Study on Preparation and Characterization of Phenyl-Modified Natural Rubber

(フェニル修飾天然ゴムの調製とキャラクタリゼーションに関する研究)

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CHAPTER 1

General Introduction

Chemical modification may have a potential to improve mechanical properties of natural rubber, since glass transition temperature of the rubber is varied by chemical modification [1,2]. For instance, phenyl-modified natural rubber may change its glass transition temperature as a function of phenyl group content. Thus, the phenyl-modified natural rubber may achieve a good balance between rebound resilience and wet skid resistance, which are necessary to prepare high performance tire, since the balance is dependent upon the glass transition temperature. In addition, to meet a requirement of the sustainable development goals (SDGs), a water process must be established for the modification of natural rubber without versatile organic solvent, since natural rubber is isolated as a latex from *Hevea brasiliensis*. It is, therefore, necessary to prepare the phenyl-modified natural rubber and to develop the water process of natural rubber.

The phenyl-modified natural rubber may be prepared by direct insertion of the phenyl groups into natural rubber. For instance, carbon-carbon bonds between the phenyl groups and natural rubber may be formed by Suzuki-Miyaura cross-coupling reaction [3-6], which is known as a homologation reaction of hydrocarbons having allylic bromide groups. In general, the Suzuki-Miyaura cross-coupling reaction begins with oxidative addition of the allylic bromide groups to form a palladium (II) complex and, then, alkyl groups of alkylboronic acid replace a halide anion on the palladium complex by transmetallation. The reaction is usually carried out in homogeneous solution. In addition, this reaction is also performed in oil/water emulsion due to stability of the palladium catalyst in water. Based on the previous works [7-

8], therefore, the phenyl-modified natural rubber may be prepared in latex stage by Suzuki-Miyaura cross-coupling reaction when a suitable catalyst is used. One of the suitable catalysts is di-μ-chloro-bis [5-hydroxy-2-[1-(hydroxyimino)-ethyl]-phenyl] palladium (II) dimer, since it exists at the interface between natural rubber particles and water in latex due to hydrophobic nature of the catalyst.

In the present study, first, Suzuki-Miyaura cross-coupling reaction was performed in solution for natural rubber after deproteinization followed by bromination. The bromination of natural rubber was carried out with N-bromosuccinimide (NBS) under nitrogen atmosphere in dichloromethane. The characterization of brominated natural rubber was performed by 1D and 2D-nuclear magnetic resonance (NMR) spectroscopy. The resulting brominated natural rubber was subjected to cross-coupling reaction with phenylboronic acid in the presence of the di-μ-chloro-bis [5-hydroxy-2-[1-(hydroxyimino)-ethyl]–phenyl] palladium (II) dimer in tetrahydrofuran to convert the allylic bromide groups to phenyl groups. Second, the preparation of phenyl-modified natural rubber was performed in latex stage by Suzuki-Miyaura cross-coupling reaction of brominated natural rubber with phenylboronic acid in the presence of the palladium catalyst. The T_g and viscoelastic properties of the phenyl-modified natural rubber were investigated by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), respectively.

1.1 Chemical modification of natural rubber

Natural rubber is known to be superior in green strength, tensile strength, tear strength and rebound resilience, whereas it is inferior in weather resistance, heat resistance, oil resistance, abrasion resistance and wet skid resistance [9-11]. Therefore, chemical modification

of natural rubber has been carried out to improve the inferior properties of natural rubber without sacrificing the superior properties. For instance, Wada *et al.* [12] reported that the environmental resistances and wet skid resistance were improved by introduction of epoxy groups to natural rubber. However, the epoxy groups are known to undergo ring-opening reaction under acidic condition [13]; that is, epoxidized natural rubber is decomposed as the acid rain falls. Therefore, it is necessary to introduce chemically stable substituent such as phenyl groups into natural rubber instead of epoxy groups. In the present study, it is, thus, important to establish a suitable method to insert the phenyl groups into natural rubber in a rational basis.

1.2. Suzuki-Miyaura cross-coupling reaction

Suzuki-Miyaura cross-coupling reaction is well-known to be a palladium-catalyzed cross-coupling reaction of organohalides with organoboron compounds [3-6]. It has become one of the most efficient homologation reactions. Therefore, many researchers have used Suzuki-Miyaura cross-coupling reaction to introduce aromatic rings into organic compounds; for instance, aromatic rings were introduced into brominated butyl rubber in the presence of di-μ-chlorobis[5-hydroxy-2-[1-(hydroxyimino) ethyl] phenyl] palladium (II) dimer (Figure 1-1) [14-17].

Catalytic cycle for palladium catalyzed cross-coupling reaction between organoboron compound and organohalide is shown in Figure 1-2. First, oxidative addition of palladium (Pd^0) and organohalide (R_2—X) produces organopalladium species (R_2—Pd^{II}—X). Transmetallation of organometallic species under base generates a palladium (II) intermediate (R_1—Pd^{II}—R_2). In this step, the base also plays important roles in the formation of R_2—Pd^{II}—OH from

R_2—Pd^{II} —X and R_1—B^-—OH from R_1—B. Second, reductive elimination generates a product (R_1—R_2) and Pd^0 catalyst.
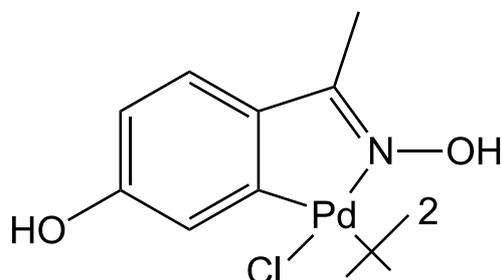

Figure 1-1 di-μ-chlorobis[5-hydroxy-2-[1-(hydroxyimino) ethyl] phenyl] palladium (II) dimer
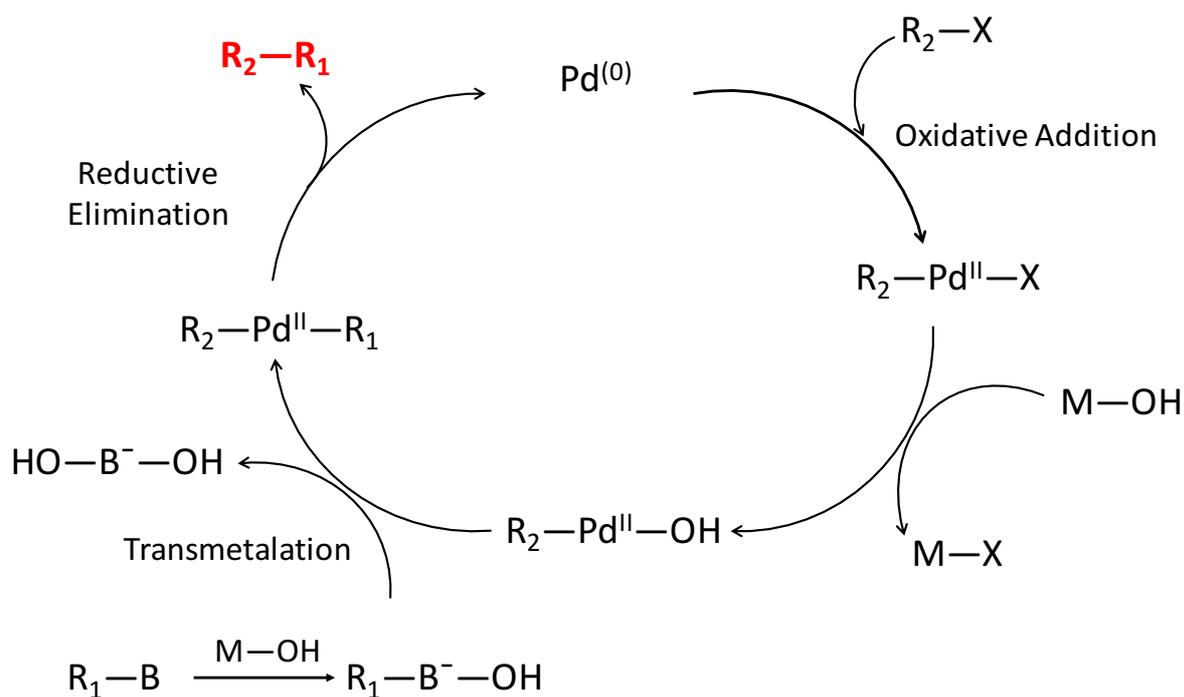

Figure 1-2 the catalytic cycle for Pd^{II} catalyzed cross-coupling between organoboronic acid and organohalide

In the present study, the Suzuki-Miyaura cross-coupling reaction of brominated natural rubber is carried out in tetrahydrofuran with phenylboronic acid in the presence of di-μ-chlorobis[5-hydroxy-2-[1-(hydroxyimino)-ethyl]-phenyl] palladium (II) dimer. Figure 1-3 shows a plausible scheme of the Suzuki-Miyaura cross-coupling reaction with the brominated natural rubber in the presence of the palladium catalyst. The oxidative addition of palladium catalyst occurs on the bromine atom of brominated *cis*-1,4-isoprene unit. The phenyl group of the phenylboronic acid is introduced into the *cis*-1,4-isoprene unit while palladium catalyst is recovered by transmetallation and reductive elimination, respectively.
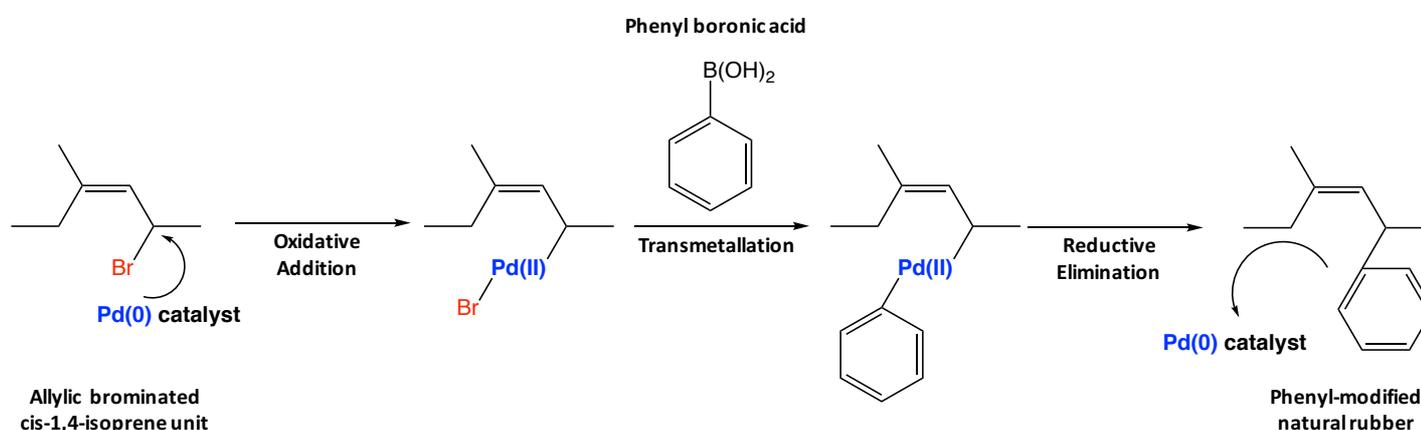
Figure 1-3 Suzuki-Miyaura cross-coupling reaction of brominated natural rubber with phenylboronic acid

1.3. Bromination of natural rubber with *N*-bromosuccinimide

Bromination of natural rubber may be carried out by Wohl-Ziegler reaction with *N*-bromosuccinimide (NBS), in which bromine atom is directly introduced to natural rubber at allylic position [18-19]. Figure 1-4 shows the bromination of *cis*-1,4-isoprene unit, according to mechanisms of Goldfinger [20-21] and Bloomfield [22-23], respectively. In initiation step, homolytic cleavage of NBS generates a succinimidyl radical and a bromine radical, according

to the Wohl-Ziegler reaction. In chain propagation step, hydrogen abstraction of the *cis*-1,4-isoprene unit occurs at the allylic position to form an allylic carbon radical. The resulting hydrogen bromide can rapidly react with NBS to provide bromine. The reaction between the allylic carbon radical and bromine produces brominated *cis*-1,4-isprene unit. In termination step, recombination of the bromine radical may occur with the allylic carbon radical of *cis*-1,4-isoprene unit and the bromine radical itself.

Step 1: Chain initiation
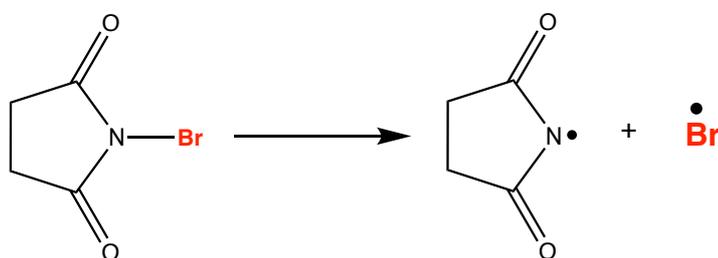
Step 2: Chain propagation
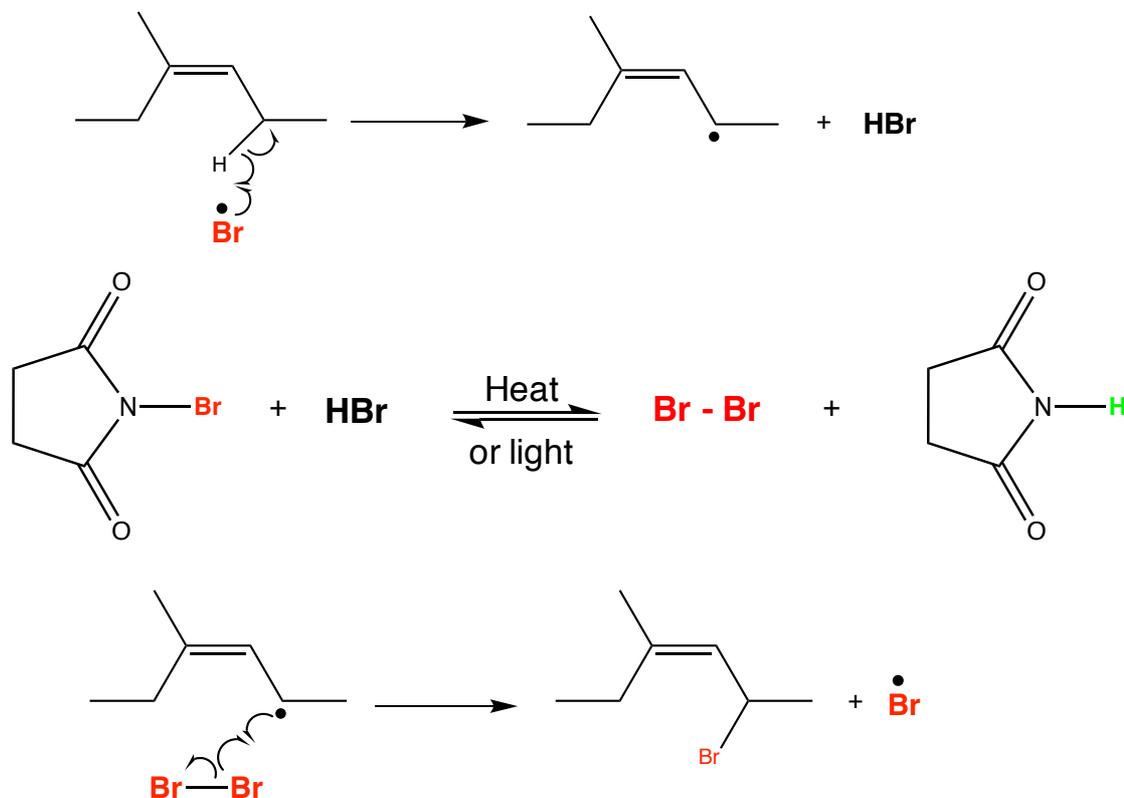
Step 3: Chain termination
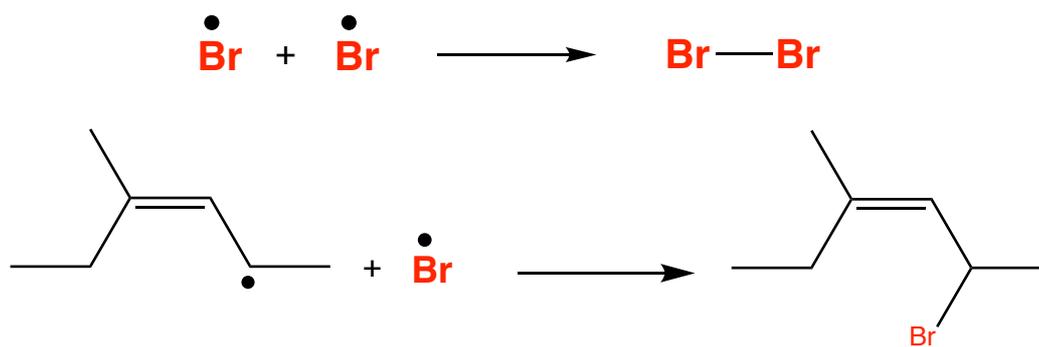
Figure 1-4 the bromination of *cis*-1,4-isoprene unit

1.4. Preparation of phenyl-modified natural rubber in latex stage

Natural rubber Brominated-natural rubber Phenyl-modified natural rubber
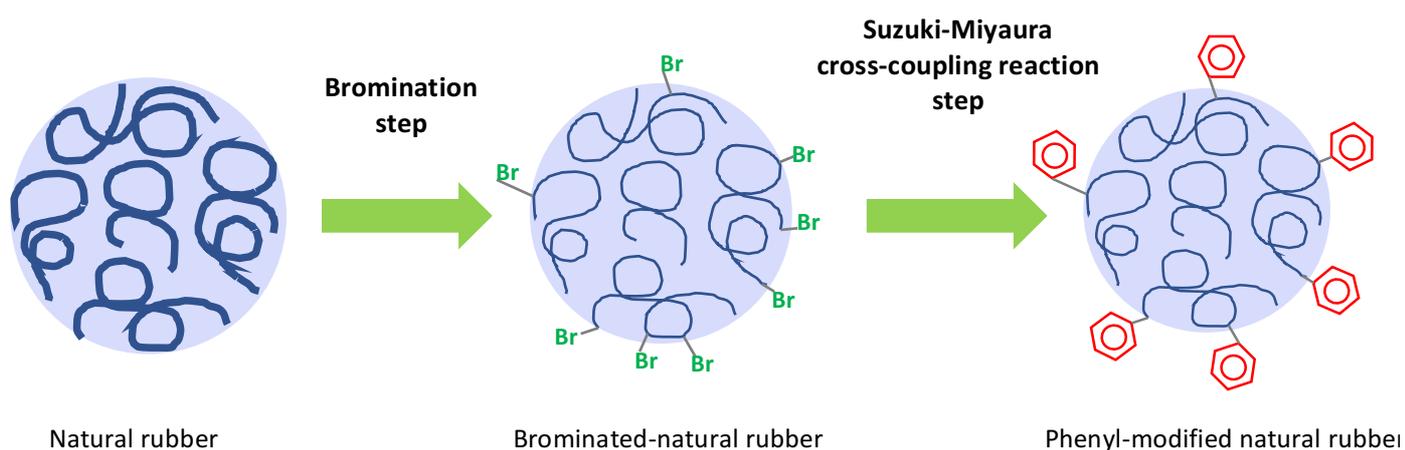
Figure 1-5 Suzuki-Miyaura cross-coupling reaction of brominated natural rubber with phenylboronic acid.

