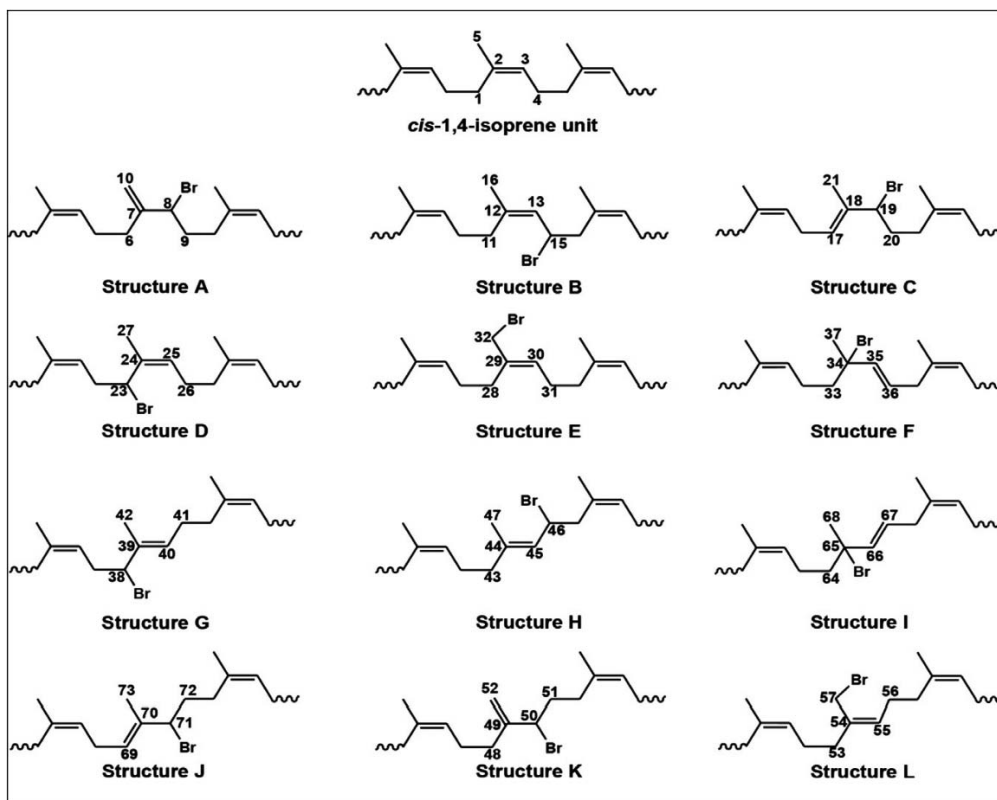
Bromination of NR with *N*-bromosuccinimide (NBS) is a very well-known method for rubber modification<sup>1–5</sup> as an allylic bromine addition, which is useful as an intermediate initiator for graft copolymerization<sup>6–8</sup> and Suzuki–Miyaura cross-coupling reaction.<sup>9,10</sup> NBS is one of the most important brominating agents, especially for use as a substitute for Br<sub>2</sub> in a radical bromination. The advantage of NBS is that it provides a low-level concentration of Br<sub>2</sub>; for example, bromine atom from NBS is introduced to a carbon adjacent to a double bond, that is, the allylic position, known as Wohl–Zeigler bromination reaction.<sup>11–14</sup>

The addition of bromine atom adjacent to the carbon double bond has considerable added value to the product. For example, superior properties of rubber such as cure reactivity, polarity of the molecular chain, and compatibility were improved due to the remaining double bond after bromination.<sup>15,16</sup> It is thus important to anticipate performing a kinetic study to investigate the bromination of NR.

Bromination with NBS has many reaction steps.<sup>17–19</sup> The bromine atom is maintained at a low concentration throughout the reaction by formation from NBS and hydrogen bromide. The bromination of *cis*-1,4-isoprene units is divided into four steps: (1) homolytic cleavage of NBS to produce a succinimidyl radical and bromine radical; (2) hydrogen abstraction of *cis*-1,4-isoprene units with the bromine radicals, which is suggested to be the hydrogen abstracting species, at the allylic position to form allylic carbon radicals; (3) rapid reaction of the resulting hydrogen bromide with NBS to provide bromine; and (4) reaction between the allylic carbon radical and bromine to produce the brominated NR.

