Quantitative Analysis of Modified Rubber through Latex-state NMR Spectroscopy

（ラテックス NMR 分光法による改質ゴムの定量分析）

A Doctor Thesis Submitted to

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論 文 内 容 の 要 旨

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Quantitative analysis through nuclear magnetic resonance (NMR) spectroscopy is widely recognized to be an important technique for polymer colloids such as emulsion, latex and so forth. It may allow to investigate reactions of the polymer colloids, which take place in polymer particles dispersed in water. The analysis may be applicable to not only determination of constitutional units of polymers but also investigation of mechanism of the reactions of the polymer colloids. One of the analytical techniques for the polymer colloids is latex-state NMR spectroscopy, which has been used for qualitative analysis of the polymer colloids. Recently, a suitable condition for the latex-state NMR spectroscopy was determined for natural rubber latex, and the latex-state NMR spectroscopy was preliminarily applied to quantitative analysis for vulcanized natural rubber. Based on the preliminary results, it may be possible to apply the latex-state NMR spectroscopy to the quantitative analysis for the polymer colloids. In the present study, epoxidation of natural rubber and prevulcanization of natural rubber and synthetic isoprene rubber (IR) were investigated by latex-state NMR spectroscopy, in which contents of epoxy groups and crosslinking junctions were determined. Time dependency of the contents during the reactions was also investigated.

Attempt to determine the epoxy group content of epoxidized natural rubber was performed by latex-state NMR spectroscopy. The epoxidized natural rubber was prepared by epoxidation of deproteinized natural rubber (DPNR) with freshly prepared peracetic acid in latex stage. Half width and signal-to-noise (S/N) ratio of signals in latex-state NMR spectrum for epoxidized DPNR (EDPNR) were similar to those of solution-state NMR spectrum at temperatures above 50 ˚C. The narrow half width and sufficient S/N ratio of the signals demonstrated that the high resolution was maintained in latex-state NMR spectrum for EDPNR. Chemical shift values of signals and the epoxy group content of EDPNR determined by latex-state NMR spectroscopy were found to be similar to those determined by solution-state NMR spectroscopy.

Prevulcanization of natural rubber was investigated by latex-state NMR spectroscopy. Natural rubber was prevulcanized with zinc-2-mercaptobenzothiazole (ZMBT) as an accelerator in latex stage at 70 - 90 ˚C. A small signal at 37 ppm, which appeared after prevulcanization, was assigned to secondary carbons adjacent to carbons linking to sulfur atoms and a signal at 50 ppm was assigned to tertiary and quaternary carbons linking to sulfur atoms. Intensity of the signals increased as the prevulcanization time was prolonged, in which kinetic constants were determined.

Activation energy of the prevulcanization of natural rubber in latex was estimated from the kinetic constants for the signals at 37 and 50 ppm: that is, 51.5 and 47.2 kJ/mol for the signals at 37 and 50 ppm, respectively.

Prevulcanization of isoprene rubber (IR) was also investigated by latex-state NMR spectroscopy. The prevulcanization of IR was carried out with zinc-dibutyldithiocarbamate (ZDBC) as an accelerator in latex stage at 70 − 90 ˚C. The signal at 44 ppm, which appeared after prevulcanization, was assigned to secondary carbons adjacent to carbons linking to sulfur atoms, whereas the signal at 58 ppm was assigned to tertiary and quaternary carbons linking to sulfur atoms. The activation energies of the prevulcanization, i.e., 83.2 and 72.7 kJ/mol, were estimated from the intensity of the signals at 44 and 58 ppm, respectively, which were similar to those of decomposition of sulfur to generate sulfur radicals. The plausible mechanism of prevulcanization was proposed to be the following two: that is, the hydrogen abstraction with sulfur radical and addition of sulfur radical to carbon-carbon double bonds.

Effect of proteins on the vulcanization of natural rubber was investigated to understand the difference in the prevulcanization between natural rubber and IR. Removal of the proteins from natural rubber was made by incubation of high ammonium natural rubber (HANR) latex with 0.1 w/w% urea for 1 hour in the presence of surfactant at room temperature to obtain DPNR latex. The DPNR latex was compounded with commercial vulcanizing agents. The compounded DPNR was prevulcanized at 60 ˚C for 25 min, followed by vulcanization to prepare thin film rubber. Contents of nitrogen, water soluble protein and volatile fatty acid of HANR, DPNR and prevulcanized DPNR latexes were determined. Size and surface charge of the particles in the latex were determined by dynamic light scattering and zeta potential, respectively. In addition, the mechanical properties of vulcanized DPNR thin films were found to be improved after mixing with polymer coating.

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CHAPTER 1
General Introduction

Quantitative analysis through nuclear magnetic resonance (NMR) spectroscopy is widely recognized to be an important technique for polymer colloids such as emulsion, latex and so forth. It may allow to investigate reactions of the polymer colloids, which take place in polymer particles dispersed in water as a heterogeneous reaction. The analysis may be applicable to not only determination of constitutional units of polymers but also investigation of mechanism of the reactions of the polymer colloids. It is, thus, necessary to develop the quantitative analysis of the NMR spectroscopy for the polymer colloids.

In the last five decades, the latex-state NMR spectroscopy has been used for qualitative analysis for polymer colloids: for instance, hydrolysis of a polymer dispersed in water as a particle. [1] It was also applied to determination of dry rubber content (DRC) of natural rubber latex. [2,3] Recently, a suitable condition for the latex-state NMR spectroscopy was determined for natural rubber latex, and the latex-state NMR spectroscopy was preliminarily applied to quantitative analysis for vulcanized natural rubber. [4] Based on the preliminary results, one may apply the latex-state NMR spectroscopy to the quantitative analysis for the polymer colloids.

In the present study, epoxidation of natural rubber and prevulcanization of natural rubber and synthetic isoprene rubber (IR) was investigated by latex-state NMR spectroscopy, in which contents of epoxy groups and crosslinking junctions were determined. Natural rubber was purified in latex stage by removal of proteins to prepare deproteinized natural rubber (DPNR). DPNR was epoxidized with peracetic acid in latex stage. Natural rubber and IR was prevulcanized with sulfur, ZnO and accelerators in latex stage. First, the latex-state NMR spectroscopy was performed for determination of epoxy group content of epoxidized

DPNR (EDPNR) latex. The results were compared with those obtained by solution-state NMR spectroscopy. Second, the time dependency of intensity ratio of small signals, assigned to crosslinking junctions of prevulcanized natural rubber, was investigated to assure the quantitative analysis through latex-state NMR spectroscopy. Third, the kinetic study was performed to investigate the prevulcanization of IR, which lead to the mechanism of the prevulcanization. Fourth, the effect of proteins on the vulcanization of natural rubber was investigated to understand the difference in the prevulcanization between natural rubber and IR.

1.1 Quantitative analysis of NMR spectroscopy

High resolution NMR spectroscopy has been applied to both qualitative and quantitative analyses for polymer solution and polymer solid. Chemical environments of constitutional atoms of the polymers are investigated by solution- and solid-states NMR spectroscopy. Here, fundamental principle of the NMR spectroscopy is shown by the following expression, using Hamilton operator:

$$\Psi H = \Psi E \qquad \text{(Eq. 1-1)}$$

$$H = H_z + H_{CSA} + H_{DD} + H_Q \qquad \text{(Eq. 1-2)}$$

where H_z represents the Zeeman term, H_{CSA} the chemical shift anisotropy term, H_{DD} the dipole-dipole interaction term and H_Q the quadrupolar interaction term. [5] Among these, the H_{CSA}, H_{DD} and H_Q must be eliminated to observe the H_z.

High resolution solution-state NMR spectroscopy has been well established for polymer solution, since a molecular movement of the polymer is sufficiently high to eliminate the H_{CSA} and H_{DD}. In contrast, high resolution solid-state NMR spectroscopy is performed for polymer solid by applying various techniques to eliminate the H_{CSA} and H_{DD}, which are expressed by the following equations:

$$H_{DD} \alpha \sum_{i<j} ((3\cos^2 \theta_{ij} - 1) \times (I_i I_j - 3I_{iz} I_{jz}))$$ (Eq. 1-3)

$$H_{CSA} \alpha (B_x, B_y, B_z) \begin{pmatrix} S_{xx} & S_{xy} & S_{xz} \\ S_{yx} & S_{yy} & S_{yz} \\ S_{zx} & S_{zy} & S_{zz} \end{pmatrix} \begin{pmatrix} I_x \\ I_y \\ I_z \end{pmatrix}$$ (Eq. 1-4)

where θ is the orientation angle between two nuclei, I the magnetic moments, B the external magnetic field and S the magnetic shielding constant. According to the expressions, the value of $(3\cos^2\theta$-1) becomes zero, when the solid material is rotated at 54.7° to the direction of the external magnetic field. The angle of 54.7° is so-called the "magic angle" and this technique is generally known as magic angle spinning (MAS). The chemical shift anisotropy and dipole-dipole interaction in solid is, thus, eliminated or at least reduced by MAS. The use of MAS together with cross-polarization provides high resolution for solid-state NMR spectroscopy. [5,6]

For rubbery materials, the dipole-dipole interaction is known to influence the resolution for solid-state NMR spectroscopy. Two methods are, in fact, developed to eliminate the dipole-dipole interaction; that is, magic angle spinning with dipole-decoupling (DD-MAS) and multi pulse sequence. [7] Recently, field-gradient fast magic-angle spinning (FG-FMAS) solid-state NMR spectroscopy was developed for the rubbery materials, [8] in which the dipole-dipole interaction was eliminated by fast magic angle spinning. This technique is useful for structural characterization of the rubbery materials, i.e., crosslinking junctions of vulcanized rubbers. The dipole-dipole interaction of the vulcanized rubbers is eliminated by FG-FMAS spectroscopy at the spinning rate of more than 20 kHz. The FG-FMAS probe allow to use various pulse sequences such as distortionless enhancement by polarization transfer (DEPT) and attached proton test (APT) measurements and two-dimensional correlation measurement.

The latex-state NMR spectroscopy originates from multi pulse sequence technique. In the latex, a rotational movement of polymer particles as a dispersoid occurs significantly in various directions. The particles may be irradiated from various directions due to changes in a rotational axis, even though irradiation with a NMR spectrometer is performed in one direction. The resolution of latex-state NMR spectroscopy may, thus, be dependent upon a diameter of the particles. The high resolution latex-state ^{13}C NMR spectroscopy is applied to a structural characterization of natural rubber, since natural rubber is isolated from *Hevea brasiliensis* as a latex. [4,9] Preliminary studies on the latex-state NMR spectroscopy have been performed for not only natural rubber latex but also various polymer latexes: for instance, the observation of hydrolysis on the surface of polymethyl methacrylate (PMMA) dispersoid in water by Tarcha [1] and the determination of DRC for natural rubber latex by Ang [2] and Gambhir [3].

1.2   Quantitative analysis through latex-state NMR spectroscopy

High resolution latex-state NMR spectroscopy may assure reliability and accuracy of the quantitative analysis. For instance, in the last decade, isomeric unit contents and sequence distribution of the isomeric units of crosslinked polybutadiene (PB) were analyzed through latex-state NMR spectroscopy. [10] The resolution of the latex-state NMR spectrum was compared with those of solution-state NMR and solid-state NMR spectra. The latex-state ^{13}C NMR spectrum for emulsion polymerized PB containing 80 w/w% gel fraction is shown in Figure 1-1, together with the solution-state NMR and solid-state NMR spectra. The latex-state NMR spectrum shows sharp signals with narrow half width, in which no background appeared.
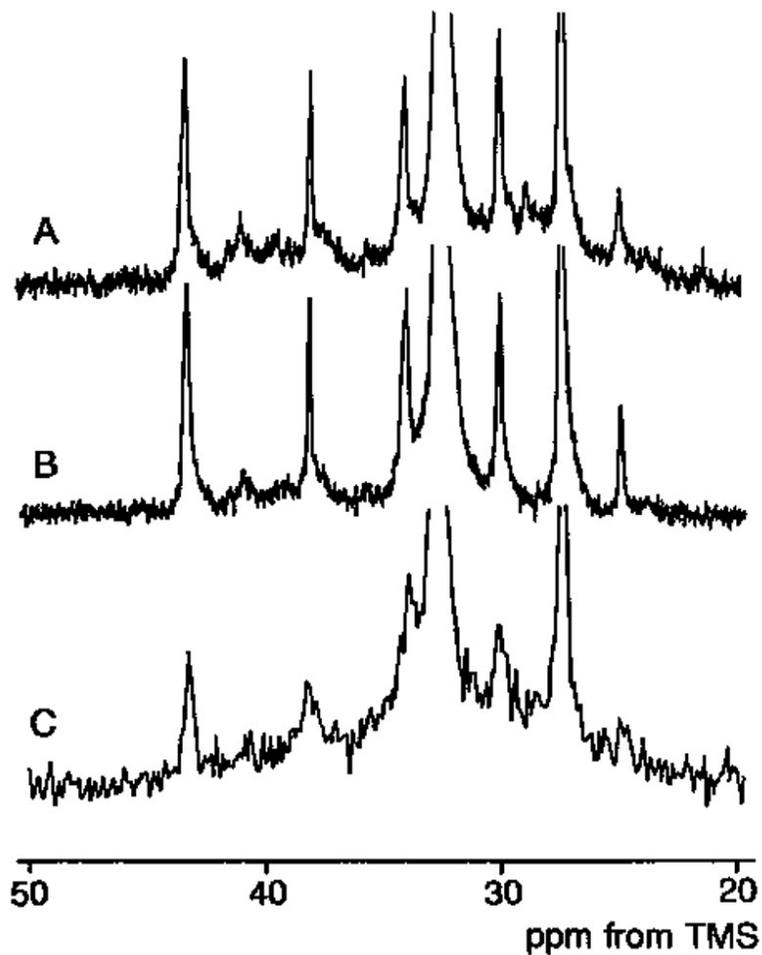
Figure 1-1 ^{13}C NMR spectra for polybutadiene containing 80 w/w% of gel: (A) solution-state (10% w/v% CDCl$_3$), (B) latex-state (10% w/v% dry rubber content) and (C) solid-state [10]

Condition of measurement was investigated for high resolution latex-state NMR spectroscopy. [11] It was reported that the high resolution latex-state NMR spectroscopy was accomplished at DRC of 10 w/w%, surfactant concentration of less than 1 w/w%, temperature of higher than T_g+70 K and no spinning of sample tube, as shown in Figure 1-2. Using the latex-state NMR spectroscopy under the suitable condition, the quantitative analysis may be achieved for the polymer colloids.

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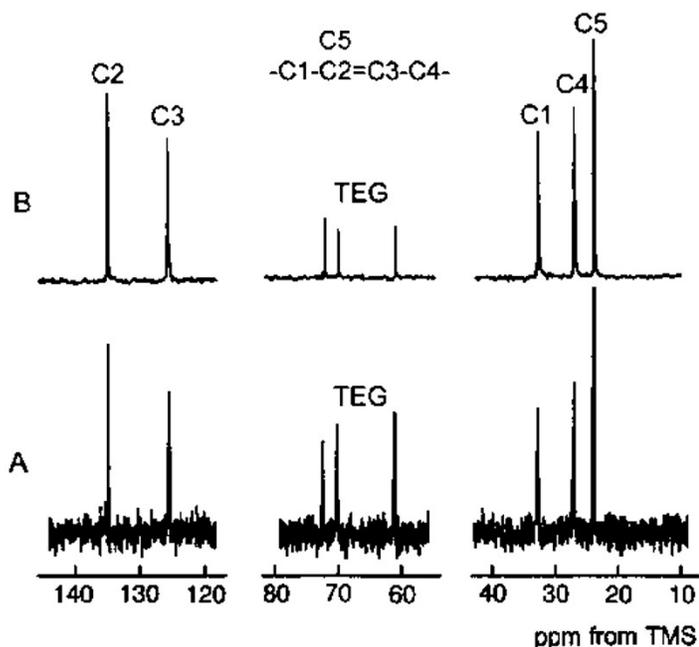
Figure 1-2 Latex-state ^{13}C NMR spectra for DPNR obtained from:

(A) with spinning of sample tube and (B) without spinning of sample tube [11]

1.3 Outline of this thesis

This thesis was divided into 6 chapters, which devoted to the quantitative analysis for polymer colloids through latex-state NMR spectroscopy. The content of each chapter was briefly described below:

In Chapter 1, "General introduction", background and current status were described for the latex-state NMR spectroscopy.

In Chapter 2, "Latex-state NMR spectroscopy for quantitative analysis of epoxidized deprotenized natural rubber", attempt to determine the epoxy group content of epoxidized natural rubber was performed by latex-state NMR spectroscopy. The epoxidized natural rubber was prepared by epoxidation of deproteinized natural rubber (DPNR) with freshly prepared peracetic acid in latex stage. Half width and signal-to-noise (S/N) ratio of signals in latex-state NMR spectrum for epoxidized DPNR (EDPNR) were similar to those of solution-

state NMR spectrum at temperatures above 50 °C. The narrow half width and sufficient S/N ratio of the signals demonstrated that the high resolution was maintained in latex-state NMR spectrum for EDPNR. Chemical shift values of signals and the epoxy group content of EDPNR determined by latex-state NMR spectroscopy were found to be similar to those determined by solution-state NMR spectroscopy.