The preparation of phenyl-modified natural rubber may be performed in latex stage, since natural rubber is isolated as a latex from *Hevea basiliensis*. The reactions may occur on the surface of the rubber particles as shown in Figure 1-5. The phenyl-modified natural rubber is prepared after bromination of deproteinized natural rubber. In bromination step, *N*-bromosucinimide is used as a brominating agent to produce an allylic brominated natural

rubber; for instance, a bromine atom is directly introduced to a carbon adjacent to a double bond of *cis*-1,4-isoprene unit, i.e., an allylic position, according to the radical mechanism (Figure 1-6) [18]. In addition, side reactions such as bromohydrin formation and elimination reaction may occur, since the reaction of natural rubber with bromine atom take place in latex stage. For bromohydrin formation, the bromine cation of NBS may attack the double bond of natural rubber to form bromonium ion (Figure 1-6) [24-29] and, then the resulting bromonium ion may react with H_2O to form bromohydrin group. Moreover, the tertiary carbon of the conjugated *cis*-1,4-isoprene unit is generated by elimination reaction of bromine atom (Figure 1-6), based on Parent *et al* [30-31]. The resulting brominated natural rubber is subjected to Suzuki-Miyaura cross-coupling reaction in latex stage.
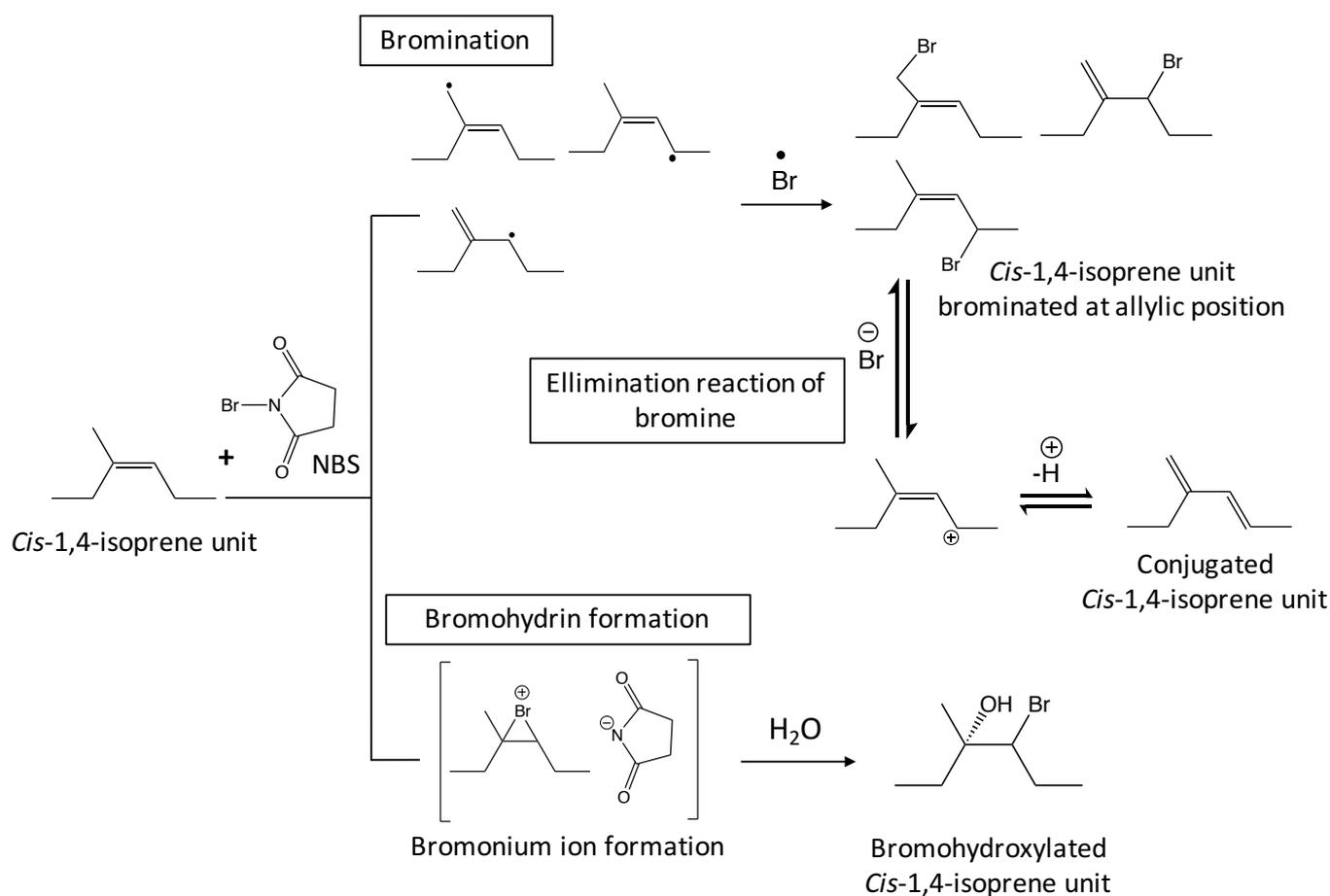
Figure 1-6 bromination, bromohydrin formation and elimination reaction of bromine atom

The Suzuki-Miyaura cross-coupling reaction of brominated natural rubber is performed with phenylboronic acid in the presence of di-μ-chloro-bis [5-hydroxy-2-[1-(hydroxyimino)-ethyl]-phenyl] palladium (II) dimer in water. This reaction is performed in oil/water emulsion due to stability of the palladium catalyst in water [7-8, 32]. The palladium catalyst may exist at the interface between natural rubber particles and water due to hydrophobic nature of the catalyst. The Suzuki-Miyaura cross-coupling reaction begins with oxidative addition of brominated *cis*-1,4-isoprene unit to form palladium (II) complex and, then, base replaces the bromine on the palladium complex. Phenyl group of the phenylboronic acid replace a bromine anion on the palladium complex by transmetallation. Finally, reductive elimination produces phenyl-modified natural rubber and generates palladium (0) catalyst to begin the catalytic cycle again.

1.4. Outline of this thesis

This thesis was divided into 5 chapters, which were devoted to the preparation and characterization of phenyl-modified natural rubber in latex stage. The content of each chapter was briefly described below:

In Chapter 1, "General introduction", background and current status is described for the chemical modification of natural rubber, the Suzuki-Miyaura cross-coupling reaction, the bromination of natural rubber with *N*-bromisuccinimide and the preparation of phenyl-modified natural rubber in latex stage.

In Chapter 2, "Preparation and properties of phenyl-modified natural rubber in solution state", an attempt to prepare phenyl-modified natural rubber (PhDPNR) was made by Suzuki-

Miyarura cross-coupling reaction in solution state. First, deproteinized natural rubber (DPNR) was brominated with *N*-bromosuccinimide (NBS) in dichloromethane solution. Second, the Suzuki–Miyaura cross-coupling reaction of the brominated natural rubber (BrDPNR) was carried out with phenylboronic acid in the presence of di-*μ*-chlorobis[5-hydroxy-2-[1-(hydroxyimino)-ethyl]-phenyl] palladium (II) dimer in tetrahydrofuran (THF) solution under nitrogen atmosphere. The resulting products, *i.e.*, BrDPNR and PhDPNR, were characterized by ^{1}H- and ^{13}C- NMR spectroscopy. Signals around 7 ppm in the ^{1}H-NMR spectra of the products were assigned to the phenyl groups. Conversion of the cross-coupling reaction and phenyl group content were estimated from intensity ratios of the assigned signals to more than 70 mol% and 4-12 mol%, respectively. The loss tangent and the T_g of PhDPNR were dependent upon the phenyl group content.

In Chapter 3, "Characterization of brominated natural rubber by solution state 2D-NMR spectroscopy", structural characterization of brominated natural rubber was carried out by 1D- and 2D-nuclear magnetic resonance (NMR) spectroscopy. The resulting BrDPNR was characterized by high resolution NMR spectroscopy such as correlation spectroscopy (COSY), hetero-nuclear multiple quantum coherence (HMQC) and Hetero-nuclear multiple bond correlation (HMBC) in conjunction with pulse field gradient technique. Small signals were assigned to nine plausible structural units of the BrDPNR. In addition, signals, newly found in ^{13}C-NMR spectra, were assigned to the brominated *trans*-1,4-isoprene units, since the isoprene units underwent *cis-trans* isomerization during the bromination of DPNR with NBS.

In Chapter 4, "Preparation of phenyl-modified natural rubber in latex stage", an attempt to prepare PhDPNR in latex stage was made by bromination of deproteinized natural rubber followed by Suzuki-Miyaura cross-coupling reaction. The bromination of natural rubber was

carried out with *N*-bromosuccinimide in latex stage. The resulting allylic bromide atom of BrDPNR was replaced in latex stage to a phenyl group by Suzuki-Miyaura cross-coupling reaction with phenylboronic acid in the presence of di-μ-chlorobis[5-hydroxy-2-[1-(hydroxyimino) -ethyl] -phenyl] palladium (II) dimer. The BrDPNR and PhDPNR were characterized by NMR spectroscopy. The conversion of the cross-coupling reaction and phenyl group content were estimated to be 23.7 mol% and 1.32 mol%, respectively.

In Chapter 5, 'General conclusion', concluding remarks of the preparation and characterization of BrDPNR and PhDPNR were described.

1.5. References

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CHAPTER 2

Preparation and properties of phenyl-modified natural rubber in solution state

2.1 Introduction

The preparation of the PhDPNR may provide a strategically synthetic pathway to control mechanical properties of naturally occurring *cis*-1,4-polyisoprene, since the phenyl group may attain a significant mechanical energy dissipation as a bulky pendant group [1-7]. This comes from the fact that the mechanical properties of styrene-butadiene rubber (SBR) are adjusted by changing the content of styrene units; that is, the higher the content of styrene units, the harder the SBR [8,9]. It is, thus, important to establish a suitable method to insert the phenyl groups into natural rubber in a rational basis.

One of the plausible methods to insert the phenyl groups into natural rubber is the Suzuki-Miyaura cross-coupling reaction [10], which is widely recognized to be a prominent method to form a carbon-carbon bond between the phenyl groups and hydrocarbons having allylic bromide groups in the presence of organometallic catalyst [11,12]. The Suzuki-Miyaura cross-coupling reaction is known to proceed in the following two steps: that is, (1) introduction of bromine atom into natural rubber at allyl position and (2) the cross-coupling reaction of BrDPNR with phenylboronic acid. In the first step, we may use either *N*-bromosuccinimide (NBS) to form allylic bromide groups [13,14] or HBr gas to perform the hydrobromination onto the rubber [15], in order to introduce bromine atom into natural rubber. In the second step, we may apply the Suzuki-Miyaura cross-coupling reaction of the BrDPNR in the presence of palladium catalyst [10], which is the pioneering approach to prepare the PhDPNR. However, we may fall into a difficulty to perform such a precise reaction, *i.e.,* Suzuki-Miyaura cross-coupling reaction, onto natural rubber, due to side reactions with proteins present in the rubber.

In the previous work, [16-21] we developed a novel purification method of natural rubber, *i.e.,* deproteinization with urea, which is an efficient method to remove the proteins from the rubber with urea. The nitrogen content of natural rubber, which was proportional to the protein content, was reduced from about 0.4 w/w% to 0.02 w/w% after removal of the proteins with urea in the presence of surfactant. From the resulting DPNR, we prepared various modified natural rubbers without the side reactions [22-25]. Therefore, we may prepare the PhDPNR, when we use DPNR as a source.

Furthermore, we have to investigate the preparation method of the BrDPNR. NBS [26-31] and HBr [32, 33] have been recognized to be a common reagent of the bromination. The bromination of natural rubber with NBS is distinguished from the hydrobromination of the rubber with HBr gas, as shown in Figure 2-1. The bromination with NBS proceeds through a radical mechanism to form allylic radical with carbon-carbon double bonds of *cis*-1,4-isoprene units as an intermediate. The product, thus obtained, contains allylic bromide, which is useful for the Suzuki-Miyaura cross-coupling reaction. In contrast, the hydrobromination with HBr gas proceeds through ionic mechanism according to Markovnikov rule. Thus, the product of hydrobromination dominantly contains quaternary carbon linking to bromine atom, but less contain tertiary carbon linking to bromine atom, *i.e.*, allylic bromide. It is important to compare the reactivity of brominated natural rubber with hydrobrominated natural rubber, since side reactions may occur among these reactions due to high molecular weight in nature.

In the present study, an attempt to insert phenyl groups into DPNR was made by Suzuki-Miyaura cross-coupling reaction. First, the introductions of bromine atom to DPNR were performed by bromination and hydrobromination of natural rubber, respectively. The BrDPNR and hydrobrominated natural rubber was subjected to Suzuki-Miyaura cross-coupling reaction with phenylboronic acid in the presence of palladium catalyst. The resulting products were characterized by ^{1}H- and ^{13}C-NMR spectroscopy, DSC and DMA.
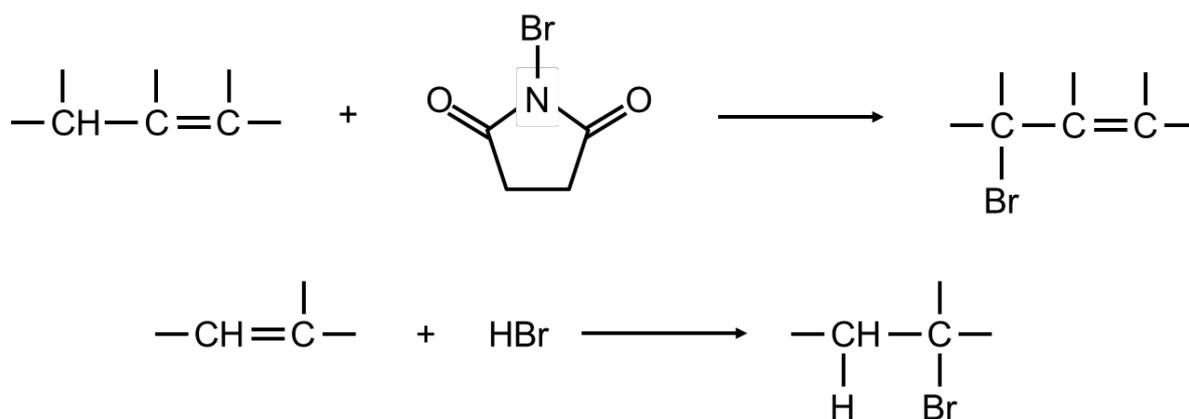
Figure 2-1 bromination of alkene with NBS and HBr

2.2 Experimental

2.2.1 Hydrobromination of deproteinized natural rubber with HBr gas

Deproteinized natural rubber (DPNR) (1 g) was dissolved into toluene (99 g). The toluene solution was charged with N_2 gas for 1 h at room temperature. Dry HBr gas was blown into the toluene solution at a rate of 5 ml min^{-1}. The reaction was carried out by stirring the solution for 2 h at room temperature. The product was coagulated with methanol and was dried under reduced pressure at 30 °C.

2.2.2 Bromination of DPNR with NBS

DPNR (2 g) was dissolved into dichloromethane (98 g). The dichloromethane solution was charged with N_2 gas for 1 h at 30 °C. NBS (2.62 g, 15 mmol) was added to the solution. The reaction was carried out by stirring the solution for 3 h at 30 °C. The product was coagulated with methanol and was dried under reduced pressure at 30 °C.

2.2.3 Insertion of phenyl groups into natural rubber by Suzuki-Miyaura cross-coupling reaction

The brominated or hydrobrominated natural rubber (1.66 g) was dissolved into THF (98 g). The THF solution was charged with N_2 gas for 1 h at room temperature. Phenylboronic acid (0.3882 g, 3.18 mmol), and water solution (2.78 g) containing potassium hydroxide (0.25 g, 4.5 mmol) and palladium catalyst (8.65 mg, $1.48{\times}10^{-2}$ mmol) were added to the solution. The reaction was carried out by stirring the solution for 6 h at refluxing temperature. The product was coagulated with methanol and was dried under reduced pressure at 50 °C.

2.2.4 Characterization

NMR measurements were carried out by using a JEOL ECA-400 NMR spectrometer operating at 399.65 and 100.4 MHz for ^{1}H and ^{13}C, respectively. The rubber was dissolved into chloroform-d without TMS. Chemical shifts were referred to chloroform in chloroform-d. ^{1}H- and ^{13}C-NMR measurements were carried out at 30 °C at the pulse repetition time of 7 s and 5 s, respectively. Two-dimensional (2D) ^{1}H-^{1}H correlation and ^{13}C-^{1}H correlation measurements were performed to collect two-dimensional hyper complex data. After weighting with shifted sine-bell function, the data was Fourier-transformed in the absolute value mode.

The T_g of the rubbers were assessed with a Seiko Instruments Inc., DSC 220, which was calibrated with standard indium and linoleic acid before measurement. The rubbers packed into an aluminum pan were heated at 100 °C. After annealing, the DSC measurement was made from −120 °C to 250 °C at a heating rate of 10 °C /min.

2.3 Results and discussion

2.3.1 Hydrobromination and bromination
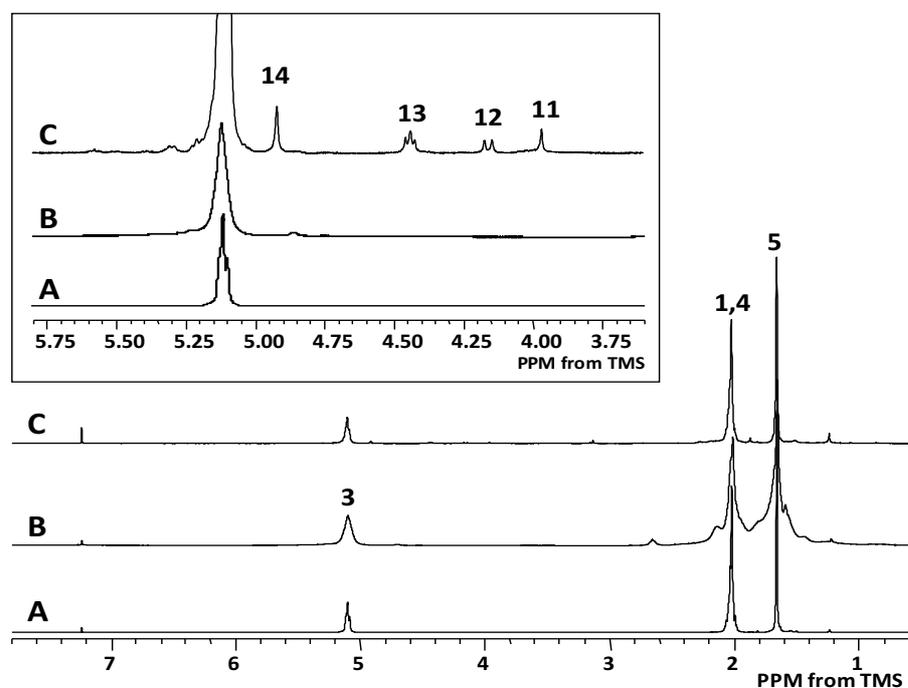
Figure 2-2 ^{1}H-NMR spectra for (A) natural rubber, (B) hydrobrominated natural rubber

prepared from HBr gas and (C) brominated natural rubber prepared from NBS

^{1}H-NMR spectra for DPNR, hydrobrominated natural rubber (HBrDPNR) prepared

with HBr gas and brominated natural rubber (BrDPNR) prepared with NBS are shown in

Figure 2-2. Signals, appearing at 1.66, 2.03 and 5.12 ppm in the ^{1}H-NMR spectra, were

assigned to methyl, methylene and unsaturated methine protons of *cis*-1,4-isoprene units [31],

respectively. After hydrobromination of DPNR, small, broad signals appeared in aliphatic

region of the spectrum (B), which overlapped with the large signals at 1.76 and 2.10 ppm,

assigned to the methyl and methylene protons of *cis*-1,4-isoprene units. The overlapping

signals made difficult to characterize the HBrDPNR, precisely.
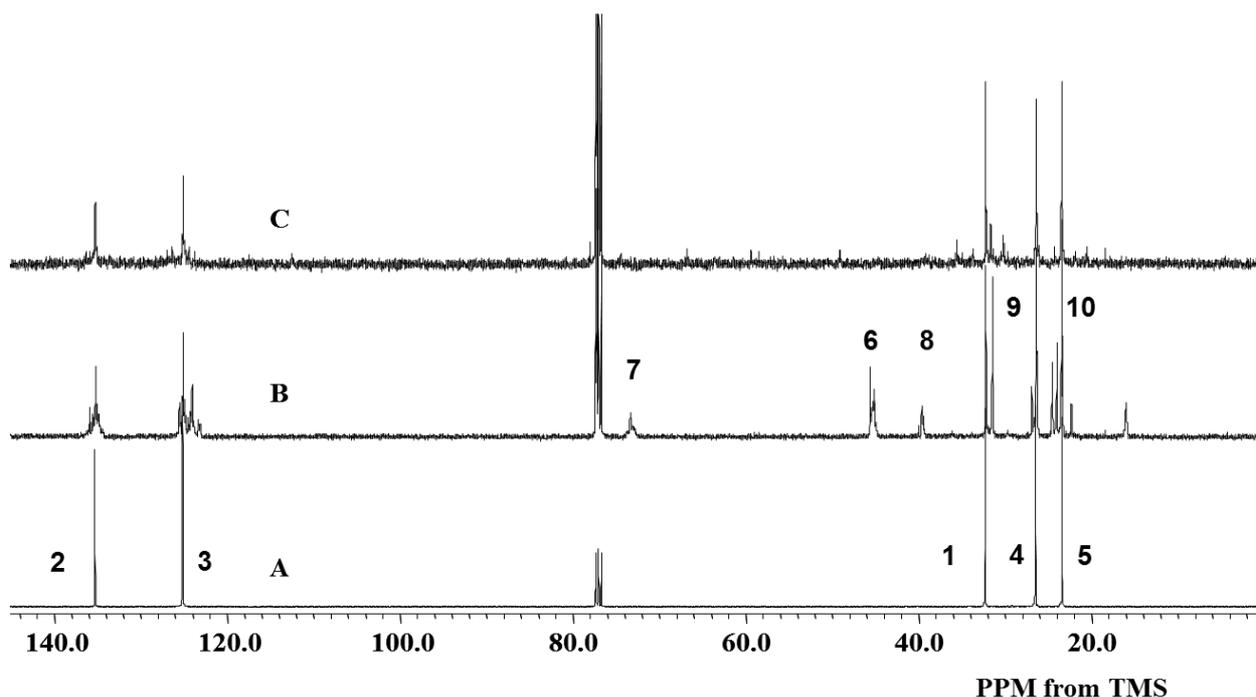
Figure 2-3 ^{13}C-NMR spectra for (A) natural rubber, (B) hydrobrominated natural rubber

prepared from HBr gas and (C) brominated natural rubber prepared from NBS.

In order to characterize the HBrDPNR, therefore, ^{13}C-NMR measurement was

performed for the rubber. Figure 2-3 shows ^{13}C-NMR spectra for DPNR and HBrDPNR,

respectively. In the ^{13}C-NMR spectra, five signals appearing at 23.4, 26.8, 32.1, 125.4 and

135.2 ppm were assigned to C5, C4, C1, C3 and C2 carbon atoms of *cis*-1,4-isoprene units

[34], respectively. After hydrobromination, many small signals appeared in aliphatic region

and a signal appeared at 74 ppm. The signals at 28, 31, 39, 45 and 74 ppm were assigned to

C10, C9, C8, C6, C7 carbon atoms of the HBrDPNR, according to the assignments of

Bradbury and co-workers [32] (Table 2-1 and Figure 2-4).

