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ORIGINAL CONTRIBUTION

Hydrogenation of natural rubber having epoxy group

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Abstract Hydrogenation of epoxidized natural rubber (ENR) was performed to introduce hydroxyl group to hydrogenated natural rubber. The ENR was prepared by epoxidation of deproteinized natural rubber (DPNR) with peracetic acid in latex stage. Hydrogenation of epoxidized DPNR (EDPNR) was performed with *p*-toluenesulfonylhydrazide in *p*-xylene. The resulting product, hydrogenated EDPNR (HEDPNR), was characterized by nuclear magnetic resonance spectroscopy with various pulse sequences, i.e., two-dimensional correlation spectroscopy, two-dimensional heteronuclear correlation measurements. Carbons linking up to hydroxyl group were assigned to be quaternary and tertiary groups. The HEDPNR was proved to be a polyolefine elastomer through differential scanning calorimetry.

Keywords Hydrogenation · Natural rubber · Epoxy group · Deproteinization · NMR measurement

Introduction

Natural rubber (NR) obtained from *Hevea brasiliensis* is well known to be superior in tensile strength, tear strength, permanent set, and so forth [1, 2]. However, NR deteriorates under sunlight, and long-term heating, in the presence of oxygen and ozone due to unsaturation of its isoprene units; hence, NR is inferior in weather resistance and ozone resistance [1, 3]. It does not withstand for long-term use under such a severe environmental condition.

Hydrogenation is one of the chemical modification techniques to improve the properties of diene elastomers [3–6]. It has been applied to reduction of the diene elastomers to enhance thermal, oxidative, and weather resistances of the rubber [5, 7, 8]. For instance, hydrogenated acrylonitrile–butadiene rubber has been prepared with a catalyst under hydrogen atmosphere [9]. Thus, when the hydrogenation is applied to NR, one may prepare ethylene–propylene alternative copolymer as a saturated elastomer, which may crystallize due to high stereo regularity of alternative ethylene–propylene units [10].

In order to prepare noncrystallizable hydrogenated NR, it is necessary to disturb the stereo-regular alternative ethylene–propylene units in terms of an addition of functional groups or substitutes. In this regard, we take a notice of epoxidized natural rubber (ENR) since epoxy groups are randomly distributed into isoprene units, and it may be converted to hydroxyl groups after hydrogenation, as shown in Fig. 1. After the addition of the hydroxyl group into the alternative ethylene–propylene units, the hydrogenated NR may not undergo crystallization, since the stereoregular ethylene–propylene repeating units are disturbed with the hydroxyl group.

ENR has been recognized to be a reactive elastomer having epoxy group, which is made from NR [11–14]. However, in most cases, side reactions may occur on ENR [15], since it contains significant amount of proteins [16]. In the previous works, we proposed enzymatic deproteinization [17–19] and urea deproteinization [20–22] to remove the proteins from natural rubber. We prepared highly deproteinized natural rubber (DPNR) and hyperdeprotei-

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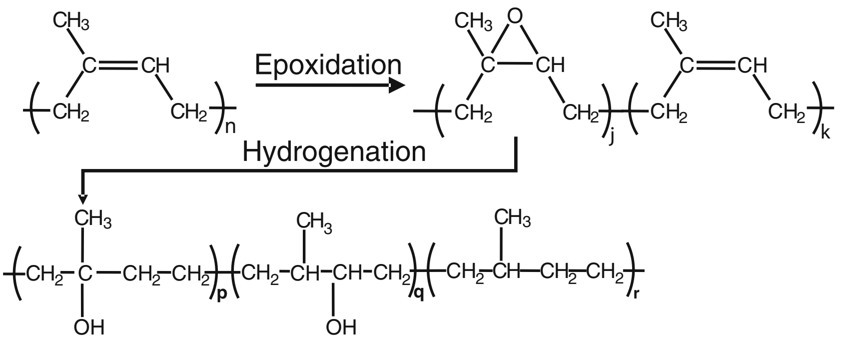


Fig. 1 Hydrogenation of epoxidized natural rubber

nized natural rubber, which contained about 0.1 wt.% and 0.02 wt.% proteins respectively, being less than about 2 wt. % proteins present in untreated natural rubber. When we prepare an epoxidized rubber from the DPNR, we may prevent the side reactions on the rubber.