In Chapter 3, "Kinetic study on prevulcanization of natural rubber latex through latex-state NMR spectroscopy", prevulcanization of natural rubber was investigated by latex-state NMR spectroscopy. Natural rubber was prevulcanized with zinc-2-mercaptobenzothiazole (ZMBT) as an accelerator in latex stage at 70 - 90 °C. A small signal at 37 ppm, which appeared after prevulcanization, was assigned to secondary carbons adjacent to carbons linking to sulfur atoms and a signal at 50 ppm was assigned to tertiary and quaternary carbons linking to sulfur atoms. Intensity of the signals increased as the prevulcanization time was prolonged, in which kinetic constants were determined. Activation energy of the prevulcanization of natural rubber in latex was estimated from the kinetic constants for the signals at 37 and 50 ppm: that is, 51.5 and 47.2 kJ/mol for the signals at 37 and 50 ppm, respectively.

In Chapter 4, "Mechanism of prevulcanization of isoprene rubber latex through latex-state NMR spectroscopy", prevulcanization of isoprene rubber (IR) was also investigated by latex-state NMR spectroscopy. The prevulcanization of IR was carried out with zinc-dibutyldithiocarbamate (ZDBC) as an accelerator in latex stage at 70 – 90 °C. The signal at 44 ppm, which appeared after prevulcanization, was assigned to secondary carbons adjacent to carbons linking to sulfur atoms, whereas the signal at 58 ppm was assigned to tertiary and quaternary carbons linking to sulfur atoms. The activation energies of the prevulcanization, i.e., 83.2 and 72.7 kJ/mol, were estimated from the intensity of the signals at 44 and 58 ppm, respectively, which were similar to those of decomposition of sulfur to generate sulfur radicals. The plausible mechanism of prevulcanization was proposed to be

the following two: that is, the hydrogen abstraction with sulfur radical and addition of sulfur radical to carbon-carbon double bonds.

In Chapter 5, "Effect of non-rubber components on vulcanization and mechanical properties of vulcanized rubber", effect of proteins on the vulcanization of natural rubber was investigated to understand the difference in the prevulcanization between natural rubber and IR. Removal of the proteins from natural rubber was made by incubation of high ammonium natural rubber (HANR) latex with 0.1 w/w% urea for 1 hour in the presence of surfactant at room temperature to obtain DPNR latex. The DPNR latex was compounded with commercial vulcanizing agents. The compounded DPNR was prevulcanized at 60 ˚C for 25 min, followed by vulcanization to prepare thin film rubber. Contents of nitrogen, water soluble protein and volatile fatty acid of HANR, DPNR and prevulcanized DPNR latexes were determined. Size and surface charge of the particles in the latex were determined by dynamic light scattering and zeta potential, respectively. In addition, the mechanical properties of vulcanized DPNR thin films were found to be improved after mixing with polymer coating.

In Chapter 6, "General conclusion", the conclusion was described on investigation of quantitative analysis through latex-state NMR spectroscopy.

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CHAPTER 2

Latex-state NMR spectroscopy for quantitative analysis of epoxidized deproteinized natural rubber

2.1   Introduction

Latex-state Nuclear Magnetic Resonance (NMR) spectroscopy is a powerful technique to analyze a primary structure of polymer, dispersed in water. It may be useful for *in-situ* determination of epoxy group content of epoxidized natural rubber, since epoxidation of natural rubber is performed in latex stage with peracetic acid or performic acid. Thus, the latex-state NMR spectroscopy is anticipated to simplify a procedure to analyze the primary structure of epoxidized natural rubber; for instance, one may omit coagulating, drying and dissolving steps for a preparation of deuterated solution of epoxidized natural rubber. Furthermore, the latex-state NMR spectroscopy makes possible to apply 2-dimensional NMR measurements to the epoxidized natural rubber in latex stage for positive assignments of unknown signals.

In the last two decades, characterization of epoxidized natural rubber has been performed by solution-state NMR spectroscopy. For instance, signals in solution-state ^{1}H NMR spectrum for epoxidized natural rubber were independently assigned by Bhattacharjee et al. [1] and Thames and Gupta [2]. Assignments of the signals, reported by Bhattacharjee and Thames, were unfortunately inconsistent with each other due to line broadening and overlapping of the signals in the solution-state NMR spectrum. This was explained to be due to the formation of gel fractions during epoxidation. In the previous work [3], liquid epoxidized natural rubber were prepared in order to solve the problem of the line broadening and overlapping of the signals, in which the insoluble gel fractions were decomposed by chain scission. High resolution NMR spectrum was obtained for liquid epoxidized natural rubber

and the assignments of the signals in ^{1}H and ^{13}C NMR spectra were completed. However, the liquid epoxidized natural rubber was not accepted for the determination of epoxy group content, since the epoxy group content changed during chain scission of the epoxidized natural rubber due to the complicated procedure. It is, thus, necessary to develop a quantitative analysis of the epoxy group content of the epoxidized natural rubber in latex stage.

In the present study, the latex-state NMR spectroscopy was applied for the quantitative analysis of the epoxy group content of epoxidized deprotenized natural rubber (EDPNR) latex. Half width, S/N ratio and epoxy group content, determined by latex-state NMR spectroscopy, were compared with those determined by solution-state NMR spectroscopy.

2.2 Experimental

2.2.1 Preparation of deprotenized natural rubber (DPNR) latex

Natural rubber latex used in this study was commercial high ammonia natural rubber (HANR) latex (Golden Hope, Malaysia). The HANR latex was incubated with 0.1 w/w% urea (Nacalai Tesque Inc., 99.5 %) in the presence of 1.0 w/w% sodium dodecyl sulfate (SDS) (Kishida Reagents Chemical Co. Ltd., 99%) at room temperature for 1 hour followed by centrifugation at 10^4 g. The cream fraction was redispersed in 1.0 w/w% SDS solution and it was centrifuged, again. Then, the cream fraction was washed twice with 0.5 and 0.1 w/w% SDS solution, respectively. The resulting DPNR latex was kept in the dark at room temperature.

2.2.2 Preparation of epoxidized deprotenized natural rubber (EDPNR) latex

Epoxidized DPNR was prepared in latex stage. The DPNR latex was diluted to 10 w/w% DRC with distilled water and pH was adjusted to 7 with acetic acid (Nacalai Tesque Inc., 99%). Epoxidation of DPNR latex (1.0 w/w% SDS) was carried out at 5 - 10 °C for 1 - 6

hour with fresh peracetic acid, which was prepared from 5 g acetic anhydride (Nacalai Tesque Inc., 93%) and 10 g hydrogen peroxide (Nacalai Tesque Inc., 30%) at 40 °C for 90 min. After epoxidation, pH of the latex was adjusted to 7 with ammonia solution (Nacalai Tesque Inc., 28%). The EDPNR latex was washed by centrifugation at 10^4 g. Cream fraction of the EDPNR latex was recovered and it was redispersed into 1.0 w/w% SDS solution to make 35 w/w% DRC latex. The resulting EDPNR latex was subjected to latex-state NMR measurement. Schematic representation of the experimental procedure is shown in Figure 2-1.
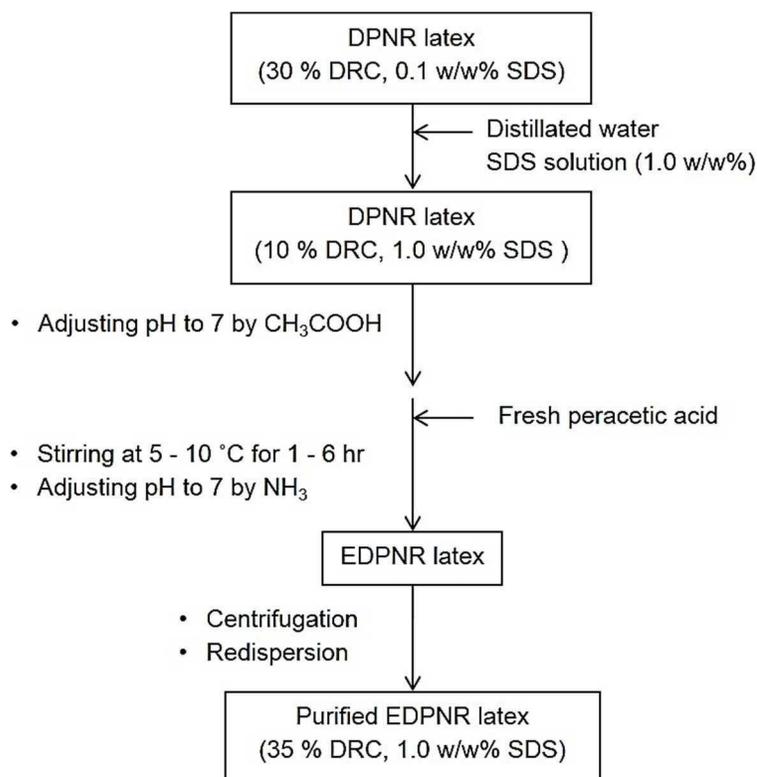

Figure 2-1 Schematic representations for experimental procedure

2.2.3   Characterization

Solution-state and latex-state NMR measurements were carried out using a JEOL ECA-400 FT-NMR spectrometer (Tokyo, Japan), operating at 399.65 and 100.40 MHz for ^{1}H and ^{13}C, respectively. The pulse width was 6.6 and 4.3 μs and spectral width was 5994.75 and 25100 Hz for ^{1}H and ^{13}C measurements, respectively. For the solution-state NMR measurements, the dried EDPNR, cut into small pieces, was dissolved into chloroform-d (CDCl$_3$, 99.8%) without TMS, whereas for the latex-state NMR measurements, the EDPNR latex with deuterium dioxide (D$_2$O, 99.9%) was used for the measurements without further treatment. ^{1}H and ^{13}C NMR measurements were carried out at the pulse repetition time of 7 and 5 s, respectively.

Differential scanning calorimetry (DSC) measurements were performed with a SII Nano Technology DSC7020 differential scanning calorimeter over the temperature range of -120 to 100 °C at the heating rate of 10 °C/min. Samples of about 10 mg were encapsulated in an aluminum pan. Glass transition temperature (T_g) of the samples was determined from a point of inflection in DSC curve.

2.3   Results and discussion

Latex-state ^{13}C NMR spectra for DPNR and EDPNR measured at 50 °C are shown in Figure 2-2, in conjunction with the solution-state ^{13}C NMR spectra. Five major signals appeared at 23.3, 26.5, 32.3, 125.1 and 135.0 ppm, which were assigned to five carbon atoms of cis-1,4-isoprene units, according to previous work [4]. Values of half width and S/N ratio of the signal at 23.3 ppm in latex-state ^{13}C NMR spectra were 12.9 Hz and 93.7 for DPNR as well as 18.5 Hz and 87.6 for EDPNR, which were similar to those in solution-state ^{13}C NMR spectra. The narrow half width and sufficient S/N ratio of the signals in the spectra may be explained to be due to not only active molecular motion of the rubbers but also rapid movement of dispersoids in the latex. Resolution of latex-state ^{13}C NMR spectra was, thus,

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found to be similar to that of solution-state ^{13}C NMR spectra even after epoxidization. This implies that the high resolution NMR spectrum may be obtained for the epoxidized natural rubber, as long as we apply latex-state ^{13}C NMR spectroscopy.
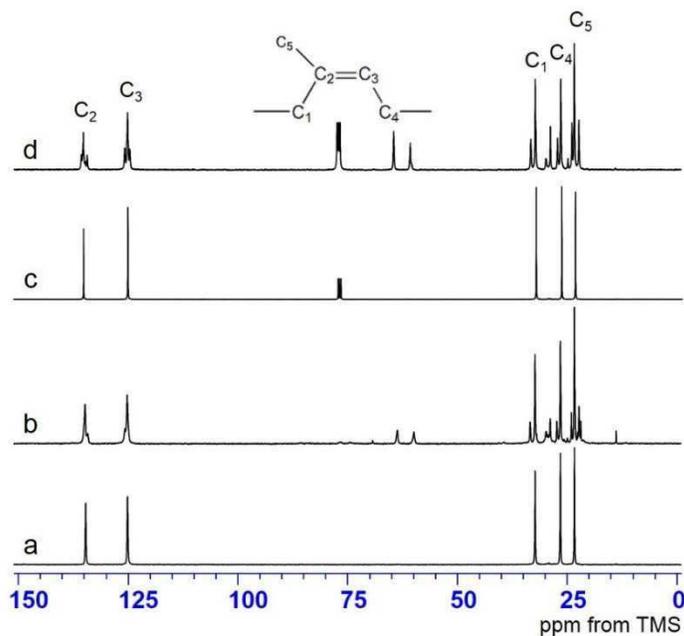

Figure 2-2 Typical ^{13}C NMR spectra measured at 50 °C: (a) latex-state for DPNR (b) latex-state for EDPNR (c) solution-state for DPNR and (d) solution-state for EDPNR

Figure 2-3 shows the expanded latex-state ^{13}C NMR and solution-state ^{13}C NMR spectra for EDPNR. Small signals appeared in aliphatic region and two signals appeared at 60.0 and 64.0 ppm in each spectrum. These signals were assigned to monad, dyad triad sequences of epoxidized isoprene units (E) and *cis*-1,4-isoprene units (C), according to Bradbury and Perera [5]. The carbon atoms of each middle unit in triad sequences were numbered to distinguish from each other. For example, the CC^5C triad sequence represents methyl carbon of *cis*-1,4-isoprene unit linking to *cis*-1,4-isoprene units at both ends, in which the C represents *cis*-1,4-isoprene unit, the CCC is a triad sequence of the *cis*-1,4-isoprene units and the superscript number belongs to the IUPAC numbering method of carbon atoms

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of the middle unit, as shown in Figure 2-4. Chemical shift values of these signals were tabulated in Table 2-1 together with the assignments, thus far proposed [3,5]. As shown in Figure 2-3, the chemical shift values of signals in latex-state ^{13}C NMR spectrum for EDPNR were similar to those in solution-state ^{13}C NMR spectrum for EDPNR. This demonstrates that the latex-state ^{13}C NMR spectroscopy was ensured to be correct to analyze the primary structure of EDPNR in latex stage.
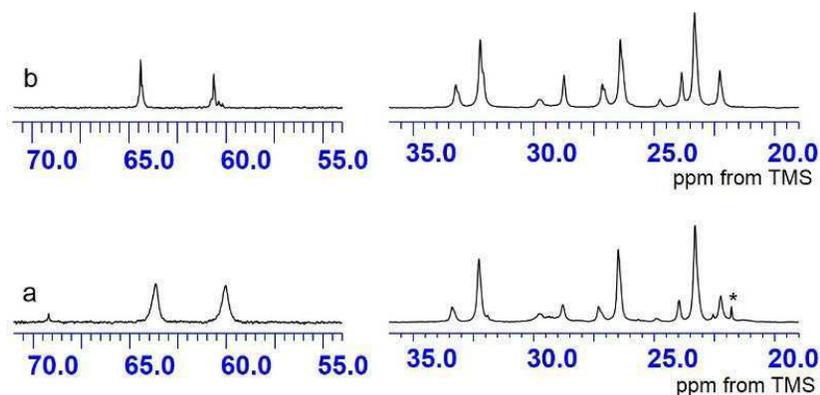

**Figure 2-3** Expanded ^{13}C NMR spectra for EDPNR: (a) latex-state and (b) solution-state
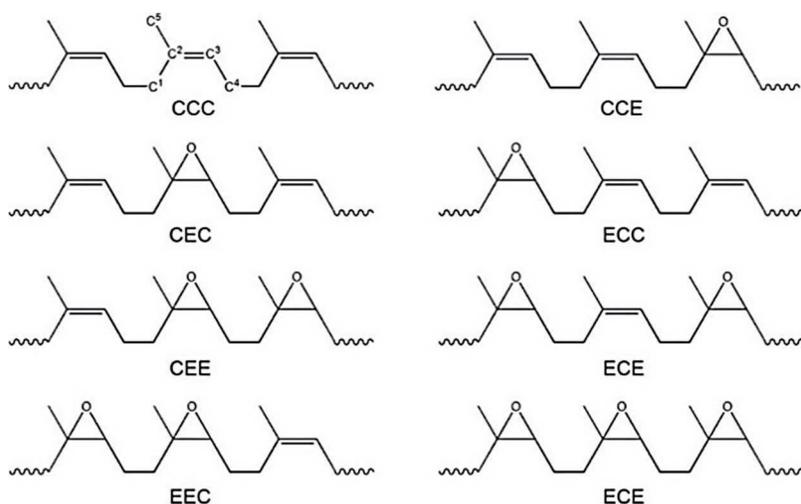
Figure 2-4 Triad sequences of epoxidized isoprene unit (E) and unepoxidized isoprene unit (C)

Table 2-1 ^{13}C NMR chemical shift of latex-state and solution-state for EDPNR

Assignment	Latex-state	Solution-state
* CH$_3$ of acetic acid in D$_2$O solvent	21.7	-
E^5	22.3	22.2
C^5	23.3	23.3
CC^{4}E, EC^{4}E	24.0	23.8
CE^{4}E, EE^{4}E	24.9	24.7
CC^{4}C, EC^{4}C	26.5	26.4
CE^{4}C, EE^{4}C	27.3	27.1
EC^{1}C, EC^{1}E	28.8	28.7
EE^{1}C, EE^{1}E	29.7	29.7
CC^{1}C, CC^{1}E	32.3	32.2
CE^{1}C, CE^{1}E	33.4	33.2
E^2	59.7	60.6
E^3	63.5	64.4
C^3	125.2	125.0
C^2	134.7	135.1

