Characterization of Poly(1-methyl-1,4-butanediol-1,4-diyl/2,3,4-trihydro-5-methylfuran-2,5-diyl) Prepared from Natural Rubber Through 2D NMR Spectroscopy

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ABSTRACT: Poly(1-methyl-1,4-butanediol-1,4-diyl/2,3,4-trihydro-5-methylfuran-2,5-diyl) was prepared by epoxidation of deproteinized natural rubber with *m*-chloroperbenzoic acid followed by hydrolysis with sulfuric acid. Characterization of the resulting product was performed through FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopies. All signals appearing in the ^{1}H and ^{13}C NMR spectra were assigned by distortionless enhancement by polarization transfer (DEPT), quaternary carbon observation (QUAT), correlation spectroscopy (COSY), and heteronuclear multiple quantum correlation (HMQC) measurements. After proving the primary structure of the product, one pot synthesis of poly(1-methyl-1,4-butanediol-1,4-diyl/2,3,4-trihydro-5-methylfuran-2,5-diyl) from deproteinized natural rubber latex was carried out with peracetic acid and 2-propanol. The resulting product was characterized by ^{1}H NMR spectroscopy on the basis of the assignments established in this study, and its gas permeability was measured for a practical application as a film. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 3423–3429, 2011

Key words: NMR; characterization; epoxidized natural rubber; hydrolysis; gas permeability

INTRODUCTION

High resolution solution state nuclear magnetic resonance (NMR) has been recognized to be a powerful tool to characterize primary structure of polymers. Especially, distortionless enhancement by polarization transfer (DEPT), quanternary carbon observation (QUAT), correlation spectroscopy (COSY), and heteronuclear multiple quantum correlation (HMQC) measurements make it possible to assign complicated signals for poly(1-methyl-1,4-butanediol-1,4-diyl/2,3,4-trihydro-5-methylfuran-2,5-diyl) (**1**), which is expected to be a green material derived from natural rubber (NR) consisting of *cis*-1,4-polyisoprene. Based on the structure of **1**, it may be possible to apply to a film having gas barrier property, since its polarity and hardness may arbitrarily vary with the composition. It is prepared by epoxidation of NR followed by hydrolysis, in which hydroxyl groups are introduced by nucleophilic attack of OH$^-$ to oxonium cation generated by protonation of epoxy groups under acidic condition (Path A), and 2,3,4-trihydro-5-methylfuran-2,5-diyl units are formed by nucleophilic attack of oxygen atom in epoxy group to neighboring it (Path B), as shown in Figure 1.

In the previous work, Perera[1] and Ng[2] tried to prepare **1** from NR in latex stage through epoxidation followed by hydrolysis with formic acid. The resulting polymer was characterized through ^{1}H and ^{13}C NMR spectroscopy. However, some signals in aliphatic region of ^{1}H and ^{13}C NMR spectra were not assigned due to analysis without 2D NMR measurement and undesired side reaction such as cyclization of NR,[3] introduction of formyloxy groups and formation of three dimensional network structure of gel fraction. Especially, the formation of gel fraction (Path C in Fig. 1) makes it difficult to assign the broad signals in ^{1}H NMR spectrum. To inhibit the side reaction such as cyclization of NR and introduction of formyloxy groups, it is necessary that epoxidized NR, prepared by epoxidation of all *cis*-1,4-isoprene units, is hydrolyzed with sulfuric acid. Additionally, the hydrolysis in diluted solution inhibits intermolecular nucleophilic attack of oxygen atom in epoxy group to the cation, which may decrease the formation of gel fraction.