Table 2-1 assignments for ^{13}C-NMR spectra for hydrobrominated natural rubber

Chemical shift of ^{13}C (ppm)	Assignments
22.3	CB^4B, BB^4B
23.4	CC^5C
24.0	CB^4C, BB^4C
24.5	CC^4B, BC^4B
26.4	CC^4C, BC^4C
31.4	BC^1C, BB^5C, BC^1B
32.2	CC^1C, CC^1B
45.2	BB^3C
45.3	BB^1C, BB^1B, CB^3B, BB^3B
45.4	CB^1B
45.6	CB^1C, CB^3C
72.7	BB^2B
73.0	CB^2B
73.2	CB^2C
73.4	BB^2C
124	BC^3B, CC^3B
125	CC^3C, BC^3C
135	CC^2C, CC^2B
136	BC^2C

Bradburry, J. H.; Elix, J. A.; Perera, M. C. S. Polymer 1987, 28, 1098-1104
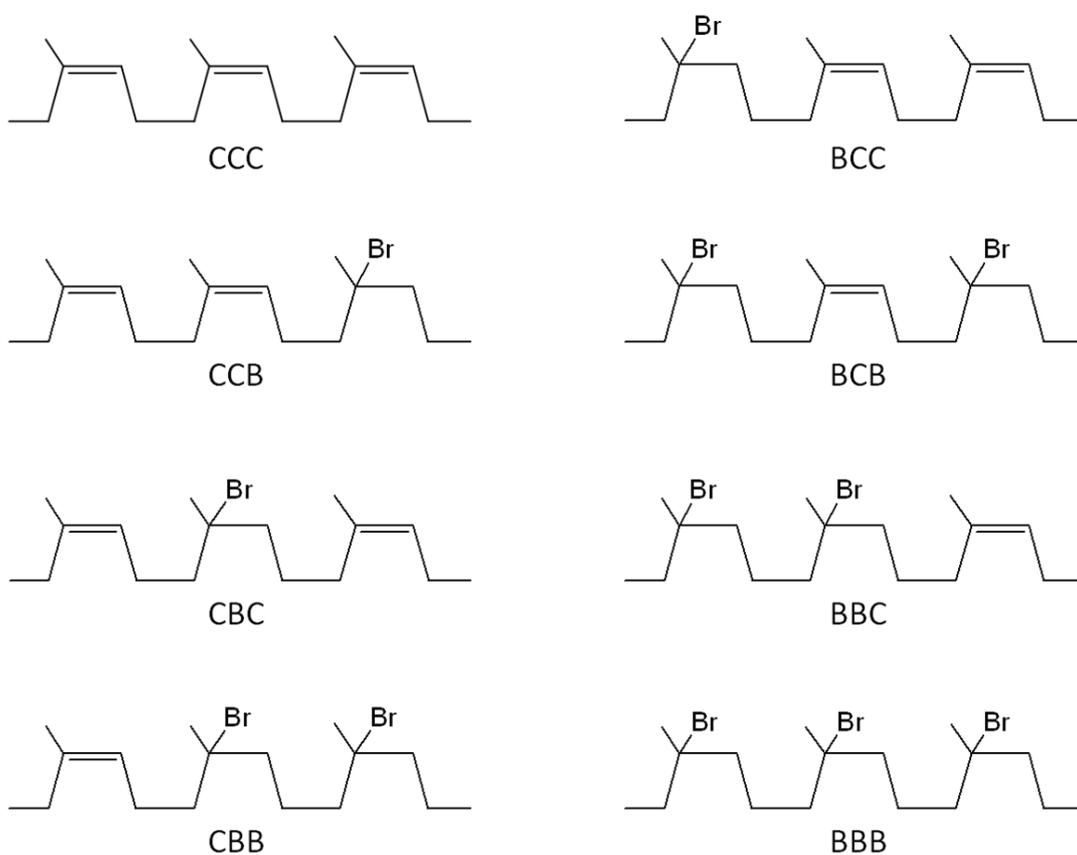
Figure 2-4 plausible structure of brominated isoprene unit for the HBrDPNR.

In Table 2-1 and Figure 2-4, the symbols C and B in triad sequences represent *cis*-1,4-isoprene units and brominated isoprene units, respectively. The superscript number represents carbon number of *cis*-1,4-isoprene units and brominated isoprene units, according to IUPAC nomenclature. Bromine atom content of the HBrDPNR, X_{HBr}, was estimated from the intensity ratio of the signals at 73 and 124 ppm, as in the following equation:

$$X_{HBr}[mol\%] = \frac{I_{73}}{I_{124} + I_{73}} \times 100 \qquad (2\text{-}1)$$

where I is intensity of the signals and subscript numbers represent values of chemical shift (ppm). The estimated content of bromine atom of the HBrDPNR used in the present study was 38 mol%.
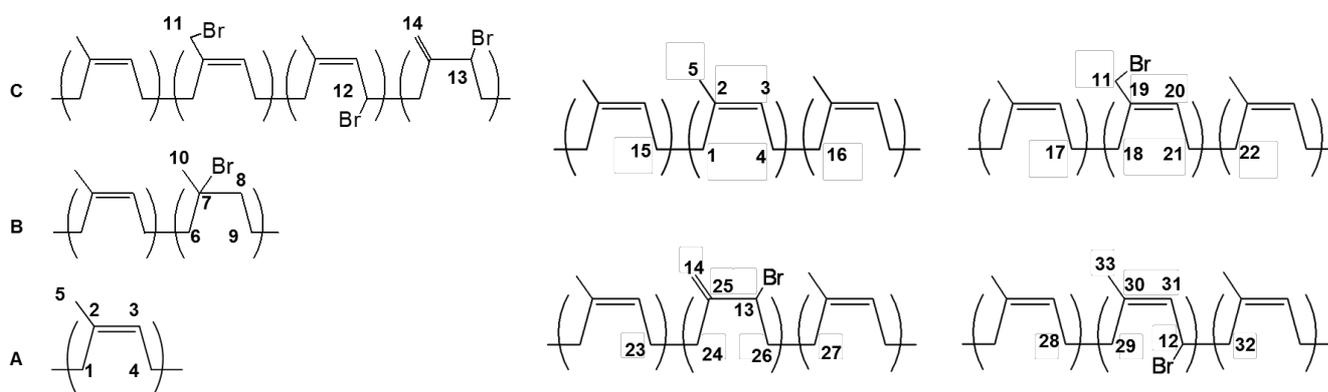
Figure 2-5 plausible structure of brominated isoprene units for the BrDPNR.

In contrast, after bromination of DPNR with NBS, small signals appeared at 3.96 (singlet), 4.14 (quartet), 4.44 (triplet) and 4.92 (singlet) ppm in the ^{1}H-NMR spectrum (Figure 2-2 (C)) for the BrDPNR, which were distinguished from the small signals overlapping with large signals at 1.66 and 2.03 ppm for the HBrDPNR. The plausible structures of the brominated isoprene units for the BrDPNR are shown in Figure 2-5. The signal at 4.92 was

assigned to an isolated vinyl groups, *i.e.*, H14 and the signals at 3.96, 4.14 and 4.44 ppm were assigned to allyl bromide groups of the BrDPNR, as marked as H11, H12 and H13, according to the previous work [29] and the splits of the signals. In order to prove the assignments, ^{1}H-^{1}H COSY measurements were performed for the BrDPNR. The ^{1}H-^{1}H COSY spectra for the BrDPNR are shown in Figure 2-6. The signal at 4.14 ppm was correlated with the signals at 1.90 and 5.12 ppm, whereas the signal at 4.44 ppm was correlated with signals at 2.03 ppm, respectively. The signals at 4.14 and 4.44 ppm were assigned to H12 and H13, respectively. In contrast, the signals at 3.96 and 4.92 ppm were not correlated with any signal, which were assigned to allylic carbons adjacent to the carbon without proton: that is, H11 and H14, respectively. The correlations of ^{1}H-^{1}H COSY are shown in Table 2-2. From the result, we confirmed that the allylic bromide groups were introduced into natural rubber by bromination with NBS.
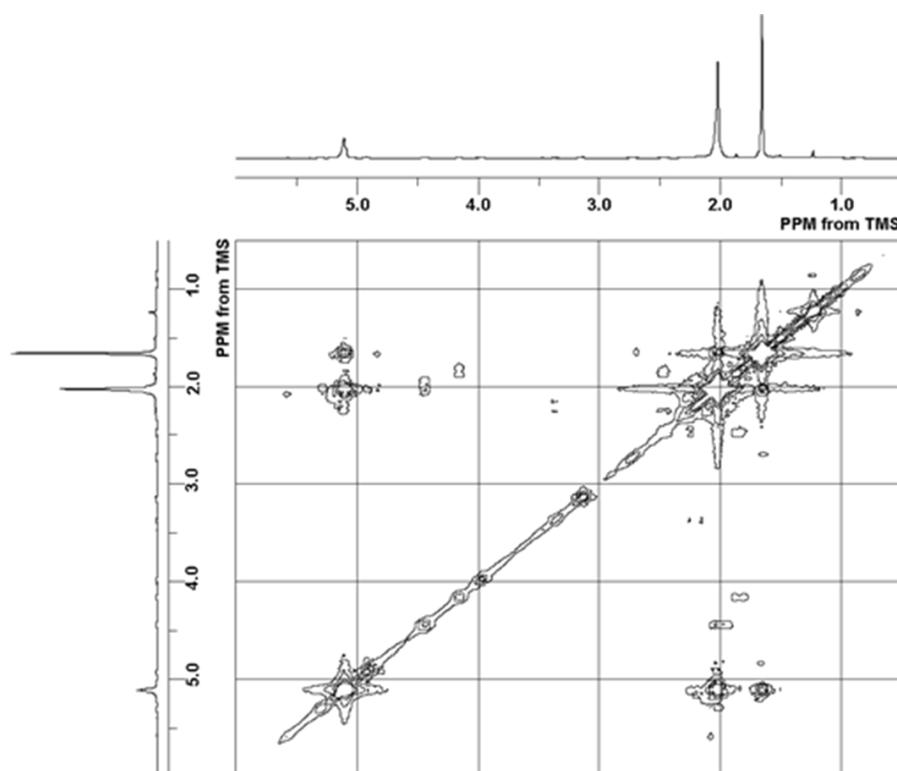

Figure 2-6 ^{1}H-^{1}H COSY spectra for BrDPNR prepared from NBS.

Table 2-2 assignments for ^{1}H-NMR spectra, spin coupling appeared in COSY spectra and HETCOR spectra for brominated natural rubber

Chemiacal shift of [1]H (ppm)	Chemical shifts of spin coupled ^{1}H signals in COSY spectra (ppm)	Assignments	Chemical shift of spin coupled ^{13}C signals in HETCOR spectra (ppm)
1.66	-	5	23.2
1.90	4.14	32	40.1
2.03	5.12	15, 4	26.3
2.03	-	1, 16	32.0
2.05	4.44	26	35.4
2.08	5.58	-	26.3
3.96	-	11	39.3
4.14	1.90	12	66.5
4.44	1.95, 2.05	13	59.2
5.12	2.03	3	125
5.58	2.08	-	132

Small signals also appeared in ^{13}C-NMR spectrum for the BrDPNR, as shown in Figure 2-3 (C). The values of chemical shift of the signals for the BrDPNR were distinguished from those of the signals for the HBrDPNR. The signals were, thus, positively assigned by 2D-NMR measurements, *i.e.,* HETCOR and HMBC. Figure 2-7 shows HETCOR spectra for the BrDPNR. The ^{1}H signals at 1.66, 2.03 and 5.12 ppm, assigned to methyl, methylene and unsaturated methane groups of *cis*-1,4-isoprene units, were correlated to the ^{13}C signals at 23.4, 26.8, 32.1 and 125.4 ppm. The small signals at 3.96, 4.14 and 4.44 ppm, assigned to the allyl bromide groups, were correlated to the signals at 39.3, 66.5 and 59.2 ppm, respectively. The signal at 4.92 ppm in ^{1}H-NMR spectrum, assigned to vinyl groups, was correlated to the signal at 112.3 ppm in ^{13}C-NMR spectrum. The ^{13}C signals at 39.3, 66.5, 59.2 and 112.3 ppm were,

thus, assigned to 11, 12, 13 and 14 carbons of triad sequences, respectively, as shown in Figure

2-5 and Table 2-3.
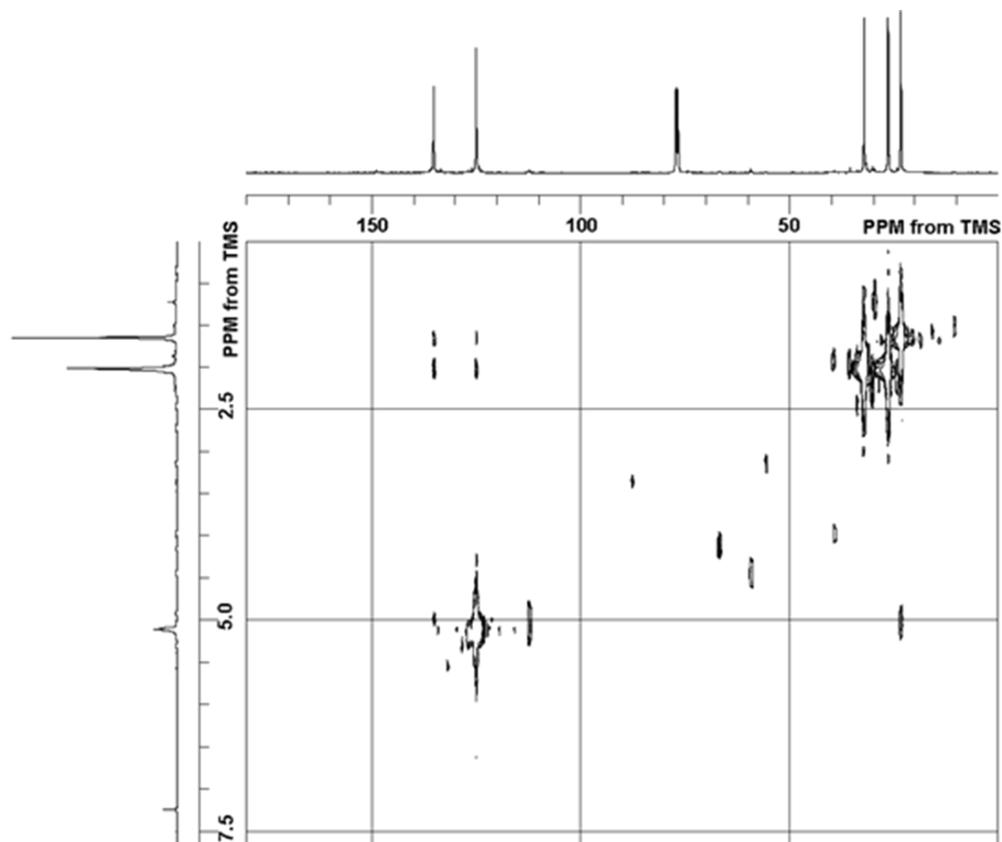
Figure 2-7 HETCOR spectra for the BrDPNR.

Table 2-3 assignments for ^{1}H-NMR spectra and spin coupling appeared in HETCOR spectra for brominated natural rubber

Chemical shifts of [1]H (ppm)	Chemical shift of spin coupled ^{13}C signals in HETCOR spectra (ppm)	Assignments
1.66	23.2	**5**
1.66	24.2	**33**
1.90	40.1	**32**
2.03	26.3	**4, 15, 17, 28**
2.03	31.3	**22**
2.03	32.0	**1, 16, 29**
2.05	35.4	**26**
2.08	26.3	**21**
2.08~2.36	28.5	**18, 23**
2.08~2.36	31.3	**24**
2.08~2.36	31.6	**27**
3.96	39.3	**11**
4.14	66.5	**12**
4.44	59.2	**13**
4.92	112	**14**
5.09	124	**31**
5.12	125	**3**
5.14	112	**14**
5.58	132	**20**
-	133	**30**
-	136	**19**
-	135	**2**
-	149	**25**
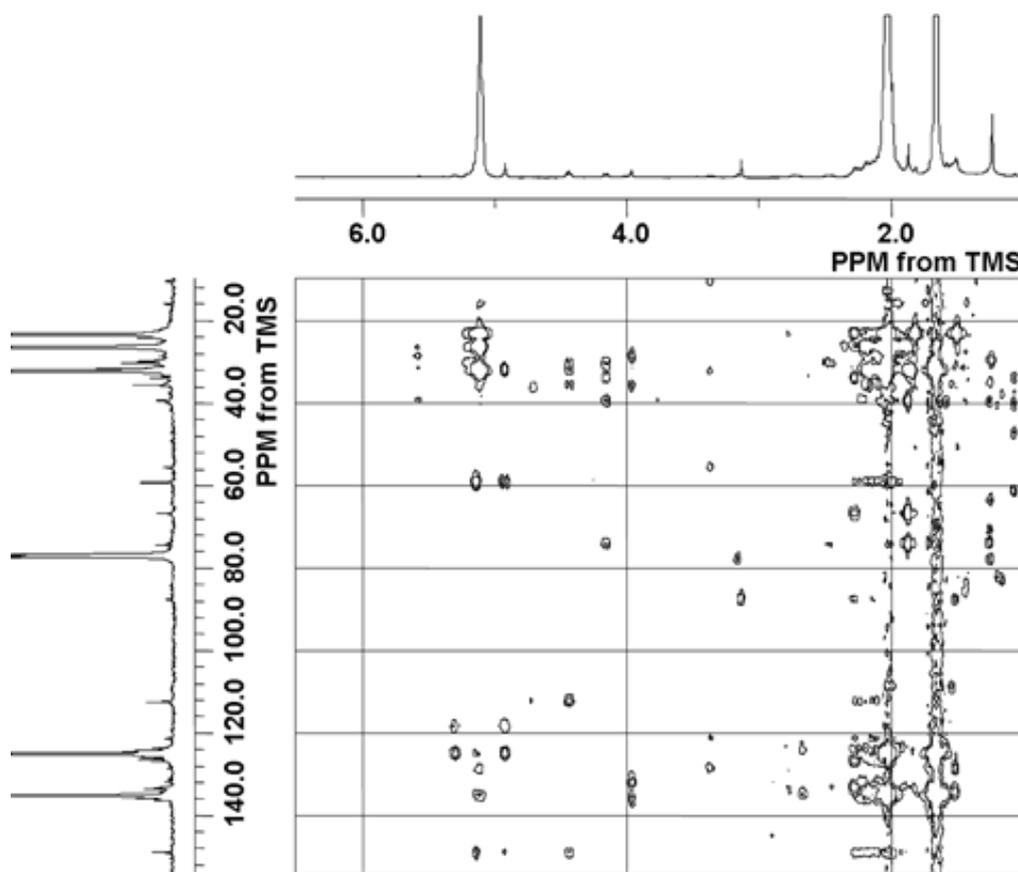
Figure 2-8 HMBC spectra for the BrDPNR.

Figure 2-8 shows HMBC spectra for the BrDPNR. In the HMBC spectra, the ^{1}H signals may correlate with the ^{13}C signals, which are one or two atoms apart from the directly linked carbon atom. The strong ^{1}H signals at 1.66, 2.03 and 5.12 ppm were well correlated to ^{13}C signals at 23.4, 26.8, 32.1, 125.4 and 135.2 ppm, since these were assigned to ^{1}H and ^{13}C of *cis*-1,4-isoprene units. The signal at 3.96 ppm, assigned to H11, was correlated to the ^{13}C signals at 28.5, 35.4, 130, 132 and 136 ppm, whereas the signal at 4.14 ppm, assigned to H12, was correlated to ^{13}C signals at 29.4, 33.7 and 40.1 ppm. In contrast, the signal at 4.44 ppm, assigned to H13, was correlated to the ^{13}C signals at 31.3, 35.4, 112 and 149 ppm. The correlations between ^{1}H and ^{13}C signals, obtained by HMBC are tabulated in Table 2-4. The unassigned signals may be attributed to chain scission and recombination of the rubber or

impurity. The product prepared by bromination with NBS was distinguished from that prepared

by hydrobromination with HBr gas.