Changes in the half width and S/N ratio of the signal at 23.3 ppm were investigated against temperature by latex-state ^{13}C NMR spectroscopy and solution-state ^{13}C NMR spectroscopy. Figure 2-5 shows a plot of the half width of the signal *versus* temperature for EDPNR, which was determined by latex-state ^{13}C NMR spectroscopy and solution-state ^{13}C NMR spectroscopy. The half width of the signal in latex-state ^{13}C NMR spectrum was significantly narrowed as temperature rose, whereas that in the solution-state ^{13}C NMR spectrum was narrowed a little. For example, the half width of the signal in the latex-state ^{13}C NMR spectrum decreased dramatically from 28.7 Hz at 25 °C to 18.5 Hz at 50 °C and, then it decreased to 16.6 Hz as temperature rose to 70 °C. In contrast, the half width of the signal in

the solution-state ^{13}C NMR spectrum decreased gradually from 9.2 Hz to 7.7 Hz, as temperature rose from 25°C to 70 °C. The difference in the temperature dependency of the half width may be explained to be due to the residual dipole-dipole interaction, since the half width of the signal in the solution-sate ^{13}C NMR spectrum reflects Zeeman Effect. This implies that the effect of the residual dipole-dipole interaction of the latex-state NMR spectroscopy is significantly reduced by active molecular motion of the rubber and rapid movement of the dispersoids, which are dependent upon temperature, respectively.
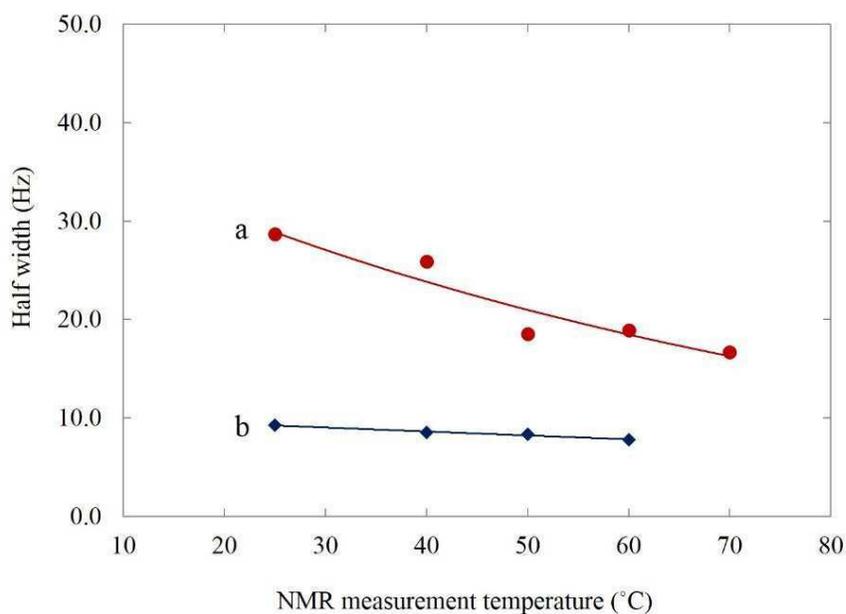

Figure 2-5 A plot of half width of (a) latex-state ^{13}C NMR and

(b) solution-state ^{13}C NMR spectroscopy *versus* measurement temperature for EDPNR

Figure 2-6 shows a plot of the S/N ratio of the signal at 23.3 ppm *versus* temperature for EDPNR. The S/N ratio of the signal in the latex-state ^{13}C NMR spectrum was dependent upon temperature; that is, the higher the temperature, the higher the S/N ratio. In contrast, the S/N ratio of the signal in the solution-state ^{13}C NMR spectrum changed a little against temperature. A value of the S/N ratio of the signal in the latex-state ^{13}C NMR spectrum was

similar to that in the solution-state NMR spectrum at 50 °C, although the difference was explicit at room temperature. Tendency of the temperature dependency of the S/N ratio is identical to that of the half width; that is, the slope changed from steep to gradual as temperature rose. Consequently, a suitable temperature for the latex-state NMR spectroscopy was determined to be 50 °C.
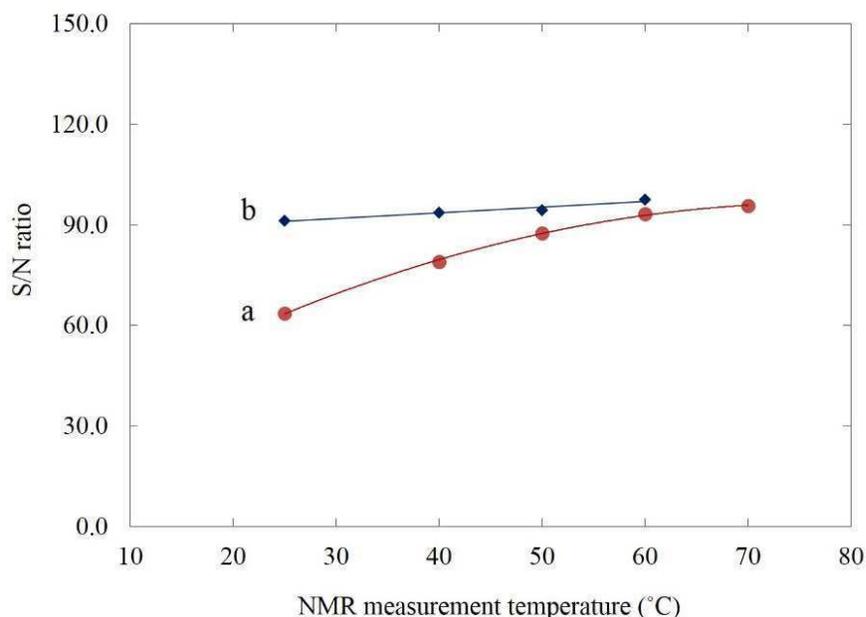

Figure 2-6 A plot of S/N ratio of (a) latex-state ^{13}C NMR and (b) solution-state ^{13}C NMR spectroscopy *versus* measurement temperature for EDPNR

The latex-state ^{13}C NMR measurements were carried out at 50 °C and 70 °C for EDPNR-1, EDPNR-2, EDPNR-3 and EDPNR-4 latexes to determine their epoxy group content. The epoxy group content of EDPNR (X_{epoxy}) was estimated from the intensity ratio of the signals, according to Burfield et al. [6], as in the following equation:

$$X_{epoxy} = \frac{I_{64.0}}{I_{64.0} + I_{125.1}} \times 100 \qquad \text{(Eq. 2-1)}$$

where I is intensity of the signals and subscript numbers represent chemical shift (ppm). The signals at 64.0 and 125.1 ppm were assigned to methine carbon of the epoxidized isoprene units and that of the cis-1,4 isoprene units, respectively. Table 2 shows the estimated values of epoxy group content of EDPNR-1, EDPNR-2, EDPNR-3 and EDPNR-4 latexes, determined by latex-state ^{13}C NMR spectroscopy at 50 °C and 70 °C, together with those determined by solution-state ^{13}C NMR spectroscopy at 50 °C. The estimated values of epoxy group content of EDPNR-1, EDPNR-2, EDPNR-3 and EDPNR-4 latexes, determined by latex-state ^{13}C NMR spectroscopy at 50 °C, were almost similar to those determined at 70 °C. The values of the epoxy group content were also similar to those determined by solution-state ^{13}C NMR spectroscopy at 50 °C. These results demonstrate that the latex-state ^{13}C NMR measurement at 50 °C is appropriate not only for determination of the epoxy group content but also for achievement of the high resolution latex-state NMR spectrum. The active molecular motion of the rubbers at 50 °C was found to be important for the quantitative analysis of the epoxy group content for EDPNR-1, EDPNR-2, EDPNR-3 and EDPNR-4, whose glass transition temperatures (T_g) were about -58.6, -51.5, -46.7 and -43.3 °C, respectively. This is consistent with the previous result that the high resolution is achieved at T-T_g > 70 K for the latex-state NMR spectroscopy [4,7].

In order to verify the epoxy group content of EDPNR-1, EDPNR-2, EDPNR-3 and EDPNR-4 latexes, determined by latex-state ^{13}C NMR spectroscopy, the solution-state ^{1}H NMR measurement was performed at 50 °C for chloroform-d solutions of the rubbers. Figure 2-7 shows the solution-state ^{1}H NMR spectra for DPNR and EDPNR. Three major signals appeared at 1.68, 2.05 and 5.1 ppm in the solution-state ^{1}H NMR spectra, which were assigned to methyl, methylene, unsaturated methine proton of cis-1,4-isoprene units, respectively. In addition, for EDPNR, two signals appeared at 1.29 and 2.7 ppm, which were assigned to methyl and methine proton of epoxidized cis-1,4-isoprene units, respectively.

The epoxy group content of EDPNR (Y_{epoxy}) was estimated from the intensity ratio of the signals, according to Bradbury and Perera [5], as in the following equation:

$$Y_{epoxy} = \frac{I_{2.7}}{I_{2.7} + I_{5.1}} \times 100 \qquad \text{(Eq.2-2)}$$

where I is intensity of the signals and subscript numbers represent chemical shift (ppm).
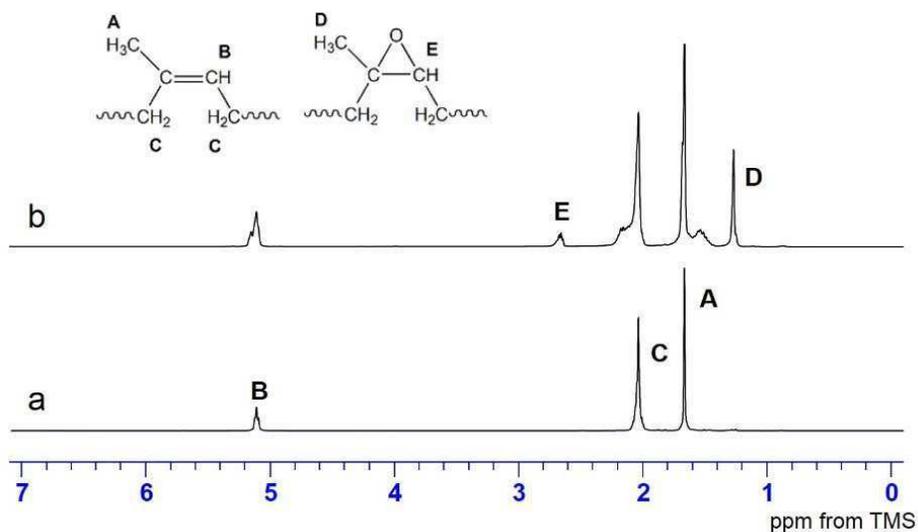

Figure 2-7 Typical solution-state ^{1}H NMR spectra for (a) DPNR and (b) EDPNR

The estimated values of epoxy group content of EDPNR-1, EDPNR-2, EDPNR-3 and EDPNR-4 latexes, determined by solution-state ^{1}H NMR spectroscopy are shown in Table 2-2. The epoxy group content of EDPNR-1, EDPNR-2, EDPNR-3 and EDPNR-4 latexes, determined by solution-state ^{1}H NMR spectroscopy, was 10.3, 18.3, 20.5 and 25.4%, respectively, which were similar to those determined by latex-state ^{13}C NMR spectroscopy. This demonstrates that the high resolution latex-state ^{13}C NMR spectroscopy is useful for the quantitative analysis of the epoxy group content of EDPNR in latex stage.

Table 2-2 Estimated values of epoxy group content of EDPNR latexes

Sample	Latex-state		Solution-state	
	^{13}C NMR 50˚C (%)	^{13}C NMR 70˚C (%)	^{13}C NMR 50˚C (%)	^{1}H NMR 50˚C (%)
EDPNR-1	10.2	10.2	10.3	10.3
EDPNR-2	18.3	18.4	18.4	18.3
EDPNR-3	20.2	20.2	20.3	20.5
EDPNR-4	24.9	25.2	25.1	25.4

2.4   Conclusion

Latex-state ^{13}C NMR spectroscopy was performed to determine the epoxy group content of EDPNR in latex stage. The chemical shift values of signals of latex-state ^{13}C NMR spectrum for EDPNR were similar to those of solution-state ^{13}C NMR spectrum for EDPNR. The latex-state ^{13}C NMR spectrum for EDPNR showed narrow half width and sufficient S/N ratio of signals at 50 °C or higher, which satisfied a suitable condition of temperature, T-T_g > 70 K. The estimated values of the epoxy group content determined by latex-state ^{13}C NMR spectroscopy were similar to those determined by solution-state ^{13}C and ^{1}H NMR spectroscopy. The latex-state ^{13}C NMR spectroscopy was found to be useful for the quantitative analysis of the epoxy group content of EDPNR.

2.5   References

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CHAPTER 3
Kinetic study on prevulcanization of natural rubber latex through latex-state NMR spectroscopy

3.1   Introduction

Latex-state NMR spectroscopy is a powerful technique to analyze crosslinking junctions of vulcanized rubber present in particles dispersed in water. [1-5] For instance, in the last decade, [3,4] the structure of the crosslinking junctions of vulcanized natural rubber were analyzed through latex-state ^{13}C NMR spectroscopy. Small signals, appearing after vulcanization, were assigned to crosslinking junctions of the rubber. Intensity ratio of the small signals in latex-state NMR spectra for vulcanized natural rubber was found to be dependent upon vulcanization time, and it was proportional to crosslink density, as well. It is, thus, possible to apply the latex-state NMR spectroscopy to an analysis of prevulcanization of rubber in latex stage.

Prevulcanization is widely recognized to be one of the important steps of the vulcanization of the rubber in latex stage as a bottle-neck process. The prevulcanization plays an important role in mechanical properties of thin film products prepared from the rubber latex. [6-9] It is, thus, expected to analyze the prevulcanization through latex-state NMR spectroscopy.

In the present study, the mechanism of prevulcanization of natural rubber was investigated through the latex-state ^{13}C NMR spectroscopy. The activation energy of the prevulcanization was determined on basis of temperature dependency of the kinetic constant of prevulcanization. The mechanism of prevulcanization of natural rubber was proposed, based on the estimated values of activation energy and signals appeared in latex-state ^{13}C NMR spectra for prevulcanized natural rubber.

3.2   Experimental

3.2.1   Materials

High ammonia natural rubber (HANR) latex with 60 w/w% dry rubber content (DRC) was purchased from Golden Hope Company, Malaysia. Sodium dodecyl sulfate (SDS) was purchased from Kishida Reagents Chemical Co. Ltd., Japan. Potassium hydroxide (KOH), sulfur (S) and zinc oxide (ZnO) were purchased from Nacalai Tesque Co., Ltd and zinc-2-mercaptobenzothiazole (ZMBT) was supplied by Ouchi Shinko Chemical Industry Co., Ltd. These chemical reagents were mixed to prepare a slurry; that is, we mixed 5 w/v% KOH solution, 50 w/w% S dispersion, 50 w/w% ZnO dispersion and 50 w/w% ZMBT dispersion. Dueterium oxide (D_2O) for NMR measurements was purchased from Wako Co. Ltd.

3.2.2   Prevulcanization of natural rubber latex

Prevulcanization of natural rubber was carried out in latex stage, using ZMBT as an accelerator. First, the natural rubber latex with 60 w/w% DRC was incubated with 2 phr S, 1.5 phr ZnO and 2 phr ZMBT for 4 hours at 40 °C. Then, the incubated latex was diluted to 20 w/w% DRC with ion exchange water followed by adding 0.5 w/w% SDS solution. Second, prevulcanization of the incubated latex was carried out by heating the latex at 70 to 90 °C for 3 to18 hours under stirring at 200 rpm. The resulting prevulcanized latex was centrifuged at 10^4 g for 30 min. Cream fraction of the latex was redispersed in 0.5 w/w% SDS solution and it was centrifuged again. Then, the washed cream fraction was redispersed in 0.5 w/w% SDS solution to make 40 w/w% DRC. As-cast film was prepared from a part of washed latex and is was dried under reduced pressure at 50 °C to obtain dried prevulcanized natural rubber.

3.2.3   Characterization

Latex-state NMR spectroscopy was performed with a JEOL EX400 FT-NMR spectrometer (Tokyo, Japan), operating at 100.40 MHz for ^{13}C. 10,000 scans were performed with a pulse repetition time of 5 s to acquire free induction decay (FID) curve. The vulcanized

natural rubber latex was mixed with D_2O and, then, it was used for the ^{13}C NMR measurements without further treatment. Solid-state NMR spectroscopy was carried out with a JEOL ECA400 FT-NMR spectrometer (Tokyo, Japan), operating at 399.95 and 99.55 MHz for ^1H and ^{13}C, respectively. The dried PVNR, loaded into a sample tube, was analyzed with a 3.2 mm FG-FMAS probe through solid-state NMR spectroscopy. The spinning rate of the sample tube for the solid-state measurements was 18 ± 5 Hz. The ^1H NMR, ^{13}C NMR, DEPT and APT measurements were performed at pulse repetition times of 7 and 5 s for ^1H and ^{13}C, respectively.