In the present study, deproteinized natural rubber (DPNR) was subjected to epoxidation with *m*-
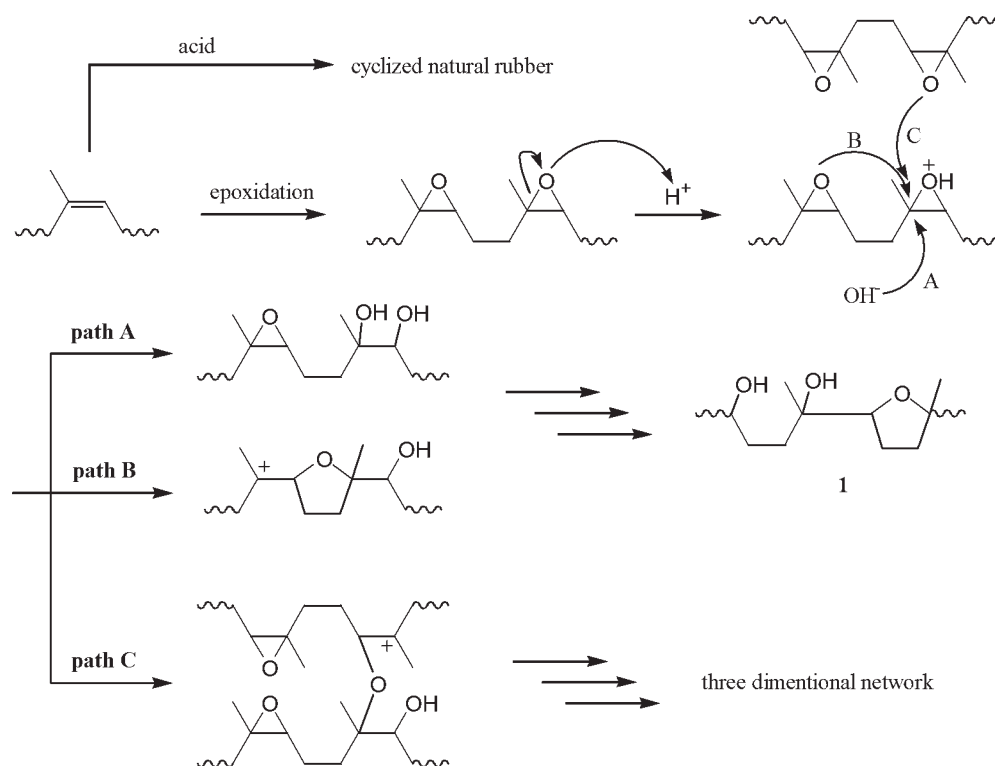
Figure 1 Proposed reaction mechanism for preparation of 1 from NR.

chloroperbenzoic acid (*m*CPBA)[4] followed by hydrolysis with sulfuric acid in THF to prepare **1** as a model. The resulting model product was characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, DEPT, QUAT, COSY, and HMQC measurements to prove the primary structure. After proving the primary structure of the product, one pot synthesis of **1** from DPNR latex was carried out with peracetic acid and 2-propanol. The resulting product was characterized by ^{1}H NMR spectroscopy on the basis of the assignments established in this study, and its oxygen gas permeability was measured for a practical application as a film having gas barrier property.

EXPERIMENTAL

Preparation of model compound

Natural rubber latex used in this study was 62.6% dry rubber content (DRC) of a commercial high ammonia natural rubber (HA-NR) latex. The deproteinization of natural rubber was made by incubation of the latex with 0.1% w/w urea (Nacalai Tesque, 99.5%) in the presence of 1.0% w/w sodium dodecyl sulfate (SDS) (Kishida Reagents Chemicals, 99%) at 303 K for 1 h followed by centrifugation at $10^4 g$.[5–7] The cream fraction was re-dispersed into 1.0% w/w SDS solution and washed twice by centrifugation to prepare DPNR latex. The DPNR latex was coagulated with excess methanol (Nacalai Tesque, 99%) and dried up at 303 K for 1 week under reduced pressure.

About 2 g of DPNR was dissolved in dichloromethane (Nacalai Tesque, 99%) to prepare 1.0% w/v solution. Epoxidation of the DPNR was initiated by adding 8.0 g of *m*CPBA (Wako Pure Chemical Industry, 69.0–75.0%) into the solution at 278 K. The *m*CPBA was added slowly and the temperature of the solution was kept at 278–288 K during the addition. After completion of the addition, the solution was stirred for 1 h at 298 K to prepare epoxidized DPNR (EDPNR). The EDPNR was coagulated with excess methanol at 243 K followed by purification with toluene (Nacalai Tesque, 99.5%) and methanol, and dried up at 303 K for 1 week under reduced pressure. About 1 g of EDPNR was dissolved in 50 mL of mixed solvent of THF and distilled water, in which the ratio of THF versus distilled water was 4 : 1. Hydrolysis of EDPNR was performed with trace amount of sulfuric acid (Nacalai Tesque, 95%) at 298 K for 3 h. After completion of the reaction, pH of the solution was adjusted to 7 with ammonia solution (Nacalai Tesque, 28%). The product was coagulated with excess acetone (Nacalai Tesque, 99%) followed by purification with acetone and toluene, and dried up at 453 K for 20 min under reduced pressure.