Table 2-4 assignments for ^{1}H-NMR spectra and spin coupling appeared in HMBC spectra for

brominated natural rubber

Chemical shift of ^{1}H (ppm)	Assignments	Chemical shifts of spin coupled ^{13}C signals in HMBC spectra (ppm)
1.66	**5**	26.3, 32.0, 125, 126, 135
1.90	**32**	23.2, 31.6, 66.5, 123, 133
2.03	**1, 4, 15, 16**	23.2, 26.3, 32.0, 109, 125, 135
2.05	**26**	23.5, 32.0, 59.1, 135, 149
3.96	**11**	28.5, 35.4, 130, 132, 136
4.14	**12**	29.4, 33.7, 40.1
4.44	**13**	31.3, 35.4, 112.3, 149
5.12	**3**	23.2, 26.3, 32.0, 36.1, 130, 133
5.58	**20**	26.3, 28.5, 31.3, 39.3

The bromine atom content of the BrDPNR, X_{Br}, was estimated from the intensity ratio

of the signals at 3.96, 4.15, 4.44, 4.92 and 5.12 ppm, as in the following equation:

$$X_{Br}[mol\%] = \frac{I_{Br}}{\left(I_{5.12} + {I_{4.92}}/{2}\right) + (I_{Br})} \times 100 \qquad (2\text{-}2)$$

$$I_{Br} = {I_{3.96}}/{2} + I_{4.14} + I_{4.44} \qquad (2\text{-}3)$$

where I is intensity of the signals and subscript numbers represent values of chemical shift

(ppm). The estimated content of bromine atom of the BrDPNR in the spectrum Figure 2-2 (C)

was 4.36 mol%. The content of bromine atom of the resulting BrDPNR was dependent upon

the amount of NBS. Figure 2-9 shows a plot of the content of bromine atom of the BrDPNR

versus the amount of NBS. The content of bromine atom of the BrDPNR was roughly

proportional to the amount of NBS; the higher the amount of NBS, the higher the content of bromine atom of the BrDPNR. This implies that the content of bromine atom is easily controlled by changing the amount of NBS.
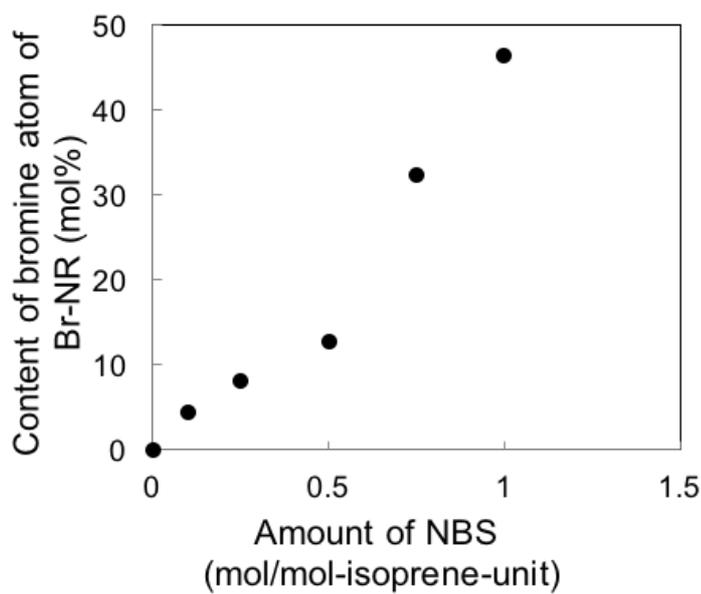
Figure 2-8 plot of amount of NBS versus content of bromine atom of brominated natural rubber

The amounts of H11, H12 and H13, which play an important role in the mechanical properties of the product, may be dependent upon the amount of NBS. Thus, mole fraction of H11, H12 and H13 were estimated as follows:

$$C_{3.96}[\%] = \frac{I_{3.96}/2}{I_{3.96}/2 + I_{4.14} + I_{4.44}} \times 100 \qquad (2\text{-}4)$$

$$C_{4.14}[\%] = \frac{I_{4.14}}{I_{3.96}/2 + I_{4.14} + I_{4.44}} \times 100 \qquad (2\text{-}5)$$

$$C_{4.44}[\%] = \frac{I_{4.44}}{I_{3.96}/2 + I_{4.14} + I_{4.44}} \times 100 \qquad (2\text{-}6)$$

where C is the mole fraction, *I* is the intensity of the signals and subscript numbers represent values of chemical shift (ppm). A plot of C3.96, C4.14 and C4.44 versus the content of bromine atom is shown in Figure 2-9. The locus of C3.96, C4.14 and C4.44 versus the content of bromine atom is convex, definite and concave, respectively.
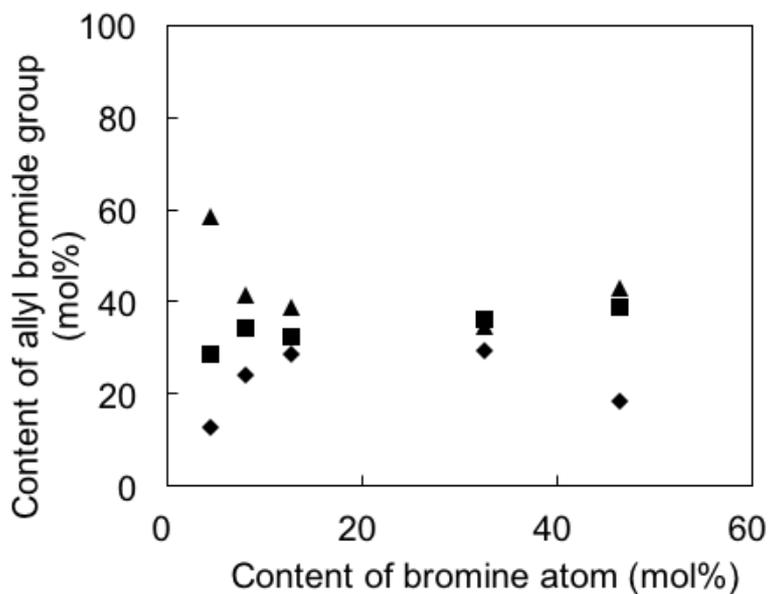
Figure 2-10 content of each brominated structure (◆: structure of 11, ■: structure of 12, ▲: structure of 13)

2.3.2 Suzuki-Miyaura cross-coupling reaction with the BrDPNR
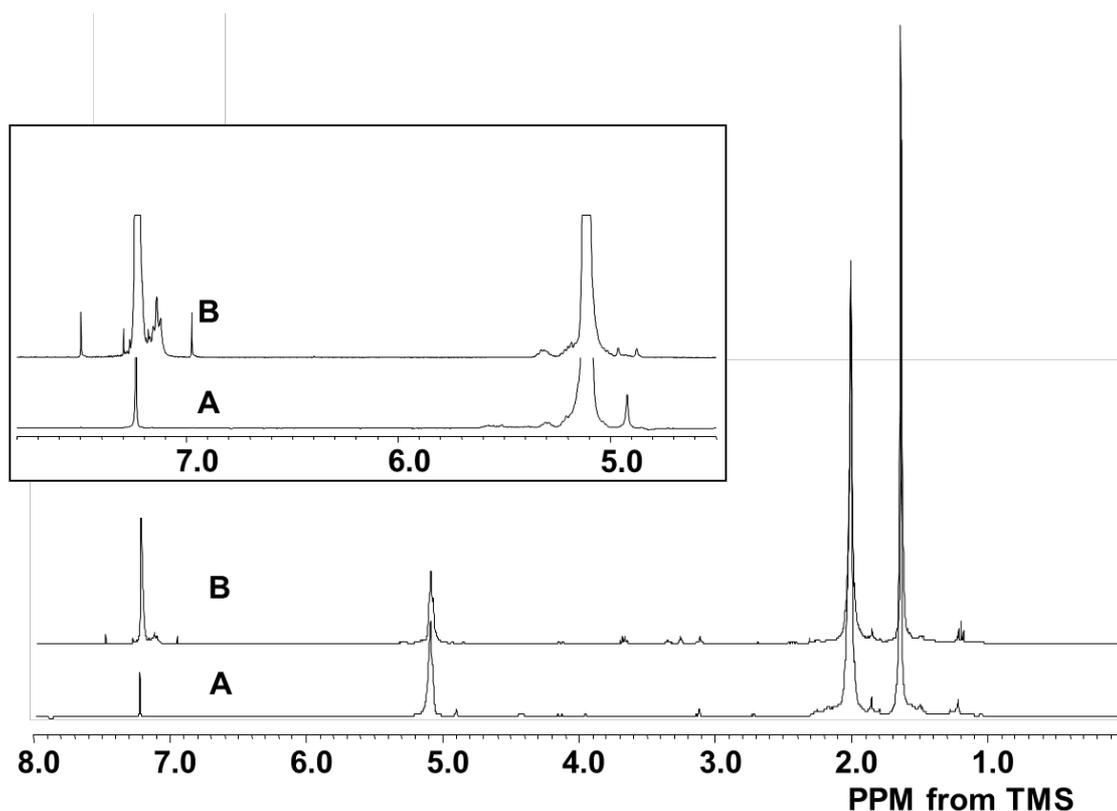
Figure 2-11 ^{1}H-NMR spectra for (A) BrDPNR and (B) product obtained after Suzuki-Miyaura cross-coupling reaction with BrDPNR.

^{1}H-NMR spectra for BrDPNR and the product prepared from the BrDPNR by Suzuki-Miyaura cross-coupling reaction are shown in Figure 2-11, in which the large signals at 1.66, 2.03 and 5.12 ppm were attributed to *cis*-1,4-isoprene units. Several small signals appeared at 7.13 ppm, after the cross-coupling reaction. These signals, which remained appearing after acetone extraction, were assigned to phenyl groups linking to natural rubber. Further, the signals were distinguished from the signals (7.3 − 7.7 ppm) for phenylboronic acid. In contrast, the signals at 3.96, 4.15 and 4.44 ppm, assigned to allyl bromide groups of BrDPNR, disappeared. The signal at 4.92 ppm also disappeared. These results demonstrate that the phenyl groups may link to natural rubber through the Suzuki-Miyaura cross-coupling reaction;

in other words, the PhDPNR was prepared from BrDPNR and phenylboronic acid. The content of phenyl groups linking to natural rubber, X_{ph}, was estimated from the intensity ratio of the signals at 5.12 and 7.13 ppm, as in the following equation:

$$X_{ph}[mol\%] = \frac{I_{7.13}/5}{I_{5.12} + I_{7.13}/5} \times 100 \tag{2-7}$$

The estimated value of the phenyl groups content was about 12 mol% for the phenyl-modified natural rubber.

Conversion of the Suzuki-Miyaura cross-coupling reaction to prepare the PhDPNR was estimated from the contents of bromine atom and phenyl groups, as in the following equation:

$$C_{cross\ coupling}[\%] = \frac{X_{ph}}{X_{Br}} \times 100 \tag{2-8}$$

Table 2-5 shows bromine atom content of the BrDPNR and the phenyl groups content of PhDPNR, the conversion of the Suzuki-Miyaura cross-coupling reaction. The conversion was found to be more than 70 mol%.

Table 2-5 bromine atom content for BrDPNR, phenyl group content for PhDPNR, conversion of Suzuki-Miyaura cross-coupling reaction and value of glass transition temperature for natural rubber and phenyl group

Content of bromine atom (mol%)	Content of phenyl group (mol%)	Conversion of Suzuki-Miyaura cross coupling Reaction (%)	Glass transition temperature (˚C)
—	—	—	-62.1
4.36	3.53	80.9	-51.2
14.1	12.0	85.2	-32.0
14.1	9.31	66.0	-32.0
14.5	11.3	78.0	-26.7
19.7	18.1	91.9	-4.17
46.4	33.2	71.4	9.61

2.3.3 Suzuki-Miyaura cross-coupling reaction with the HBrDPNR

^{1}H-NMR spectra for HBrDPNR and the product prepared from HBrDPNR by Suzuki-Miyaura cross-coupling reaction are shown in Figure 2-12. A small signal appeared at 4.7 ppm, after Suzuki-Miyaura cross-coupling reaction. This signal was assigned to an isolated vinyl group [35], formed by side reaction. It is well-known that signals characteristic of phenyl groups appeared around 7 ppm. However, in Figure 2-12, no signal appeared around 7 ppm, even after the cross-coupling reaction. This implies that only side reaction occurs, but not expected reaction. From the results, it is found that the β-hydrogen abstraction preferentially occurs to form the isolated vinyl groups.
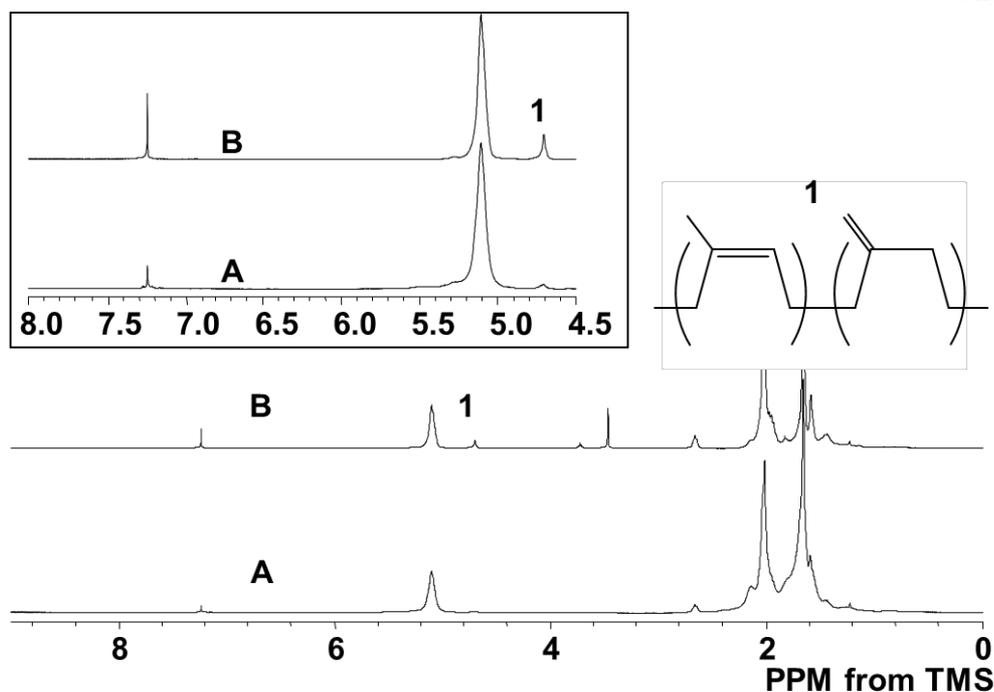
**Figure 2-12** ^{1}H-NMR spectra for (A) brominated natural rubber and (B) product obtained

after Suzuki-Miyaura cross-coupling reaction with HBrDPNR.

### 2.3.4 Glass transition temperature of phenyl-modified natural rubber
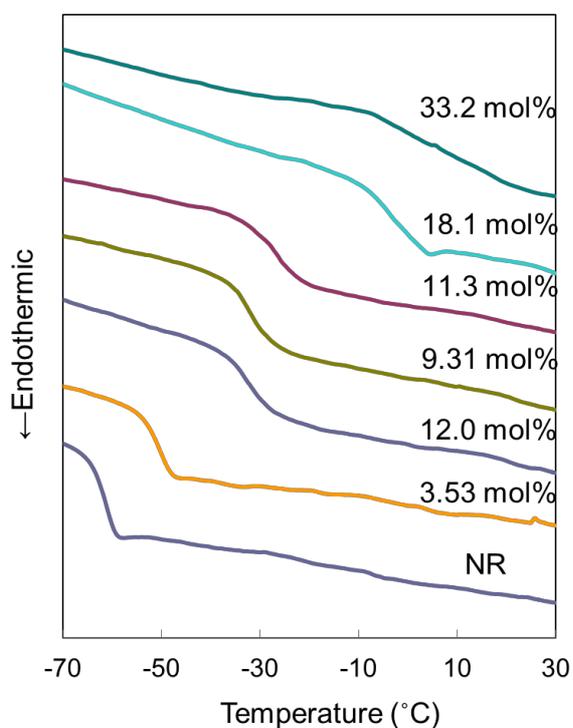
Figure 2-13 DSC thermograms for natural rubber and phenyl-modified natural rubber.
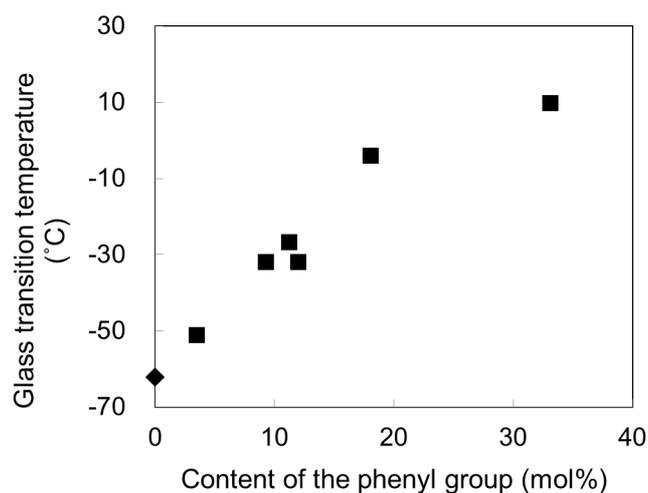
Figure 2-14 value of T_g versus content of phenyl group for phenyl-modified natural

The phenyl group is significantly bulky pendant group, which may decrease the free volume fraction of natural rubber. The glass transition temperature, T_g, is, thus, expected to raise as the phenyl group content increases, since the T_g is a function of the free volume fraction. DSC thermograms for NR and the PhDPNR are shown in Figure 2-13. The DSC thermograms show sudden decrease in heat capacity at T_g. We determined a value of T_g as a point of inflection. Figure 2-14 shows a plot of the T_g versus the content of phenyl group. The value of T_g of DPNR was -62.1 ˚C. In contrast, the value of T_g of the PhDPNR increased as the phenyl group content increased. The T_g was proportional to the content of phenyl group; the higher the content of phenyl group, the higher the T_g. Thus, it is suggested that introduction of phenyl group in DPNR directly relate increase of T_g. At 9 - 12 mol% of content of phenyl group, the value of the T_g was about -30 ˚C.

2.3.5 Loss tangent of phenyl-modified natural rubber
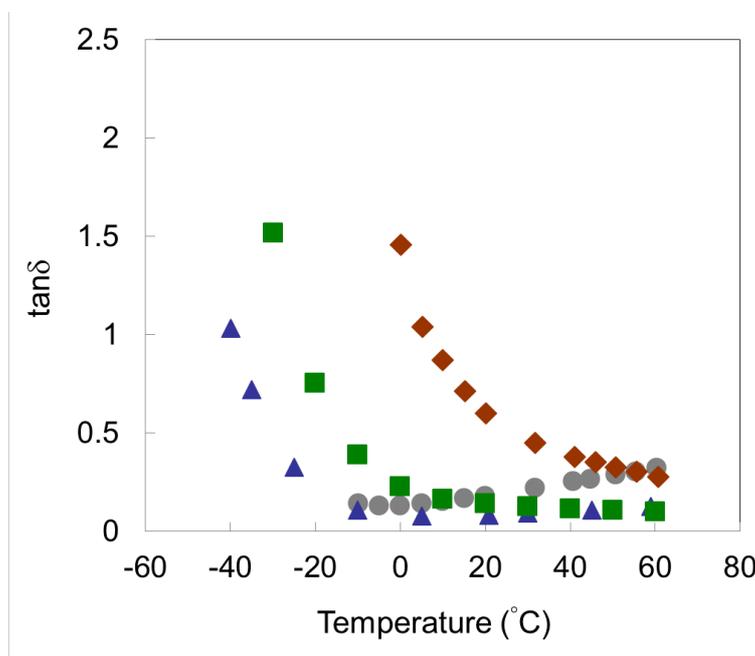
Figure 2-15 value of tanδ at 10 Hz *versus* temperature for (■) PhDPNR of 4 mol% phenyl group, (◆) PhDPNR of 12 mol% phenyl group, (▲) DPNR and (●) commercial styrene-butadiene rubber (SBR: 23.5 mol% styrene unit content).

A plot of loss tangent (tanδ) at 10 Hz versus temperature for the PhDPNR with 4 mol% phenyl group, the PhDPNR with 12 mol% phenyl group and DPNR is shown in Figure 2-15, in conjunction with tanδ at 10Hz for a commercial styrene-butadiene rubber (SBR: 23.5 mol% styrene unit content). The measurements were performed above T_g of the rubbers, in order to avoid slippage of the rubbers on plates. A locus of tanδ for NR depicted a concave curve in nature; that is, tanδ value decreased as the temperature rose and it was lowest at −10 °C. When the temperature went up to more than −10 °C, the tanδ value increased a little. As for PhDPNR with 4 mol% phenyl group, the locus of tanδ moved to about 20 °C higher temperature region; hence, the tanδ value at 0 °C increased, whereas that at 50 °C decreased. Moreover, a locus of tanδ for the PhDPNR with 12 mol% phenyl group moved to about 40 °C higher temperature region. The tanδ value at 0 °C for the PhDPNR with 12 mol% phenyl group increased dramatically, rather than that for the PhDPNR with 4 mol% phenyl group. In contrast, the tanδ value at 50 °C for the PhDPNR with 12 mol% phenyl group was a little bit higher than that for the PhDPNR with 4 mol% phenyl group.
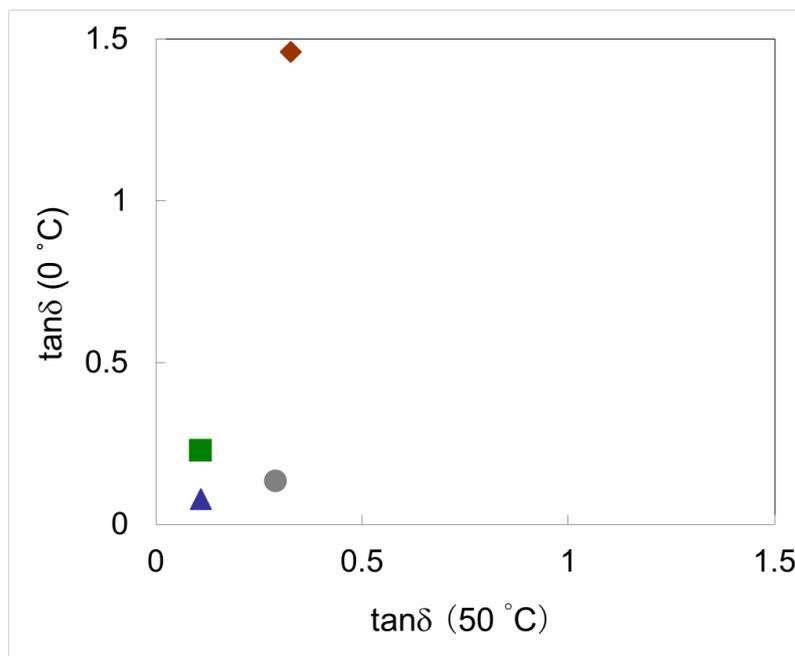
Figure 2-16 value of tanδ at 0 °C and 50 °C for (■) PhDPNR of 4 mol% phenyl group, (◆) PhDPNR of 12 mol% phenyl group, (▲) DPNR and (●) commercial styrene-butadiene rubber (SBR: 23.5 mol% styrene unit content).