Crosslink density of the prevulcanized natural rubber was determined by the swelling method. The dried PVNR film was immersed in 50 ml of toluene in the dark for a week at room temperature. The swollen sample was blotted with tissue paper and weighed with an analytical balance. It was dried under reduced pressure at 50 °C and reweighed again. The crosslink density was estimated using Flory-Rehner equation. [10]

$$v = -\frac{1}{2V_s}\frac{\ln(1-V_r)+V_r+X(V_r)^2}{(V_r)^{1/3}-(V_r/2)}$$ (Eq. 3-1)

where v is crosslink density (mol/cm^3), V_s is molar volume of the solvent (106.52 cm^3/mol), X is Flory – Huggins interaction parameter (0.393) and V_r is volume fraction of the rubber, which was determined by the following equation.

$$V_r = \frac{1}{\left[(\rho_r/\rho_s)((W_s-W_u)/W_u)+1\right]}$$ (Eq. 3-2)

where ρ_r is density of the rubber (0.913 g/cm^3), ρ_s is density of the solvent (0.865 g/cm^3), W_s is weight of swollen rubber (g) and W_u is weight of unswollen rubber (g)

3.3   Results and discussion

Latex-state ^{13}C NMR spectra for the HANR and PVNR90 latexes, obtained from prevulcanization time of 3, 6 and 12 hours are show in Figure 1. Signals at 23.4, 26.5, 32.3, 125.1 and 134.6 ppm in each spectrum were assigned to C5, C4, C1, C3 and C2 of the *cis*-1,4-isoprene unit, respectively. [11-13] The narrow half width and high signal-to-noise (S/N) ratio of the signals in latex-state ^{13}C NMR spectra for PVNR90 latexes implies that the high-resolution NMR spectrum is attained for the latex-state ^{13}C NMR spectroscopy even after prevulcanization.
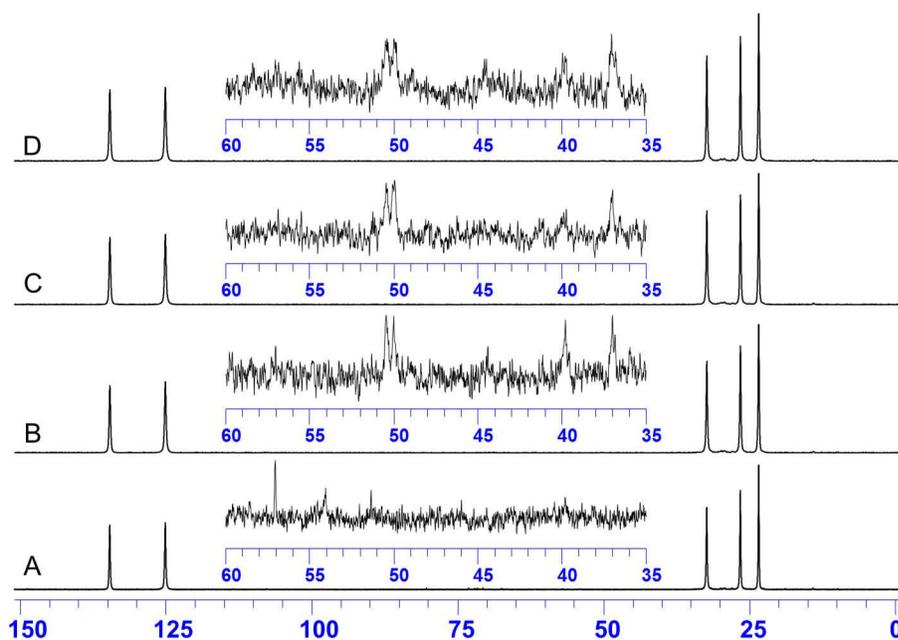
Figure 3-1 Latex-state ^{13}C NMR spectra for A) the HANR latex, B) PVNR90 for 3 hours, C) PVNR90 for 6 hours and D) PVNR90 for 12 hours

In Figure 3-1, small signals also appeared at 37, 40, 50 and 50.5 ppm in the latex-state ^{13}C NMR spectra for PVNR90 latexes, which were not shown for the HANR. The signal at 40 ppm was assigned to C4 of *trans*-1,4-isoprene units, whereas the signals at 50 and 50.5 ppm were assigned to quaternary and tertiary carbons linking to sulfur. However, the

signal at 37 ppm was not assigned due to lack of library data. In order to assign the signal at 37 ppm, an as-cast film was prepared from PVNR90 latex (18 hours prevulcanization) and it was subjected to field-gradient fast-magic angle spinning (FG-FMAS) solid-state NMR spectroscopy. Figure 3-2 shows the FG-FMAS solid-state ^{13}C NMR spectrum, together with the latex-state ^{13}C NMR spectrum for PVNR90. The five major signals at 23.4, 26.5, 32.3, 125.1 and 134.6 ppm characteristic of five carbon atoms of *cis*-1,4-isoprene units and the small signals at 37, 40 and 50 ppm appeared in the FG-FMAS solid-state ^{13}C NMR spectrum for PVNR90.
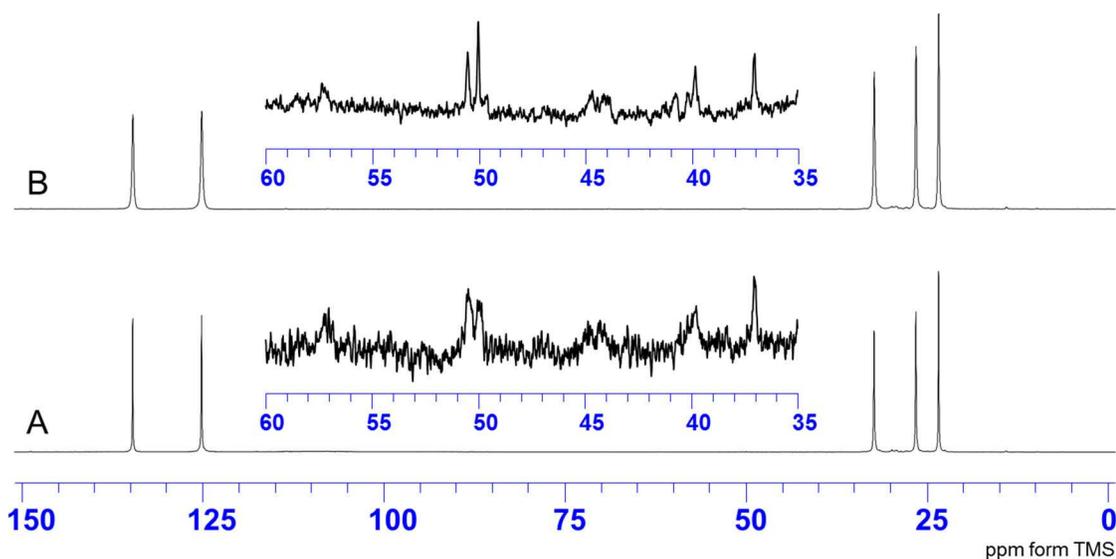
Figure 3-2 Typical ^{13}C NMR spectra for PVNR90 for 18 hours:

A) latex-state and B) solid-state

Figure 3-3 shows the DEPT at 45° (DEPT45), 90° (DEPT90), 135° (DEPT135) and APT spectra for PVNR90 (18 hours prevulcanization). In the spectra, the signals at 23.4, 26.5 and 32.3 ppm characteristic to methyl, methylene and methine carbons of *cis*-1,4-isoprene units appeared upward, upward and upward in the DEPT45 spectrum, while they were almost null in the DEPT90 spectrum. These signals appeared upward, downward and downward, respectively, in the DEPT135 and APT spectra. In contrast, signals at 37 and 40

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ppm appeared upward in the DEPT45 spectrum, null in DEPT90 spectrum, downward in the DEPT135 spectrum and downward in the APT spectrum, respectively. The signals were, thus, assigned to secondary carbons. The signal at 50 ppm didn't appear in the DEPT45, DEPT90 and DEPT135 spectra, whereas it appeared downward in the APT spectrum. The signal at 50.5 ppm appeared in the DEPT45, DEPT90, DEPT135 and APT spectra. Thus, the signal at 50 ppm was assigned to quaternary carbon, whereas the signal at 50.5 ppm was to tertiary carbon.
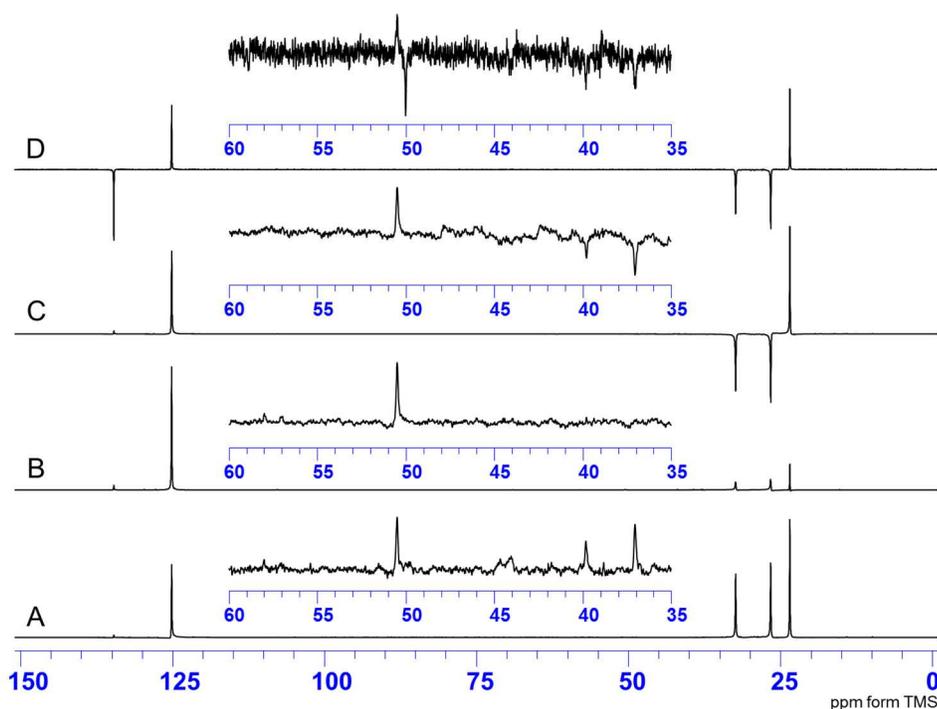
Figure 3-3 FG-FMAS solid-state ^{13}C NMR spectra with: A) DEPT45, B) DEPT90, C) DEPT135 and D) APT for PVNR90 for 18 hours

Figure 3-4 shows plausible structures of crosslinking junctions of vulcanized natural rubber. The signal at 37 ppm may be assigned to the secondary carbons adjacent to the quaternary and tertiary carbons linking to sulfur atoms, which are marked as 50 and 50.5 ppm, respectively. This may correspond to the signal at 44 ppm, assigned to the secondary carbons adjacent to the quaternary and tertiary carbons linking to sulfur atoms, which are

marked as 57.3 and 58 ppm, respectively. These crosslinking junctions may be formed through pathway A (hydrogen abstraction with sulfur radical) and pathway B (addition of sulfur radical to carbon-carbon double bonds), as shown in Figure 3-5.
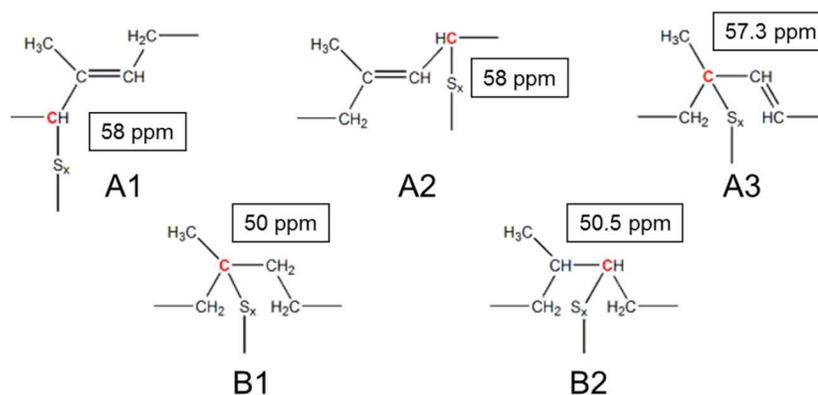
**Figure 3-4** Plausible crosslinking junctions for the vulcanized natural rubber
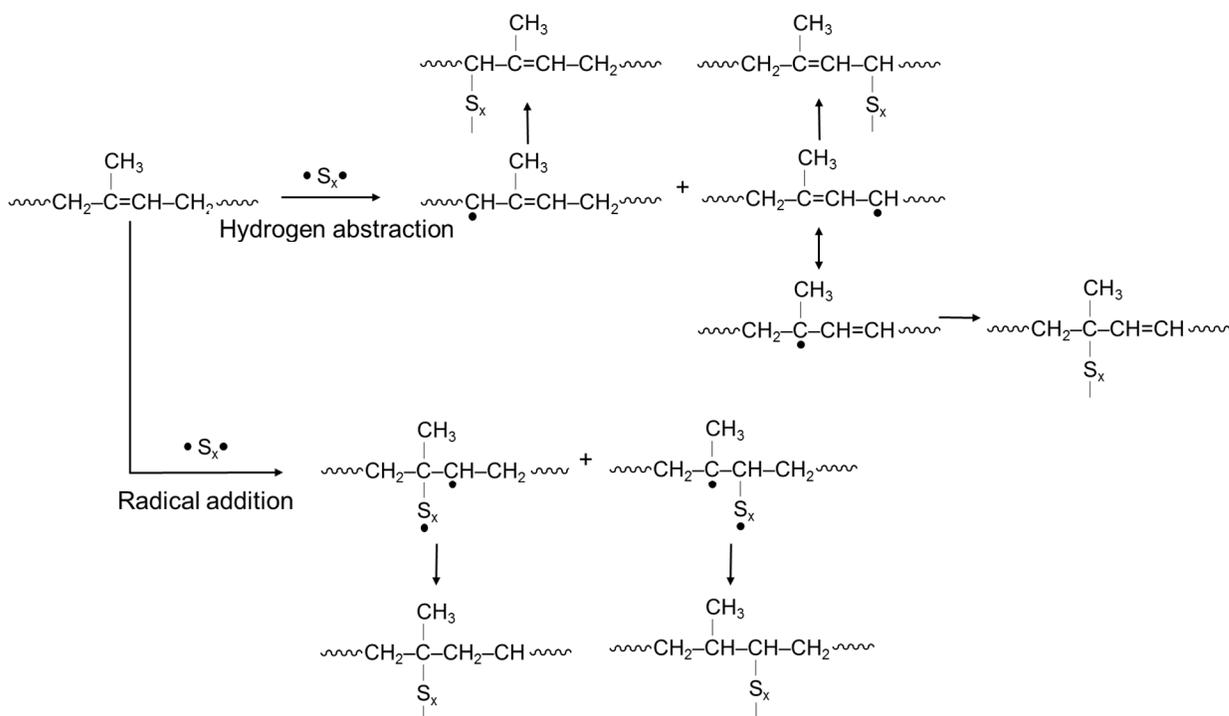
Figure 3-5 Plausible mechanism of prevulcanization of natural rubber

In order to investigate the mechanism of the prevulcanization of natural rubber, effects of time and temperature on the structure of crosslinking junctions were investigated for the prevulcanization. Figure 3-6 shows a plot of crosslink density *versus* prevulcanization time for the PVNR70, PVNR75, PVNR80, PVNR85 and PVNR90, which were prepared from the prevulcanized natural rubber latex at various temperatures between 70 and 90 °C as an as-cast film. The value of crosslink density of the as-cast films increased as the prevulcanization time was prolonged. It was also dependent on temperature; that is, the higher the temperature the larger the value of the crosslink density.
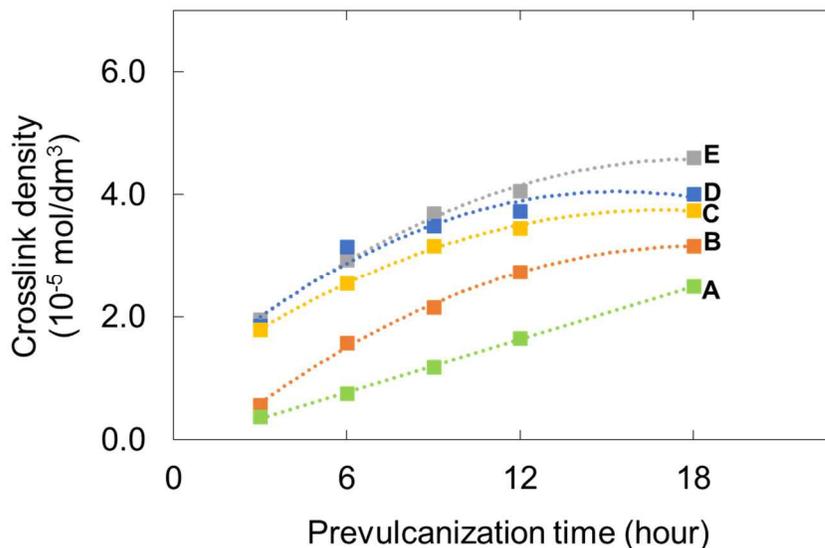
Figure 3-6 Crosslink density of the A) PVNR70, B) PVNR75, C) PVNR80,

D) PVNR85 and E) PVNR90

Figures 3-7 and 3-8 show semi-logarithmic plots of intensity of the signals at 37 and 50 ppm *versus* the prevulcanization time for PVNR70, PVNR75, PVNR80, PVNR85 and PVNR90. The intensity of the signals at 37 ppm (X_{37ppm}) and 50 ppm (X_{50ppm}) was normalized, as follows:

$$X_{37ppm}(\%) = \frac{I_{37ppm}}{I_{23.4ppm}} \times 100 \qquad \text{(Eq.3-3)}$$

$$X_{50ppm}(\%) = \frac{I_{50ppm}}{I_{23.4ppm}} \times 100 \qquad \text{(Eq.3-4)}$$

where I is intensity of the signals and the subscripts represent the value of the chemical shift. The logarithmic intensities of the signals at 37 and 50 ppm were linearly dependent upon not only the prevulcanization time but also temperature. From the results, rate constants of prevulcanization (k) were determined as a slope of the linear line in the semilogarithmic plot of the intensity of signals at 37 and 50 ppm *versus* the prevulcanization time. The estimated values of k are tabulated in Table 3-1. The value of k was dependent upon the prevulcanization temperature at 70, 75, 80, 85 and 90 ˚C.