Preparation of 1 in latex stage

About 14 g of peracetic acid was added to 20 g of DPNR latex at 273 K and stirred for 16 h to prepare **1**, in which 2 mL of 2-propanol was used as a
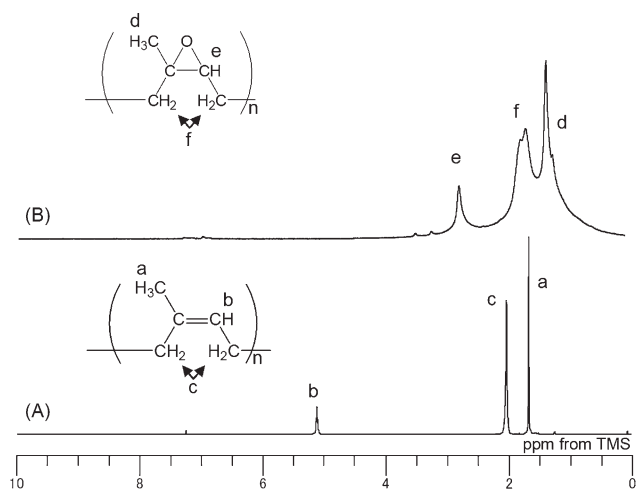
Figure 2 ^{1}H NMR spectra for (A) DPNR, and (B) EDPNR.

cosolvent. After 16 h of the reaction, pH of the latex was adjusted to 7 with ammonia solution, and then, the latex was washed with distilled water by centrifugation. The product was coagulated with excess acetone, and dried up at 453 K for 20 min under reduced pressure.

Characterization

FT-IR measurement of the products was made with a JASCO FTIR-410 spectrometer at a resolution of 4 cm^{-1}. The product was dissolved into chloroform to make 2% w/v solution. The solution was dropped on NaCl plate, and dried at room temperature.

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 (TMS) to make 2% w/v solution for ^{1}H NMR and 10% w/v solution for ^{13}C NMR spectroscopy. 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, the pulse width of 6.1 and 5.0 μs, and pulse delay of 4.24 and 3.79 s, respectively. DEPT and QUAT measurements were carried out by using a JEOL EX-400 NMR spectrometer. The 90° pulse widths used for DEPT and QUAT measurements were 14.6 μs for ^{13}C observation and 27.6 μs for ^{1}H irradiation. COSY and HMQC measurements were made to collect 2D hyper complex data. After weighing with shifted sine-bell function, the data were Fourier-transformed in the absolute value mode.

Measurement of gas permeability

Oxygen gas permeability coefficient of the product was measured with gas transmission rate tester BT-3

(Toyo seiki seisaku-syo) using a standard constant volume, variable pressure method. The measurements were conducted at 296 K under 1 atom upstream pressure. The permeability coefficient was calculated from the slope of the steady-state line.

RESULTS AND DISCUSSION

Characterization of model compound

Figure 2 shows ^{1}H NMR spectra for DPNR and EDPNR. As for DPNR, three signals characteristic of methyl, methylene, and unsaturated methine protons of *cis*-1,4-isoprene unit appeared at 1.7, 2.1, and 5.1 ppm, respectively. After epoxidation of DPNR, the signal at 5.1 ppm disappeared, while new signals appeared at 1.3 and 2.7 ppm, which were assigned to methyl and methine protons of epoxidized *cis*-1,4-isoprene unit, respectively.[8] Since almost all double bonds of the *cis*-1,4-isoprene units were converted to the epoxidized *cis*-1,4-isoprene units, the resulting EDPNR was subjected to hydrolysis with sulfuric acid.

Figure 3 shows typical FT-IR spectra for the EDPNR and the hydrolyzed product. After hydrolysis of the EDPNR, new absorption bands appeared at about 1100 and 3200–3500 cm^{-1}. These may be identified to five-membered ring of the 2,3,4-trihydro-5-methylfuran-2,5-diyl unit and hydroxyl group of the 1-methyl-1,4-butanediol-1,4-diyl unit, respectively, according to the previous work.[9] Based upon the identification of the FT-IR spectra, it is suggested that 2,3,4-trihydro-5-methylfuran-2,5-diyl unit and 1-methyl-1,4-butanediol-1,4-diyl unit were formed by the hydrolysis of EDPNR.

