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Crosslinking junctions of vulcanized natural rubber analyzed by solid-state NMR spectroscopy equipped with field-gradient-magic angle spinning probe

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ABSTRACT

Crosslinking junctions of vulcanized natural rubber were analyzed by solid-state NMR spectroscopy equipped with a field-gradient high speed magic angle spinning probe. Resolution of ^{1}H and ^{13}C NMR spectra and correlations between ^{1}H and ^{13}C of the vulcanized natural rubber were investigated by one- and two-dimensional measurements, including inverse correlation measurements. The number of substitution of the carbon atom at the crosslinking junctions was determined by solid-state NMR spectroscopy.

1. Introduction

Solid-state Nuclear Magnetic Resonance, NMR, spectroscopy is a powerful technique to analyze crosslinking junctions of elastomers and gels, since a chemical shift of signals appearing after crosslinking reflects a chemical environment of surroundings of the atoms of the crosslinking junctions [1,2]. The chemical environment may be positively analyzed by measuring correlations between ^{13}C and ^{1}H. Thus, we must apply various pulse sequences to the analysis of the crosslinking junctions through NMR spectroscopy. However, in many literatures [3–8], only solid-state ^{13}C NMR spectroscopy under high power ^{1}H-decoupling, i.e. dipolar decoupling, has been performed to analyze the crosslinking junctions, since a residual dipole–dipole interaction was so significant after crosslinking due to constrained motions of the elastomers and gels. To assign the signals appearing after vulcanization through solid-state ^{13}C NMR spectroscopy, therefore, Mori and Köenig [5,6] adopted empirical correlations with shift factors to estimate values of chemical shifts of plausible crosslinking junctions proposed by Coran [9]. Small signals at 44, 50, 57 and 64 ppm of vulcanized natural rubber were assigned to tertiary carbons linking to S atoms [5,6], respectively.

In the previous works [10,11], we carefully assigned the signal at 44 ppm to secondary carbons and the signals at about 58 ppm to tertiary and quaternary carbons through latex-state NMR spectroscopy with distortionless enhancement by polarization transfer (DEPT) and attached proton test (APT) measurements. The assignment was proved by solution-state NMR spectroscopy for vulcanized liquid *cis*-1,4-polyisoprene and vulcanized squalene with DEPT, APT, 2-dimensional ^{1}H–^{13}C correlation (HETCOR), 2-dimensional heteronuclear single coherence (HSQC) and 2-dimensional heteronuclear multiple bond correlation (HMBC) measurements. Furthermore, we proposed a method to prepare latex from vulcanized rubber sheets with a cryogenic sample crusher, in order to apply latex-state NMR spectroscopy to various vulcanized rubbers prepared in the solid state [11]. However, due to a complicated procedure to prepare the latex, it is anticipated to develop a novel solid-state NMR spectroscopy for the vulcanized rubber, in which various pulse sequences are applied to the analysis of the crosslinking junctions.

For the rubbery materials, high-resolution solid-state NMR spectroscopy without dipolar decoupling is performed with high speed magic angle spinning (HS-MAS) that is higher than about 20 kHz [12–18]. This may be attained even after vulcanization; hence, the residual dipole–dipole interaction of the vulcanized rubber is eliminated with HS-MAS. In this case, we may apply various pulse sequences, i.e. DEPT, APT, HETCOR and so forth to solid-state NMR spectroscopy for the vulcanized rubber.