Table 3-1 Estimated values of rate constant of reactions (k)

| Prevulcanization temperature (˚C)	Rate constant of reaction (s^{-1})	
	37 ppm	50 ppm
70	0.0360	0.0276
75	0.0683	0.0595
80	0.0817	0.0797
85	0.0971	0.0844
90	0.0936	0.0791
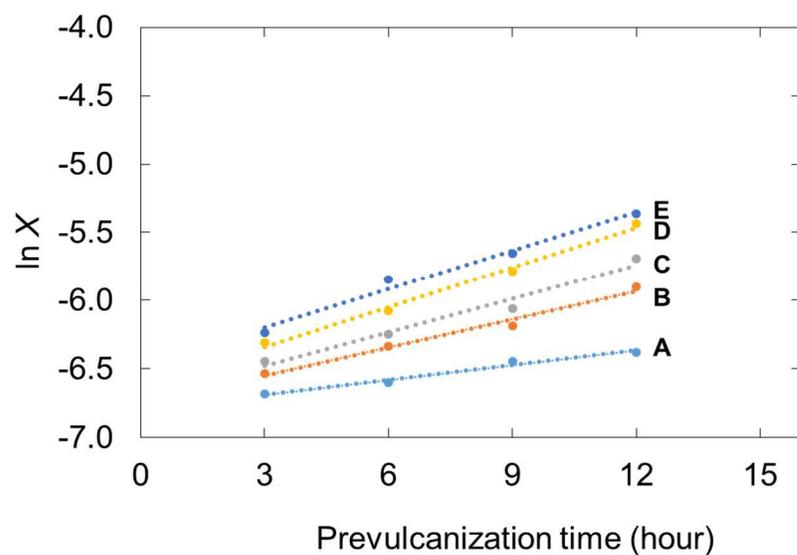
Figure 3-7 Semilogarithmic plots of intensity of the signal at 37 ppm for A) PVNR70,

B) PVNR75, C) PVNR80, D) PVNR85 and E) PVNR90 *versus* prevulcanization time
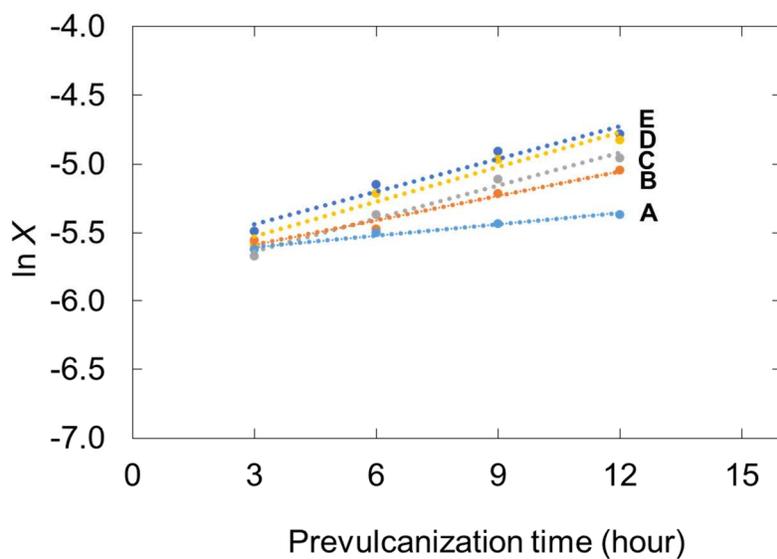
Figure 3-8 Semilogarithmic plots of intensity of the signal at 50 ppm for A) PVNR70,

B) PVNR75, C) PVNR80, D) PVNR85 and E) PVNR90 *versus* prevulcanization time

The activation energy was estimated from k by the following Arrhenius equation,

$$\ln k = \frac{-E_\alpha}{RT} + \ln A \qquad\qquad \text{(Eq. 3-5)}$$

where k is the rate constant (s^{-1}), A the frequency factor, E_α the activation energy (kJ/mol), R the gas constant (J/mol·K) and T the absolute temperature (K). Figure 3-9 shows the semilogarithmic plot of k *versus* reciprocal temperature, which was well known as Arrhenius plot. The activation energy was estimated from a slope of the Arrhenius plot. The estimated values of activation energy for the signals were almost similar to each other; that is, the value of the activation energy estimated from intensity of the signal at 37 ppm was 51.5 kJ/mol and that of the signal at 50 ppm was 47.2 kJ/mol. These values correspond to the activation energy of decomposition of sulfur. This demonstrates that the prevulcanization of the rubber is dominated by decomposition of the sulfur in latex.
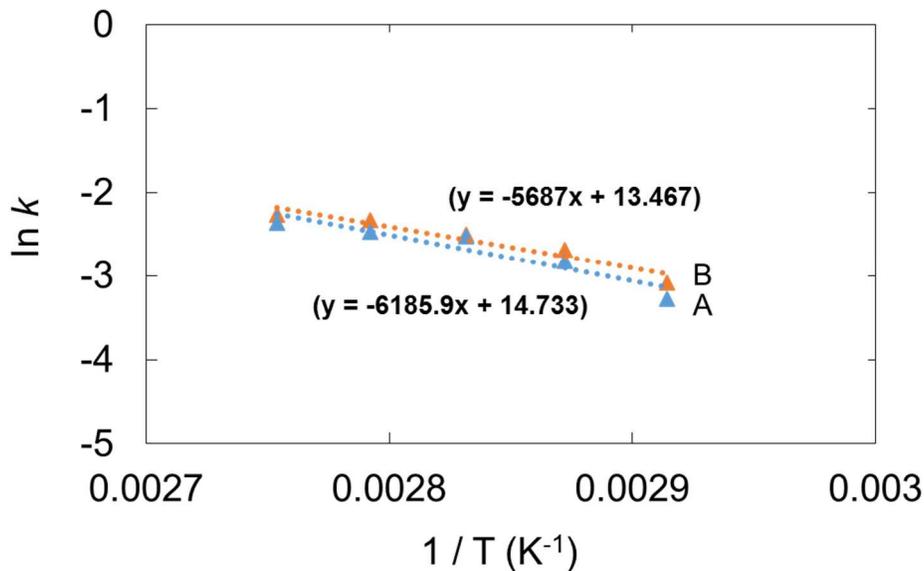

Figure 3-9 Plot of logarithmic value of rate constant of reaction for the signals at

A) 37 and B) 50 ppm *versus* reciprocal temperature

3.4   Conclusion

The latex-state ^{13}C NMR spectroscopy was perform for *in-situ* analysis of crosslinking junctions of prevulcanized natural rubber latex. The mechanism of prevulcanization of natural rubber was investigated on the basis of kinetic study through those of *in-situ* analysis. The signals at 37 and 40 ppm were assigned to secondary carbons adjacent to carbons linking to sulfur atoms and C4 of *trans*-1,4-isoprene units, respectively. On the other hand, the signal approximately at 50 ppm was distinguishable to be doublet signals at 50 and 50.5 ppm, which were assigned to quaternary carbons and tertiary carbons linking to sulfur atoms, respectively. The intensity ratio of these signals was dependent upon not only time evolution but also prevulcanization temperature, in which the activation energy of the prevulcanization was determined from these intensity ratio of the signals. The estimated values of activation energy of the prevulcanization of natural rubber for the signal at 37 and 50 ppm were 51.5 and 47.2 kJ/mol, respectively. The plausible mechanism of prevulcanization of natural rubber latex, using ZMBT as an accelerator was suggested that to mainly proceed in radical reaction, which was preceded by the addition of sulfur radical to carbon-carbon double bonds.

3.5   References

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CHAPTER 4

Mechanism of prevulcanization of isoprene rubber latex through latex-state NMR spectroscopy

4.1   Introduction

Latex-state NMR spectroscopy is a powerful technique to analyze reactions of colloidal dispersion system, since it is applicable to crosslinked rubbery polymers in latex stage. For instance, in the last decade, vulcanization of natural rubber in latex stage was investigated through latex-state ^{13}C NMR spectroscopy. [1,2] Small signals appearing after vulcanization were carefully assigned to crosslinking junctions of natural rubber. This implies that the latex-state NMR spectroscopy open a new field of the in-situ analysis of the crosslinked rubbery polymers in latex stage. One may, thus, investigate the mechanism of prevulcanization of rubbery polymer latex through latex-state NMR spectroscopy, as well as field gradient fast magic angle spinning (FG-FMAS) solid-state NMR spectroscopy, which were developed in our previous works. [3]

Prevulcanization of rubbery polymer latex is one of the important steps of the vulcanization of the polymer in latex stage, since it plays an important role in mechanical properties of thin film products prepared from the latex. [4,5] In the previous work, Ho and coworkers [6] reported that the prevulcanization has been divided into three steps: that is, (1) dissolution of the vulcanizing agents into water, (2) sufficient contact of the rubber particles with the vulcanizing agents, and (3) the reaction of the rubber with the vulcanizing agents. The reaction was considered to proceed from surface to inside of the rubber particles, as well as the diffusion of sulfur, on the basis of observation of the surface of the film specimen. However, no conclusive mechanism has been proposed due to a lack of kinetic data on the prevulcanization through *in-situ* analysis.

Vulcanization is well known to be one of the important processes to form crosslinking junctions of the rubbery polymers. The resulting crosslinking junctions may govern the properties of final products. Thus, the structure of the crosslinking junctions has been extensively investigated and the mechanism of vulcanization has been proposed by Coran. [7] Based on the mechanism, the crosslinking junctions were analyzed by Koenig [8-10] through dipolar decoupling magic angle spinning (DD-MAS) NMR spectroscopy. However, assignments of the signals appearing after vulcanization were inaccurate due to overestimation of the chemical shift values. In order to analyze the crosslinking junctions of vulcanized natural rubber, thus, it is necessary to apply and latex-state NMR spectroscopy to the rubber.

In the previous work, Oraphin [3,11] assigned the small signals of vulcanized natural rubber through FG-FMAS solid-state NMR spectroscopy with various pulse sequences, i.e. DEPT, APT and two-dimensional correlation measurements. The signal at 44 ppm was assigned to the secondary carbons adjacent to carbons linking to S atoms and the signal at 58 ppm to the tertiary and quaternary carbons linking to S atoms. The plausible crosslinking junctions of vulcanized rubber were proposed, as shown in Figure 4-1.

Secondary carbons   Tertiary carbons   Quaternary carbons
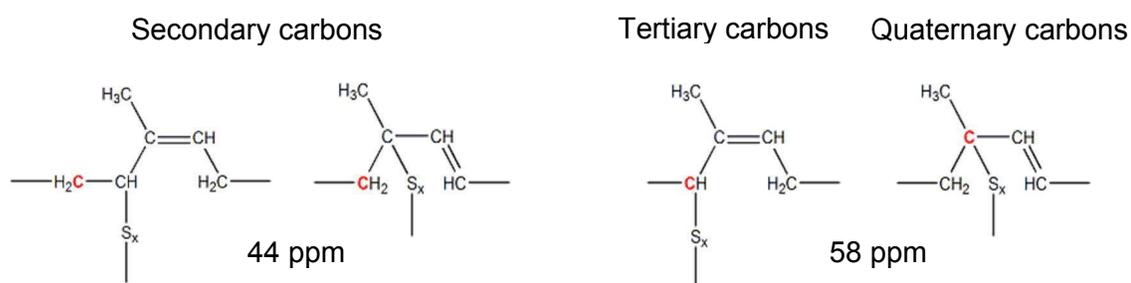
Figure 4-1 Plausible crosslinking junctions for the vulcanized natural rubber

In the present study, an attempt to investigate the prevulcanization of isoprene rubber latex was performed through latex-state ^{13}C NMR spectroscopy, based on the chemical shift

values of signals assigned by FG-FMAS solid-state NMR spectroscopy with DEPT, APT and HMQC measurements. The activation energy of the prevulcanization was determined by temperature dependency of the kinetic constant of the prevulcanization, estimated from the intensity ratio of the signals.

4.2   Experimental

4.2.1   Materials

Synthetic isoprene rubber (IR) latex, used in the present work, was an industrial product of about 55 w/w% dry rubber content (DRC). Sodium dodecyl sulfate (SDS) was purchased from Kishida Chemical Co., Ltd. Potassium hydroxide (KOH), methanol, and toluene were purchased from Nacalai Tesque Co., Ltd. Dispersion sulfur (dispersion S) 50 w/w%, dispersion zinc oxide (dispersion ZnO) 50 w/w% and dispersion zinc-dibutyldithiocarbamate (dispersion ZDBC) 50 w/w% were obtained from Nippon Zeon Co., Ltd. Dueterium oxide (D_2O) was purchased from Wako Co., Ltd.

4.2.2   Preparation of prevulcanized isoprene rubber

Prevulcanization of isoprene rubber was made in latex stage, using synthetic rubber latex as a raw material. The latex was diluted with distilled water to 30 w/w% DRC followed and then added SDS 0.5 w/w%. The pH of latex was adjusted with KOH solution to 10.5. The dispersion S, dispersion ZnO and dispersion ZDBC were added into latex. The prevulcanization was carried out by stirring the latex at about 200 rpm for 15 to 360 min at 70 to 90 ˚C (hereby abbreviated to PVIR70, PVIR75, PVIR80, PVIR85, and PVIR90). The prevulcanized isoprene rubber latex was centrifuged at 9000g for 30 min. Cream fraction of the latex was redispersed in SDS 0.5 w/w% followed by centrifugation again. The washed cream faction was redispered in SDS 0.5 w/w% to make 40 w/w% DRC. The resulting prevulcanized IR latex was subjected to latex-state NMR measurement. Schematic representation of the experimental procedure is shown Figure 4-2.

```
┌─────────────────────────────────┐
│      IR latex (DRC 55 w/w%)      │
└─────────────────────────────────┘
                │  ←──── SDS
                │        KOH (aq)
                ↓
┌─────────────────────────────────┐
│            IR latex             │
│ (DRC 30 w/w%, SDS 0.5 w/w%, pH 10.5) │
└─────────────────────────────────┘
```

- Stirring 200 rpm   ←──── S (1.5 phr)
- Temp 70 to 90 °C   ZnO (1.5 phr)
- Time 15 to 360 min   ZDBC (1.5 phr)

- Centrigation 9000g, 30 min   ←──── SDS
- Redispersion 30 min, twice

```
┌─────────────────────────────────┐
│       Prevulcanized IR latex    │
│   (DRC 40 w/w%, SDS 0.5 w/w%)    │
└─────────────────────────────────┘
```
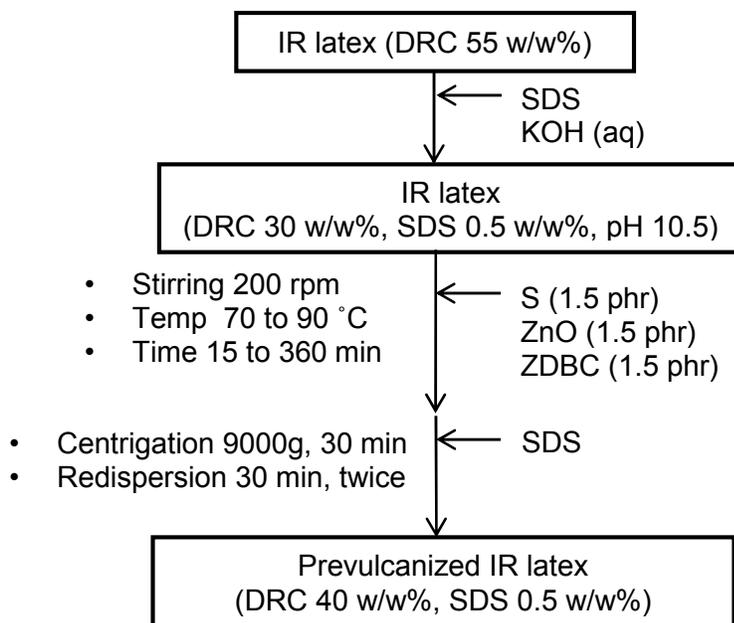
Figure 4-2 Preparation procedure of prevulcanized isoprene rubber latex

4.2.3   Characterization

Latex-state NMR spectroscopy was performed with a JEOL EX-400 FT-NMR spectrometer (Tokyo, Japan), operating at 100.40 MHz for ^{13}C. The prevulcanized isoprene rubber latex with deuterium dioxide was used for the measurement without further treatment. For the quantitative analysis, the pulse sequence of gated decoupling without Nuclear Overhauser Effect (NOE) was applied at 30° pulse. The NOE measurement was carried out at room temperature. The number of scans for the acquisition of spectra was 10,000 with a pulse repetition time of 5 s for ^{13}C. In this case, 90% reliability of the quantitative analysis was ensured for the NOE measurements.