In previous work,<sup>20</sup> nine plausible structural units of brominated *cis*-1,4-isoprene units, which were prepared by the bromination of NR with NBS in a refluxing solution of dichloromethane, were investigated by using one- and two-dimensional solution-state NMR spectroscopy. The small <sup>1</sup>H signals at 3.98, 4.16, and 4.44 ppm appeared in <sup>1</sup>H-NMR spectra for brominated NR. These signals were assigned to the allylic bromine position adjacent to the double bond of the brominated *cis*-1,4-isoprene units shown in Scheme 1. The signal at 3.98 ppm was due to the methylene protons of H32 and H57. The signal at 4.16 ppm was assigned to the methine protons of H15, H23, H38, and H46,

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SCHEME 1. — Structural units of the *cis*-1,4-isoprene unit and the brominated *cis-trans*-1,4-isoprene units.<sup>20</sup>

whereas the signal at 4.44 ppm was assigned to the methine protons of H8, H19, H50, and H71. However, the brominated atom position of the resulting brominated NR may induce the creation of the new product, for example, the graft copolymerization of styrene onto allylic brominated NR through activators regenerated by electron transfer atom transfer radical polymerization.<sup>21</sup> Thus, it is important to ensure the mechanism of bromination of *cis*-1,4-isoprene units with NBS on the basis of kinetic data estimated from the intensity ratio of the <sup>1</sup>H-NMR signals.

Herein, the bromination of deproteinized NR was performed with NBS in dichloromethane solution. The bromination was analyzed through solution-state <sup>1</sup>H-NMR spectroscopy. The activation energy ( $E_a$ ) of the bromination was determined on the basis of temperature dependency of the kinetic constant of bromination. The mechanism of the bromination of NR was concluded, based on the estimated values of  $E_a$  and signals that appeared in <sup>1</sup>H-NMR spectra for brominated *cis*-1,4-isoprene units.

## EXPERIMENTAL

### MATERIALS

NR latex used in this study was commercial high ammonia NR latex (Goldenhope, Malaysia). Urea (99.5%, Nacalai Tesque, Tokyo, Japan) and sodium dodecyl sulfate (99%, Kishida Reagents Chemicals, Osaka, Japan) were used to prepare the deproteinized NR latex.<sup>22,23</sup> Dichloromethane, toluene (99%), methanol (99%), and chloroform-*d* (99.8%) were purchased from Wako Pure

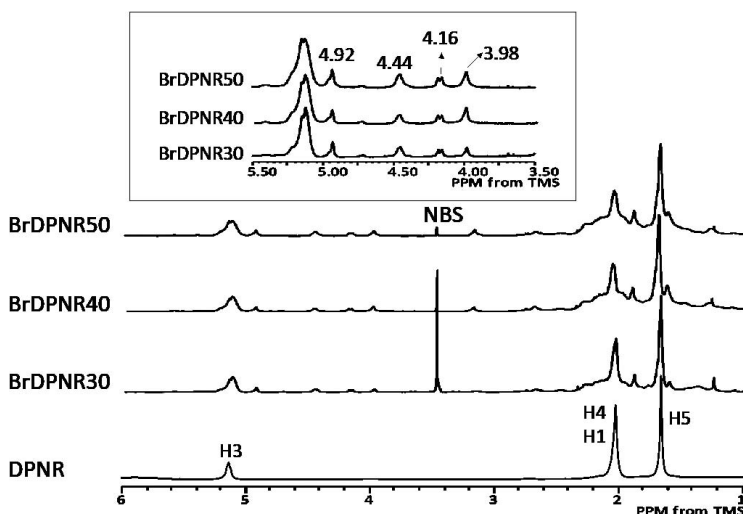


FIG. 1. —  $^1\text{H}$ -NMR spectra for DPNR, BrDPNR30, BrDPNR40, and BrDPNR50.

Chemical Industry (Osaka, Japan). NBS was purchased from Tokyo Chemical Industry (Tokyo, Japan). All reagents were purified before use.