Figure 2-16 shows the values of tanδ at 0 °C and 50 °C for the PhDPNR with 4 mol% phenyl group, the PhDPNR with 12 mol% phenyl group, DPNR and SBR. Upper left side in Figure 2-16 represents a good balance of the mechanical energy dissipations, such as both large value of tanδ at 0 °C and small value of tanδ at 50 °C, which are empirical rule useful for the rubbers. When we compare DPNR with SBR, it is possible to understand the difficulty to achieve the balance of large value of tanδ at 0 °C and small value of tanδ at 50 °C. The value of tanδ at 0 °C of natural rubber was improved after inserting the phenyl group to natural rubber. The values of tanδ at 0 °C and tanδ at 50 °C for the PhDPNR with 4 mol% phenyl group were quite similar to those of epoxidized natural rubber. Furthermore, the value of tanδ at 0 °C of natural rubber increased dramatically by inserting 12 mol% phenyl group into natural rubber without sacrificing the rebound resilience. The change in the values of tanδ at 0 °C and tanδ at 50 °C may be associated with the change in values of T_g: for instance, −62.1 °C for

DPNR, $-51.2\ ^{\circ}$C for the PhDPNR with 4 mol% phenyl group, $-32.0\ ^{\circ}$C for the PhDPNR with 12 mol% phenyl group and $-49.8\ ^{\circ}$C for SBR. Consequently, we assured that the PhDPNR, which possesses unique mechanical energy dissipation, was successfully prepared by Suzuki-Miyaura cross-coupling reaction of the brominated natural rubber.

2.4. Conclusions

PhDPNR was prepared by bromination of DPNR with NBS followed by Suzuki-Miyaura cross-coupling reaction with phenylboronic acid in the presence of di-μ-chloro-bis [5-hydroxy-2-[1-(hydroxyimino)-ethyl]-phenyl] palladium (II) dimer as a catalyst. The bromine atom content of BrDPNR was dependent upon the amount of NBS; that is, the higher the amount of NBS, the higher the content of bromine atom of the BrDPNR. Three allyl bromide groups, *i.e.*, H11, H12 and H13, were found for the BrDPNR. The BrDPNR was converted to the PhDPNR by Suzuki-Miyaura cross-coupling reaction, whose conversion was more than 70 mol% under a suitable condition. The value of T_g of PhDPNR increased as the phenyl group content increased. At 9 - 12 mol% of phenyl group content, the value of the T_g was about -30 $^{\circ}$C. The PhDPNR with 9 - 12 mol% phenyl groups achieved a superior balance of large value of tanδ at 0 °C and small value of tanδ at 50 °C.

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CHAPTER 3

Characterization of brominated natural rubber by solution state 2D-NMR spectroscopy

3.1 Introduction

Bromination is an important reaction to modify natural rubber since the bromine groups of brominated natural rubber are useful for living radical polymerizations [1-3] and Suzuki-Miyaura cross-coupling reactions [4,5]. To prepare brominated natural rubber, a bromine atom is introduced to a carbon adjacent to a double bond (*i.e.,* the allylic position). One plausible reaction is the Wohl-Ziegler reaction [6] with *N*-bromosuccinimide (NBS), which is a common and versatile reagent for radical bromination [3,7,8]. For instance, hydrogen abstraction of alkene may take place at the allylic position and bromine may react with the resulting allyl radicals, according to the radical mechanism, which may contribute side reactions during reaction. It is, thus, important to analyze the structure of brominated natural rubber.

Nuclear magnetic resonance (NMR) spectroscopy is a powerful technique to characterize organic materials, since NMR spectrum reflects the chemical environment of individual atoms. One-dimensional (1D) NMR spectroscopy has been used to investigate the primary structure of organic materials. For instance, the signals in the ^{1}H- and the ^{13}C-NMR spectra are assigned to the primary structure based on the chemical shift values estimated for the plausible structural units of an organic material. The assignments may be positively proved by proficient techniques such as two-dimensional (2D) NMR spectroscopy, making it possible to investigate the correlations between homo- and hetero-nuclei (*i.e.,* ^{1}H-^{1}H, ^{1}H-^{13}C and ^{13}C-^{13}C). Various pulse sequences [*i.e.,* heteronuclear single-quantum coherence (HSQC) heteronuclear multiple-quantum coherence (HMQC), and heteronuclear multiple-bond coherence (HMBC)] are indispensable in determining the primary structures of organic

materials. Thus, we apply 2D-NMR spectroscopy together with the distortionless enhancement by polarization transfer (DEPT) measurements to the structural analysis of the brominated natural rubber.

In Chapter 2, we prepared the BrDPNR through the Wohl-Ziegler bromination with NBS. The BrDPNR was subjected to 1D- and 2D-NMR measurements to analyze its primary structure. The small signals in the ^{1}H-NMR spectra were assigned to the allylic methylene and methine groups linking bromine atoms. Furthermore, the signals in the ^{13}C-NMR spectra were assigned based on the assignments of bromobutyl rubber [9]. However, several expected correlations between ^{1}H-^{13}C and ^{1}H-^{1}H did not appear in the 2D-NMR spectra, when the assignments of the signals in ^{1}H- and ^{13}C-NMR spectra were investigated by 2D-NMR spectroscopy. This inconsistency may be explained to be due to inadequate assignments of the signals for brominated natural rubber. Thus, it is necessary to take account of the *cis-trans* isomerization of the *cis*-1,4-isoprene units, which has been neglected in Chapter 2.
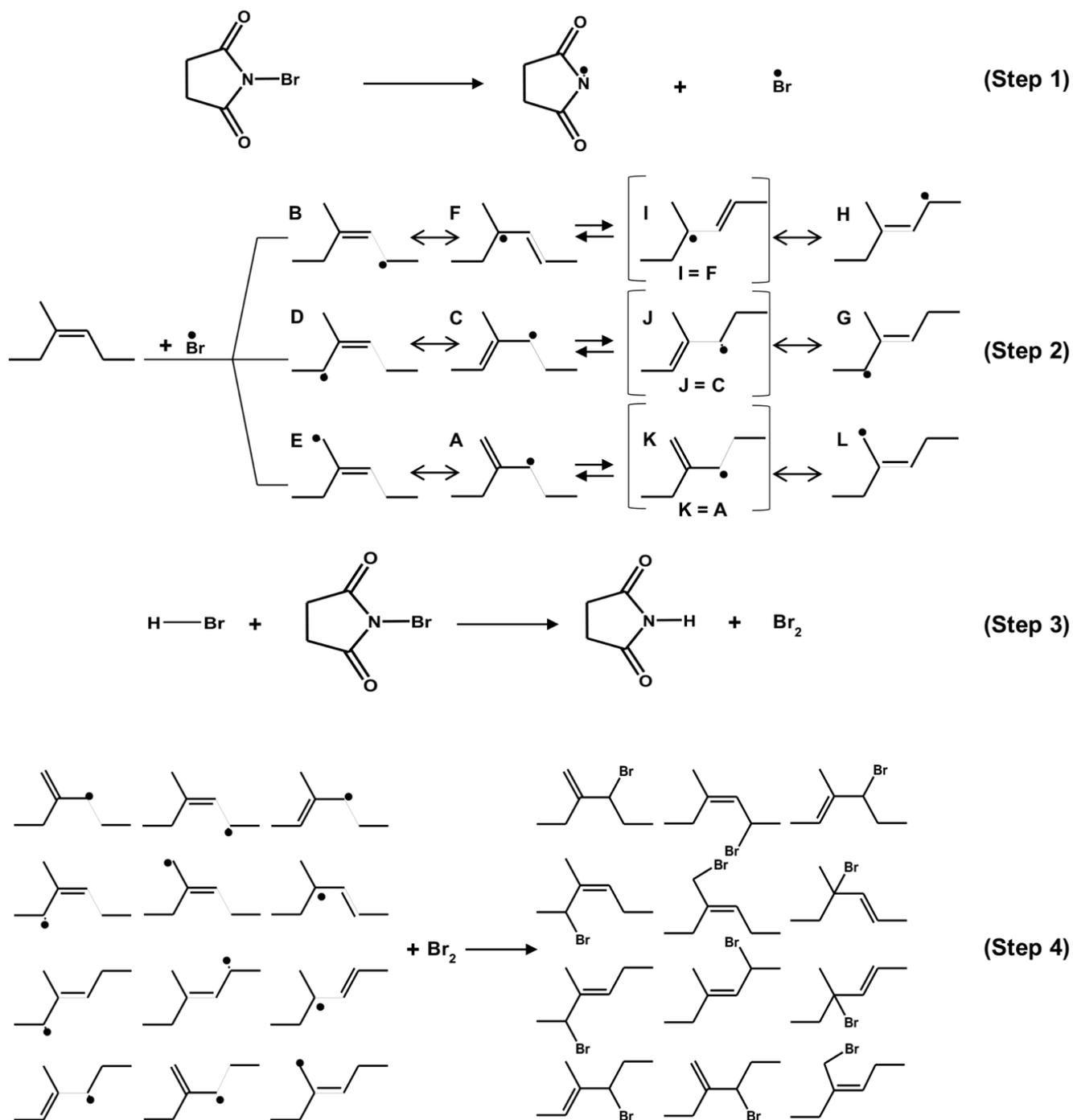
Figure 3-1 bromination of natural rubber and plausible structural units of the brominated

natural rubber (BrDPNR)

Figure 3-1 shows the bromination of natural rubber and the plausible structural units of the brominated natural rubber. The plausible structures are formed in four steps. First, homolytic cleavage of NBS initiates bromination, which generates a succinimidyl radical and a bromine radical, according to the Wohl-Ziegler reaction (step 1) [6,10,11]. Hydrogen abstraction of the *cis*-1,4-isoprene units occurs at the allylic position to form an allylic carbon radical (step 2). In this step, *cis-trans*-isomerization is induced due to the delocalization of free electrons on the double bond. The resulting hydrogen bromide can rapidly react with NBS to provide bromine (step 3). Finally, the reaction between an allylic carbon radical and bromine produces brominated natural rubber (step 4). According to this mechanism, we may have nine plausible structural units for the brominated isoprene units.

In Chapter 3, 1D- and 2D-NMR measurements were performed to analyze the structure of the BrDPNR. Attempts to assign the small signals, appearing after the Wohl-Ziegler bromination reaction, were made to prove the nine plausible structural units by correlation spectroscopy (COSY), heteronuclear multiple-quantum coherence (HMQC), heteronuclear multiple-bond coherence (HMBC) and so forth.

3.2 Experimental

3.2.1 Preparation of deproteinized natural rubber (DPNR) latex

Deproteinization of natural rubber was carried out by incubation of HANR latex with 0.1 w/w% urea in the presence of 1.0 w/w% sodium dodecyl sulfate (SDS) at room temperature (303 K) for 1 hour and subsequent centrifugation at 104g. The cream fraction in the centrifugation tube was re-dispersed in a 1.0 w/w% SDS solution. The resulting latex was centrifuged again. The cream fraction was washed with a 0.5 w/w% SDS solution and then with a 0.1 w/w% SDS solution. The resulting DPNR latex was poured into a petri dish and

dried at 323 K to prepare as cast film, the film was subsequently dried for an additional three days at a reduced pressure before use.

3.2.2 Bromination of natural rubber with NBS

Bromination of DPNR was carried by a Wohl-Ziegler reaction with NBS. The dried DPNR (2 g) was cut into small pieces, which were dissolved in dichloromethane (100 g). The dichloromethane solution was charged with N_2 gas for 1 h at 303 K. The bromination of DPNR was performed by stirring the solution at 303 K for 3 h after adding NBS (2.62 g, 15 mmol). The reaction was terminated when the solution changed from colorless to yellowish. The product was recovered as a precipitate by pouring the resulting solution into an excess amount of methanol. The precipitate, BrDPNR, was washed twice by the toluene-methanol precipitation method and subsequently dried at 303 K under a reduced pressure.

3.2.3 Characterization

Solution state NMR spectroscopy was performed with a JEOL ECA-400 NMR spectrometer (JEOL, Tokyo, Japan) for BrDPNR (10 mg for ^{1}H-NMR and 100 mg for ^{13}C-NMR measurements), which was dissolved into chloroform-d without tetramethylsilane (TMS) (~ 4 ml) in a 5-mm ϕ tube. The ^{1}H-NMR measurement at 399.65 MHz and 303 K was performed by 512 scans with a pulse repetition time of 7 s at 45°pulse of 1.8 μsec and a relaxation delay of 4.24 s. The ^{13}C-NMR and DEPT measurements at 100.4 MHz and 303 K were carried out by 10000 scans with a pulse repetition time of 5 s at 30°pulse of 3.5 μsec and a relaxation delay of 3.68 s.

2D-NMR measurements were performed by collecting 2D hyper complex data at 303 K, which was Fourier-transformed in the absolute value mode, after weighting with a shifted sine-bell function. The COSY measurement at 395.88 MHz was performed by 516 scans. For

the F2 and F1 dimensions, the measurement was carried out at repetition time of 1.67 s using 1024 and 256 data points at 90° pulse of 14 μsec, respectively. The HMQC and HMBC measurements at 395.88 MHz were performed by 256 scans. The HMQC measurement was carried out by using 1024 data points at 90° pulse, 13.9 μsec, for F1 dimension and 256 data point at 90° pulse, 14 μsec, for F2 dimension. The both dimensions were zero-filled and processed with a sine-bell function. The repetition time was 1.64 s and the bond coupling constant for HMQC, ^{1}JCH, was 140 Hz. Furthermore, the HMBC measurement was carried out by using 2048 data points at 90° pulse, 13.9 μsec, for F1 dimension and 256 data points at 90° pulse, 14 μsec, for F2 dimension. Both dimensions were zero-filled and processed with a sine-bell function. The repetition time was 1.64 s, the bond coupling constant for HMBC, ^{1}JCH, was 140 Hz and a long-range coupling constant, $^{2\text{-}4}$JCH, was 8 Hz.

3.3 Results and discussion
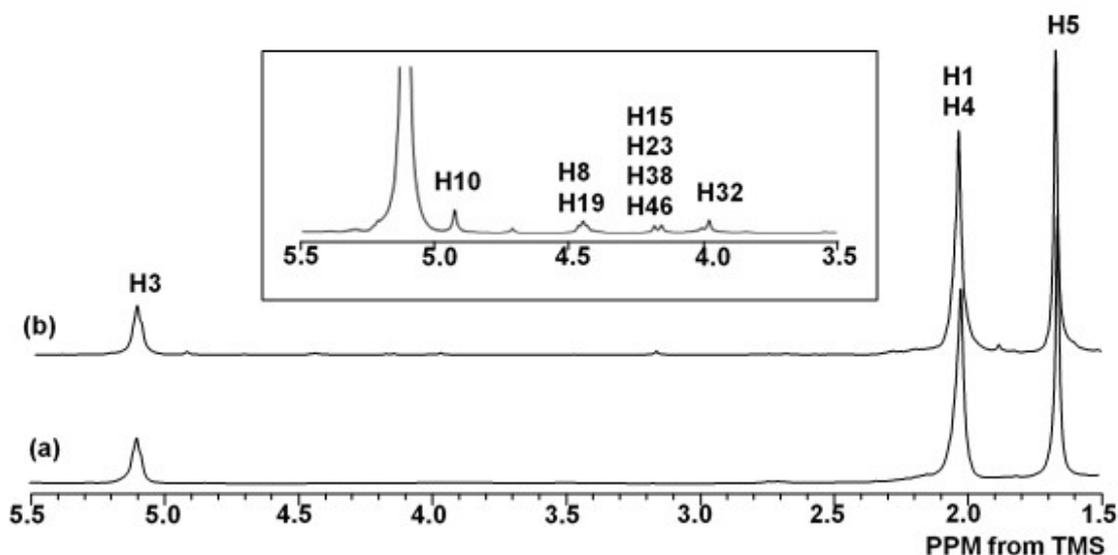
Figure 3-2 ^{1}H-NMR spectra for (a) natural rubber and (b) BrDPNR

Figure 3-2 shows ^{1}H-NMR spectra for DPNR and BrDPNR. The inset is an enlarged ^{1}H-NMR spectrum between 3.5 and 5.5 ppm. The three major signals appeared at 1.66, 2.02 and 5.10 ppm were assigned to the methyl proton (H5), the methylene protons (H1, H4) and the methine proton (H3) of the *cis*-1,4-isoprene units, respectively. After bromination of DPNR with NBS, small broad signals appeared at 3.98 (singlet), 4.16 (triplet and quartet), 4.44 (triplet) and 4.92 (singlet) ppm. These signals were assigned to the plausible structural units listed in Figure 3-3, according to the previous work [5]. The signal at 4.92 ppm was assigned to the unsaturated methylene protons of H10 and H52, while the signal at 3.98 ppm was assigned 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, whereas the signal at 4.44 ppm was assigned to the methine protons of H8, H19, H50 and H71.
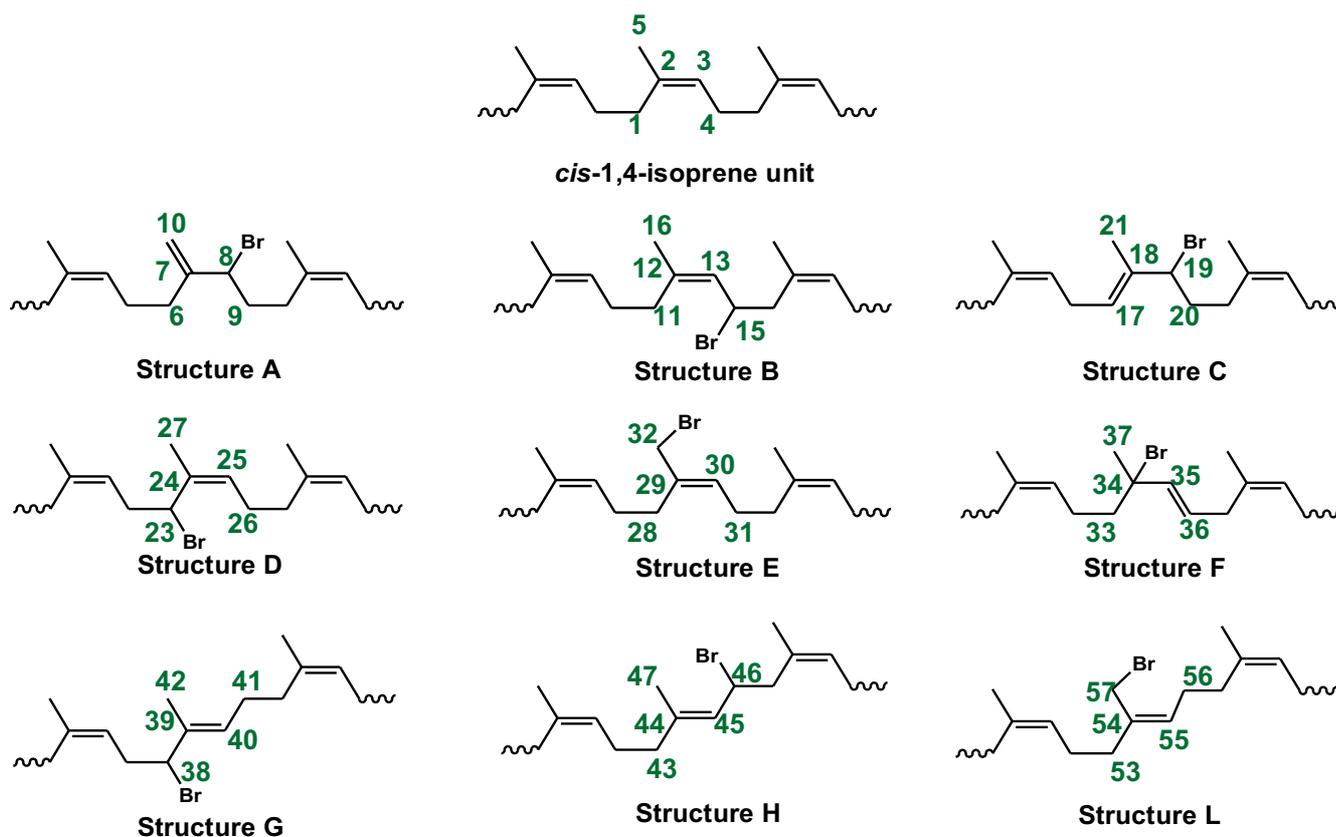
Figure 3-3 the structural units of *cis*-1,4-isoprene units and brominated *cis-trans*-1,4-isoprene units as marks as structure A to L