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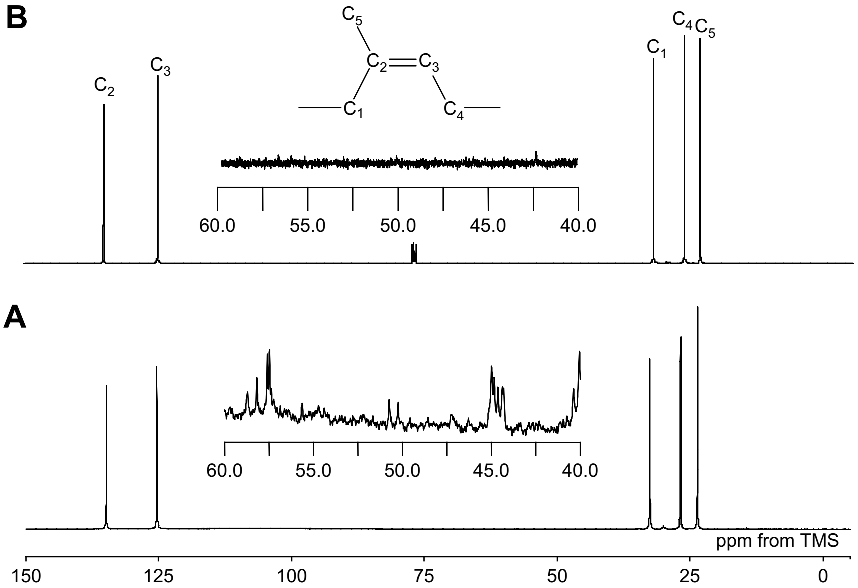

Fig. 1. Typical ^{13}C NMR spectra: (A) solid-state ^{13}C NMR spectrum for the vulcanized natural rubber, (B) solution-state ^{13}C NMR spectrum for unvulcanized natural rubber. The solid-state ^{13}C NMR measurement was performed with a 4 mm FG-MAS probe at 18 kHz in spinning rate. The solution-state ^{13}C NMR measurement was performed with an NM-40TH5AT/FG2SL probe at 12 Hz in spinning rate.

Furthermore, in order to detect very small signals of fewer amounts of crosslinking junctions, it is necessary to measure inverse correlations of ^{1}H with ^{13}C, i.e. HSQC, HMQC and HMBC, which make possible to enhance sensitivity through solid-state NMR spectroscopy equipped with field-gradient HS-MAS (FG-HS-MAS) probe. In the present study, we apply newly developed FG-HS-MAS probe to the analysis of the crosslinking junctions of the vulcanized natural rubber through solid-state NMR spectroscopy, as the first trial. The crosslinking junctions of the vulcanized rubber were analyzed through solid-state NMR spectroscopy with DEPT, APT, HSQC and HMQC.

2. Experimental

Natural rubber latex used in this study was commercial high ammonia natural rubber latex of 60 w/w% dry rubber content (DRC). Vulcanization of natural rubber was made in latex stage. One example for the vulcanization of natural rubber was as follows; first, natural rubber latex (ca. 1000 ml) was prevulcanized with 88.5 g of 20 w/v% KOH solution, 17.5 g of 30%S/15%ZnO suspension and 99.5 g of 50 w/v% sodium di-n-butyldithiocarbamate solution at 40 °C for 4 h. Second, vulcanization of the prevulcanized natural rubber latex was carried out at 90 °C for 1–72 h, after dilution of the prevulcanized latex with water to adjust 20 w/w% DRC followed by adding 1 w/w% sodium dodecyl sulfate (SDS). The resulting vulcanized latex was filtered with 40 μm mesh followed by centrifugation at 10,000g. Cream fraction of the latex was redispersed in 1 w/w% SDS solution to make 30 w/w% DRC latex and was washed by centrifugation, again. The washed cream fraction was redispersed in 0.1 w/w% SDS solution with deuterium oxide to make 50 w/w% DRC. A part of the cream fraction was coagulated and dried under reduced pressure. It was subjected to the solid-state NMR measurement.