In this work, an attempt to prepare hydrogenated epoxidized DPNR (HEDPNR) was performed by epoxidation of DPNR with peracetic acid followed by hydrogenation with *p*-toluenesulfonylhydrazide (PTSH) in *p*-xylene at 135 °C. The resulting product was characterized by ^{1}H-nuclear magnetic resonance (NMR), ^{13}C-NMR, two-dimensional correlation spectroscopy (COSY), two-dimensional heteronuclear correlation (HETCOR) measurements and differential scanning calorimetry (DSC).

Experimental

Materials

NR latex used in this study was commercial high ammonia NR (HA-NR) latex. Deproteinization of HA-NR was made by incubation of the latex with 0.1% *w*/*w* urea (Nacalai Tesque Inc., 99.5%) in the presence of 1% *w*/*w* sodium dodecyl sulfate (Kishida Reagents Chemicals Co. Ltd., 99%) at 303 K for 1 h followed by centrifugation at 10^4 rpm [20, 21]. Resulting DPNR latex, precooled at 283 K, was epoxidized in the latex stage with fresh peracetic acid (33%, *v*/*v* concentration) for 3 h [23–25]. After completion of the reaction, pH of the solution was adjusted to 7 with ammonia solution (Nacalai Tesque Inc., 28%) and followed by coagulation with an excess amount of methanol and purified with toluene/methanol then dried under reduced pressure at 303 K for a week. The EDPNR was dissolved in *p*-xylene (Nacalai Tesque Inc., 99.5%) for a night. Hydrogenation of EDPNR was carried out in the presence of 4 molar amount of PTSH (Nacalai Tesque Inc., 99.5%) to isoprene unit at 408 K for 6 h. The resulting solution was coagulated with methanol and purified with toluene/methanol before the coagulum was dried up at 303 K for a week under reduced pressure. The procedure to prepare the product was schematically represented in Fig. 2.

Characterization

NMR measurements were carried out using a JEOL ECA-400 NMR spectrometer operating at 399.65 and 100.4 MHz for ^{1}H and ^{13}C, respectively. The polymer was dissolved into chloroform-*d* without tetramethylsilane. Chemical shifts were referred to chloroform in chloroform-*d*. ^{1}H- and ^{13}C-NMR measurements were carried out at 323 K at the pulse repetition time of 7 and 5 s, respectively. COSY and HETCOR measurements were made to collect two-dimensional hyper complex data.