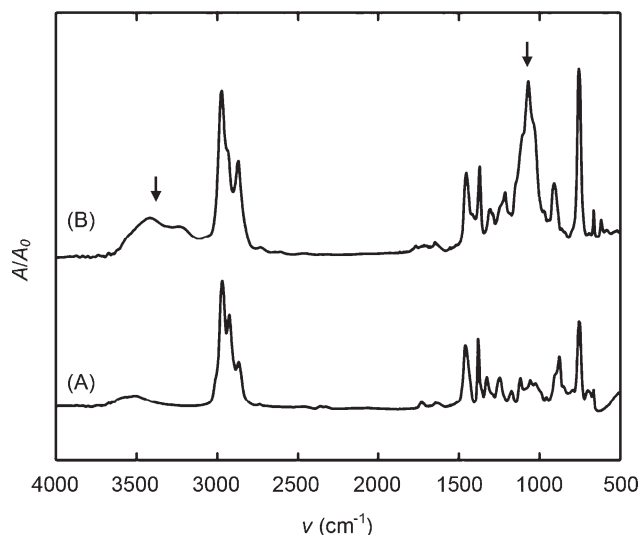Figure 4 shows ^{1}H NMR spectrum for the hydrolyzed EDPNR. In the spectrum, signals appeared at

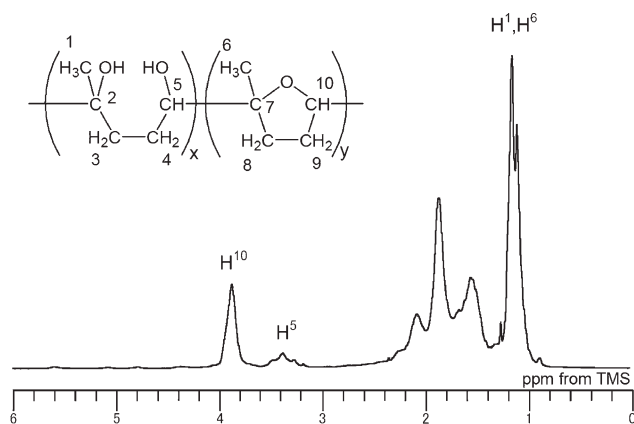**Figure 3** FT-IR spectra for (A) EDPNR and (B) hydrolyzed EDPNR.

Figure 4 ^{1}H NMR spectrum for the hydrolyzed EDPNR.

about 1.15, 1.55, 1.85, 2.07, 3.38, and 3.87 ppm. According to the previous work,[1] the signals at 1.15, 3.38, and 3.87 ppm may be assigned: that is, 1.15 ppm assigned to methyl protons of the 1-methyl-1,4-butanediol-1,4-diyl unit and the 2,3,4-trihydro-5-methylfuran-2,5-diyl unit, 3.38 ppm to methine proton of the 1-methyl-1,4-butanediol-1,4-diyl unit, and

3.87 ppm to methine proton of the 2,3,4-trihydro-5-methylfuran-2,5-diyl unit. The assignment is shown in the Figure 4, in which H represents the protons, and superscript numbers represent the position of the protons. To assign the signals in aliphatic region of the spectrum, COSY measurement was made of the hydrolyzed EDPNR.