Solid-state NMR spectroscopy was performed with a JEOL JNM-ECA600 FT-NMR spectrometer, operating at 600 and 150 MHz for ^{1}H and ^{13}C, respectively. A spinning rate of the sample tube for the solid-state measurement was 18 kHz ± 5 Hz. N_2 gas was used as MAS bearing and driving gas sources in order to protect samples from oxidation and NMR probe head. The vulcanized natural rubber was loaded into a sample tube and its crosslinking junctions were analyzed with a 4 mm FG-MAS probe through solid-state NMR spectroscopy. Solution-state NMR spectroscopy was carried out with a JEOL JNM-ECA400 FT-NMR spectrometer, operating at 399.7 and 100.4 MHz for ^{1}H and ^{13}C, respectively. The vulcanized natural rubber latex with deuterium oxide was used for the measurements without further treatment with NM-40TH5AT/FG2SL probe. ^{1}H NMR, ^{13}C NMR, DEPT and APT measurements were carried out at 323 K at pulse repetition times of 7 s and 5 s, respectively, since the liquid-like molecular motion should be accomplished at 323 K, which was about 100 K higher than the glass transition temperature of natural rubber [19]. The actual temperature of the surroundings in NMR probes was calibrated on the basis of the temperature dependence of the ^{207}Pb chemical shift of $Pb(NO_3)_2$. Two-dimensional ^{1}H–^{13}C and heteronuclear multiple bond correlation measurements were made to collect two-dimensional hyper complex data. After weighting with shifted sine-bell function, the data was Fourier-transformed in the absolute value mode.

3. Results and discussion

Solid-state ^{13}C NMR spectrum for the vulcanized natural rubber, measured with the FG-HS-MAS probe, is shown in Fig. 1, in conjunction with solution-state ^{13}C NMR spectrum for unvulcanized natural rubber. Five major signals in the spectrum were

Table 1
Summary of relevant parameters for the spectra shown in Fig. 1.

Figure	1A	1B
Sample	Vulcanized NR	Unvulcanized NR
Instruments (kHz)	150	100.4
T (K)	323	323
No. of transients	90,000	90,000
Rec delay (s)	2.0	2.0
S/N	4882	5295
Half width (Hz)	17.05	11.47
Time (h)	76.5	76.5

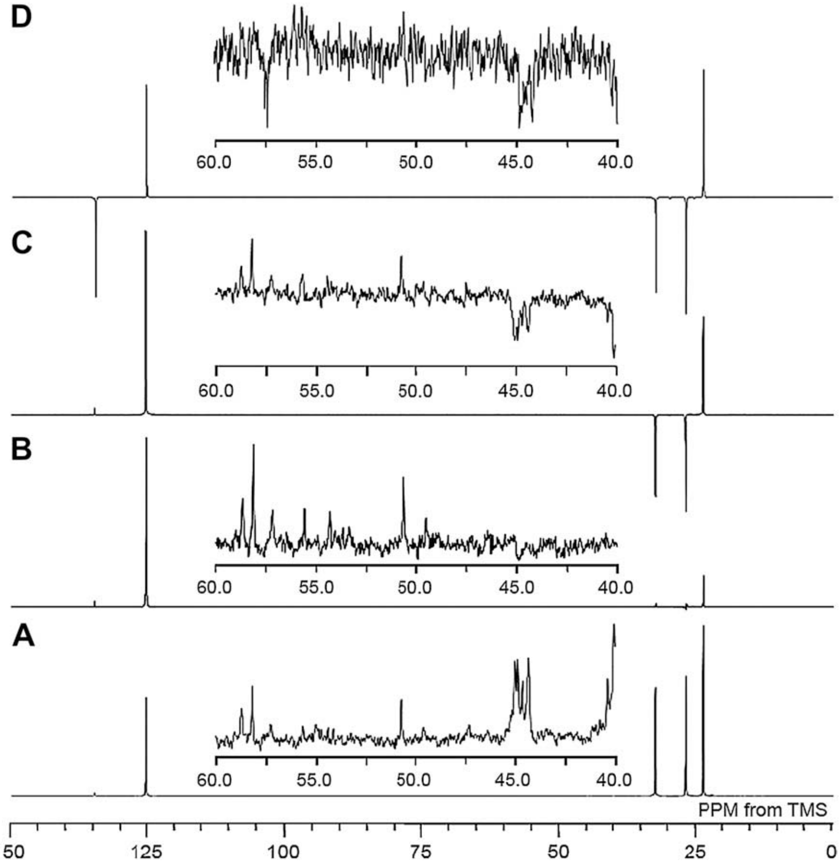

Fig. 2. Solid-state ^{13}C NMR spectra with pulse sequences of distortionless enhancement by polarization transfer (DEPT) and attached proton test (APT) for the vulcanized natural rubber: (A) DEPT45, (B) DEPT90, (C) DEPT135, (D) APT.