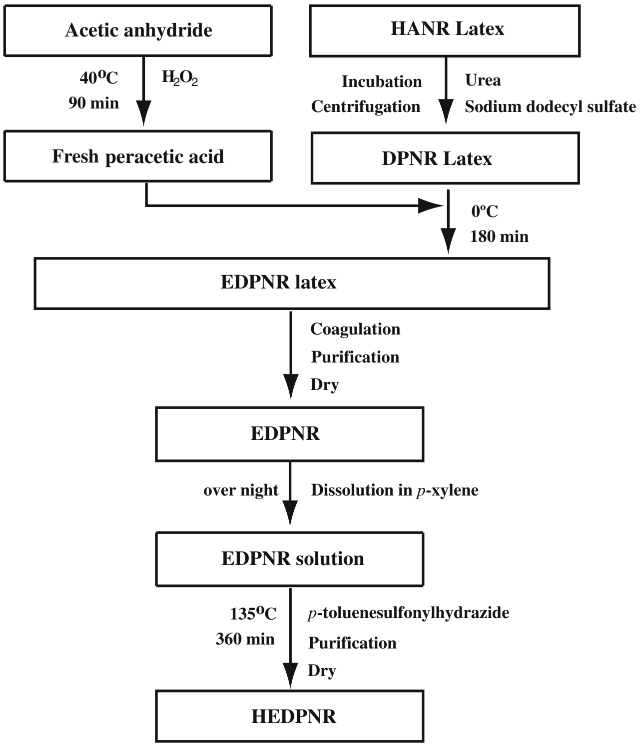


Fig. 2 Schematic illustration for preparing HEDPNR

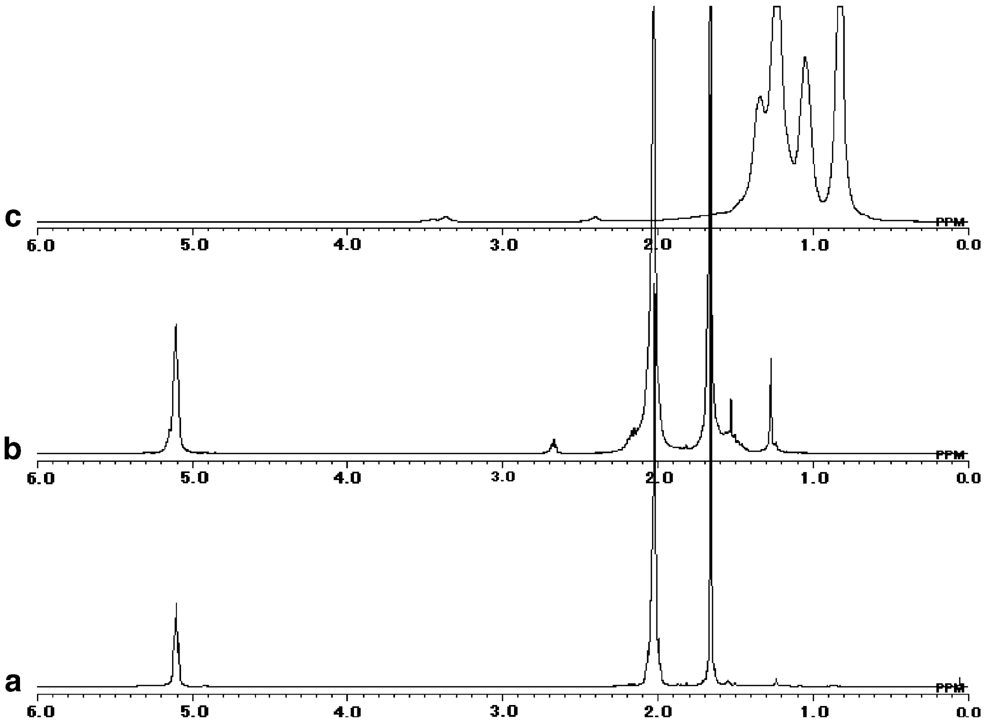


Fig. 3 ^{1}H-NMR spectra for **a** DPNR, **b** EDPNR, and **c** HEDPNR

Results and discussion

^{1}H-NMR spectra for DPNR, EDPNR, and HEDPNR are shown in Fig. 3. As for DPNR, three signals characteristic of methyl, methylene, and unsaturated methine protons of *cis*-1,4 isoprene units appeared at 1.68, 2.05, and 5.1 ppm, respectively. In contrast, for EDPNR, other two signals appeared at 1.29 and 2.7 ppm, which were assigned to methyl and methine protons of the resulting epoxy group, respectively. The epoxy group content of EDPNR, X_{epoxy},

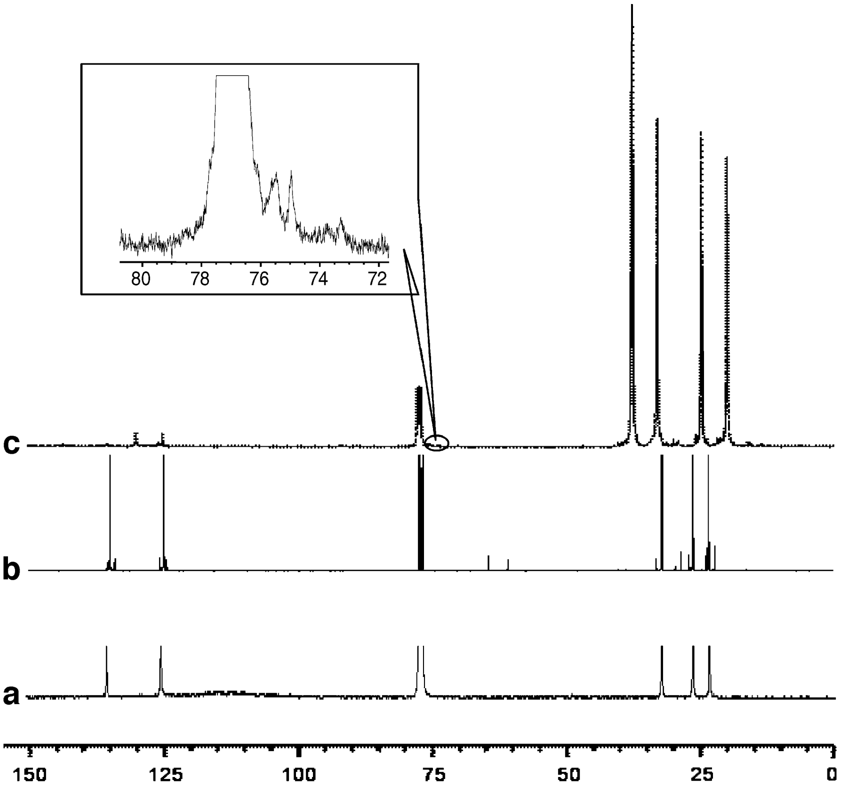
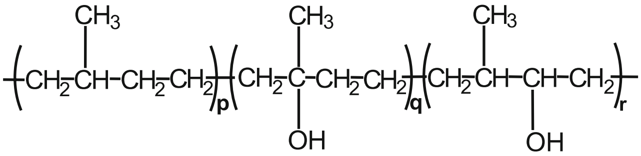