#### PREPARATION OF BROMINATED NR IN SOLUTION STATE

Bromination of NR was performed with NBS. The dried deprotonized NR (DPNR) was dissolved into dichloromethane and then charged with  $\text{N}_2$  gas for an hour at  $30\text{--}50^\circ\text{C}$  (hereafter abbreviated to BrDPNR30, BrDPNR40, and BrDPNR50). The bromination of DPNR was performed by stirring the solution after adding NBS for  $30\text{--}240$  min. The product, brominated NR (BrDPNR), was recovered as a precipitate by pouring the resulting precipitate into excess amount of methanol. The precipitate, BrDPNR, was washed, twice, by toluene–methanol precipitation method, and dried at  $30^\circ\text{C}$  under reduced pressure.

#### CHARACTERIZATION

Solution-state NMR spectroscopy was performed with a ECA-400 NMR spectrometer (JEOL, Tokyo, Japan) for DPNR and BrDPNR. The DPNR and BrDPNR were dissolved into chloroform-*d* without tetramethylsilane. Chemical shifts were referred to chloroform in chloroform-*d*.  $^1\text{H}$ -NMR measurement at  $399.65$  MHz and  $30^\circ\text{C}$  was performed by 512 scans with a pulse repetition time of 7 s at  $45^\circ$  pulse of  $1.8\ \mu\text{s}$  and a relaxation delay of 4.24 s.

#### RESULTS AND DISCUSSION

Figure 1 shows the  $^1\text{H}$ -NMR spectra for DPNR. Three major signals appeared at 1.66, 2.02, and 5.10 ppm that were assigned to the methyl proton (H5), methylene proton (H1, H4), and methine proton (H3) of the *cis*-1,4-isoprene units, respectively. After bromination, the  $^1\text{H}$ -NMR spectra for brominated NR, with bromination with NBS at  $30^\circ\text{C}$  (BrDPNR30),  $40^\circ\text{C}$  (BrDPNR40), and  $50^\circ\text{C}$  (BrDPNR50), are shown in Figure 1. The insets are enlarged  $^1\text{H}$ -NMR spectra ranging from 3.3 to 5.5 ppm. Three major signals appearing at 1.66, 2.02, and 5.10 ppm were assigned to the methyl proton H5, the methylene protons H1 and H4, and the methine proton H3 of the *cis*-1,4-

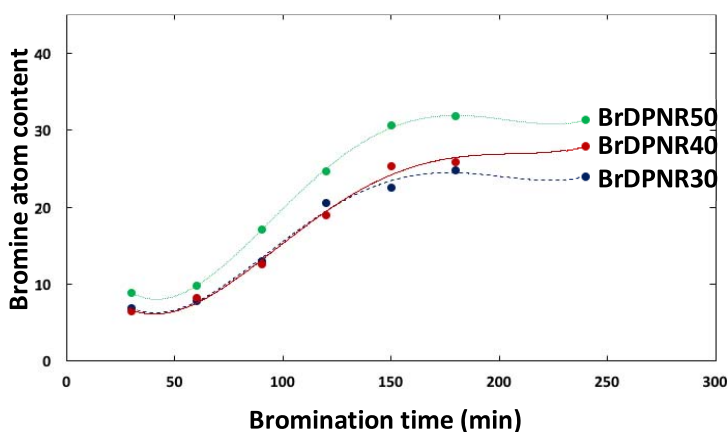


FIG. 2. — Bromine atom content for BrDPNR30, BrDPNR40, and BrDPNR50 vs the bromination time.

isoprene units, respectively. After bromination of DPNR with NBS at 30, 40 and 50 °C, a small signal appeared at 3.98, 4.16, and 4.44 ppm. These signals were assigned to the structural units of brominated NR (Scheme 1), according to previous work.<sup>20</sup> The signal at 3.98 ppm was assigned to the methylene protons of H32 and H57 (Scheme 1). The signal at 4.16 ppm was assigned to the methine protons of H15, H23, H38, and H46, whereas the signal at 4.44 ppm was assigned to the methine protons of H8, H19, H50, and H71 (Scheme 1). Moreover, the signal at 4.92 ppm was assigned to the methine protons of H10 and H52 (Scheme 1).

The bromine atom content of BrDPNR was estimated from intensity ratio of the signals 3.98, 4.16, 4.44, 4.92, and 5.10 ppm by using the following equations:

$$x_{\text{Br}}(\text{mol}\%) = \frac{I_{\text{Br}}}{(I_{5.10} + I_{4.92}/2) + (I_{\text{Br}})} \times 100 \quad (1)$$

$$I_{\text{Br}} = I_{3.98}/2 + I_{4.16} + I_{4.44} \quad (2)$$

where  $I$  is the signal intensity and the subscript denotes the chemical shift (ppm).

