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INVITED ARTICLE

Molecular dynamics and orientation of stretched rubber by solid-state ^{13}C NMR

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The molecular dynamics and orientation of vulcanized natural rubber (NR) stretched at a low extension ratio (α=stretched length/original length) were studied by carbon-13 direct polarization-magic angle spinning nuclear magnetic resonance (^{13}C DP-MAS NMR), ^{13}C cross-polarization (CP)-MAS NMR, ^{13}C DP NMR without MAS, ^{13}C CP NMR without MAS and density functional theory (DFT) calculations. Gradual peak broadening was observed in the ^{13}C DP-MAS NMR spectra of stretched NR with an increasing extension ratio, indicating that the molecular mobility of NR chains is restricted by stretching. The static ^{13}C NMR spectra of uniaxially stretched NR (α=2) changed slightly depending on the angle, θ, between the stretching direction and the applied magnetic field, although the spectra of unstretched NR did not change even if θ was changed. Thus, it is noted that NR chains oriented slightly as a time average by stretching even at a low extension ratio, α=2, although there still exists rapid rotation around the oriented NR chain. Motionally narrowed anisotropies in the ^{13}C spectra of stretched NR and the directions of chemical shift anisotropy principal axes determined by DFT calculations suggest that isoprene units of oriented rubber chains in stretched NR rotate rapidly around the axis that almost aligned with the C=C bond direction of polyisoprene.
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INTRODUCTION

An important question in designing industrial rubber products is whether vulcanized natural rubber (NR) is oriented under strain even at low extensions. Industrial rubbers, such as tires, are always used at a low extension ratio, $\alpha \leqslant 2$, and therefore designs of tires are influenced by the molecular orientation of stretched rubbers with a low extension. Until now, there have been two contrasting views about the orientation of stretched NR.[1–11] One is that stretched NR is not oriented at a low extension ratio of $\alpha \leqslant 2$.[1–8] This opinion has been supported by X-ray diffraction (XRD) and birefringence experiments. Only an amorphous halo was observed at stretched NR $\alpha \leqslant 2$, and strain-induced crystallization of NR occurred from an extension ratio of $\alpha=2.5$ by XRD experiments.[1–7] The birefringence result shows that growth of the crystal in definitional constraint programming (DCP)-cured NR occurred at an extension ratio of $\alpha=2.5$–3.5.[8] On the other hand, Fourier transform infrared dichroism, pulse-nuclear magnetic resonance (NMR) and solid-state NMR support another opinion that stretched rubber is oriented even at a low extension of $\alpha \leqslant 2$, although the degree of orientation is not so large.[9–11] From Fourier transform infrared dichroism, the average orientation function derived from Fourier transform infrared spectra as a function of α tends to show a linear relationship in the range of α from 1 to ~4.[9] The short T_2 component in the pulse-NMR experiments of stretched NR also shows a linear relationship between T_2 and α from 1 to ~4.[10] In our previous study using carbon-13 direct polarization (^{13}C DP) NMR, we showed that isoprene units of rubber polymers oriented by uniaxial stretching even at $\alpha=2$.[11] The study also suggests that a high molecular motion remains in molecular orientation.[11] We assume that the different opinions about the molecular orientation of stretched NR at low extensions comes from the high motion of the stretched NR chain. It is likely that orientation occurs partially even if the value of α is less than 2. However, such an orientation cannot be detected by XRD and birefringence because of high molecular motion and the small degree of orientation. At a value of α more than 2, the degree of orientation is speculated to be larger and then crystallization can be detected at $\alpha=2.5$ by these methods. Solid-state NMR and Fourier transform infrared are forceful methods for detecting molecular orientations, even for mobile amorphous samples, and therefore may be more suitable for disclosing the molecular orientation and dynamics of stretched rubber samples.[12–18]

In this study, the molecular dynamics and orientation of vulcanized NR stretched at a low extension ratio α were studied by ^{13}C DP-magic angle spinning (MAS) NMR, ^{13}C CP-MAS NMR, ^{13}C DP NMR without MAS, ^{13}C cross-polarization (CP) NMR without MAS and density functional theory (DFT) calculations.

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EXPERIMENTAL PROCEDURE

Materials

Table 1 summarizes the recipe of the vulcanized NR samples used in this study. These rubber samples, which consist of rubber bands with an inner diameter of 2.5 mm and rubber discs with a diameter of 7 mm, were cured at 170 °C for 10 min.