Fig. 4 ^{13}C-NMRspectra for *a* DPNR, *b* EDPNR, and *c* HEDPNR



$$-\left(CH_2-\overset{CH_3}{CH}-CH_2-CH_2\right)_p\left(CH_2-\overset{CH_3}{\underset{OH}{C}}-CH_2-CH_2\right)_q\left(CH_2-\overset{CH_3}{CH}-\underset{OH}{CH}-CH_2\right)_r-$$

Fig. 5 Chemical structure of HEDPNR

was thus estimated from the intensity ratio of the signals at 2.7 and 5.1 ppm, as in the following Eq. 1:

$$X_{\text{epoxy}} = I_{2.7}/(I_{2.7} + I_{5.1}) \times 100\% \tag{1}$$

where I is the intensity of the signals and the subscripts represent a value of the chemical shift. The estimated epoxy group content of EDPNR used in the present study was 8.8%; hence, the estimated double bond content was 91.2%. After hydrogenation of EDPNR with PTSH for 6 h, new signals appeared around 0.8–1.8 and 3.4 ppm, whereas the signals at 2.7 and 5.1 ppm disappeared. The residual double bond content, $X_{\text{residual double bond}}$, was estimated from the intensity ratio of the signals at 5.1 and 0.88 ppm, as in the following Eq. 2:

$$X_{\text{residual double bond}} = I_{5.1}/(I_{5.1} + I_{0.8}/3) \times 100\% \tag{2}$$

where I is the intensity of the signals and the subscripts represent a value of chemical shift. The estimated residual double bond content was less than 2%.

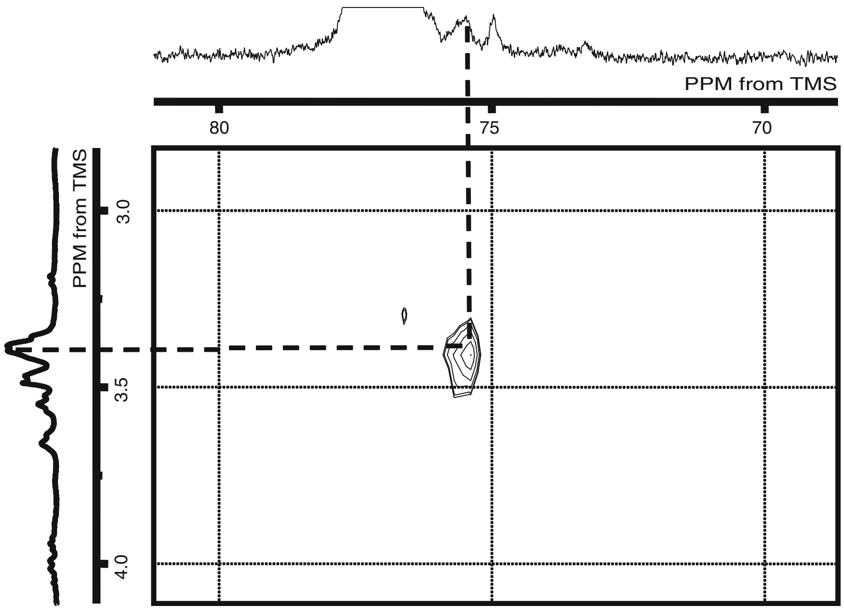
Typical ^{13}C-NMR spectra for DPNR, EDPNR, and HEDPNR are shown in Fig. 4. Signals characteristic of methyl (C5), methylene (C4), and methylene (C1) carbons of *cis*-1,4 isoprene units appeared at 24.5, 26.7, and 32.8 ppm, respectively, in which figures in parenthesis represent positions of the carbon atoms, respectively, according to International Union of Pure and Applied Chemistry nomenclature. After epoxidation, some signals appeared in an aliphatic region of the ^{13}C-NMR spectrum. These are assigned to diad and triad sequences of isoprene units and epoxidized isoprene units, as shown in Fig. 4 (b). Among these, the signals at 61 and 64 ppm, assigned to C2 and C3 atoms of epoxidized *cis*-1,4 isoprene unit were independent of the diad and triad sequences; hence, they are considered to be the characteristic signals of the epoxy groups of EDPNR. After hydrogenation of EDPNR, two signals newly appeared at 75.0 and 75.5 ppm, though the signals at 61 and 64 ppm disappeared. The signals characteristic of HEDPNR at 75.0 and 75.5 ppm may be considered to be tertiary and quaternary carbons linking to hydroxyl group, as in Fig. 5. Consequently, we considered that the epoxy groups of EDPNR were converted to the hydroxyl groups, after hydrogenation.