Figure 2 shows a plot of bromine atom content versus the bromination time for BrDPNR30, BrDPNR40, and BrDPNR50. The value of bromine atom content for BrDPNR30, BrDPNR40, and BrDPNR50 increased at the initial stage and reached to 30% when the bromination time was 150 min. Thereafter, it was constant, even though the reaction time was prolonged to 240 min. Therefore, the rate of formation of bromine atoms may be calculated from the value within 150 min from the bromination time of 60 min.

Figure 3 shows a plot of the intensity of the signals at 3.98, 4.16, and 4.44 ppm versus the bromination time for BrDPNR30. The intensity of the signals at 3.98, 4.16, and 4.44 ppm was dependent upon the bromination time. The value of the intensity reached the maximum value at the bromination time of 150 min and then was constant. Therefore, the bromination of NR was investigated on the reaction time. Figure 4 shows semi-logarithmic plots of the intensity of the signals at 3.98, 4.16, and 4.44 ppm versus the bromination time. The intensity of the signals at 3.98, 4.16, and 4.44 ppm were proportional to the bromination time at 60–150 min.

The value of rate constant of reaction,  $k$ , for BrDPNR30, BrDPNR40, and BrDPNR50 was determined as a slope of the semi-logarithmic plot of the intensity of the signals at 3.98, 4.16, and 4.44 ppm versus the bromination time. The estimated values of  $k$  are presented in Table I.

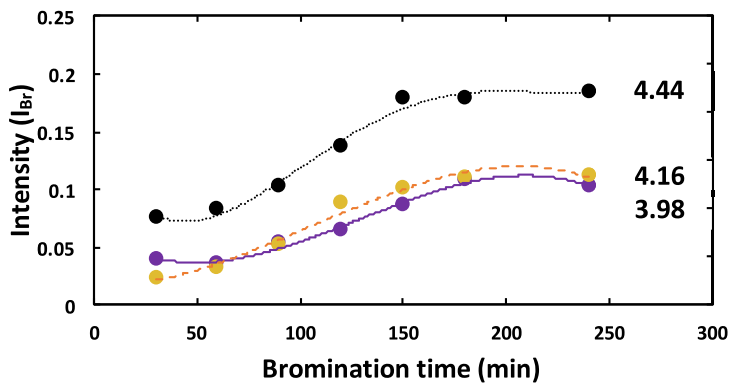


FIG. 3. — Intensity of the signals at 3.98, 4.16 and 4.44 ppm vs bromination time.

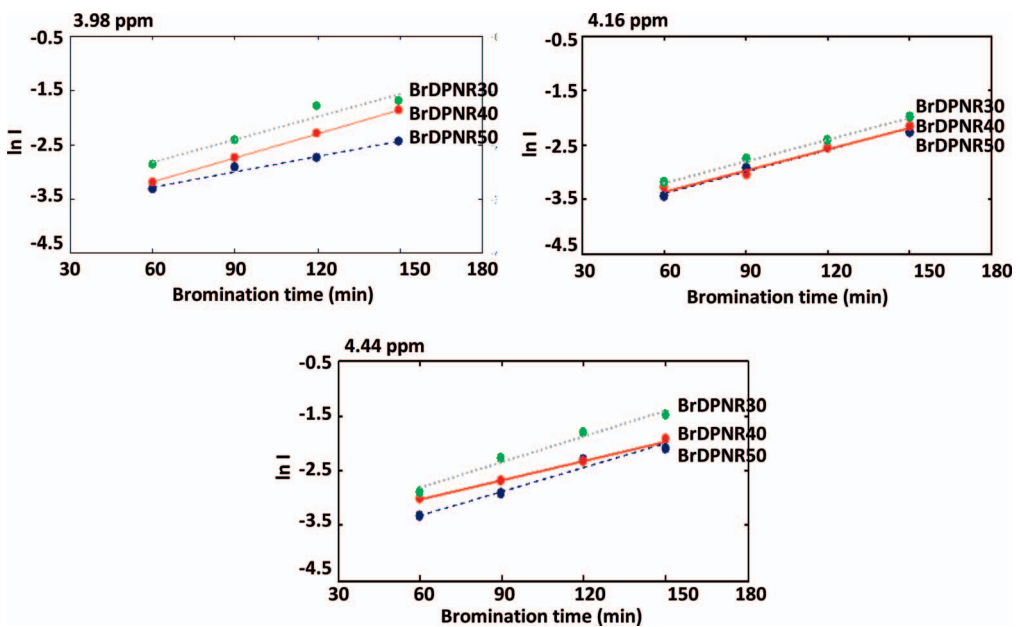


FIG. 4. — Semi-logarithmic plots of intensity of the signals at 3.98, 4.16, and 4.44 ppm for BrDPNR30, BrDPNR40, and BrDPNR50 vs bromination time.