Figure 3-4 shows the ^{13}C-NMR spectra for DPNR and BrDPNR. The five characteristic signals for the *cis*-1,4-isoprene units of natural rubber appeared at 23.5, 26.8, 32.6, 125 and 135 ppm, which were assigned to the carbon atoms of C5, C4, C1, C3 and C2 of the *cis*-1,4-isoprene units, respectively. After bromination, several small signals appeared in the ^{13}C-NMR spectrum for BrDPNR. According to the previous work [5], the signals at 24.5, 32.6, 39.8, 59.8 and 66.9 ppm were attributed to the carbon atoms of the brominated *cis*-1,4-isoprene units. The signal at 24.5 ppm was assigned to the primary carbon of C16, while that at 32.6 ppm was attributed to the secondary carbon of C11. The signal at 39.8 ppm was assigned to the secondary carbon of C32, the signal at 59.8 ppm was due to the secondary carbons of C8 and C19 and the signal at 66.9 ppm was assigned to the secondary carbons of C15 and C23. In addition, we observed unknown signals at 20.5, 24.8, 29.8 and 40 ppm.
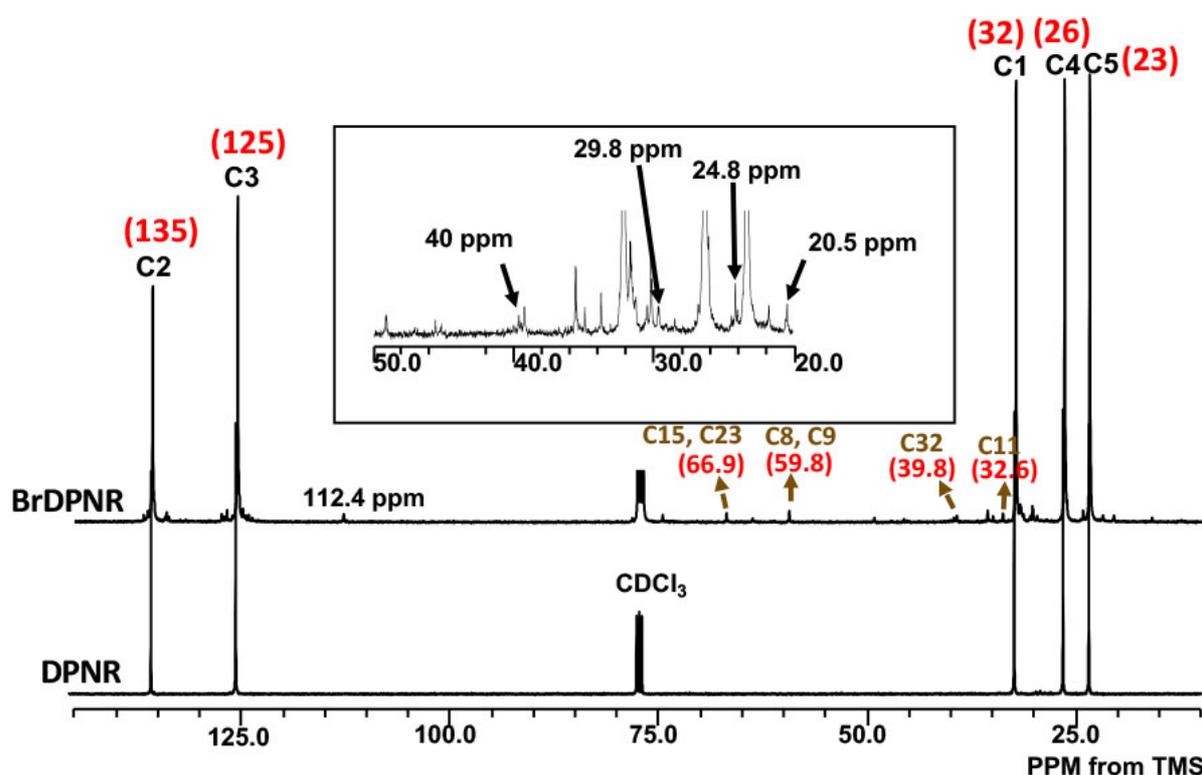
Figure 3-4 ^{13}C-NMR spectra for (a) DPNR and (b) BrDPNR

To identify the unknown signals, we applied DEPT measurements at 45° (DEPT45), 90° (DEPT90) and 135° (DEPT135) pulses to solution state ^{13}C-NMR spectroscopy. Figure 3-5 shows the DEPT45, DEPT90 and DEPT135 spectra for BrDPNR. The signals at 23.5, 26.8 and 32.6 ppm were characteristic of the methyl, the methylene and the methine carbons of the *cis*-1,4-isoprene units. These signals appear upward, upward and upward in the DEPT45 spectrum, but they were almost null in the DEPT90 spectrum. On the other hand, in the DEPT135 spectrum, the signals appeared upward, downward and downward. Thus, the pulse width determined for the DEPT measurements was confirmed to be correct to assign the unknown signals at 20.5, 24.8, 29.8 and 40 ppm. The signals at 20.5 and 29.8 ppm were due to primary carbons because appearance of the upward signals in DEPT45, null in DEPT90 and upward signals in DEPT135 spectra. On the other hand, the signals at 24.8 and 40 ppm were assigned to the secondary carbons due to upward signals in DEPT45, null in DEPT90 and downward signals in DEPT135 spectra.
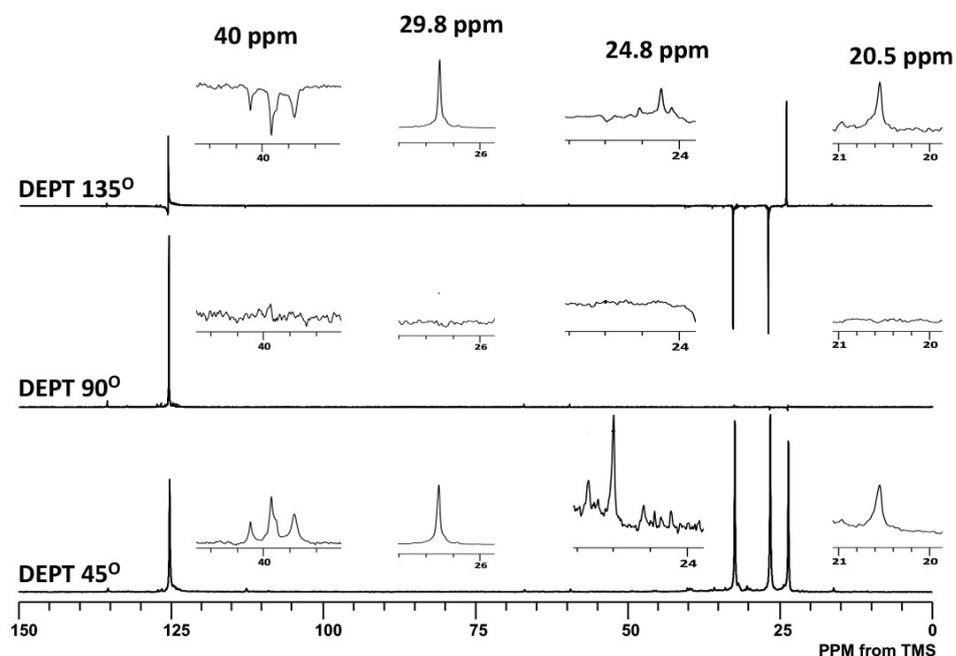
Figure 3-5 ^{13}C-NMR spectra with pulse sequences of DEPT for BrDPNR; DEPT (a) 45°, (b) DEPT 90°, and (C) DEPT 135°

The signals were positively assigned by 2D-NMR measurements. The ^{1}H signal at 1.66 ppm in the HMQC spectra for BrDPNR (Figure 3-6) was correlated with the ^{13}C signals at 20.5 and 29.8 ppm. The ^{1}H signal at 2.02 ppm was correlated with ^{13}C signal at 40 ppm. The ^{1}H signal at 2.18 ppm was correlated with ^{13}C signal at 24.8 ppm. The correlations between ^{13}C signals and ^{1}H signals were attributed to the brominated *trans*-1,4-isoprene units, based on the chemical shift values estimated by Furst's method [12,13]. The signals at 20.5 and 29.8 ppm were assigned to the primary carbons of C47 and C42 of the triad sequences (Figure 3-3), respectively. The signals at 24.8 and 40 ppm were assigned to the secondary carbons of C53 and C43, respectively. These assignments imply that the brominated *trans*-1,4-isoprene units are formed by *cis-trans* isomerization during bromination. Table 3-1 summarized the assignments for the signals and spin couplings of the HMQC spectra for BrDPNR.

Table 3-1 Assignments for the ^{13}C-NMR spectrum, DEPT measurements, spin couplings in the HMQC and HMBC spectra for BrDPNR

Chemical shift of [13]C (ppm)	Assignments	DEPT measurements[a]	δ for spin coupled ^{1}H signals in HMQC spectra (ppm)	δ for spin coupled ^{13}C signals in HMBC spectra (ppm)
32.6	1	s	2.02	23.7, 26.8, 125.25, 135.37
135.37	2	q	-	-
125.25	3	t	5.1	23.7, 26.8, 32.6, 135.37
26.8	4	s	2.02	32.6, 125.25, 135.37
23.7	5	p	1.66	32.6, 125.25, 135.37
31.3	6	s	2.08	26.8, 59.78, 112.54, 125.25, 149
149	7	q	-	-
59.2	8	t	4.44	32.6, 35.2, 112.7, 149
35.4	9	s	2.05	32.6, 59.78, 135.37, 149
112	10	s	4.92	31.6, 59.78, 149
32	11	s	2.03	24.5, 26.8, 112.6, 125.25, 134
133	12	q	-	-
124	13	t	5.09	24.5, 32.6, 39.8, 134

66.9	15	t	4.16	39.5
24.2	16	p	1.66	32.6, 112.6, 134
112.4	17	t	5.14	22, 29.8, 59.8, 125, 149
149	18	q	-	-
59.8	19	t	4.44	32.08, 35.8, 22, 112.4, 149
35.21	20	s	2.02	32.08, 59.4, 135.35, 149
22	21	p	1.66	59.8, 112.4, 149
66.9	23	t	4.16	30.15, 33.44
136	24, 29,39	q	-	-
125.25	25	t	5.12	26.8, 30.15, 32.6, 136
26.8	26	s	2.02	32.6, 125.25, 135.35, 136
30.15	27	p	1.66	66.9, 125.25, 136
30.8	28	s	2.18	26.8, 39.8, 125.25, 132.06, 136
132.06	30	t	5.58	28.76, 30.8, 32.6, 39.8, 136
28.76	31	s	2.02	32.6, 132.06, 135.37, 136
39.8	32	s	3.97	30.8 132.06, 136
45.6	33	s	2.01	29, 32.6, 74, 112.7, 125.25
74	34	q	-	-
112.7	35	t	5.13	32.36, 36.08, 45.6, 74, 125.05
125.05	36	t	5.1	32.36, 74, 112.7, 135.37
29	37	p	1.67	45.6, 74, 112.7
66.9	38	t	4.16	29.8, 39.8
125.25	40	t	5.1	26.8, 29.8, 32.6, 136
26.8	41	s	2.02	26.8, 125.25, 135.35, 136
29.8	42	p	1.66	66.9, 125.25, 136
40	43	s	2.02	20.5, 26.8, 125.25, 134, 135.37
135.37	44	q	-	-
125.25	45	t	5.58	30.5, 35.8, 40
66.9	46	t	4.16	35.8
20.5	47	p	1.66	40, 125.25, 135.37
24.8	53	s	2.18	30.8, 132, 136
136	54	q	-	-
132	55	t	5.58	24.8, 28.76, 30.8, 132, 136
28.76	56	s	2.02	132, 136
30.8	57	s	3.97	24.8, 132, 136

[a] p: primary carbon, s: secondary carbon, t: tertiary carbon and q: quaternary carbon
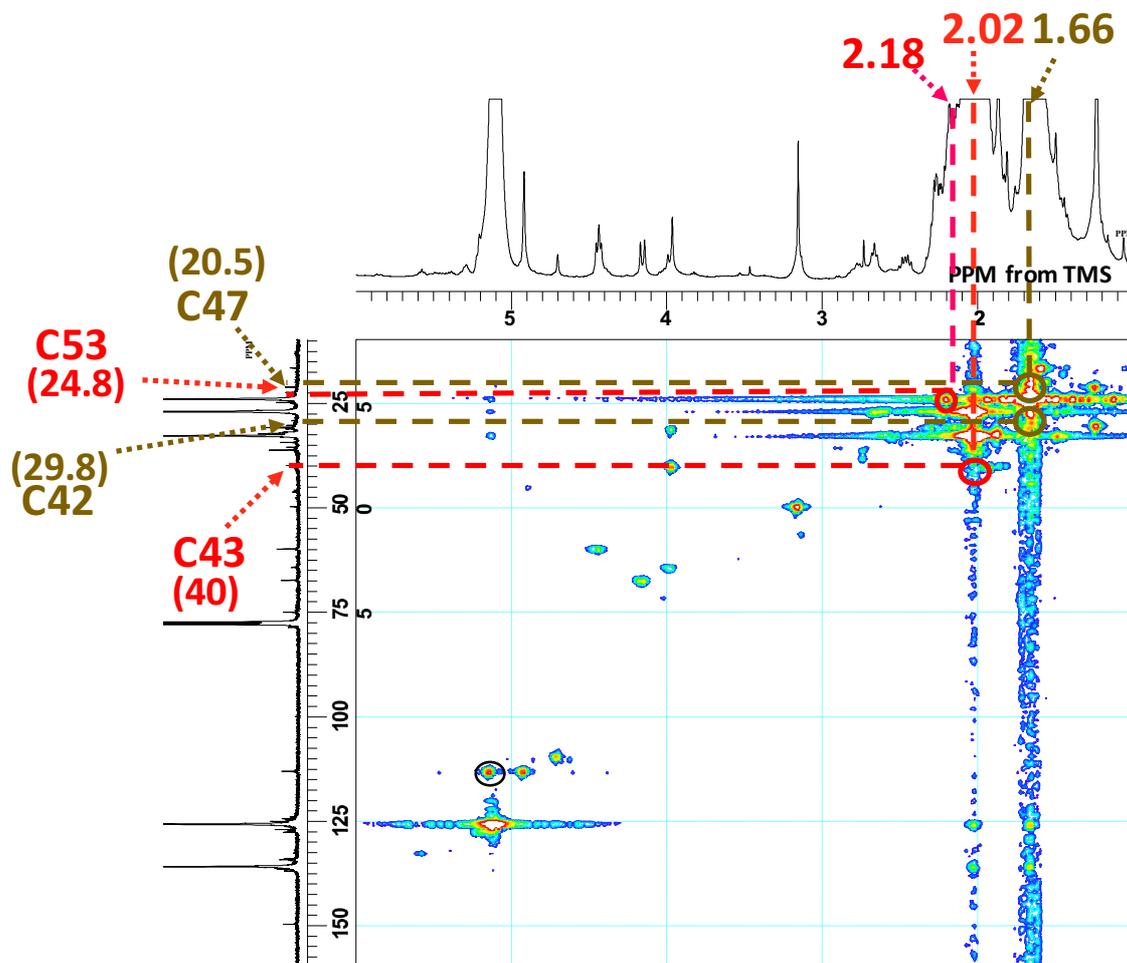
Figure 3-6 HMQC spectra for BrDPNR
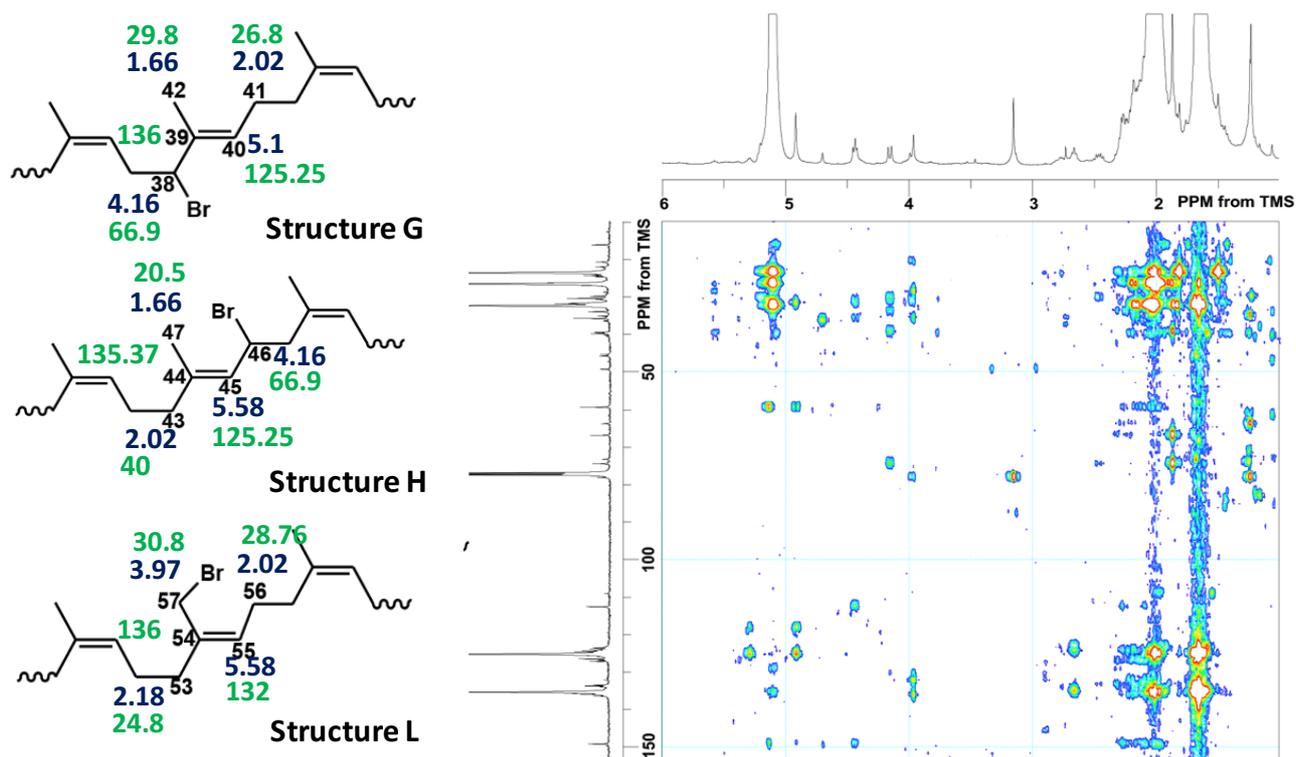
Figure 3-7 HMBC spectra for BrDPNR

Figure 3-7 shows the HMBC spectra for BrDPNR. The ^{1}H signals in the HMBC spectra are correlated with the ^{13}C signals that are one or two atoms apart from the directly linked carbon atom. The ^{1}H signal at 1.66 ppm, which was assigned to methyl proton of H47, was correlated to the ^{13}C signals at 40 (C43), 125.25 (C45) and 135.37 (C44) ppm, where the carbon number in parenthesis denotes the carbon position shown in Figure 3-3. In contrast, the ^{1}H signal at 2.02 ppm, which was assigned to methylene proton of H43 and was correlated with the ^{13}C signal at 40 ppm in the HMQC spectra, was correlated to the ^{13}C signals at 20.5 (C47), 26.8 (C4), 135.37 (C44), 125.25 (C45) and 135 (C3) ppm in the HMBC spectra. Therefore, we assigned the ^{13}C signals at 20.5 and 40 ppm to the brominated *trans*-1,4-isoprene unit of structure H (Figure 3-3). In contrast, the ^{1}H signal at 1.66 ppm, which was assigned to the methyl proton of H42, was correlated to the ^{13}C signals at 66.9 (C38), 125.25 (C40) and 136

53

(C39) ppm. Thus, the signal at 29.8 ppm is assigned to the brominated *trans*-1,4-isoprene unit of structure G (Figure 3-3). Additionally, the ^{1}H signal at 2.18 ppm, which was assigned to the methyl proton of H53, was correlated to the ^{13}C signals at 30.8 (C57), 132 (C55) and 136 (C54) ppm. Thus, the ^{13}C signals at 24.8 ppm are assigned to the brominated *trans*-1,4-isoprene of structure L (Figure 3-3). Table 3-1 summarizes the assignments for the signals and spin couplings of the HMBC spectra for BrDPNR.
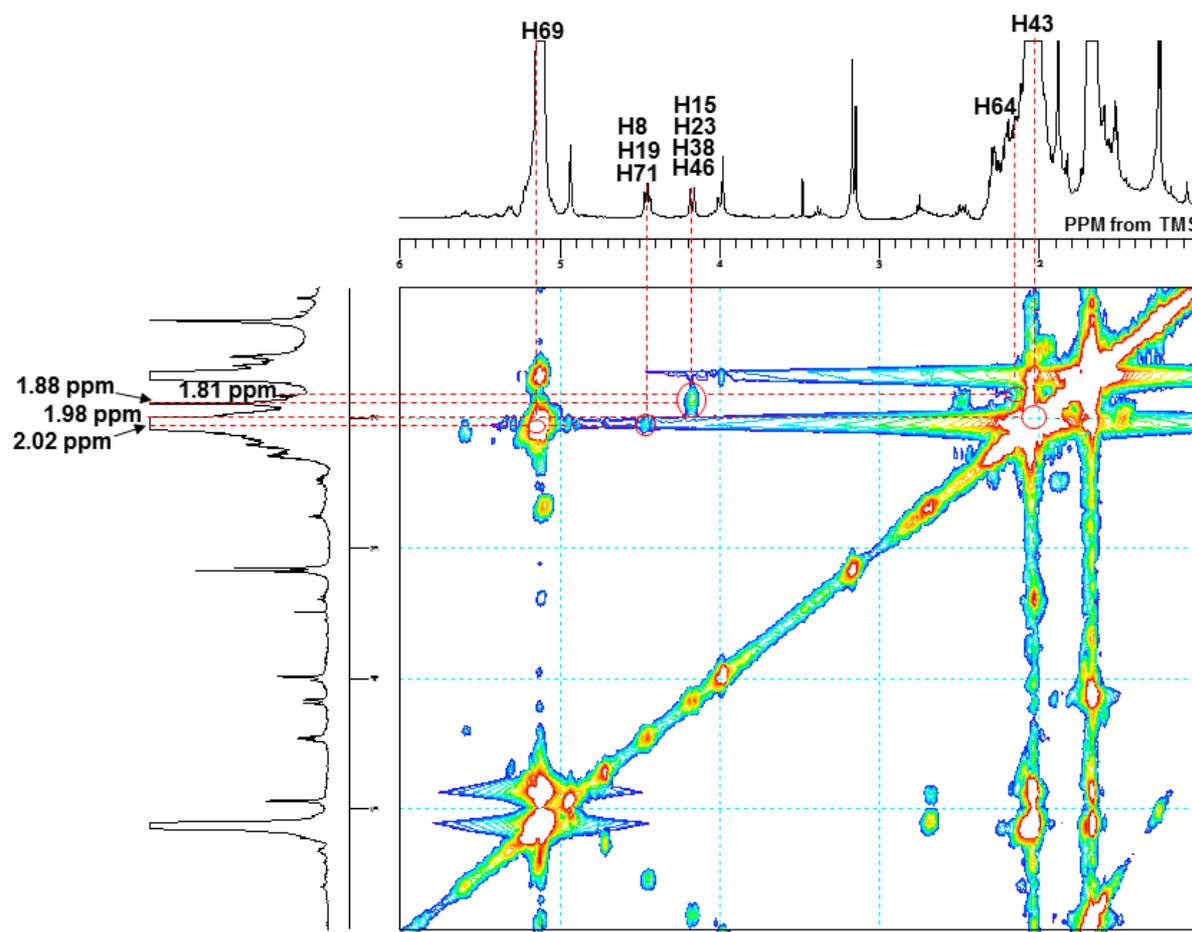

Figure 3-8 ^{1}H-^{1}H COSY spectra for BrDPNR

These assignments were supported by the COSY spectra for BrDPNR (Figure 3-8). The signal at 2.02 ppm, which was assigned to the methylene proton of H43, was correlated with the signal at 1.98 ppm. The signal at 2.19 ppm, which was assigned to the methylene proton of

H64, was correlated with the signal at 1.81 ppm. The signal at 5.14 ppm, which was assigned to the methane proton of H69, was correlated with the signal at 2.02 ppm. In contrast, based on these structures, the signal at 1.66 ppm, which did not appear in the COSY spectra, was assigned to the methyl proton adjacent to the carbon without a proton; that is, H42 and H47. Table 3-2 shows the correlation of ^{1}H—^{1}H COSY. These results demonstrate that the brominated *trans*-1,4-isoprene units of structures G, H and L are generated by *cis-trans* isomerization that occurred during the bromination of natural rubber through the Wohl-Ziegler reaction with NBS according to the radical mechanism.