Solid-state NMR measurements

^{13}C solid-state NMR spectra were observed by using a Bruker Avance 400 spectrometer (Bruker Biospin GmbH, Rheinstette, German), equipped with a 7 mmϕ MAS or a 10 mmϕ static probehead operating at 100.6 MHz. To observe the high-resolution NMR spectra of stretched NR, we designed a rubber-stretching kit[19] (Sumitomo Rubber Industries Ltd., Chuo-ku, Kobe, Japan) that enables MAS measurements. Rubber bands were stretched by the rubber-stretching kit (Figure 1), after which the ^{13}C DP-MAS NMR spectra of stretched rubbers at α=2 and 4 were measured under a ^{1}H dipolar decoupling condition at 25 °C. ^{13}C DP-MAS spectra with dipolar decoupling of 29.4 kHz at 25 °C, and ^{13}C CP-MAS spectra with dipolar decoupling of 57.5 kHz at −55 °C were observed for rubber samples without stretching (α=1). MAS speed was 5.0 kHz for the former measurements, and 3.0 or 4.0 kHz for the latter measurements. The $\pi/2$ pulse width was 4.35 μs and the repetition time was 6 s. Rubber bands with α=2 were uniaxially stretched, as reported in the previous study.[13] The $\pi/2$ pulse width was 8.5 μs and the delay time was 5 s. The dmfit program[20] was used for spectral fittings.

Table 1 Recipe of the samples used in this study (in phr)

Sample	NR	Carbon	Sulfur	Stearic acid	ZnO	Accelerator	Antioxidant
Natural rubber (NR)	100	0	1.5	2.0	3.0	0.5	1.0

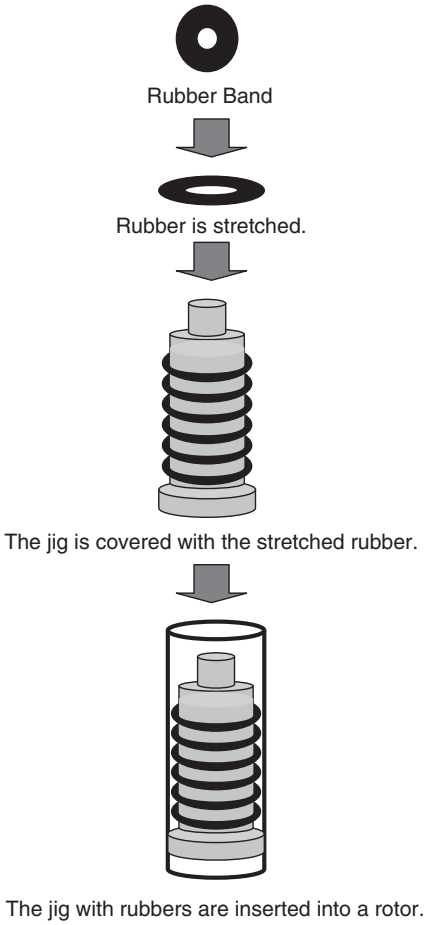

Figure 1 Schematic diagram of a kit used to obtain ^{13}C NMR MAS spectra of stretched rubbers.

DFT calculations of ^{13}C-shielding components

The Gaussian 03 Rev.D.02 program package (Gaussian, Inc., Wallingford, CT USA) was used for DFT calculations of ^{13}C-shielding tensor components. The B3LYP exchange-correlation functional and the 6-311++G(d,p) basis set were used. A simplified model of polyisoprene, CH_3-CH_2-$C(CH_3)$=CH-CH_2-CH_3 with *cis* form was used for the calculation. As DFT calculations provided absolute shielding values, we converted the calculated chemical shielding to chemical shift values using the following equation:

$$\delta_{13C} = 184.05 - \sigma_{13C} \text{ (p.p.m.)}$$

In this equation, the value of 184.05 p.p.m. was the absolute shielding of the ^{13}C nucleus of tetramethylsilane calculated using the same basis set.

RESULTS AND DISCUSSION

Restriction of molecular mobility of NR by stretching

Figure 2 shows the ^{13}C DP-MAS NMR spectra of vulcanized NR without stretching (α=1 (a)) and with stretching (α=2 (b) and α=4 (c)).