TABLE I  
ESTIMATED VALUE OF  $k$  OF REACTION

Bromination temp., °C	Rate constant of reaction, s <sup>-1</sup>		
	3.98 ppm	4.16 ppm	4.44 ppm
30	0.0099	0.013	0.0134
40	0.013	0.013	0.0149
50	0.0159	0.0149	0.0165

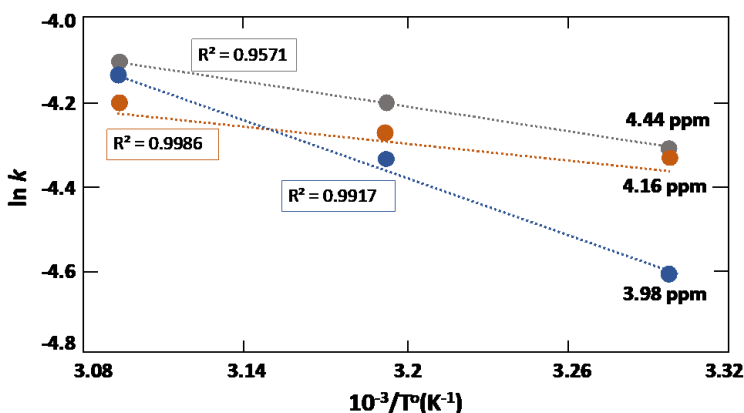


FIG. 5. — Plot of logarithmic value for the  $k$  for the signals at 3.98, 4.16, and 4.44 ppm vs reciprocal temperature (Arrhenius plot).

The value of  $k$  is a proportionality factor of the chemical kinetics that depends upon the bromination temperature. From Table I, the temperature is increased as the  $k$  of three different structures increases. Thus, the logarithmic value of  $k$  was plotted against a reciprocal temperature, that is, the Arrhenius plot. The  $E_a$  was estimated from a slope of the Arrhenius equation, as follows:

$$\ln k = \frac{-E_a}{RT} + \ln A \quad (3)$$

where  $k$  is the rate constant of reaction ( $s^{-1}$ );  $A$  is the frequency factor;  $E_a$  is the activation energy ( $kJ mol^{-1}$ ), the minimum energy required to initiate a chemical reaction and specific to a particular reaction;  $R$  is the gas constant ( $J mol^{-1} K^{-1}$ ) that is equal to  $8.314 J mol^{-1} K^{-1}$ ; and  $T$  is the absolute temperature (K).

As shown in Figure 5 and Table II, the estimated value of the  $E_a$  of the signal at 3.98 ppm was  $19.3 kJ mol^{-1}$ , the signal at 4.16 ppm was  $5.5 kJ mol^{-1}$ , and the signal at 4.44 ppm was  $5.8 kJ mol^{-1}$ . These were similar to the value of the  $E_a$  of the hydrogen abstraction of bromine in the reaction (Table III), because the hydrogen abstraction step is rate limiting and the product composition is governed by the selectivity of the hydrogen abstraction step.<sup>24</sup> In addition, the difference in  $E_a$  may be explained by the possibility of the bromine atom position as a dominate structure. However, the proportions of three structures, which were assigned from the signals 3.98, 4.16, and 4.44 ppm, were unclear. Therefore, how the precise proportions relate with the  $E_a$  diagram was examined, and the results will be reported in the subsequent paper.