assigned to C atoms of *cis*-1,4-isoprene units, according to the previous paper [11]. Values of half width of the signals and signal to noise (S/N) ratio of the solid-state ^{13}C NMR spectrum for the vulcanized natural rubber were quite similar to those in the solution-state ^{13}C NMR spectrum for unvulcanized natural rubber, as shown in Table 1. The narrow half width and the sufficient S/N ratio of the solid-state ^{13}C NMR spectrum for the vulcanized natural rubber may imply that high resolution was maintained for solid-

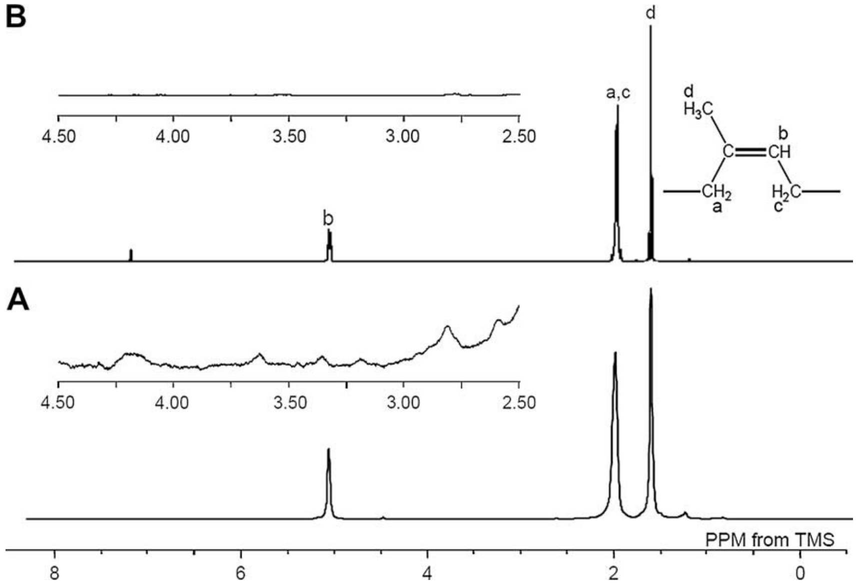

Fig. 3. Typical ^{1}H NMR spectra: (A) solid-state ^{1}H NMR spectrum for the vulcanized natural rubber, (B) solution-state ^{1}H NMR spectrum for the unvulcanized natural rubber. The solid-state ^{1}H NMR measurement was performed with a 4 mm FG-MAS probe at 18 kHz in spinning rate. The solution-state ^{1}H NMR measurement was performed with an NM-40TH5AT/FG2SL probe at 12 Hz in spinning rate.

Table 2
Summary of relevant parameters for the spectra shown in Fig. 3.

Figure	3A	3B
Sample	Vulcanized NR	Unvulcanized NR
Instruments (kHz)	600	399.7
T (K)	323	323
No. of transients	128	128
Rec delay (s)	5.0	4.2
S/N	26,732	27,178
Half width (Hz)	7.00	5.20
Time (min)	13	13

state ^{13}C NMR spectroscopy even after vulcanization, since the dipole–dipole interaction between hetero-nuclei was eliminated by HS-MAS. This is distinguished from very low resolution of the solid-state NMR spectrum for the vulcanized natural rubber reported by Klüppel [17] and Köenig [3–8].