Figure 5 shows COSY spectra for the hydrolyzed EDPNR, in which cross-peaks appeared due to spin couplings between ^{1}H and ^{1}H. The signal at 1.85 ppm was assigned to methylene protons neighbor with the methine proton of the 2,3,4-trihydro-5-methylfuran-2,5-diyl unit, since the signal at 3.87 ppm, assigned to the methine proton of the 2,3,4-tri-hydro-5-methylfuran-2,5-diyl unit, was correlated to the signal at 1.85 ppm. The signal at 1.85 ppm was also correlated to the signals at 1.55 and 2.07 ppm. Thus, the signals at 1.55 and 2.07 ppm were assigned to methylene protons neighbor with quaternary carbon of the 2,3,4-trihydro-5-methylfuran-2,5-diyl unit, respectively. These assignments were supported by the strong correlation between the signals at 1.55 and 2.07 ppm. On the other hand, the signal of the methine proton of the 1-methyl-1,4-
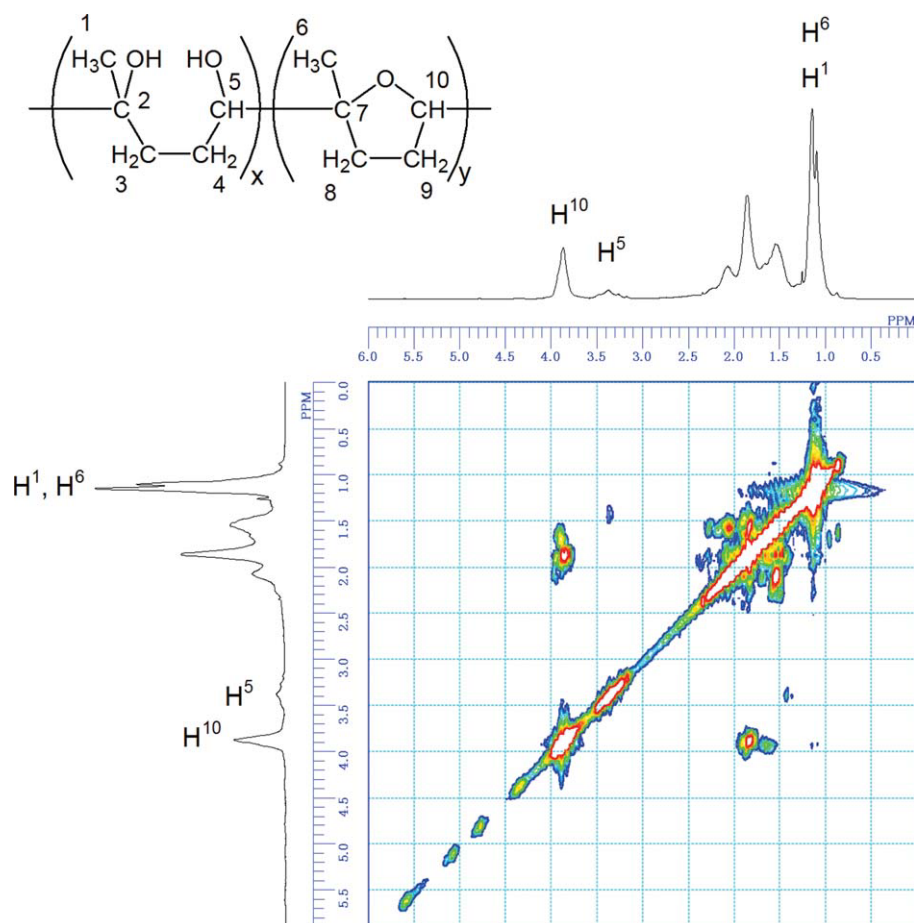

Figure 5 COSY spectra for hydrolyzed EDPNR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Chemical Shift, δ, of Signals in ^{1}H NMR Spectrum, Correlated Signals in COSY Spectra, and Assignment of Signals

δ of ^{1}H (ppm)	δ of correlated ^{1}H (ppm)	Assignment
1.15	–	H^1, H^6
1.43[a]	1.91, 3.38	H^4
1.55	1.85, 2.07	H^8
1.85	1.55, 2.07, 3.87	H^9
1.91[a]	1.43	H^3
2.07	1.55, 1.85	H^8
3.38	1.43	H^5
3.87	1.85	H^{10}

[a] Indistinguishable signal in ^{1}H NMR spectrum due to the overlapping of signals.

butanediol-1,4-diyl unit at 3.38 ppm correlated to signal at 1.43 ppm. Thus, the signal at 1.43 ppm was assigned to methylene protons neighbor with the methine proton of the 1-methyl-1,4-butanediol-1,4-diyl unit. Since the signal at 1.43 ppm was also correlated to the signal at 1.91 ppm, the signal at 1.91 ppm was assigned to methylene protons neighbor with quaternary carbon of the 1-methyl-1,4-butanediol-1,4-diyl unit. The correlation and the resulting assignment were tabulated in Table I, in which H represents the protons, and superscript numbers represent the position of atoms, as shown in Figure 5.