Moreover, there is a substantial kinetic preference for hydrogen abstraction in the order secondary > primary. It is demonstrated that the reaction of NR with NBS in dichloromethane

TABLE II  
ESTIMATED  $E_a$  VALUES

Signals at	$E_a$ , kJ/mol
3.98 ppm	19.3
4.16 ppm	5.5
4.44 ppm	8.5

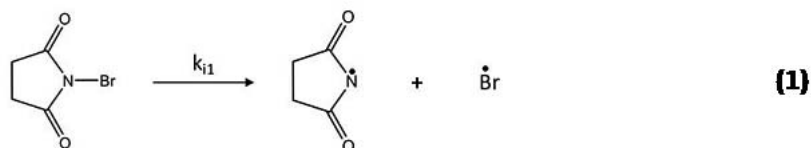
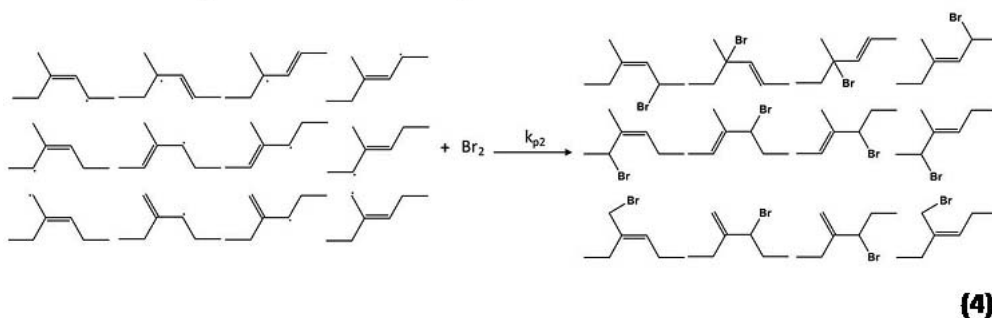
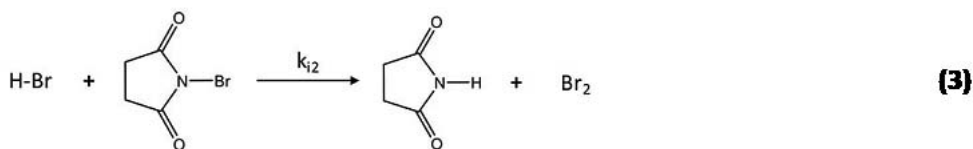
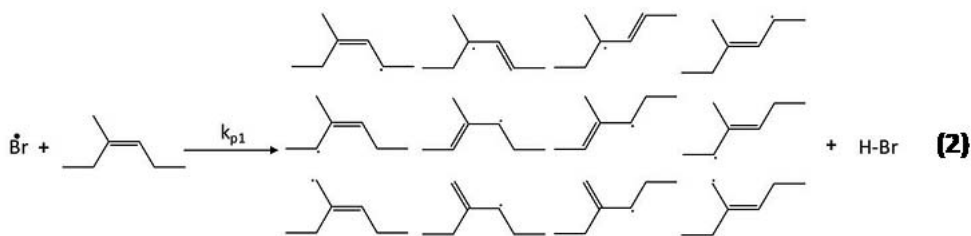
**Initiation:****Propagation:****Termination:**

FIG. 6. — Mechanism of the bromination of NR with NBS.

solution occurs by a radical process. The plausible mechanism of the bromination of NR is shown in Figure 6. The bromination is initiated by homolytic cleavage of NBS, which generates a succinimidyl radical and a bromine radical. In the propagation step, the hydrogen abstraction with bromine radical and the reaction between the allylic carbon radical and bromine are realized.

TABLE III  
 $E_a$  OF FREE RADICAL BROMINATION AT HYDROGEN ATOM ABSTRACTION  
 STEP 2<sup>a</sup>

	$E_a$ , kJ/mol
Primary	18.0
Secondary	11.7

<sup>a</sup> See introduction for the four steps involved in bromination of *cis*-1,4-isoprene units.

## CONCLUSION

The bromination of *cis*-1,4-isoprene units with *N*-bromosuccinimide (NBS) was found to be first-order reaction; that is, the reaction rate is independent with the concentration of NR. The activation energy of bromination of NR was 19.3, 5.5, and 5.8 kJ mol<sup>-1</sup> for signals at 3.98, 4.16, and 4.44 ppm, respectively. The value of the activation energies was similar to the value of the activation energy of the hydrogen abstraction of bromine in the reaction. It was found that the plausible mechanism of the bromination of NR with NBS was suggested to start with the hydrogen abstraction at the allylic position to form allylic brominated *cis*-1,4-isoprene unit.

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