In Fig. 1, small signals appeared at 40, 44, 50 and 58 ppm in the solid-state ^{13}C NMR spectrum for the vulcanized natural rubber, which were not shown in the solution-state ^{13}C NMR spectrum for the unvulcanized natural rubber. To assign the signals, we applied DEPT measurement at 45° (DEPT45), 90° (DEPT90) and 135° (DEPT135) pulses and APT measurement to solid-state ^{13}C NMR spectroscopy. Fig. 2 shows DEPT45, DEPT90 and DEPT135 spectra for the vulcanized natural rubber. The signals at 24, 26 and 32 ppm characteristic of methyl, methylene and methine carbons of *cis*-1,4-isoprene units were shown to be upward, upward and upward in the DEPT45 spectrum and they were almost null in the DEPT90 spectrum. On the other hand, in the DEPT135 spectrum, the signals were upward, downward and downward. Thus, the pulse width determined for DEPT measurements was confirmed to be correct to assign the small signals at 44, 50 and 58 ppm.

The small signals at 40 and 44 ppm were shown to be upward in the DEPT45 spectrum, null in the DEPT90 spectrum and downward in the DEPT135 spectrum; hence, they were assigned to secondary carbons. The signal at 50.5 ppm was assigned to quaternary carbon due to null signal in the spectra, while the signal at 50 ppm was assigned to tertiary carbon due to upward signals in the spectra, respectively. In contrast, the signal at 58 ppm was assigned to tertiary and quaternary carbons due to the very small upward signals in the DEPT45, DEPT90 and DEPT135 spectra and null signals. In Fig. 2, the APT spectrum is also shown for the vulcanized natural rubber. The APT spectrum represented downward signals at 40 and 44 ppm, upward and downward signals at 50 ppm, and upward and downward signals at about 58 ppm. Thus, we assigned the signals at 40 and 44 ppm to the secondary carbons and the signals at 50 and 58 ppm to the tertiary and quaternary carbons.

Fig. 3 shows solid-state ^{1}H NMR spectrum for the vulcanized natural rubber and solution-state ^{1}H NMR spectrum for the unvulcanized natural rubber with acquisition parameters listed in Table 2. Major signals at 1.7, 2.1 and 5.1 ppm in the spectra were assigned to methyl, methylene and unsaturated methine protons of *cis*-1,4-isoprene units, respectively. Values of half width and signal to noise (S/N) ratio of the signals in the solid-state ^{1}H NMR spectrum for the vulcanized natural rubber were a little bit larger and smaller, respectively, than the values of the half width and the S/N ratio of the signals in the solution-state ^{1}H NMR spectrum for the unvulcanized natural rubber. For instance, the value of half width of the signals in the solid-state spectrum was about 1.5 times as large as that in the solution-state spectrum. This may be explained to be due to a reduced effect of the dipole–dipole interaction between homo-nuclei in the solid-state ^{1}H NMR spectrum; that is, a major portion of the dipole–dipole interaction between homo-nuclei is eliminated by HS-MAS. The dipole–dipole interaction between homo-nuclei may be completely eliminated by extremely high speed MAS with smaller sample tube. However, we are not interested in the smaller sample tube and extremely high speed MAS, because the aim of the present study is to detect the correlation