The crosslink density of the prevulcanized isoprene rubber was determined by the swelling method. The rubber was immersed in 50 ml of toluene in the dark for a week at room temperature. The swelled sample was blotted with tissue paper and weighed on an analytical balance to nearest 10^4 *g*. It was dried under reduced pressure at 50 °C for more

than one week and reweighed again. The crosslink density was estimated using Flory-Rehner equation. [12]

$$v = \frac{1}{M_c} = -\frac{1}{2V_s} \frac{\ln(1-V_r) + V_r + X(V_r)^2}{(V_r)^{1/3} - (V_r/2)}$$

(Eq. 4-1)

where v is crosslink density (mol/cm^3), M_c is molecular weight between crosslinks, V_s is molar volume of the solvent (106.52 cm^3/mol), V_r is volume fraction of the rubber and X is Flory – Huggins interaction parameter (0.393).

The volume fraction of the rubber was determined as followed equation below;

$$V_r = \frac{1}{\left[(\rho_r / \rho_s)((W_s - W_u)/W_u) + 1 \right]}$$

(Eq 4-2)

where ρ_r is density of the rubber (0.913 g/cm^3), ρ_s is density of the solvent (0.865 g/cm^3), W_s is weight of swollen rubber (g) and W_u is weight of unswollen rubber (g).

4.3 Results and discussion

4.3.1 Effect of prevulcanization temperature

Figure 4-3 shows latex-state ^{13}C NMR spectra for the PVIR50, PVIR70, PVIR90 and IR latexes. Five major signals at 24, 26, 32, 124 and 132 ppm in the latex-state ^{13}C NMR spectra for PVIR50, PVIR70 and PVIR90 latexes were assigned to the five carbon atoms of cis-1,4-isoprene units, according to the previous work. [3] The narrow half-width and high signal-to-noise (S/N) ratio of the latex-state ^{13}C NMR spectra for PVIR50, PVIR70 and PVIR90 latexes may imply that the high-resolution is attained for the latex-state ^{13}C NMR spectroscopy even after prevulcanization.
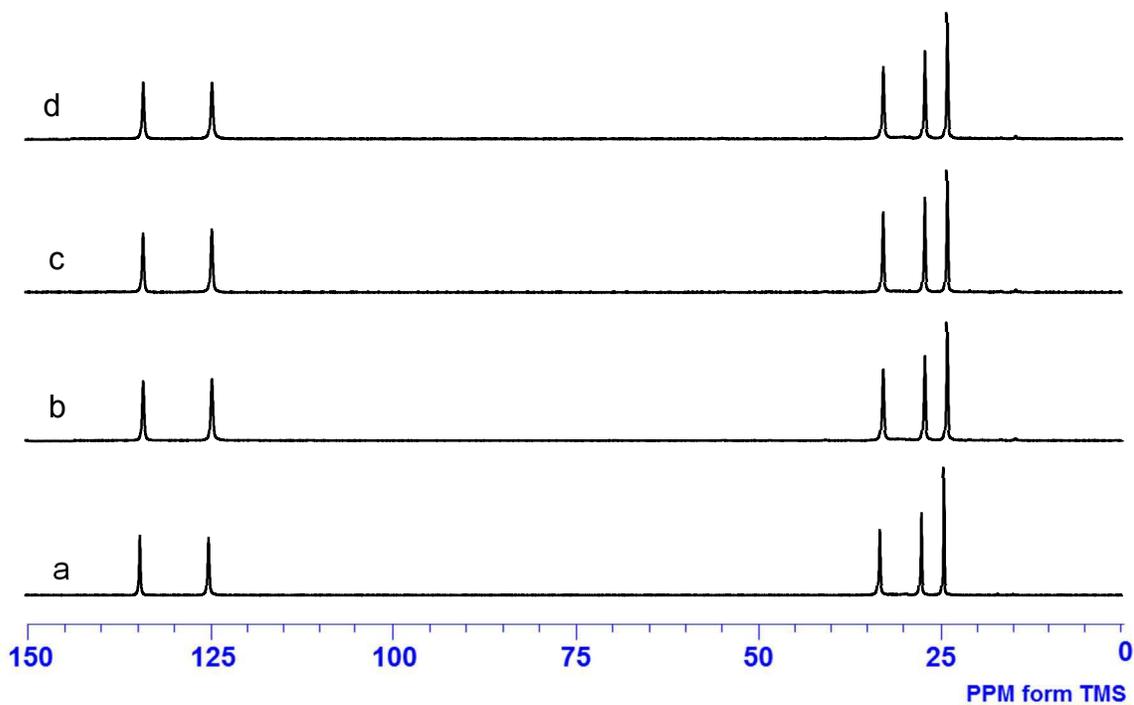
**Figure 4-3** Typical latex-state ^{13}C NMR spectra (a) the IR latex (b) PVIR50 latex

(c) PVIR70 latex and (d) PVIR90 latex, prepared by prevulcanization

The expanded latex-state ^{13}C NMR spectra for the PVIR50, PVIR70, PVIR90 latexes and IR latexes are shown in Figure 4-4. The small signals at 40, 44 and 58 ppm appeared in the latex-state ^{13}C NMR spectra for PVIR70 and PVIR90 latexes, whereas these signals did not appear in latex-state ^{13}C NMR spectrum for PVIR50 latex. The integral intensity of the signals was dependent up on temperature; that is, the higher the temperature, the higher is the integral intensity of the signals. The signals at 40 and 44 ppm were assigned to C4 of the *trans*-1,4-isoprene units and secondary carbons adjacent to carbons linking to S atoms, respectively. In contrast, the signal at 58 ppm was assigned to the tertiary and quaternary carbons linking to S atoms. These assignments were carried out on the basis of literature values of chemical shift for the signals. This implies that the prevulcanization of IR latex may occur at temperature above 70 $^{\circ}C$.
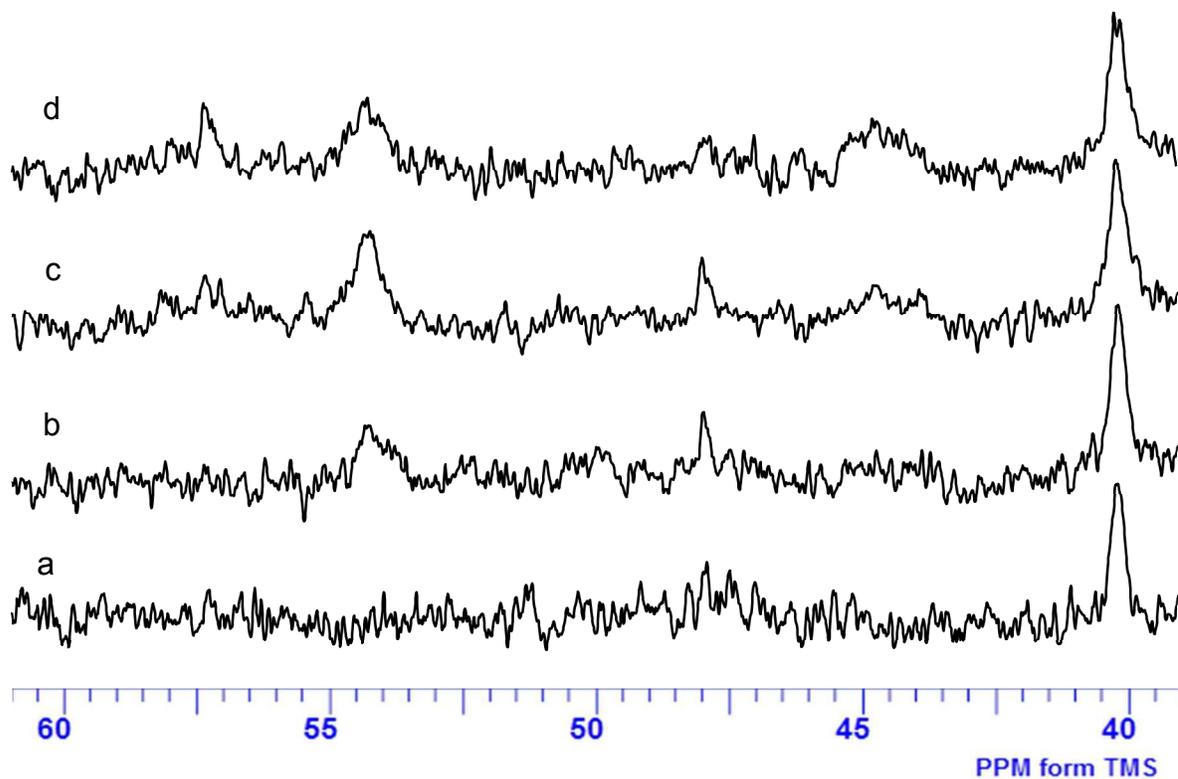
Figure 4-4 Typical latex-state ^{13}C NMR spectra, ranging from 40 to 60 ppm (a) the IR latex (b) PVIR50 latex (c) at PVIR70 latex and (d) PVIR90 latex, prepared by prevulcanization

4.3.2   Effect of prevulcanization time

Figure 4-5 shows a plot of crosslink density *versus* prevulcanization time for the PVIR70, PVIR80 and PVIR90 latexes. The value of crosslink density for the PVIR70, PVIR80 and PVIR90 latexes monotonically increased at initial stage, as the prevulcanization time was prolonged. The value of the crosslink density reached maximum at prevulcanization time of 90 min and, then, it decreased to a definite value. The first abrupt increase in the value of the crosslink density may be explained to be due to a significant formation of the crosslinking junctions, which may be related

to a rigorous generation of sulfur radicals at the initial stage. However, the formation of the crosslinking junctions may be reduced due to suppressed generation of sulfur radicals. At this moment, the decomposition of IR may increase and it may decrease against time. Eventually, a steady state may be achieved between the formation of crosslinking junctions and the decomposition of IR; in other words, a rate of formation of crosslinking junctions may become similar to a rate of decomposition of IR. It is, thus, necessary to perform the kinetic study on the formation of crosslinking junctions within 90 min from crosslinking start.
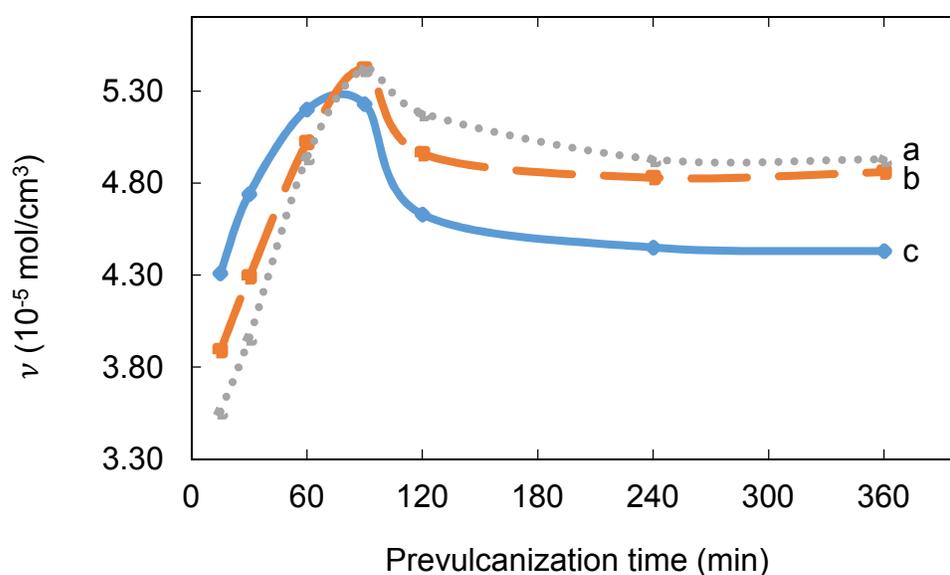
Figure 4-5 Crosslink density for the (a) PVIR70 latex, (b) PVIR80 latex and

(c) PVIR90 latex *versus* prevulcanization time

4.3.3 Mechanism of prevulcanization of isoprene rubber

Figure 4-6 shows a plot of the intensity of signals at 44 and 58 ppm *versus* prevulcanization time for PVIR90 latex, in which the intensity of signals at 44 ppm ($X_{44\,ppm}$) and 58 ppm ($X_{58\,ppm}$) was normalized with the integral intensity of the signals at 24 ppm, as follows:

$$X_{44\,ppm}(\%) = \frac{I_{44\,ppm}}{I_{24\,ppm}} \times 100 \tag{Eq.4-3}$$

$$X_{58\,ppm}(\%) = \frac{I_{58\,ppm}}{I_{24\,ppm}} \times 100 \tag{Eq.4-4}$$

where I is integral intensity of the signals and the subscripts represent the value of the chemical shift. [11] The intensity of the signals was, in most cases, determined at the S/N ratio of more than 5, whereas it was estimated by averaging the intensities of the spectra for several experiments as the S/N ratio was smaller than 5. As shown in Figure 4-6, the intensity of signals at 44 and 58 ppm were dependent upon the prevulcanization time and it reached maximum value at the prevulcanization time of 90 min. The locus of the intensity of signals at 44 and 58 ppm versus prevulcanization time was similar to the dependency of crosslink density on the time. This demonstrates that the number of crosslinking junctions is directly related to the crosslink density of prevulcanized IR latex, as the prevulcanization is performed at 90 ˚C.
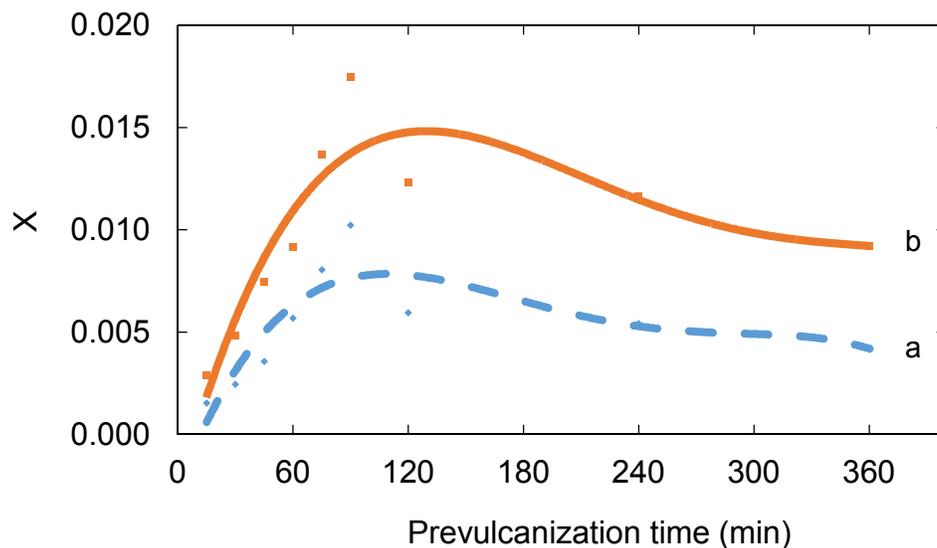
Figure 4-6 Integral intensity of the signals at approximately (a) 44 ppm and

(b) 58 ppm *versus* prevulcanization time

The prevulcanization of IR latex was further investigated by kinetic study on the crosslinking reaction. [13] Figure 4-7 and 4-8 show semi logarithmic plots of the integral intensity of the signals at 44 and 58 ppm *versus* the prevulcanization time. The integral intensity of the signals at 44 and 58 ppm was proportional to the prevulcanization time in the initial stage of the reaction. The value of k for PVIR70, PVIR 75, PVIR 80, PVIR 85 and PVIR90 latexes was, thus, determined as a slope of the semi logarithmic plot of the integral intensity of the signals at 44 and 58 ppm *versus* the prevulcanization time.
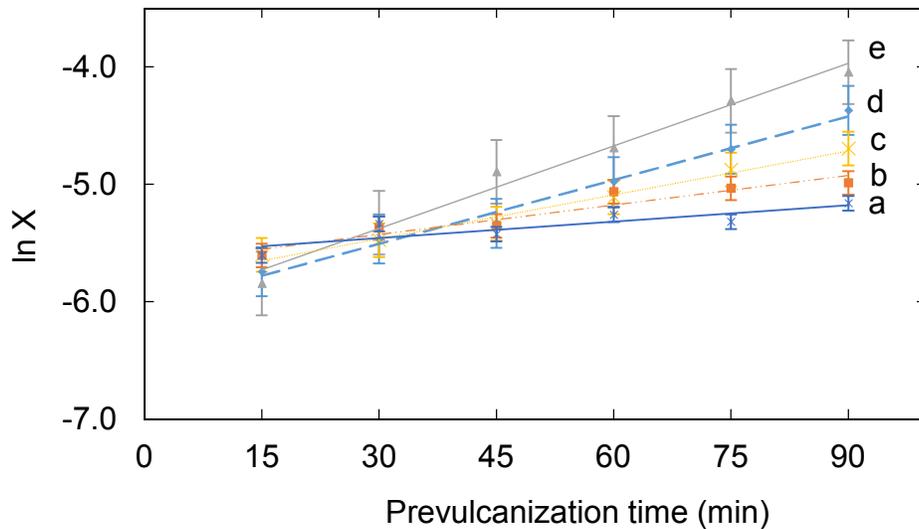
Figure 4-7 Semi logarithmic plots of intensity of the signal at 44 ppm for (a) PVIR70,

(b) PVIR75, (c) PVIR80, (d) PVIR85 and (e) PVIR90 latexes *versus* prevulcanization time
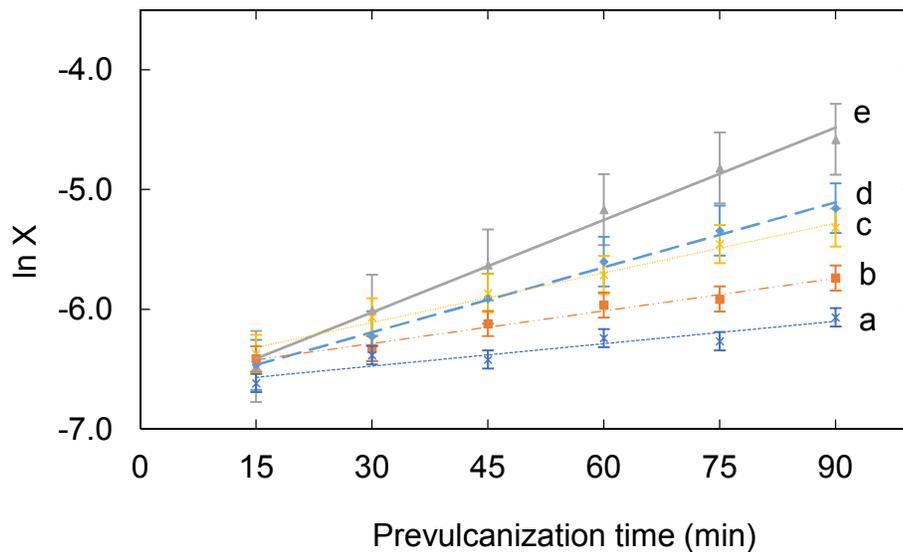
Figure 4-8 Semi logarithmic plots of intensity of the signal at 58 ppm for (a) PVIR70,

(b) PVIR75, (c) PVIR80, (d) PVIR85 and (e) PVIR90 latexes *versus* prevulcanization time

The estimated values of k are tabulated in Table 4-1. The value of k was dependent upon the prevulcanization temperature. Thus, the logarithmic value of k was plotted against a reciprocal temperature: that is, Arrhenius plot. The activation energy was estimated from a slope of the Arrhenius equation, as follows:

$$\ln k = \frac{-E_\alpha}{RT} + \ln A \qquad\qquad (Eq.4\text{-}5)$$

where k is rate constant of reaction (s^{-1}), A is frequency factor, E_α is activation energy (kJ/mol), R is gas constant (J/mol·K) and T is absolute temperature (K).