Figure 6 shows the HETCOR spectrum for HEDPNR. The signal at 75.5 ppm in ^{13}C-NMR spectrum was clearly correlated to the signal at 3.4 ppm in ^{1}H-NMR spectrum. Thus, the signal at 75.5 ppm in ^{13}C-NMR spectrum was assigned to the tertiary carbon linking to the hydroxyl group. On the other hand, the signal at 75.0 ppm was not correlated to any signal in ^{1}H-NMR spectrum, reflecting the quaternary carbon.

These assignments were supported with COSY spectrum for HEDPNR. The COSY spectrum for HEDPNR is shown in Fig. 7. The signal at 3.4 ppm in ^{1}H-NMR spectrum was correlated with the signals at 1.25 and 1.4 ppm in ^{1}H-NMR spectrum which were assigned methylene proton and methine proton of secondary and tertiary carbons, respectively, next to the tertiary carbon linking to the hydroxyl group.

According to the assignments, the hydroxyl group content of HEDPNR, X_{hydroxyl}, was estimated from the

Fig. 6 HETCOR spectra for HEDPNR



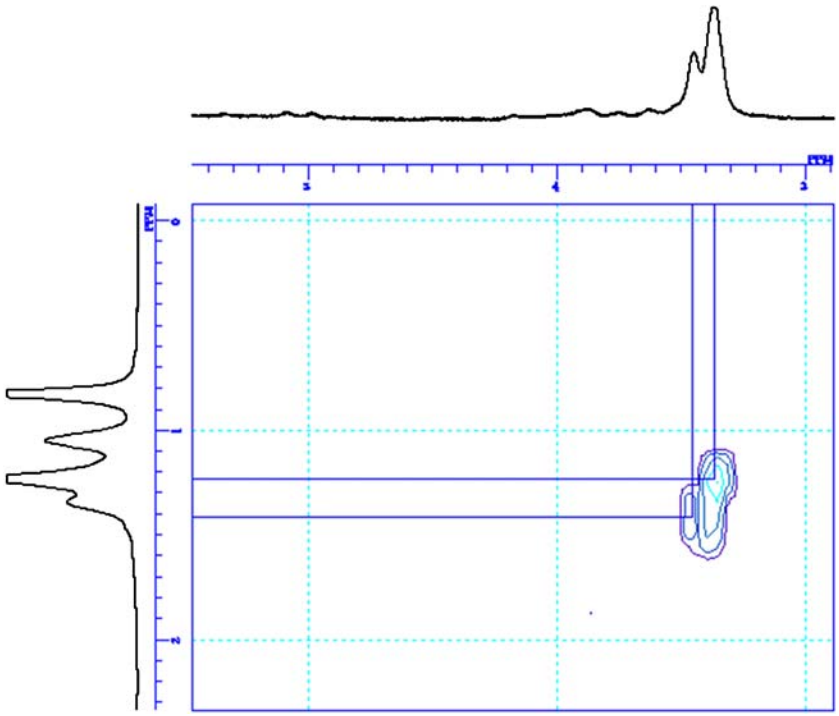


Fig. 7 COSY spectrum for HEDPNR

intensity ratio of the signals at 32.8 and 75.0–75.5 ppm, as in the following Eq. 3:

$$X_{\mathrm{hydroxyl}}=I_{75.0}/\left(I_{33.8}+I_{75.0-75.5}\right)\times 100\% \qquad (3)$$