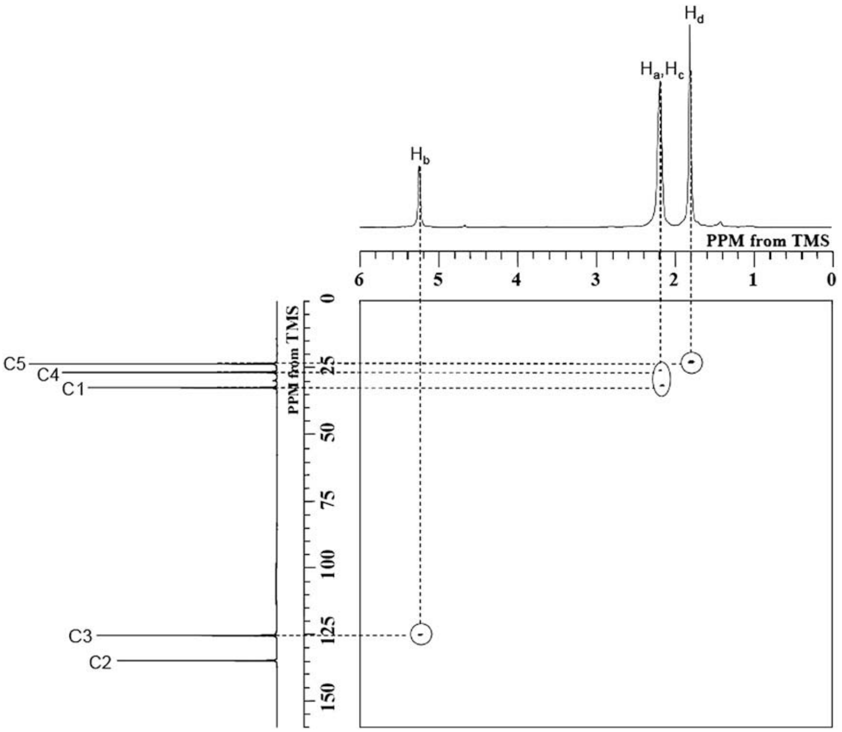

Fig. 4. HSQC spectra for the vulcanized natural rubber, obtained through solid-state NMR spectroscopy equipped with a 4 mm FG-MAS probe at 18 kHz in spinning rate for 1 h 2 min.

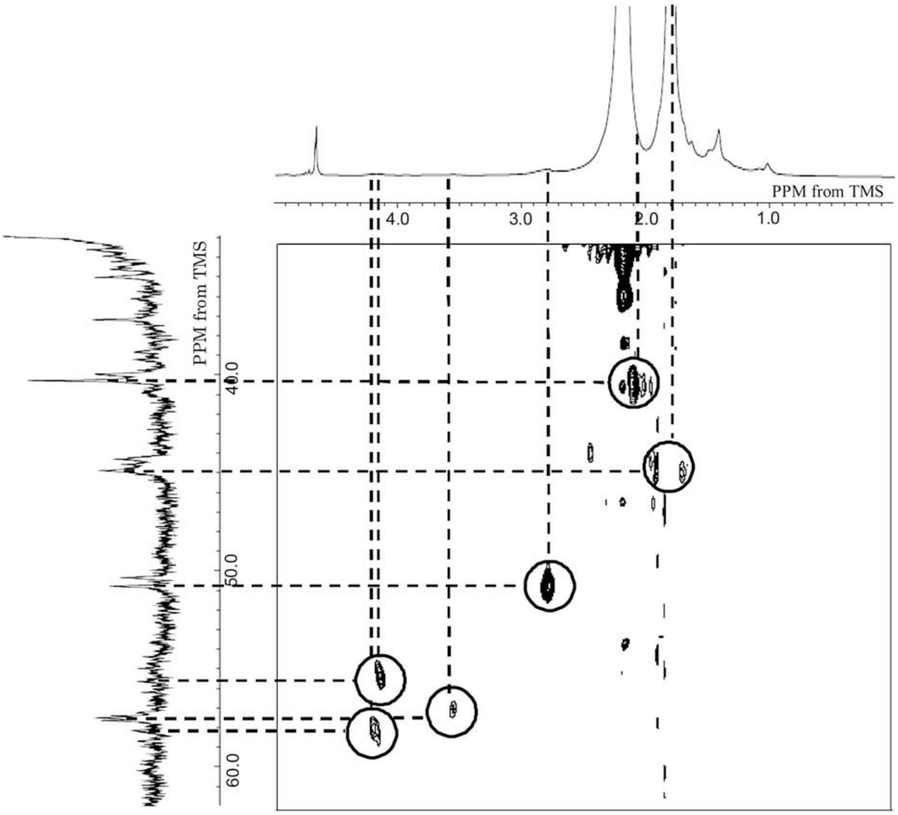

Fig. 5. HMQC spectra for the vulcanized natural rubber, obtained through solid-state NMR spectroscopy equipped with a 4 mm FG-MAS probe at 18 kHz in spinning rate for 71.5 h. HMQC measurement was performed in a selective region of chemical shift: 2–4 ppm in ^{1}H domain and 35–70 ppm in ^{13}C domain.

between the small ^{13}C and ^{1}H-signals assigned to the crosslinking junctions of vulcanized natural rubber. In Fig. 3, small signals at 3.4 and 4.2 ppm appeared in the solid-state ^{1}H NMR spectrum for the vulcanized natural rubber, but not in the solution-state ^{1}H NMR spectrum for the unvulcanized natural rubber. The signal at 3.4 ppm was assigned to aliphatic ^{1}H linking to –C-**CH**-S_x group and the signal at 4.2 ppm to unsaturated aliphatic ^{1}H linking to =C-**CH**-S_x group, according to the literature [20], which subscript x represents a number of S atoms.