Table 4-1 Estimated value of rate constant of reaction (k)

Prevulcanization Temperature (˚C)	Rate constant of reaction (s^{-1})	
	44 ppm	58 ppm
70	0.0045	0.0060
75	0.0084	0.0091
80	0.0125	0.0138
85	0.0181	0.0181
90	0.0235	0.0257

As shown in Figure 4-9, the slopes of the Arrhenius plots were nearly identical to each other. For instance, the estimated value of activation energy of the signal at 44 ppm was 83.2 kJ/mol and that of the signal at 58 ppm was 72.7 kJ/mol. These were similar to the value of the activation energy of the decomposition of the peroxide and sulfur. [14,15] This may be explained to be due to the bottle-neck nature of the decomposition of the peroxide and sulfur in the reactions. When the decomposition of the peroxide and sulfur occurs, the primary radicals may be quickly formed; especially, in the case of the prevulcanization,

crosslinking junctions are suddenly formed in the rubber. According to this mechanism, the decomposition of sulfur is, thus, considered to dominate a major portion of the prevulcanization of the rubber; that is, the formation of the crosslinking junctions rapidly occurs, as the sulfur radicals are generated.
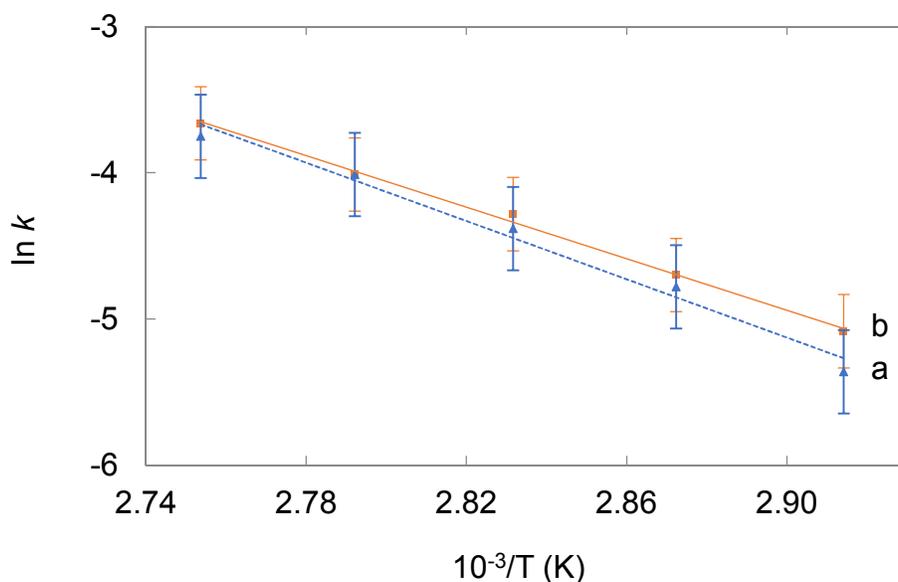

Figure 4-9 Plot of logarithmic value for the k for the signals at (a) 44 ppm and (b) 58 ppm *versus* reciprocal temperature (Arrhenius plots)

The plausible mechanism of prevulcanization of isoprene rubber latex is shown in Figure 4-10. The formation of the crosslinking junctions may be considered to precede two paths: that is, hydrogen abstraction with sulfur radical (pathway A) and addition of sulfur radical (pathway B). The low value of the activation energy may suggest that the decomposition reaction requires low energy to generate the primary radicals such as (RO•), (HO•) and (R•) etc. to form the crosslinking junctions.

The crosslinking junctions A1, A2 and A3 may be formed by hydrogen abstraction at C1 methylene or C4 methylene of *cis*-1,4-isoprene units. The carbon-sulfur linkages of A1, A2 and A3 are tertiary and quaternary carbons, whose value of chemical shift is

approximately 58 ppm. On the other hand, the crosslinking junctions B1 and B2 are formed by the addition of sulfur radicals onto carbon-carbon double bond of *cis*-1,4-isoprene units. The carbon-sulfur linkages of B1 and B2 are tertiary carbon and quaternary carbons, whose value of chemical shift are approximately 50 ppm, according to the literature. In Figure 4-4, the signals, assigned to tertiary and quaternary carbons, appeared at 58 ppm for prevulcanized IR latexes, whereas no signal appeared at 50 ppm. From the results, it is proven that the prevulcanization of IR latex precedes in Pathway A (hydrogen abstraction with sulfur radicals).
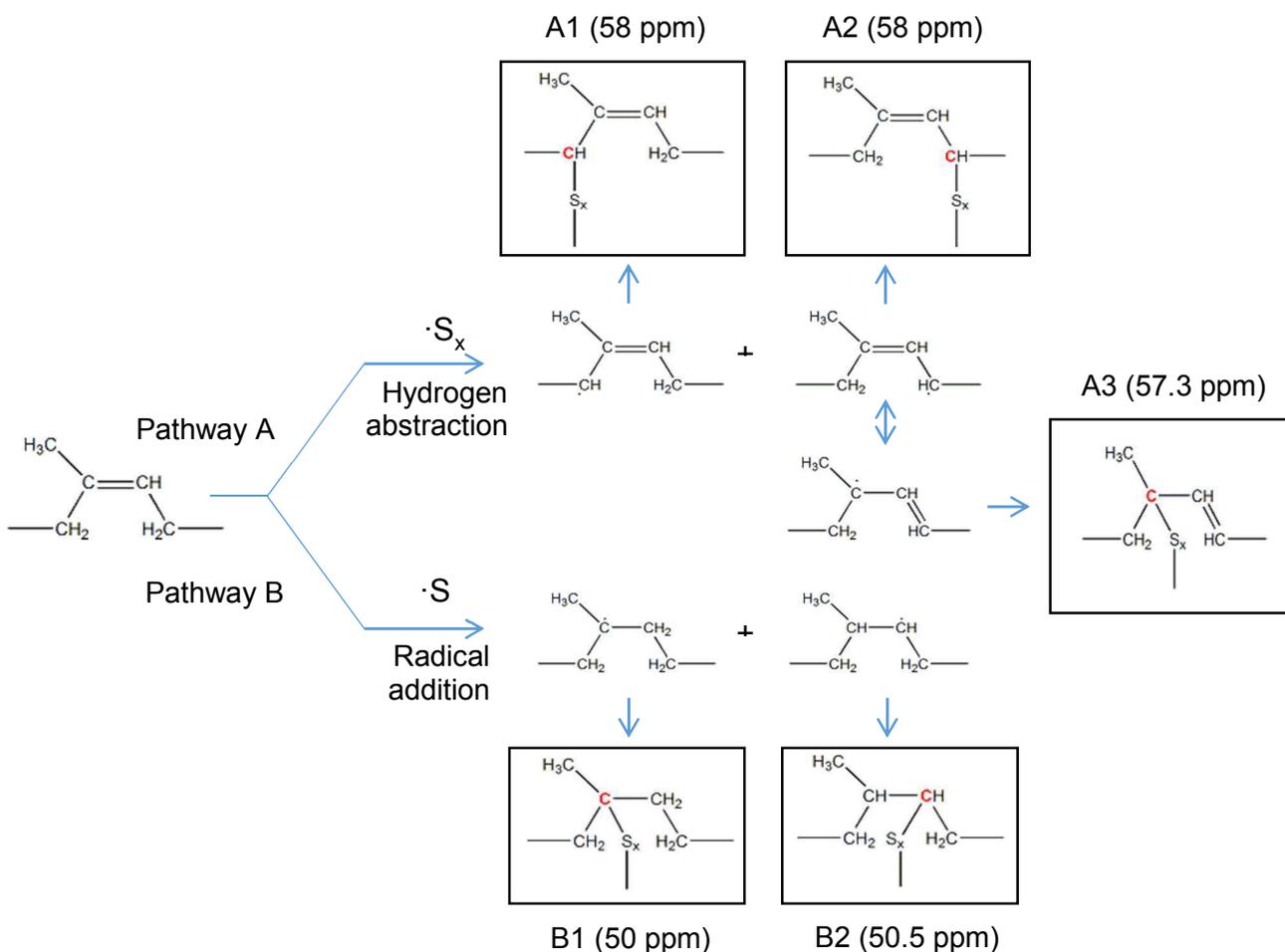
Figure 4-10 Plausible of mechanism of prevulcanization of isoprene rubber latex

4.4   Conclusion

The mechanism of the prevulcanization of IR in latex stage was investigated through latex-state ^{13}C NMR spectroscopy. The signals at 40 and 44 ppm were assigned to C4 of the *trans*-1,4-isoprene units and secondary carbons adjacent to carbons linking to S atoms, respectively. In contrast, the signal at 58 ppm was assigned to the tertiary and quaternary carbons linking to S atoms. The time evolution of intensity of these signals was analyzed at various temperatures by latex-state ^{13}C NMR spectroscopy to investigate the mechanism for prevulcanization of the IR in latex stage. The activation energies of the prevulcanization were estimated for signals at 44 ppm and 58 ppm, which were 83.2 kJ/mol and 72.7 kJ/mol, respectively. The value of the activation energies was similar to that of the decomposition of sulfur at the initial stage, suggesting that the decomposition of the sulfur was a bottle-neck process, which dominated the prevulcanization of IR in latex stage. The plausible mechanism of the prevulcanization of IR latex was suggested to begin with the abstraction of hydrogen at allylic position of isoprene units.

4.5   References

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CHAPTER 5

Effect of non-rubber component on vulcanization and mechanical properties of vulcanized rubber

5.1 Introduction

Removal of proteins from natural rubber (NR) with urea is conducted to prepare a vulcanized deproteinized natural rubber latex, rapidly and efficiently. The proteins present on the surface of NR particle in the latex stage may sometimes cause an allergy [1-3] to sensitive individual and side reaction during chemical modification of NR latex. [4] In our previous work [5-7], the removal of proteins can be successfully prepared in latex stage using proteolytic enzyme to decompose the proteins and urea treatment to denaturation of the proteins. However, in order to improve deproteinized natural rubber (DPNR) latex as a rubber product it is necessary to investigate the properties of vulcanized latex.

In this study, physical and mechanical properties of DPNR latex treated with urea as a denaturant in the presence of surfactant was investigated. DPNR latex was also applied for vulcanization in latex stage in order to prepare a thin film product.

5.2 Experimental

5.2.1 Materials

Natural rubber latex (HANR), Sulfur (S), Zinc oxide (ZnO), Zincdiethyldithiocarbomate (ZDEC), Zinc mercaptobenzothaizole (ZMBT), Wingstay-L and Terric acid were purchased from Rubber Research Institute of Thailand. Sodium dodecyl sulphate (SDS) was supported by Nagaoka University of Technology. Calcium nitrate (Ca(NO$_3$)2 4H2O) were purchased from TTK science. Ltd. Urea was purchased from BDH Laboratory Supplies Ltd. Potassium

hydroxide (KOH) was purchase from VWR International Ltd. Polymer coating (C1 and C2) was donated from Glove Company.

5.2.2   Preparation of deproteinized natural rubber (DPNR)

HANR latex was incubated with 0.1 wt% urea in the presence of 1.0 wt% SDS solution at room temperature for 1 h. the centrifugation was used to separate the cream fraction, which was redispersed in 1.0 wt% SDS solution. Then, the cream fraction was washed twice with 0.5 and 0.1 wt% SDS solution, respectively.

5.2.3   Preparation of prevulcanized latex

The DPNR latex was prepared by compounding of DPNR latex according to the formulations shown on Table 5-1. The mixtures were incubated at room temperature   for 96 h, then were prevulcanized at 60ºC for 25 min.

Table 5-1 Formulation of prevulcanized DPNR latex compound

Component	Weight (g)
60% DPNR latex	167.0
10% KOH	2.0
10% Terric acid	0.2
50% Sulfur	1.6
50% ZDEC	0.8
50% ZMBT	0.8
50% Wingstay-L	2.0
50% ZnO	2.0
30% Coating polymer (C1 and C2)	10, 20

5.2.4   Preparation of DPNR latex films

The DPNR film was prepared by dipping method as shown in Figure 5-1. The dipping was achieved by using ceramic bar as mold. The mold was dipping into the coagulant for 30 s followed by drying in the oven at 100˚C for 1 min. The dried mold was dipped into the

prevulcanized DPNR latex. The soaking time was 1 min, after that was vulcanized in the oven

at 100 ˚C for 30 min
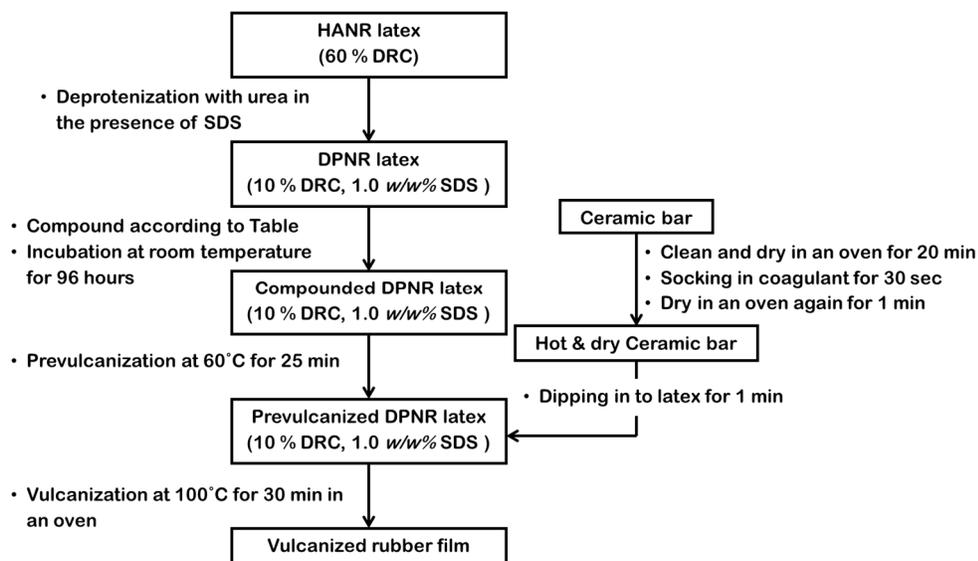
Figure 5-1 Preparation of vulcanized DPNR film

5.2.5   Characterization

The physical properties of latex were investigated by Thai Industrial Standard (TIS 980

– 2009) i.e. determination of total solids content (ISO 124 - 1997), determination of dry rubber

content (ISO 126 - 1995) and determination of volatile fatty acid number (ISO 506 - 1992).

The amount of water soluble protein of rubber dry film prepared from concentrated NR

was measured using a Standard Test Method for Analysis of Aqueous Extractable Protein in

Natural Rubber and Its Products Using the Modified Lowry Method.

The testing was performanced according to determination of tensile stress – strain

properties (ISO 37 - 2005) type 2. The two pieces of dumbbell were cut from each film. Also,

the average thickness was evaluated and used for the measurement. Mechanical properties

of tensile strength and elongation at break for NR vulcanized films were investigated by

universal testing machine. The crosshead was operated at speed of 500mm/min.

Particle size distribution and zeta potential analysis was determined using a Malvern 2000 laser particle analyzer. About 5–10% (v/v) of rubber latex was dispersed in distilled water before the analysis. The stock buffer solution was freshly prepared in the pH range of 4–12 for dispersing the prevulcanized natural rubber latex, as given in Table 1. Samples were prepared by adding one drop of latex to 20 ml of buffer solution. Zeta-potential values for natural rubber particles were determined using zeta potential analyzer (MALVERN S4700 version 1.27). The rubber latex was dropped into de-ionized water and then injected into the sample handling for re-flush and measurement, respectively. Zeta potential was observed using the conversion of the frequency and scattering intensity function. The Measurement of particle size in suspensions with Brownian motion based on the theory of the Stokes-Einstein equation.