Figure 6(A,B) show ^{13}C NMR spectra for the EDPNR and the hydrolyzed EDPNR measured with chloroform-d, respectively. As for the EDPNR, signals appeared at 22.2, 24.6, 29.7, 60.5, and 64.5 ppm, which were assigned to primary, secondary, secondary, quaternary, and tertiary carbons of the epoxidized cis-1,4-isoprene unit, according to the previous work.[8] After the hydrolysis of the EDPNR, the signals characteristic of the epoxidized cis-1,4-isoprene unit disappeared, while many signals appeared at 20–40, 73, 84, and 86 ppm, together with a small signal at 78 ppm. To observe the signal at 78 ppm, ^{13}C NMR measurement of the hydrolyzed EDPNR was carried out with deuterated benzene as a solvent. The resulting ^{13}C NMR spectrum is shown in Figure 6(C). The chemical shifts of the signals were almost identical to those obtained with chloroform-d solution. The chemical shifts of the signals are tabulated in Table II. To assign these signals, QUAT and DEPT measurements were carried out, in which QUAT spectrum shows quaternary carbons as the upward signals, DEPT45 spectrum shows primary, secondary, and tertiary carbons as the upward signals, DEPT90 spectrum shows tertiary carbons as the upward signals, and DEPT135 spectrum shows primary and tertiary carbons as the upward signals, and secondary carbons as the downward signals, respectively.
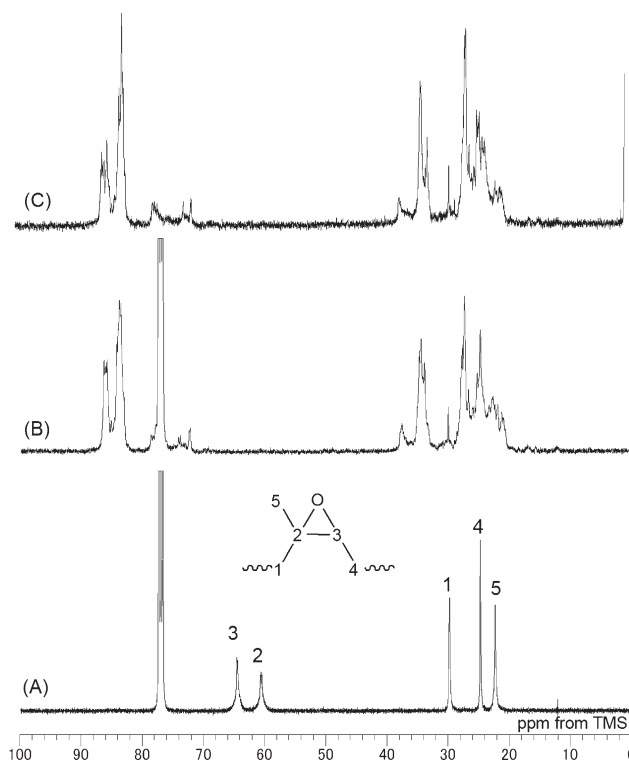

Figure 6 ^{13}C NMR spectra for (A) EDPNR, (B) hydrolyzed EDPNR measured with CDCl$_3$, and (C) hydrolyzed EDPNR measured with C$_6$D$_6$.

Figure 7 shows QUAT and DEPT spectra for the hydrolyzed EDPNR. In the QUAT spectrum, the signals at about 73, 84, and 86 ppm appeared. Further, the signals at 84 and 86 ppm appeared in not only QUAT spectrum but also the DEPT spectrum. Among these signals, the signal at 73 ppm was assigned to the quaternary carbon of the 1-methyl-1,4-butanediol-1,4-diyl unit, according to the chemical shift of the model compound.[10–13] The signals at 84 and 86 ppm are assigned to the quaternary and

TABLE II
Chemical Shifts, δ, of Signals in ^{13}C NMR Spectrum, the Results from QUAT and DEPT Measurements, δ of Correlated ^{1}H (ppm) in HMQC Spectra, and Assignment of Signals

δ of ^{13}C (ppm)	Results from QUAT and DEPT measurement[a]	δ of correlated ^{1}H (ppm)	Assignment
21	p	1.15	C^1
22–24	p	1.15	C^6
27	s	1.85	C^9
34	s	1.55, 1.91, 2.07	C^3, C^8
37	s	1.43	C^4
74	q	–	C^2
78	t	3.38	C^5
84	t, q	3.87	C^7, C^{10}
86	t, q	3.87	C^7, C^{10}

[a] p: primary carbon, s: secondary carbon, t: tertiary carbon, q: quaternary carbon.
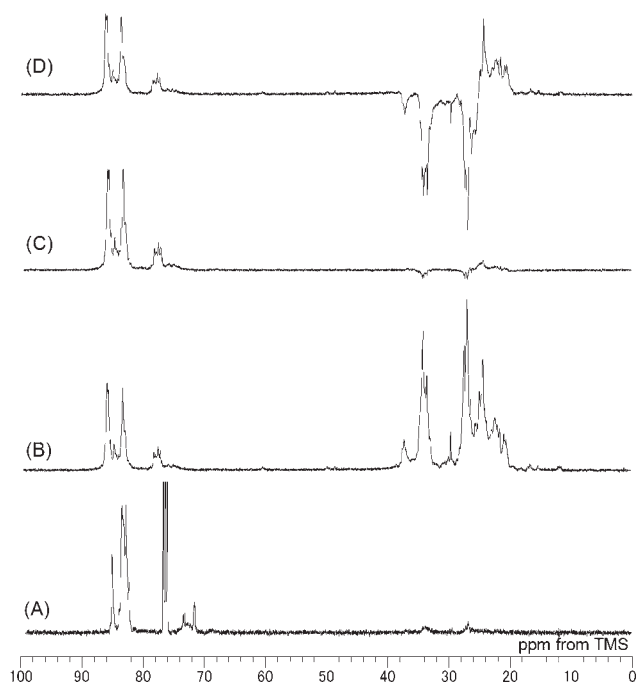
Figure 7 NMR spectra obtained from (A) QUAT, (B) DEPT 45, (C) DEPT 90, and (D) DEPT 135 measurement.

