

## 論文内容の要旨

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Chemical modification may have a potential to improve mechanical properties of natural rubber, since glass transition temperature ( $T_g$ ) of the rubber is varied by chemical modification. For instance, phenyl-modified natural rubber (PhDPNR) may change its  $T_g$  as a function of phenyl group content. Thus, the PhDPNR may achieve a good balance between rebound resilience and wet skid resistance, which are necessary to prepare high performance tire. The PhDPNR may be prepared by direct insertion of the phenyl groups into natural rubber. One of the plausible methods to insert the phenyl group is Suzuki-Miyaura cross-coupling reaction, which is known as a homologation reaction of a carbon-carbon formation between phenyl groups and hydrocarbons with allylic bromide groups in the presence of an organometallic catalyst. In addition, this reaction is also performed in oil/water emulsion due to stability of the palladium catalyst in water. Therefore, the PhDPNR may be prepared in latex stage by Suzuki-Miyaura cross-coupling reaction when a suitable catalyst is used; that is, di- $\mu$ -chloro-bis [5-hydroxy-2-[1-(hydroxyimino)-ethyl] palladium (II) dimer. In the present study, Suzuki-Miyaura cross-coupling reaction was performed in solution and latex for DPNR followed by bromination. The characterization of the products, *i.e.*, BrDPNR and PhDPNR, was performed by 1D and 2D-nuclear magnetic resonance (NMR) spectroscopy. The  $T_g$  and viscoelastic properties of the PhDPNR were investigated by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), respectively.

An attempt to prepare PhDPNR was made by Suzuki-Miyaura cross-coupling reaction in solution state. First, DPNR was brominated with NBS in dichloromethane solution. Second, the Suzuki-Miyaura cross-coupling reaction of the BrDPNR was carried out with phenylboronic acid in the presence of di- $\mu$ -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  $^1\text{H}$ - and  $^{13}\text{C}$ - NMR spectroscopy. Signals around 7 ppm in the  $^1\text{H}$ -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.

Structural characterization of BrDPNR was carried out by 1D- and 2D-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  $^{13}\text{C}$ -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.

An attempt to prepare PhDPNR in latex stage was made by bromination of DPNR followed by Suzuki-Miyaura cross-coupling reaction. The bromination of DPNR was carried out with NBS 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- $\mu$ -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.