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

$$X_{Br}[mol\%] = \frac{I_{Br}}{\left(I_{5.10} + {I_{4.92}}/{2}\right) + (I_{Br})} \times 100 \qquad (3\text{-}1)$$

$$I_{Br} = {I_{3.98}}/{2} + I_{4.16} + I_{4.44} \qquad (3\text{-}2)$$

where I is the signal intensity and the subscript denote the chemical shift (ppm). The estimated bromine atom content of BrDPNR prepared in the present study was 6.56%.

3.4 Conclusion

The BrDPNR, which was prepared by bromination of DPNR through the Wohl-Ziegler reaction with NBS, was analyzed by solution state 1D and 2D-NMR spectroscopy such as HMQC, HMBC and COSY measurements. The signals at 20.5 and 29.8 ppm were assigned to the primary carbons of C47 and C42 of the brominated *trans*-1,4-isoprene units, respectively. The signals at 24.8 and 40 ppm were assigned to the secondary carbons of C53 and C43 of the brominated *trans*-1,4-isoprene units. The bromination of DPNR with NBS occurred after

hydrogen abstraction of the *cis*-1,4-isoprene units. The reaction between the allylic carbon radicals and bromine radicals generates the brominated *trans*-1,4-isoprene units.

3.5 References

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CHAPTER 4

Preparation of phenyl-modified natural rubber in latex stage

4.1 Introduction

The bromination and the Suzuki-Miyaura cross-coupling reaction must be performed in latex stage, since natural rubber is isolated as a latex from Para-rubber tree, *Hevea brasiliensis*. In Chapter 2, the Suzuki-Miyaura cross-coupling reaction on BrDPNR was performed in THF solution. Its reaction scheme is shown in Figure 4-1. First, the bromination of natural rubber was made with *N*-bromosuccinimide (NBS) under nitrogen atmosphere in dichloromethane. Hydrogen atoms at allylic position of natural rubber were replaced to bromine atoms, according to the radical mechanism [1-3]. Second, allylic bromine atoms of the resulting brominated natural rubber were replaced to phenyl groups by Suzuki-Miyaura cross-coupling reaction with phenylboronic acid in the presence of di-μ-chloro-bis [5-hydroxy-2-[1-(hydroxyimino)-ethyl]-phenyl] palladium (II) dimer under nitrogen atmosphere in THF [4]. Eventually, the PhDPNR was obtained. The T_g of PhDPNR was found to be dependent upon the phenyl group content and it was $-30\,°C$ at 10 mol% phenyl group content. In addition, the PhDPNR met the requirement that value of loss tangent must be smaller at $50\,°C$ and larger at $0\,°C$, when the phenyl group content was 4 mol%.
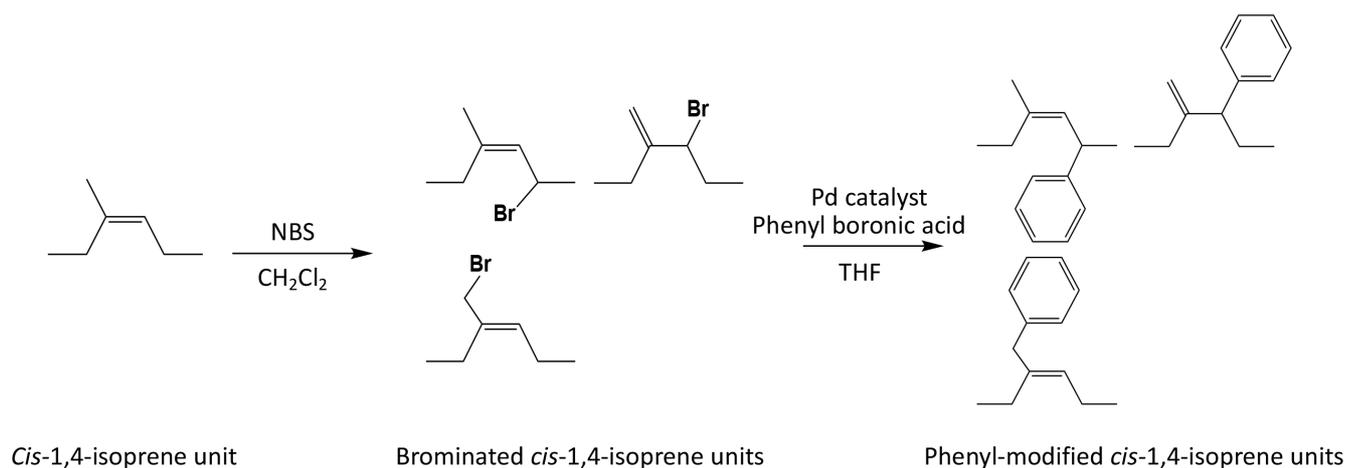
Figure 4-1 Suzuki-Miyaura cross-coupling reaction of *cis*-1,4-isoprene unit.

However, dichloromethane and THF used in the previous work are known to be volatile organic solvents, which are uneasy to use in future. To accomplish the sustainable development goals, natural rubber latex isolated from *Hevea brasiliensis* must be used without further treatment. It is, thus, necessary to develop a water process with natural rubber latex to prepare PhDPNR without volatile organic solvents. The DPNR latex [5-7] may meet this demand to establish a promising water process, since it suppressed side reactions with proteins [8].

In Chapter 4, the Suzuki-Miyaura cross-coupling reaction of DPNR was carried out in the latex stage. First, the bromination of DPNR with NBS was carried out under nitrogen atmosphere in latex stage. Second, the BrDPNR latex was subjected to Suzuki-Miyaura cross-coupling reaction with phenylboronic acid in the presence of the palladium catalyst under nitrogen atmosphere in latex stage. The BrDPNR and PhDPNR, prepared in latex stage, were characterized by NMR spectroscopy and DSC.

4.2 Experimental

4.2.1 Bromination of natural rubber with NBS in latex stage

The BrDPNR was prepared in the latex stage. DPNR latex (100 g, 2.0 w/w% dry rubber content, DRC) with 2.0 w/w% SDS solution was charged with N_2 gas for 1 h at 313 K. The bromination of DPNR latex was performed by stirring the latex at 313 K for 2h after adding NBS (1 *wt*%). The obtained BrDPNR was subjected to a Suzuki-Miyaura cross-coupling reaction without purification. Schematic representation of the experimental procedure is shown in Figure 4-2.

4.2.2 Insertion of phenyl groups into natural rubber by Suzuki-Miyaura cross-coupling reaction in latex stage

The BrDPNR was charged with N_2 gas for 1h at room temperature. Phenylboronic acid (0.75 mol%), palladium catalyst (0.005 mol%), and potassium carbonate (1.0 mol%) were added and stirred for 6 h at a refluxing temperature. The PhDPNR, was coagulated with methanol, and dried under a reduced pressure at 50 °C. Schematic representation of the experimental procedure is shown in Figure 4-2.

4.2.3 Characterization

Solution state NMR spectroscopy was performed with JEOL ECA-400 NMR spectrometer (JEOL, Tokyo, Japan) for BrDPNR and PhDPNR. The rubbers were dissolved into chloroform-*d* without tetramethylsilane (TMS). The chemical shifts were referenced to chloroform-*d*. The ^{1}H-NMR measurement at 399.65 MHz was performed by 128 scans with a pulse repetition time of 7 s at 45° pulse of 1.8 μs and a relaxation delay of 4.24 s. The measurement temperature was 303 K for BrDPNR, and 323 K for PhDPNR. ^{13}C-NMR

measurement at 100.4 MHz and 303 K was carried out by 5,000 scans with a pulse repetition time of 5 s at 30°pulse of 3.5 μs and a relaxation delay of 3.68 s.

The T_g of the rubbers was assessed with DSC 220 (Seiko Instruments, Chiba, Japan), which was calibrated with standard indium and linoleic acid. The rubbers (10 mg), which were packed into an aluminum pan, were heat at 100 ˚C. After annealing, the temperature range and heating rate were set to −120 °C to 100 °C at a heating rate of 10 °C/min.

```
                    ┌─────────────────────────┐
                    │      DPNR latex         │
                    │ (2.0% DRC, 2.0 w/w% SDS)│
                    └─────────────────────────┘
                              │
Inserting N₂ gas for 1h at 313K  ←──  N-bromosuccinimide (NBS)
                              │         1wt% at 313K for 2h
                    ┌──────────────┐
                    │  BrDPNRlatex │
                    └──────────────┘
                              │
                              │  ←──  Phenyl boronic acid 0.75 mol equivalent*
Stirring at 333K for 2h       │       Palladium catalyst 0.005 mol equivalent*
                              │       Potassium carbonate 1.0 mol equivalent*
                    ┌────────────────┐
                    │  PhBrDPNRlatex │    *For amount of N-bromosuccinimide
                    └────────────────┘
                              │
Coagulation with excess MeOH  │
Purification with toluene and MeOH
                              │
Drying under pressure at 323K │
                    ┌──────────────────────┐
                    │  Dried PhBrDPNRlatex │
                    └──────────────────────┘
```

Figure 4-2 Bromination and Suzuki-Miyaura cross-coupling reaction of natural rubber in

latex stage

4.3 Results and discussion
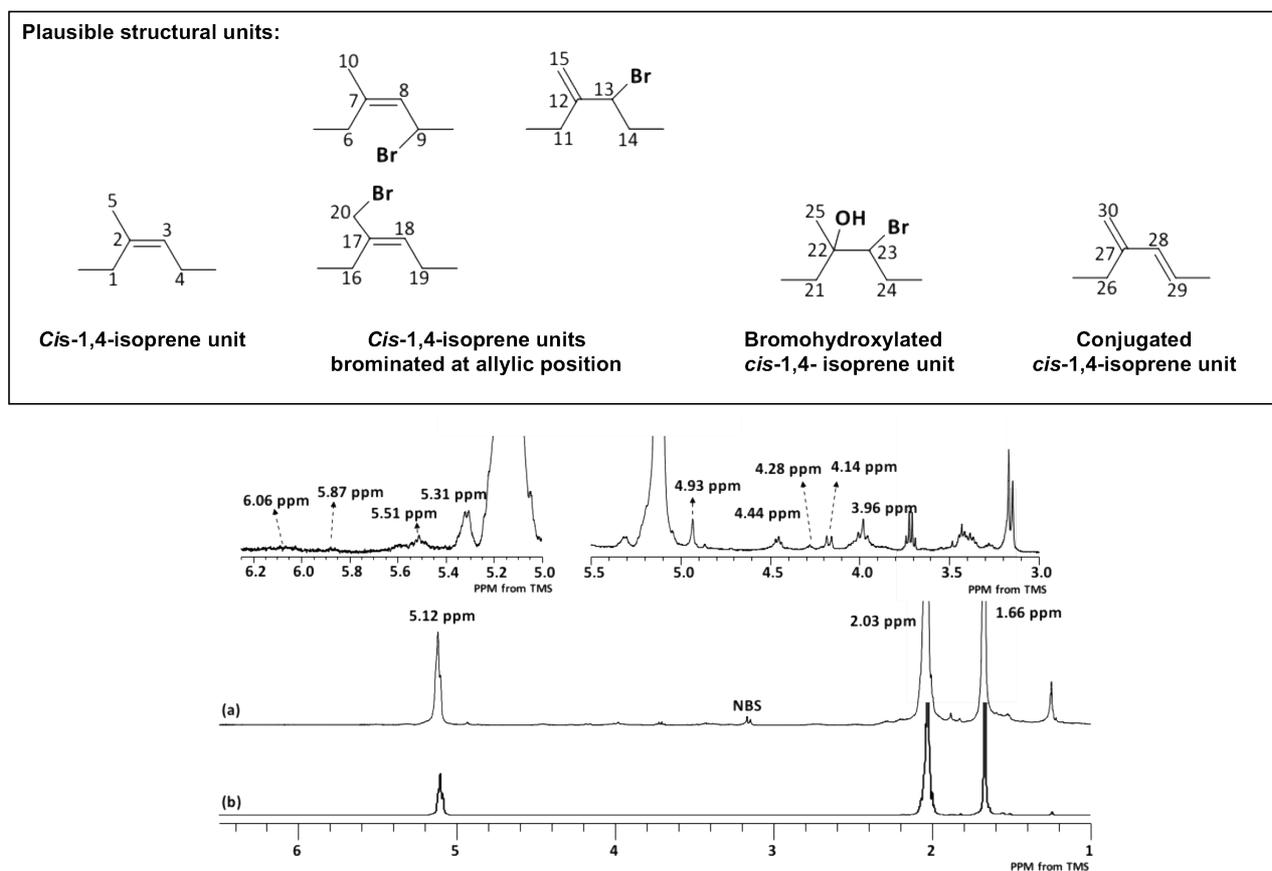
Figure 4-3 ^{1}H-NMR spectra of BrDPNR (a), and DPNR (b) and plausible structural units.

The ^{1}H-NMR spectrum for BrDPNR prepared in latex stage (BrDPNR) is shown in Figure 4-3, in conjunction with that for DPNR. The inserts are enlarged ^{1}H-NMR spectra ranging from 3.0 to 5.5 ppm and from 5.0 to 6.3 ppm, respectively. Three major signals at 1.66, 2.03 and 5.12 ppm were assigned to methyl, methylene and unsaturated methine protons of *cis*-1,4-isoprene units. After bromination of DPNR with NBS in latex stage, many small signals appeared in ^{1}H-NMR spectra. The signals at 3.96, 4.14, 4.44 and 4.93 ppm were assigned to the plausible structural units of BrDPNR that possessed bromine atom at allylic position of *cis*-1,4-isoprene units, according to the previous work (Figure 4-3) [1]. The signal at 3.96 ppm was assigned to the methylene proton of H20, while the signal at 4.14 ppm was to the methine proton of H9. The signal at 4.44 ppm was assigned to the methine proton of H13, while the

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signal at 4.93 ppm was to the methylene proton of H15. In addition, we found unknown signals at 4.28, 5.87 and 6.06 ppm. The signal at 4.28 ppm was assigned to the methine proton of H23 (Figure 4-3). The signals at 5.87 and 6.06 ppm were assigned to methine protons of H29 and H28 (Figure 4-3), respectively. The assignments of signals at 4.28, 5.87 and 6.06 ppm is explained, in detail, by using ^{13}C-NMR spectroscopy as in the following paragraph.
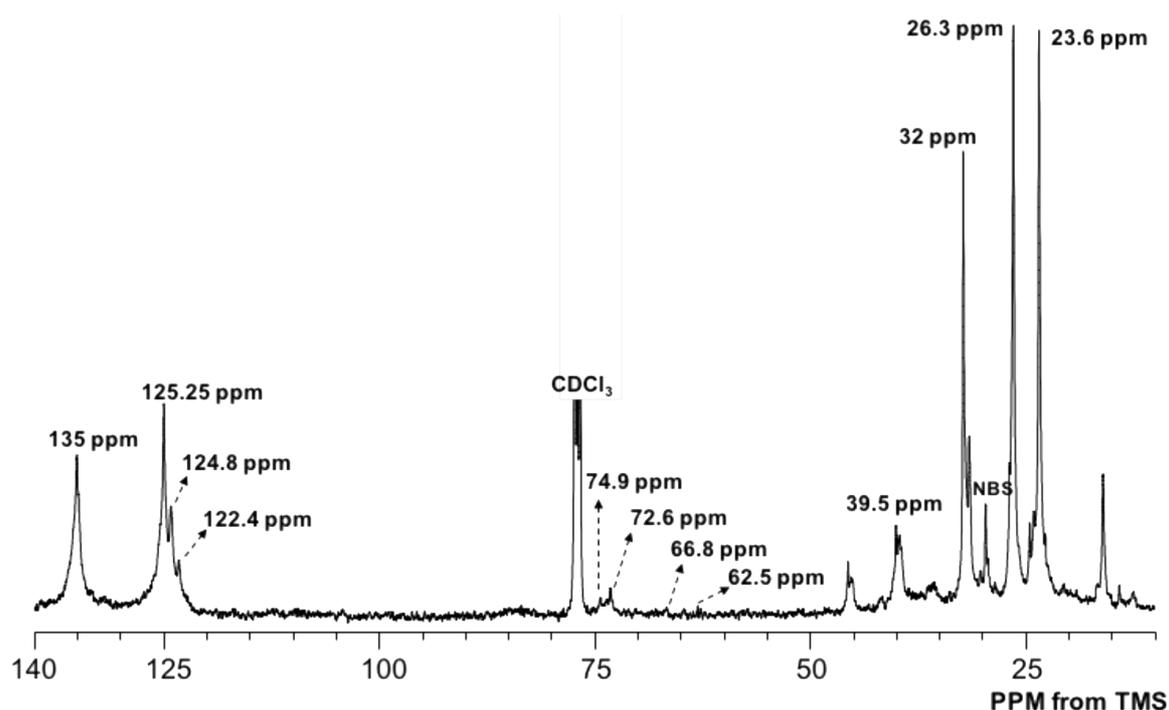

Figure 4-4 ^{13}C-NMR spectrum for BrDPNR

Figure 4-4 shows ^{13}C-NMR spectrum for BrDPNR. The five characteristic signals at 23.6, 26.3, 32, 125.25, and 135 ppm were assigned to the C5, C4, C1, C3, and C2 of the *cis*-1,4-isoprene units [9], respectively. According to the previous work [1], the signals at 39.5, 62.5, and 66.8 ppm were assigned to the secondary carbons of C20, C13, and C9 (Figure 4-3) of the BrDPNR, respectively. In addition, the signals at 74.9 and 72.2 ppm appeared in the ^{13}C-NMR spectrum for BrDPNR. These signals were assigned to the carbons of bromohydroxylated *cis*-1,4-isoprene units (Figure 4-3). The signal at 74.9 ppm was assigned

to quaternary carbon of C22, whereas the signal at 72.2 ppm was assigned to tertiary carbon of C23. From the results, it is considered that the reactions of natural rubber with bromine atom and H_2O take place in latex stage. For instance, first, the bromine cation of NBS may attack the double bond of natural rubber to form bromonium ion (Figure 4-5) [20-23]. Second, the resulting bromonium ion may react with H_2O to form bromohydrin group. Furthermore, the signals at 122.4 (C29) and 124.8 (C28) ppm were assigned to tertiary carbons of the conjugated *cis*-1,4-isoprene units generated by elimination reaction of bromine atoms (Figure 4-5), based on Parent *et al* [14,15]. These results demonstrate that natural rubber is brominated with NBS in latex stage, according to mechanism shown in Figure 4-5. Consequently, it is proved that bromine atom is introduced into the natural rubber at the allylic position of *cis*-1,4-isoprene units while the bromohydrin structure of BrDPNR is formed since the reaction takes place in the water. In addition, BrDPNR prepared in the latex stage contains not only bromine atoms but also conjugated dienes due to the elimination of bromine atoms.