the tertiary carbons of the 2,3,4-trihydro-5-methyl-furan-2,5-diyl unit, since quaternary carbon appeared in QUAT spectrum but not in DEPT spectrum. The signal at 78 ppm was assigned to the tertiary carbon of the 1-methyl-1,4-butanediol-1,4-diyl unit, since the signal at 78 ppm appeared in the DEPT 45 and 90 spectra. Furthermore, in the DEPT 135 spectrum, the signals at 20–25 ppm appeared upward, while the signals at 26–40 ppm appeared downward. Thus, the signals at 20–25 ppm were assigned to the primary carbon of the 1-methyl-1,4-butanediol-1,4-diyl unit and that of the 2,3,4-trihydro-5-methylfuran-2,5-diyl unit, and the signals at 26–40 ppm is assigned to the secondary carbons of the 1-methyl-1,4-butanediol-1,4-diyl unit and the 2,3,4-trihydro-5-methylfuran-2,5-diyl unit. The results from QUAT and DEPT measurements are tabulated in Table II. To confirm the assignment, HMQC measurement was carried out.

Figure 8 shows HMQC spectra for the hydrolyzed EDPNR, in which ^{13}C correlates to directly connected ^1H. The correlations are summarized in Table II. One example of the assignments was as follows: The ^1H signals at 1.55, 1.91, and 2.07 ppm were
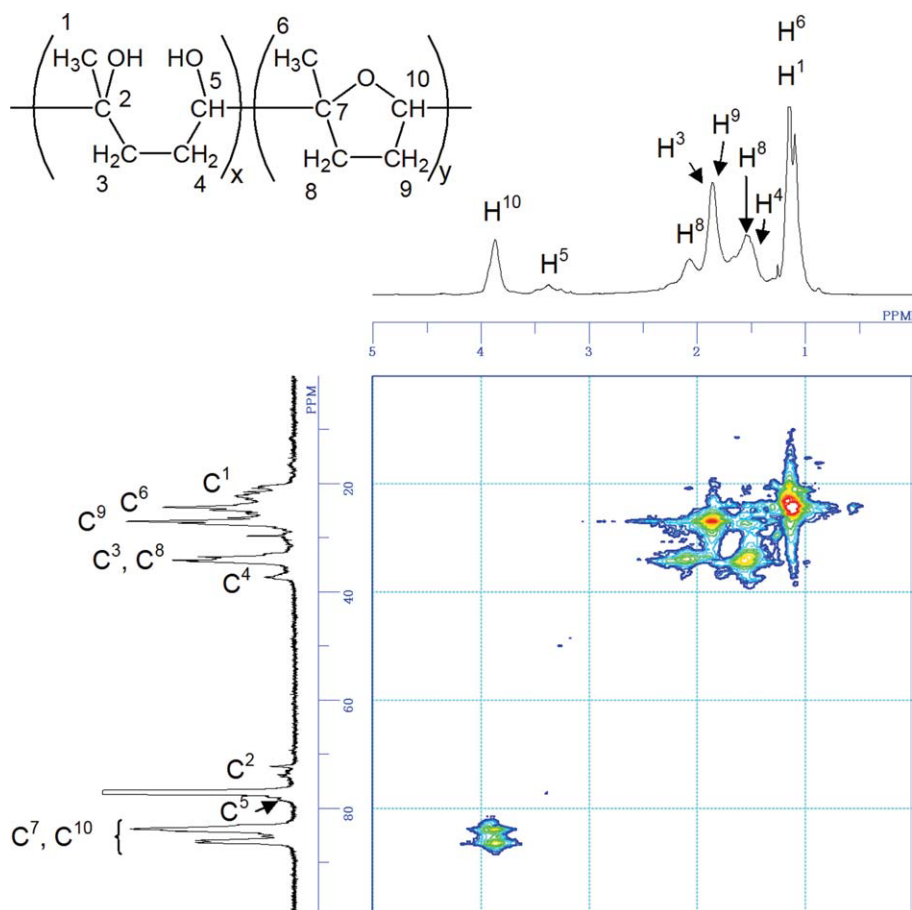

Figure 8 HMQC spectra for hydrolyzed EDPNR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Oxygen Gas Permeability Coefficient of 1 and DPNR