Fig. 4 shows HSQC spectra obtained through solid-state NMR spectroscopy equipped with the FG-HS-MAS probe. The signals at 1.7, 2.1 and 5.1 ppm in the ^{1}H NMR spectrum were reasonably correlated with the signals in the ^{13}C NMR spectrum; for instance, the signal at 1.7 ppm was correlated with the signal at 23 ppm, the signal at 2.1 ppm was with the signals at 26 and 32 ppm, and the signal at 5.1 ppm was with the signal at 135 ppm. However, no hetero-nuclei correlation between the small signals was detected in HSQC spectra due to unsatisfactory accumulation time for HSQC measurement.

To detect the hetero-nuclei correlation between the small signals, HMQC measurement was performed in a selective region of chemical shift: 2–4 ppm in ^{1}H domain and 35–70 ppm in ^{13}C domain. Fig. 5 shows HMQC spectra obtained by the selective measurement. The ^{13}C-signals at 40, 44, 50 and 58 ppm were well correlated to the ^{1}H-signals at 2.1, 1.7, 2.8 and more than 3.6 ppm. In the previous works [10,11], the signals at 40, 44 and 58 ppm of the vulcanized liquid *cis*-1,4-polyisoprene as a model were assigned through solution-state NMR spectroscopy with various pulse sequences, i.e. DEPT, APT, HETCOR, HSQC and HMBC. The signal at 40 ppm was assigned to C4 of *trans*-1,4-isoprene units, obtained by isomerization of *cis*-1,4-isoprene units. In contrast, the signals at 44 ppm in the ^{13}C NMR spectrum were assigned to the secondary carbons adjacent to carbons linking to S atoms. The signals at 58 ppm in ^{13}C NMR spectrum were assigned to the tertiary and quaternary carbons linking to S atoms. In the present work, the same results were obtained by solid-state NMR spectroscopy equipped with the FG-HS-MAS probe. Furthermore, the ^{13}C-signals at 58 ppm were correlated to the ^{1}H-signals at 3.4 and 4.2 ppm, which were assigned to the –C-**CH**-S_x group and =C-**CH**-S_x group. More detailed assignments through solid-state NMR spectroscopy will be reported in our subsequent paper.

4. Conclusions

The crosslinking junctions of the vulcanized natural rubber were analyzed by solid-state NMR spectroscopy equipped with the FG-HS-MAS probe. The resolution of the solid-state ^{13}C NMR spectra for the vulcanized natural rubber was sufficiently high, which was comparable to the resolution of the solution-state ^{13}C NMR spectra for the unvulcanized natural rubber. The resolution of the solid-state ^{1}H NMR spectra for the vulcanized natural rubber was also similar to that of the solution-state NMR spectrum for the unvulcanized natural rubber. It was confirmed that the inverse correlation between ^{1}H and ^{13}C-signals, assigned to the crosslinking junctions for the vulcanized natural rubber, was investigated by solid-state NMR spectroscopy equipped with the FG-HS-MAS probe. The signals at 40 and 44 ppm were assigned to C4 of *trans*-1,4-isoprene units and secondary carbons adjacent to carbons linking to S atom, respectively, and the signals at 58 ppm were to the tertiary and quaternary carbons linking to S atoms. Furthermore, the ^{13}C-signals at 58 ppm were distinguishably correlated to the ^{1}H-signals at 3.4 and 4.2 ppm, which were assigned to the –C-**CH**-S_x group and =C-**CH**-S_x group, respectively.

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