The estimated hydroxyl group content of HEDPNR prepared with PTSH for 6 h was 3.8%. This suggests that the 8.8% epoxy group is converted to 3.8% hydroxyl group and 5.0% saturated hydrocarbon group. This may be due to a conversion of a part of the resulting hydroxyl group to the saturated hydrocarbon group. In order to confirm the conversion, we made the longer hydrogenation of EDPNR for 12 h. The dependence of hydroxyl group content on the hydrogenation time of EDPNR is shown in Table 1. The hydroxyl group content decreased from 3.8% for 6 h to 2.0% for 12 h. This is a strong evidence that a part of hydroxyl group is converted to the hydrocarbon group. In addition to the conversion of epoxy group, the double bond content was reduced from 2.0% for 6 h to 0.5% for 12 h. Thus, for reaction time, it is necessary to carry out hydrogenation in 6 h. Consequently, sequence length of alternative ethylene–propylene units are proved to be longer, after longer hydroxylation.

Table 1 Hydrogenation of EDPNR

Hydrogenation time (hour)	Epoxy group content (mol%)	Double bond content (mol%)	Hydroxyl group content (mol%)
0	8.8	91.2	–
6	0	2.0	3.8
12	0	0.5	2.0

Figure 8 shows DSC thermograms of HEDPNR prepared by hydrogenation of EDPNR for 6 h (a) and for 12 h (b) and hydrogenated DPNR (HDPNR) prepared by hydrogenation of DPNR for 4 h (c) and for 6 h (d). In the thermogram (d), a strong endothermic peak appeared at about 130 °C with an endothermic drop at −60 °C. The former peak is attributed to a melting of crystal of HDPNR for 6 h, whereas the latter drop is attributed to a glass

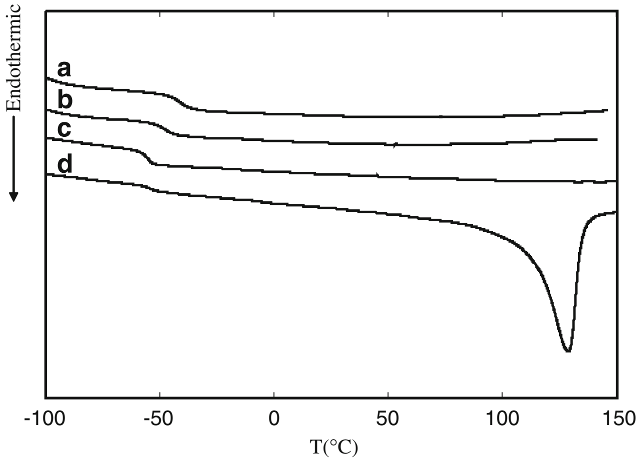


Fig. 8 DSC thermograms of HEDPNR prepared for *a* 6 h, *b* 12 h and HDPNR prepared for *c* 4 h, *d* 6 h

transition. In contrast, in the thermogram (c) for HDPNR for 4 h, only endothermic drop, due to the glass transition, appeared at −60 °C. Since HDPNR for 6 h consists of 97% ethylene–propylene units and 3% isoprene units and HDPNR for 4 h consists of 96% ethylene–propylene units and 4% isoprene units, it is found that higher conversion of hydrogenation makes rubber thermoplastic. Thus, to prepare the saturated elastomer, irregular structural units are required. The (a) and (b) showed the endothermic drop in thermograms without any endothermic peak, which is the characteristic of the elastomer. The T_g of HEDPNR for 6 h (a) and 12 h (b) were −44.0 °C and −46.9 °C, respectively. Though HEDPNR for 12 h contained 0.5% isoprene units, it did not undergo the crystallization, due to 2.0% hydroxyl groups. This implies that a long sequence of the stereoregular ethylene–propylene repeating units is disturbed with the hydroxyl group.

Conclusion

The epoxidation of NR followed by hydrogenation was proved to be effective to prepare the polyolefine elastomer from the rubber. The signals at 75.0 and 75.5 ppm in the ^{13}C-NMR spectrum were assigned to quaternary and tertiary carbons which are connected with the hydroxyl group. The melting endothermic peak, found for HDPNR, disappeared due to the presence of the hydroxyl groups.

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