Specimen	Oxygen gas permeability coefficient/cm^3·μm·m^{-2}·day^{-1}·atm^{-1}
1	3.98×10^4
DPNR	1.61×10^6

correlated to the ^{13}C signal at 34 ppm. Thus, the ^{13}C signal at 34 ppm was assigned to the secondary carbon neighbor with the quaternary carbon of the 2,3,4-trihydro-5-methylfuran-2,5-diyl unit as well as that of the 1-methyl-1,4-butanediol-1,4-diyl unit. The other signals were assigned in the similar way. The assignments are tabulated in Table II, in which C represents the carbons, and the superscript numbers represent the position of the carbons. The hydrolyzed EDPNR was confirmed to be poly(1-methyl-1,4-butanediol-1,4-diyl/2,3,4-trihydro-5-methylfuran-2,5-diyl), since ^{1}H and ^{13}C signals were rationally assigned through 1D and 2D NMR spectroscopy.

The 1-methyl-1,4-butanediol-1,4-diyl unit content, $X_{hydroxy}$, and 2,3,4-trihydro-5-methylfuran-2,5-diyl unit content, Y_{fran}, was estimated from intensity ratio of the signals at 3.38 and 3.87 ppm in the ^{1}H NMR spectrum, as in the following equation:

$$X_{hydroxy} = \frac{I_{3.38}}{I_{3.38} + I_{3.87}} \times 100$$

$$Y_{furan} = \frac{I_{3.87}}{I_{3.38} + I_{3.87}} \times 100$$

where I is the intensity of the signals, subscript numbers represent the chemical shift (ppm), and the signal at 3.38 ppm was separated from the overlapped signals at 3.17, 3.27, and 3.48 ppm by curve fitting process before the estimation. The estimated $X_{hydroxy}$ and Y_{furan} of the sample prepared in the present study were 17 and 83%, respectively.

Gas permeability of 1 prepared in latex stage

Since the primary structure of **1** was successfully proved by NMR spectroscopy, one pot synthesis of **1** was attempted in latex stage. The estimated $X_{hydroxy}$ and Y_{furan} of **1** prepared in latex stage were 25 and 75%, respectively. The higher $X_{hydroxy}$ compared to that prepared in solution state may be attributed to excess water surrounding NR particles and 2-propanol, which improves the affinity of NR particles and peracetic acid. Since **1** prepared in latex stage showed higher $X_{hydroxy}$, oxygen gas permeability coefficient was measured to apply as a film having a gas barrier property. Table III shows oxygen gas permeability coefficient of **1** and that of DPNR as a reference. The oxygen gas permeability coefficient of **1** was 3.98×10^4 cm^3·μm/m^2·day atm, which was quite smaller than that of DPNR. This may be due to the higher polarity of **1** compared to DPNR.

CONCLUSIONS

Poly(1-methyl-1,4-butanediol-1,4-diyl/2,3,4-trihydro-5-methylfuran-2,5-diyl) was prepared by hydrolysis of epoxidized natural rubber with sulfuric acid in THF solution as a model. After hydrolysis of epoxidized natural rubber, new signals appeared at 3.38 and 3.87 ppm in ^{1}H NMR spectrum, which were assigned to the methine protons of the 1-methyl-1,4-butanediol-1,4-diyl unit and the 2,3,4-trihydro-5-methylfuran-2,5-diyl unit, respectively. The 1-methyl-1,4-butanediol-1,4-diyl unit content and the 2,3,4-trihydro-5-methylfuran-2,5-diyl unit content were estimated to be 16.6 and 83.4%, respectively.

After proving the primary structure of the poly(1-methyl-1,4-butanediol-1,4-diyl/2,3,4-trihydro-5-methylfuran-2,5-diyl), one pot synthesis from DPNR latex was attempted with peracetic acid and 2-propanol. The estimated 1-methyl-1,4-butanediol-1,4-diyl unit content and the 2,3,4-trihydro-5-methylfuran-2,5-diyl unit content of **1** prepared in latex stage were 25.0 and 75.0%, respectively. The oxygen gas permeability coefficient of the product was 3.98×10^4 cm^3·μm/m^2·day atm, which was quite smaller than that of DPNR. Consequently, poly(1-methyl-1,4-butanediol-1,4-diyl/2,3,4-trihydro-5-methylfuran-2,5-diyl) was successfully prepared not only in solution state but also in latex state, and it was found that the poly(1-methyl-1,4-butanediol-1,4-diyl/2,3,4-trihydro-5-methylfuran-2,5-diyl) shows superior gas barrier property compared to NR.

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