Bromination:
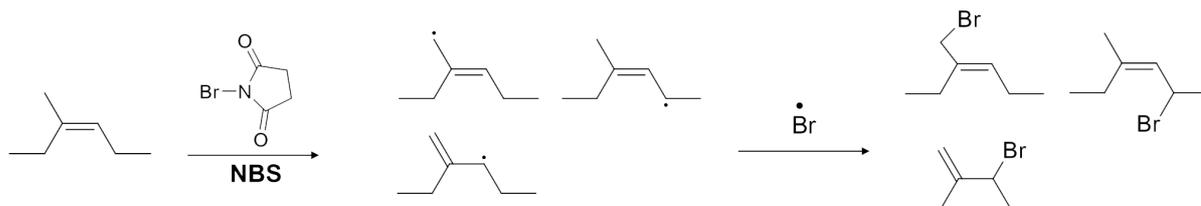
Cis-1,4-isoprene unit

Cis-1,4-isoprene unit
brominated at allylic position

Bromohydrin formation:
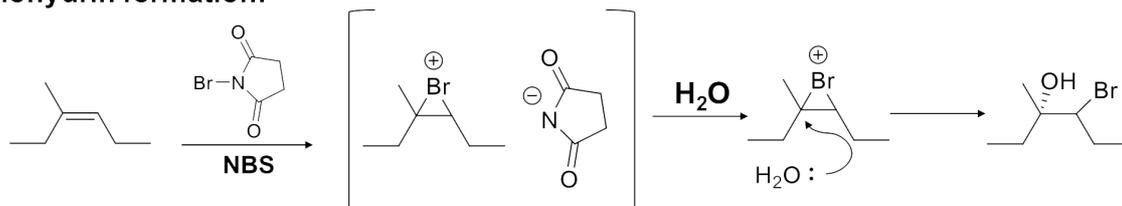
Cis-1,4-isoprene unit   Bromonium ion formation

Bromohydroxylated
cis-1,4-isoprene unit

Elimination reaction of bromine:
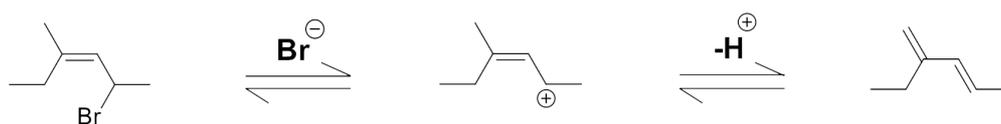
Cis-1,4-isoprene unit
brominated at allylic position

Conjugated
cis-1,4- isoprene unit

Figure 4-5 bromination, bromohydrin formation and elimination reaction of bromine atom

The bromine atom content (X_{BrL}) and the conjugated diene content (X_{diene}) of BrDPNR were estimated from the intensity ratio of the signals at 3.96, 4.16, 4.28, 4.44, 4.92, 5.13 and 6.06 ppm.

$$X_{BrL}[mol\%] = \frac{I_{Br}}{\left(I_{5.13} + {I_{4.93}}/{2}\right) + (I_{Br}) + I_{6.06}} \times 100 \qquad (4\text{-}1)$$

$$X_{diene}[mol\%] = \frac{I_{6.05}}{\left(I_{5.13} + {I_{4.93}}/{2}\right) + (I_{Br}) + I_{6.06}} \times 100 \qquad (4\text{-}2)$$

$$I_{Br} = {I_{3.96}}/{2} + I_{4.14} + I_{4.44} + I_{4.28} \qquad (4\text{-}3)$$

where *I* is the signal intensity and the subscript denotes the chemical shift (ppm). The estimated bromine atom content in BrDPNR and conjugated diene content are 5.43 mol% and 1.66 mol%, respectively. The bromine atom content and conjugated diene content of BrDPNR depended on the amount of NBS. Figure 4-6 shows plots of bromine atom content and conjugated diene content versus amount of NBS. The bromine atom content and conjugated diene content linearly increased as the amount of NBS increased.
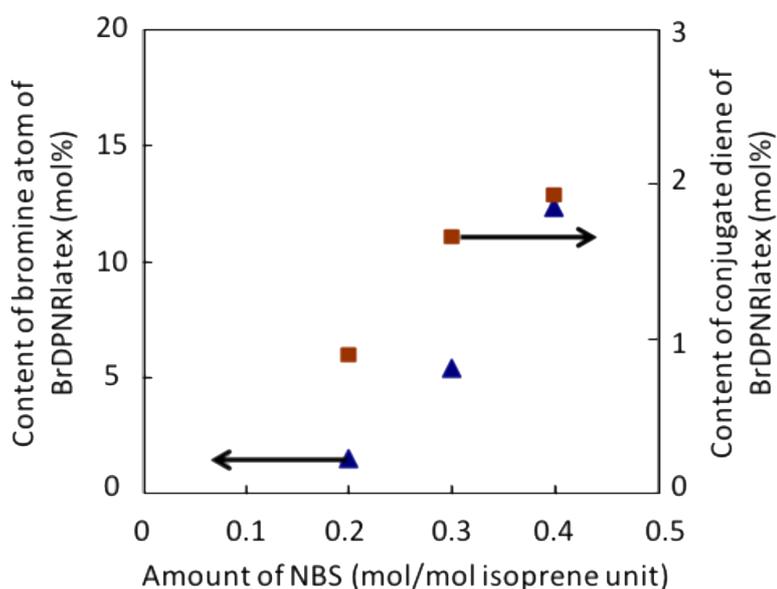

Figure 4-6 plots of amount of NBS versus bromine atom content (▲) and conjugate diene content (■) of BrDPNR.

The molar fraction of H20, H9, H23 and H13, which were related to the structural units of BrDPNR listed in Figure 4-3, were calculated according to the following equations:

$$C_{H20}[mol\%] = \frac{I_{3.96}/2}{I_{3.96}/2 + I_{4.28} + I_{4.14} + I_{4.44}} \times 100 \qquad (4\text{-}4)$$

$$C_{H9}[mol\%] = \frac{I_{4.14}}{I_{3.96}/2 + I_{4.28} + I_{4.14} + I_{4.44}} \times 100 \qquad (4\text{-}5)$$

$$C_{H23}[mol\%] = \frac{I_{4.28}}{I_{3.96}/2 + I_{4.28} + I_{4.14} + I_{4.44}} \times 100 \qquad (4\text{-}6)$$

$$C_{H13}[mol\%] = \frac{I_{4.44}}{I_{3.96}/_2 + I_{4.28} + I_{4.14} + I_{4.44}} \times 100 \qquad (4\text{-}7)$$

where C is the molar fraction, *I* is the intensity of the signal and the subscripts represent the chemical shift (ppm). The molar fraction of H20 (C_{H20}), H9 (C_{H9}), H23 (C_{H23}) and H13 (C_{H13}) were 54.2, 15.1, 3.5 and 27.2 mol%, respectively. It is worthy of note that the molar fraction of H13 of the BrDPNR was 27.2 mol%, which was distinguish from that, *i.e.*, 40 mol%, for brominated natural rubber prepared in solution state [16]. This may be explained to be due that the conjugated dienes are formed by elimination reaction of bromine atoms at position 13 (Figure 4-5). In addition, the BrDPNR contained large amount of allylic brominated *cis*-1,4-isoprene units; that is, the molar fraction of allylic brominated *cis*-1,4-isoprene units was 96.5 mol%, while the molar fraction of H23 of bromohydroxylated *cis*-1,4-isoprene units was 3.5 mol%. It is, thus, considered that the BrDPNR is suitable for Suzuki-Miyaura cross-coupling reaction since it consists of the *cis*-1,4-isoprene units and the allylic brominated *cis*-1,4-isoprene units as major components.
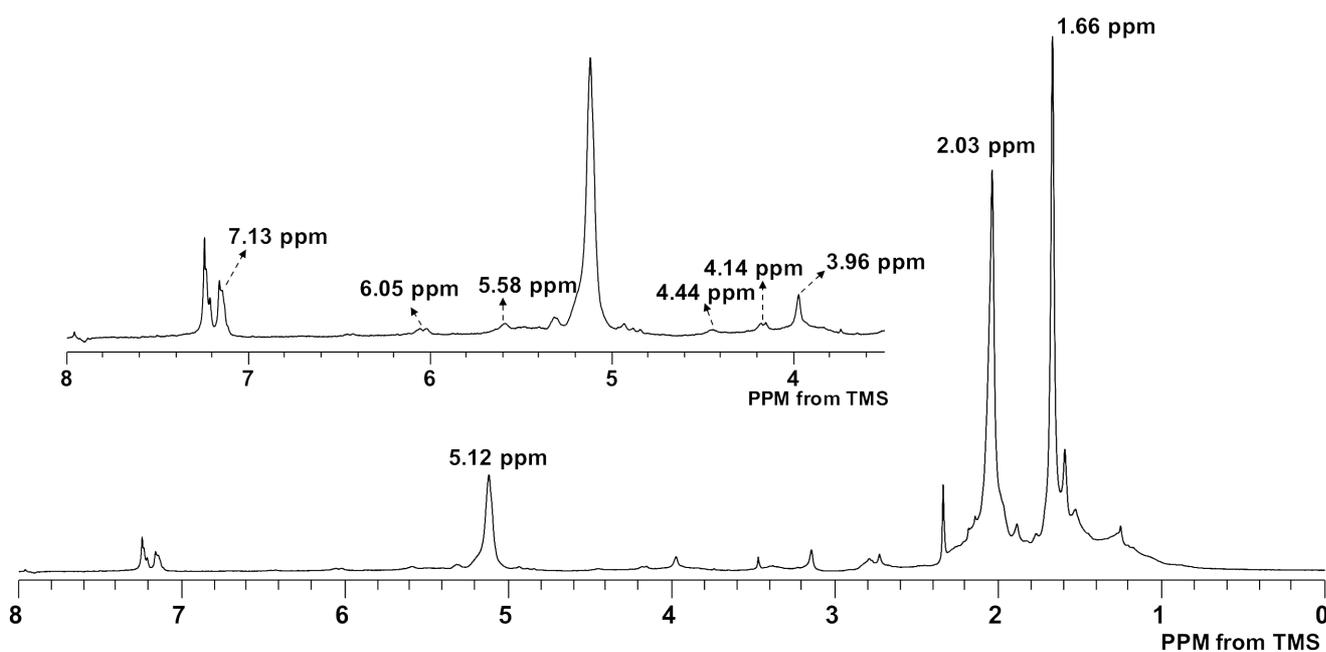

Figure 4-7 ^{1}H-NMR spectrum for PhDPNR

Figure 4-7 shows ^{1}H-NMR spectrum for PhDPNR prepared in latex stage. The insert is an enlarged ^{1}H-NMR spectrum ranging from 3.5 to 8.0 ppm. Three major signals at 1.66, 2.03 and 5.12 ppm were attributed to methyl, methylene and unsaturated methine protons of *cis*-1,4-isoprene units, respectively. After Suzuki-Miyaura cross-coupling reaction, small signals appeared around 7.13 ppm. These were assigned to the phenyl groups linking to PhDPNR, according to the previous work [16]. Moreover, we found that signals at 3.96, 4.14, 4.44, 5.87 and 6.05 ppm appeared in ^{1}H-NMR spectrum for PhDPNR. The signals at 3.96, 4.14, 4.44 were assigned to H20, H9 and H13 of the BrDPNR; so that, PhDPNR contained bromine atoms as unreated units. This may be explained to be due to the low conversion; *i.e.*, 23.7 mol%, of Suzuki-Miyaura cross-coupling reaction in latex stage ($C_{cross\text{-}coupling}$), which calculated from equation 4-9. In contrast, the signals at 5.87 and 6.05 ppm were assigned to H29 and H28 of the conjugated *cis*-1,4-isoprene units. The conjugated diene content (X_{diene}) of PhDPNR was similar to the conjugated diene content of BrDPNR. This implies that the phenyl group is replaced from bromine atom but not from conjugated *cis*-1,4-isoprene units, based on the mechanism of Suzuki-Miyaura cross-coupling reaction. From these results, it is found that PhDPNR consists of phenyl-modified *cis*-1,4-isoprene units, allylic brominated *cis*-1,4-isoprene units, bromohydroxylated *cis*-1,4-isoprene units and conjugated *cis*-1,4-isoprene units in addition to *cis*-1,4-isoprene units.

The phenyl group content (X_{phL}) and the conversion of the Suzuki-Miyaura cross-coupling reaction ($C_{cross\text{-}coupling}$) of the PhDPNR was calculated as follows:

$$X_{phL}[mol\%] = \frac{I_{7.13}/5}{I_{5.13} + I_{7.13}/5} \times 100 \qquad (4\text{-}8)$$

$$C_{cross-coupling}[\%] = \frac{X_{phL}}{X_{BrL}} \times 100 \qquad (4\text{-}9)$$

where I is the intensity of the signal and the subscripts denote the chemical shift (ppm). Conversion of the Suzuki-Miyaura cross-coupling reaction ($C_{\text{cross-coupling}}$) was calculated from the bromine atom content (X_{BrL}) and the phenyl group content (X_{PhL}). The phenyl group content was estimated to be 1.32 mol%. The value of conversion of the Suzuki-Miyaura cross-coupling reaction is shown in Table 4-1.

Table 4-1 shows the bromine atom content of BrDPNR prepared with DPNR latex, the phenyl group content of PhDPNR, the conversion of Suzuki-Miyaura cross-coupling reaction and T_g. The conversion of the cross-coupling reaction using BrDPNR with bromine contents of 1.52, 5.57 and 12.9 mol% were 90.7, 23.7 and 58.3%, respectively.

Table 4-1 bromine atom content, phenyl group content, conversion of Suzuki-Miyaura cross-coupling reaction and the glass transition temperature of PhDPNR, prepared in latex stage

Bromine atom content (mol%)	Phenyl group content (mol%)	Conversion of Suzuki-Miyaura cross coupling reaction (%)	Glass transition temperature (°C)
0.80	-[a]	-	-60.6
1.52	1.38	90.7	-53.2
5.57	1.32	23.7	-46.7
12.91	7.53	58.3	-43.1

[a] Signal for phenyl proton was overlapped with large signal for chloroform
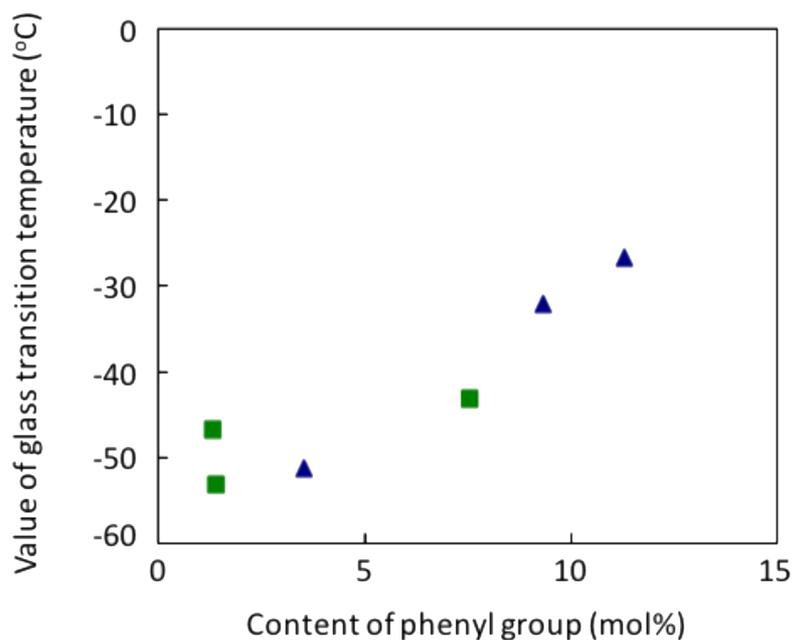
Figure 4-8 plot of the T_g versus phenyl group content for PhDPNR (■) in conjunction with

PhDPNR prepared in solution state (▲)

Figure 4-8 shows a plot of the T_g versus phenyl group content for PhDPNR in conjunction with the PhDPNR prepared in solution state. The value of T_g of DPNR increased from −62.1 °C to −46.7 °C when the phenyl group was introduced into the rubber. This may be explained to be due to the introduction of the phenyl group as a bulky pendent group, which decrease the free volume fraction of the natural rubber. The value of T_g of PhDPNR was related to the phenyl group content, that is; the value of T_g increased as the phenyl group content increased.

4.4 Conclusions

The PhDPNR was prepared in latex stage by bromination of DPNR with NBS followed by Suzuki-Miyaura cross-coupling reaction with phenylboronic acid in the presence of palladium catalyst. It was found that the PhDPNR consisted of phenyl-modified *cis*-1,4-isoprene units, allylic brominated *cis*-1,4-isoprene units, bromohydroxylated *cis*-1,4-isoprene

units and conjugated *cis*-1,4-isoprene units in addition to *cis*-1,4-isoprene units, as was evident from the structural characterization of PhDPNR through NMR spectroscopy. The allylic bromine groups (*i.e.*, H9, H13 and H20) were converted to phenyl group by Suzuki-Miyaura cross-coupling reaction in latex stage. The conversion of Suzuki-Miyaura cross-coupling reaction was 23.7 mol%. The value of T_g of DPNR increased when the phenyl group was introduced into the structure. At 1.32 mol% of phenyl group, T_g of PhDPNR was about $-46.7\ ^{\circ}\text{C}$.

4.5 References

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CHAPTER 5

General conclusion

In the present work, the PhDPNR was prepared in solution and latex from deproteinized natural rubber after bromination of the rubber with NBS.

In Chapter 2, the PhDPNR was prepared in THF solution by Suzuki-Miyaura cross-coupling reaction of the BrDPNR, which was prepared from DPNR in CH_2Cl_2 solution by bromination with NBS. After bromination of DPNR, signals appeared at 3.96, 4.14 and 4.44 ppm in ^{1}H-NMR spectrum and 39.3, 66.5 and 59.2 ppm in ^{13}C-NMR spectrum, which were assigned to allyl bromide groups of brominated *cis*-1,4-isoprene unit. The bromine atom content of BrDPNR increased as the amount of NBS increased. After Suzuki-Miyaura cross coupling reaction of the BrDPNR, several small signals of PhDPNR appeared at 7.13 ppm, which were assigned to phenyl groups linking to the rubber, whereas the signals at 3.96, 4.14 and 4.44 ppm disappeared. The phenyl group content of PhDPNR changed from 4 mol% to 34 mol%, which was associated with the T_g of PhDPNR, i.e., -51 ^{o}C – 10 ^{o}C. The T_g of PhDPNR was found to be about -30 ˚C, when the phenyl group content was 9 - 12 mol%. The PhDPNR realized the good balance between rebound resilience and wet skid resistance at the phenyl group content of 4 mol%.

In Chapter 3, structural characterization of BrDPNR was performed through 2D-NMR spectroscopy. The small signals at 20.5, 24.8, 29.8 and 40 ppm were assigned to brominated *trans*-1,4-isoprene units of the BrDPNR; that is, the signals at 20.5 and 29.8 ppm were assigned to the primary carbons, whereas the signals at 24.8 and 40 ppm were assigned to the secondary

and unsaturated carbons of C53 and C43. The BrDPNR was found to contain the brominated *cis*- and *trans*-1,4-isoprene units, since the isoprene units undergo *cis-trans* isomerization during the bromination of DPNR with NBS.

In Chapter 4, the PhDPNR was prepared in latex stage. After Suzuki-Miyaurs cross-coupling reaction, small signals in ^{1}H-NMR spectrum appeared around 7.13 ppm. These signals were assigned to the phenyl groups linking to PhDPNR. In addition, the signals at 3.96, 4.14, 4.44, 5.87 and 6.05 ppm were assigned to allylic brominated *cis*-1,4-isoprene units and conjugated *cis*-1,4-isoprene units, respectively. The PhDPNR was found to consists of phenyl-modified *cis*-1,4-isoprene units, allylic brominated *cis*-1,4-isoprene units and conjugated *cis*-1,4-isoprene units in addition to *cis*-1,4-isoprene units. The phenyl group content of PhDPNR changed from 1.3 mol% to 7.5 mol%, which was related with T_g of PhDPNR, *i.e.*, −53.2 °C to −46.7 °C. when the phenyl group content was about 1.32 mol%.

List of publications

1. "Preparation and properties of phenyl-modified natural rubber"
   S. Kawahara, S. Shioyama, **N. Choothong**, L. Fukuhara, H. Ishii, Y. Yamamoto and K. Takenaka,
   Polym. Adv. Technol., 26, (2014), 546-554.

2. "Characterization of brominated natural rubber by solution-state 2D NMR spectroscopy"
   N. Choothong, K. Kosugi, Y. Yamamoto, S, Kawahara,
   React. Funct. Polym., 113, (2017), 6-12.

3. "Preparation of phenyl-modified natural rubber in latex stage"
   N. Choothong, Y. Yamamoto, S, Kawahara,
   Polym. Adv. Technol., **in press**

List of presentations

1. "Preparation and properties of phenyl-modified natural rubber" (Poster)
   S. Kawahara, S. Shioyama, **N. Choothong**, L. Fukuhara, H. Ishii, Y. Yamamoto and K. Takenaka,
   15-1 NMR meeting, May 15th, 2015; SEKISUI CHEMICAL (Kyoto R&D Laboratories), Kyoto, Japan.

2. "Preparation of phenyl-modified natural rubber though Suzuki-Miyaura cross-coupling reaction" (Poster)
   N. Choothong, S. Kawahara,
   4th Gigaku Conference, June 19-22th, 2015; Nagaoka University of Technology, Nagaoka, Japan.

3. "Preparation and Properties of Phenyl-modified Natural Rubber" (Oral)
   N. Choothong, S. Kawahara,
   International Polymer Conference of Thailand (PCT-5), June 18-19th, 2015; Pathumwan Princess Hotel, Bangkok, Thailand.

4. "Preparation and Properties of Phenyl-modified Natural Rubber" (Oral)

N. Choothong, S. Kawahara,

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

5. "Preparation and Properties of Phenyl-modified Natural Rubber" (Poster)

N. Choothong, S. Kawahara,

4th Joint symposium CU-NUT, October 22nd, 2015; Chulalongkorn University (Faculty of Science), Bangkok, Thailand.

6. "Characterization of brominated natural rubber by solution-state 2D NMR spectroscopy" (Oral)

N. Choothong, S, Kawahara,

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

7. "Preparation and Mechanical Properties of Phenyl-modified Natural Rubber" (Poster)

S. Kawahara, S. Shioyama, **N. Choothong**, L. Fukuhara, H. Ishii, Y. Yamamoto and K. Takenaka,

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

8. "Characterization of brominated natural rubber by solution-state 2D NMR spectroscopy" (Oral)

N. Choothong, S, Kawahara,

191st spring technical meeting by ACS (Rubber division American Chemical Society) April 25-26th, 201; Double Tree by Hilton, Cleveland, America.

9. "Bromination of Natural Rubber with N-bromosuccinimide" (Oral)

N. Choothong, K. Kosugi, Y. Yamamoto, S, Kawahara,

International Polymer Conference of Thailand (PCT-7), June 01-02nd, 2017; Amari Watergate Hotel, Bangkok, Thailand.

10.   "Characterization of brominated natural rubber by solution-state 2D NMR spectroscopy" (Oral)

N. Choothong, K. Kosugi, Y. Yamamoto, S, Kawahara,

The Society of Rubber Science and Techonlogy, Japan, 28th Elastomer Symposium, November 29-30, 2017, Kyoto, Japan.