5.3   Results and discussion

5.3.1   Physical properties

Total nitrogen content of HANR and DPNR, which is proportional to the amount of proteins present in the rubber latex, is shown in Table 5-2. The total nitrogen content of HANR decreased from 0.45 wt% to 0.06 wt% after incubation with urea for 1 hours at room temperature. It may demonstrate that most proteins present in NR latex are attached to the rubber with weak attractive forces, can be detached with urea.

Table 5-2 Total solid content (% TSC), dry rubber content (%DRC), nitrogen content, water soluble protein and volatile fatty acid (VFA) number of HANR and DPNR latex

Sample	TSC (%)	DRC (%)	Nitrogen content (wt%)	Water soluble protein (μg/g)	VFA number
HANR	60.87	60.05	0.45	4,215	0.028
DPNR	60.75	59.83	0.06	1.52	0.014

The amount of water soluble protein content of HANR was 4,215 μg/g, which was very much higher than those of DPNR (1.5 μg/g), respectively. The result confirms that urea treatment is quite effective to prepare low protein rubber latex.

Physical properties i.e. total solid content (TSC), dry rubber content (DRC) and volatile fatty acid (VFA) of NR were also tabulated in Table 2. %TSC and % DRC of DPNR latex were lower than a neat HANR after centrifugation twice. Then we kept the both DPNR latex (preservation with NH_4 content about 0.2 wt%) for 2 weeks before testing of VFA. Volatile fatty acid number indicates a quality of preservation latex in which occurred from degradation of protein by bacteria present in the latex. VFA number of DPNR was lower than HANR two times. This may be due to the lower amount of protein in the latex.

5.3.2 Particle size distribution and zeta potential

The rubber latex were usually maintain colloidal stability via their surface charges having either lower of -30 mV or higher of +30 mV. [8] Table 5-3 shows a zeta potential value of HANR, DPNR and prevulcanized DPNR latex. It was found that all rubber samples were negative charge at pH 8.5-9.8. The zeta potential values of DPNR latex and prevulcanized DPNR were lower than HANR. This may be due to the surface of NR latex was covered with protein molecules which was contains both carboxyl and amino groups. Therefore after removal of protein, the negative charge of rubber particles was reduced but still maintain stable without self-coagulation. We found that the DPNR latex and prevulcanized DPNR latex at pH of 8.5 and 8.9, were -45.90 and -37.69 mV, respectively.

The particle size distribution of rubber latex was shown in Figure 5-2 and mean diameter of particle size for HANR, DPNR and prevulcanized DPNR latex was tabulated in Table 5-3. It was found that the average mean diameter of HANR was lower than DPNR and prevulcanized DPNR latex. This may be due to the reduction of zeta potential of the latex.

There are a potential to coagulation after removal of negative charge (proteins) and when we stirred the DPNR latex for preparing the prevulcanized latex.

Table 5-3 Particle size distribution and Zeta potential value of natural rubber latex

Sample	Mean diameter of particle size (nm)	Zeta potential (mV)	pH
HANR	440.57	-58.83	9.88
DPNR	643.67	-45.90	8.54
Prevulcanized DPNR	804.60	-37.69	8.90
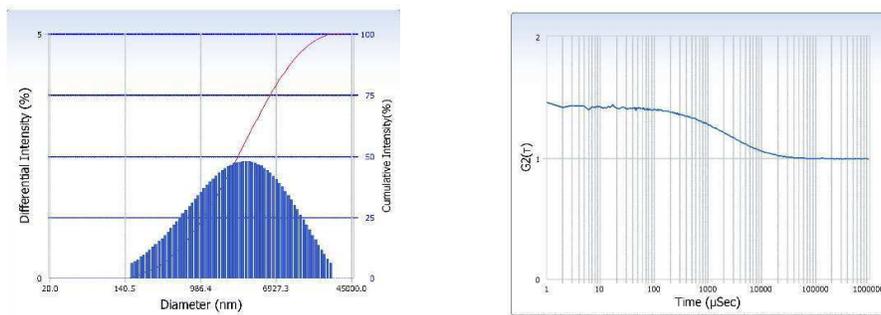
Figure 5-2 Particle size distributions of DPNR latex

5.3.3 Mechanical properties

The DPNR latex was then compounding using sulfur vulcanization as shown in Table 5-1. Figure 5-3 shows a typical stress-strian curve of prevulcanized DPNR. The Tensile strength, modulus100, modulus 300 and elongation at break of the DPNR after vulcanization at various curing times (5, 10, 15 and 20 mins) was estimanted from Figure 5-3.
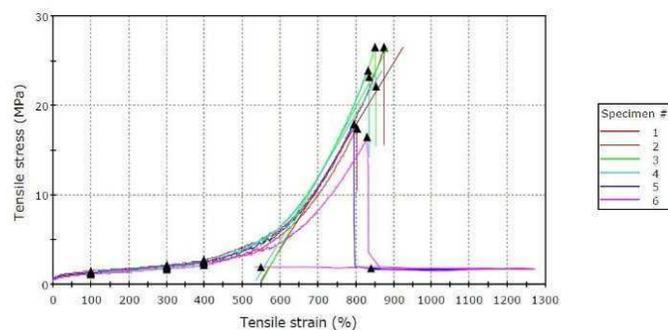
Figure 5-3 Stress-strain curve of vulcanized DPNR/C2 at curing time 20 min

As can be seen in the Figure 5-4, tensile strength of DPNR/C1 was increased with increasing curing time while tensile strenght of DPNR/C2 was decreased.   It was found that after mix DPNR with C2 at 10 wt% shows the higest value of tensile strenght. From Figure 5-5, elongation at break of DPNR was higher than that of HANR (843%) in selected conditions.
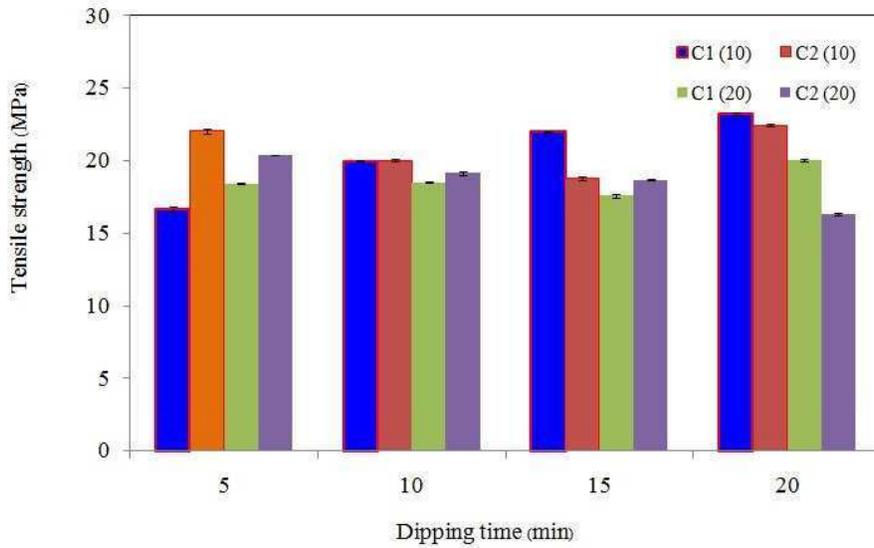
Figure 5-4 Tensile strength of vulcanized DPNR/C1 and vulcanized

DPNR/C2 at various curing time
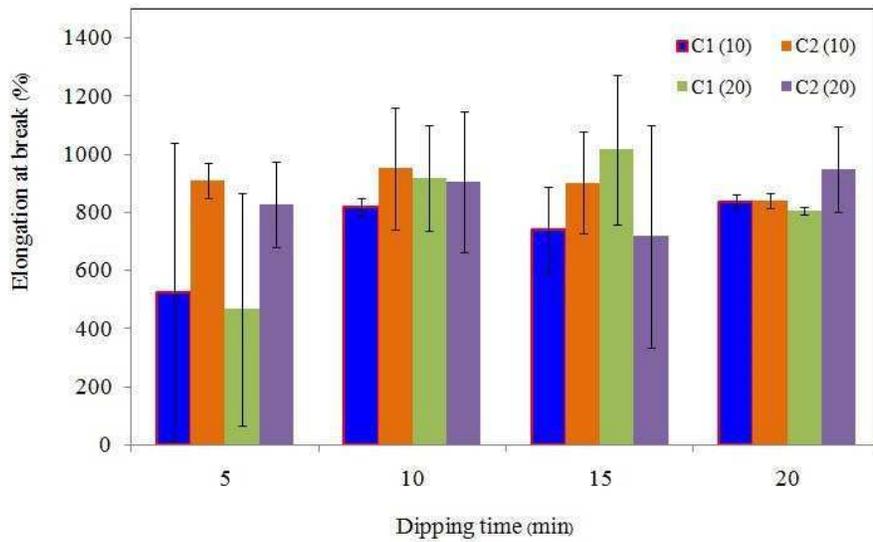
Figure 5-5 Elongation at break of vulcanized DPNR/C1 and vulcanized

DPNR/C2 at various curing time

Table 5-4 and 5-5 show the modulus at 100% and 300 % of DPNR/C1 and vulcanized DPNR/C2 at various curing time. It was found that the modulus tended to increased when curing time increased. The modulus at 300% was higher than modulus 100% for all samples. It is worth to note that modulus of vulcanized DPNR was higher than that of HANR. It may suggest the possibility to develop a preparation of low protein natural rubber product when elongation higher than 500%.

Table 5-4 Modulus 100% of vulcanized DPNR/C1 and vulcanized DPNR/C2 at various curing time

Curing time	Modulus 100% (MPa)			
(mins)	(C1 10)	(C2 10)	(C1 20)	(C2 20)
5	0.90±0.16	1.14±0.15	0.80±0.07	0.95±0.01
10	0.88±0.01	1.15±0.07	0.69±0.05	0.94±0.11
15	1.10±0.05	1.17±0.12	0.77±0.14	0.98±0.04
20	1.12±0.10	1.26±0.10	0.92±0.07	0.94±0.09

Table 5-5 Modulus 300% of vulcanized DPNR/C1 and vulcanized DPNR/C2 at various curing time

Curing time	Modulus 300% (MPa)			
(mins)	(C1 10)	(C2 10)	(C1 20)	(C2 20)
5	1.54±0.11	1.82±0.24	1.47±0.10	1.63±0.04
10	1.50±0.03	1.81±0.06	1.39±0.06	1.65±0.17
15	1.85±0.11	1.85±0.23	1.51±0.14	1.74±0.06
20	1.83±0.23	1.95±0.12	1.64±0.12	1.63±0.13

5.4 Conclusion

Removal of protein from natural rubber latex using urea treatment was proved to be effective method to prepare vulcanized DPNR rapidly and efficiently. It was confirmed by nitrogen content and amount of water soluble proteins. The DPNR latex are able to void a self coagulation due to a presence of negative charge even after removal of protein. From the present study of vulcanized DPNR, we found that a mechanical properties of vulcanized DPNR can be improved by mixed with polymer coating therefore the quality of DPNR materials can be enhanced more for specific applications.

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CHAPTER 6
Conclusion

In the present study, the quantitative analysis of the latex-state NMR spectroscopy was established for the polymer colloids. The epoxidation of natural rubber and the prevulcanization of natural rubber and IR were quantitatively analyzed by latex-state NMR spectroscopy.

The chemical shift values of the signals in the latex-state NMR spectrum were the same as those in the solution-state NMR spectrum. In addition, the values of half width and S/N ratio of signals in the latex-state ^{13}C NMR spectrum were found to be sufficiently narrow and small, which were similar to those in the solution-state NMR spectrum, when the NMR measurements were performed at the temperature of 50°C or higher. The epoxy group contents of EDPNR determined by latex-state NMR spectroscopy was almost similar to those determined by solution-state NMR spectroscopy. It was proved that the quantitative analysis was performed by latex state NMR spectroscopy.

The quantitative analysis through latex-state NMR spectroscopy was performed for prevulcanization of natural rubber, which was carried out with zinc-2-mercaptobenzothiazole (ZMBT) as an accelerator. The structure of the crosslinking junctions of prevulcanized natural rubber (PVNR) was quantitatively analyzed by latex-state NMR spectroscopy. Small signal at 37 ppm was assigned to secondary carbon adjacent to carbons linking to sulfur atoms, whereas the signals at 50 and at 50.5 ppm were assigned to quaternary carbons linking to sulfur and the tertiary carbon linking to sulfur, respectively. The kinetic constants of the prevulcanization at 70, 75, 80, 85 and 90 °C were determined as a slope in the plot of logarithmic intensity of the signals *versus* prevulcanization time. The activation energy of

prevulcanization of natural rubber was 51.5 and 47.2 kJ/mol, which was estimated from the intensities of the signals at 37 and 50 ppm, respectively.

The latex-state NMR spectroscopy was applied to the quantitative analysis of the prevulcanization of IR latex, which was carried out with zinc-dibutyldithiocarbamate (ZDBC) as an accelerator. Small signals at 40 and 44 ppm were assigned to C4 of the *trans*-1,4-isoprene units and secondary carbons adjacent to carbons linking to sulfur atoms, respectively, whereas the signals at 58 ppm was assigned to the tertiary and quaternary carbons linking to sulfur atoms. The intensity of the signals was dependent upon not only prevulcanization time but also prevulcanization temperature. The kinetic constants at 70, 75, 80, 85 and 90 °C were determined as a slope in the plot of logarithmic intensity of the signals *versus* prevulcanization time. The activation energy of prevulcanization of IR was 83.2 and 72.7 kJ/mol, which were estimated from the intensity of the signals at 44 and 58 ppm, respectively. From the results, the plausible mechanism of prevulcanization of IR was proposed to be the following two: that is, one starting from the hydrogen abstraction of IR with sulfur radical and the other starting from addition of sulfur radical to carbon-carbon double bonds.

The effect of proteins on the prevulcanization of natural rubber was investigated to understand the difference in the prevulcanization between natural rubber and IR. The deproteinzation of natural rubber was carried out by incubation of HANR latex with urea in the presence of surfactant. The HANR, DPNR and prevulcanized DPNR latexes were characterized by measurements of the zeta potential and particle size distribution. It was found that the average mean diameter of HANR was smaller than those of DPNR and prevulcanized DPNR. The value of the zeta potential decreased in the order of HANR, DPNR and prevulcanized DPNR, i.e., -58.3, -45.9 and -37.9 mV, respectively.

In this thesis, the latex-state NMR spectroscopy was found to be a powerful technique to investigate not only constitutional units of polymers in latex but also mechanism

of the reactions of the polymer colloids. It ensured high reliability and accuracy for the quantitative analysis of polymer colloids.

List of publications

1. "The mechanism properties of vulcanized deproteinized natural rubber"

   Ariyawiriyanan W., Nuinu J., **Sae-heng K.**, Kawahara S.

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2. "Prevulcanization of isoprene rubber latex"

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   Colloid and Polymer Science. **2015**; *293(5)*, 1457–1464.

3. "Latex-state NMR spectroscopy for quantitative analysis of epoxidized deproteinized natural rubber"

   Sae-heng K., Kanya T., Choothong N., Kosugi K., Ariyawiriyanan W., Kawahara S.

   Polymer for Advance Technology. in press.

Presentations

1. "Study on Prevulcanization of Isoprene Rubber" (Oral)

   Sae-heng K., Kawahara S.

   63rd SPSJ Symposium on Macromolecules, September 24-26th, 2014; Nagasaki University, Nagasaki, Japan.

2. "Mechanism of prevulcanization of isoprene rubber latex" (Oral)

   Sae-heng K., Kawahara S.

   The 10th SPSJ International Polymer Conference (IPC 2014), December 2-5th, 2014; Tsukuba International Congress Center, Ibaraki, Japan.

3. "Latex-state NMR spectroscopy for analysis of reaction between polyisoprene and sulfur" (Poster)

   Sae-heng K., Kawahara S.

   15-1 NMR meeting, May 15th, 2015; SEKISUI CHEMICAL (Kyoto R&D Laboratories), Kyoto, Japan.

4. "Latex-state NMR spectroscopy for analysis of prevulcanization of isoprene rubber latex" (Poster)

   Sae-heng K., Kawahara S.

   4th Gigaku Conference, June 19-22th, 2015; Nagaoka University of Technology, Nagaoka, Japan.

5. "Effect of accelerator on crosslinking junctions and mechanical properties of vulcanized natural rubber" (Oral)

   Sae-heng K., Kawahara S.

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6. "Analysis of reaction between polyisoprene rubber latex and sulfur" (Oral)

   Sae-heng K., Kawahara S.

   64th SPSJ Symposium on Macromolecules, September 15 -17th, 2015; Tohoku University (Kawauchi Campus), Miyaki, Japan.

7. "Latex-state NMR spectroscopy for analysis of prevulcanization of isoprene rubber latex" (Poster)

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10. "Prevulcanization of isoprene rubber latex" (Poster)

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The International Rubber Conference (IRC) 2016, October 24-28th, 2016; Kitakyushu International Conference Center, Fukuoka, Japan.

11. "Latex-state NMR spectroscopy for quantitative analysis of epoxidized deprotenized natural rubber" (Oral)

Sae-heng K., Kawahara S.

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