The five peaks observed at 24.1, 27.3, 33.0, 125.9 and 135.4 p.p.m. are assigned to individual carbons of *cis*-1,4-polyisoprene as indicated.[21] By stretching the vulcanized NR, the ^{13}C chemical shifts of the five peaks are unchanged and any strain-induced new peaks cannot be observed. However, the linewidths of the five peaks become slightly large with increasing α, although the degree of broadening is small. As linewidth is inversely proportional to the T_2 relaxation time that relates to molecular mobility,[22] the molecular motion of vulcanized NR seems to be slightly restricted by stretching.

Molecular orientation of the stretched NR at α=2

The main factor causing the restriction of molecular mobility is likely to be the molecular orientation of stretched NR. To verify the molecular orientation of the stretched NR, we carried out static NMR experiments of stretched and unstretched NR by changing the angle of the stretched direction relative to the applied magnetic field. Here, we concentrate on the behavior of two carbon signals, C_2 and C_3 in NR, with large chemical shift anisotropies.

Figures 3a–c show the ^{13}C DP-static NMR spectra of two carbons, C_2 and C_3, of the stretched NR with α=2 at θ=0°, 45° and 90°, where the angle, θ, is defined as the angle between the stretching direction and the applied magnetic field.

By tilting θ from 0° to 90°, gradual downfield shifts of $\Delta\delta$=3.0–3.1 p.p.m. were observed for both the C_2 and C_3 carbons. This result indicates that isoprene units of rubber polymers are slightly oriented by stretching even at α=2.[11] However, the amount of downfield shifts is quite small compared with the common range of ^{13}C chemical shift anisotropies (generally $\Delta\delta=\delta_{11}-\delta_{33}$=approximately several tens to several hundred p.p.m.).[23,24] In the circularly stretched NR at α=2, mixed patterns of oriented peaks are observed for each carbon (Figure 3d). Thus, the circularly stretched NR includes various directions of orientation in the spectrum. These results also confirm that rubber polymers are oriented by stretching at α=2.

In addition, to prove that θ-dependent shifts of stretched NR are not artificial, θ-dependent observation was also performed for the mixture of stretched and unstretched NR samples. In the spectrum of Figure 4a of the stretched NR containing unstretched NR, an

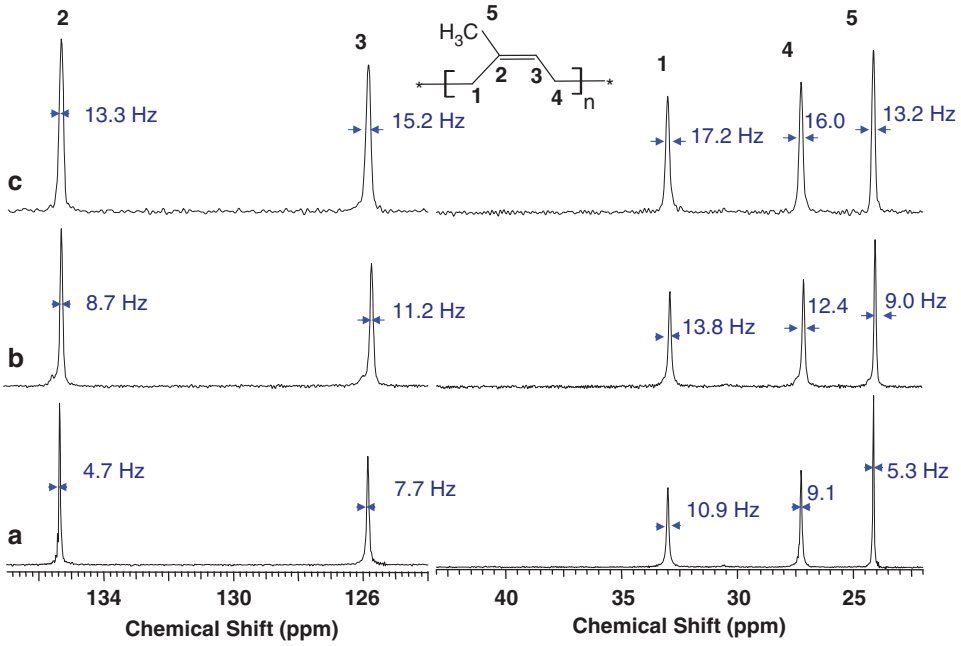

Figure 2 ^{13}C DP-MAS NMR spectra of vulcanized natural rubber (NR) without stretching ($\alpha=1$) (**a**), with stretching of $\alpha=2$ (**b**) and $\alpha=4$ (**c**). The structure of polyisoprene, which is the major constituent of NR, and signal assignment are also shown.

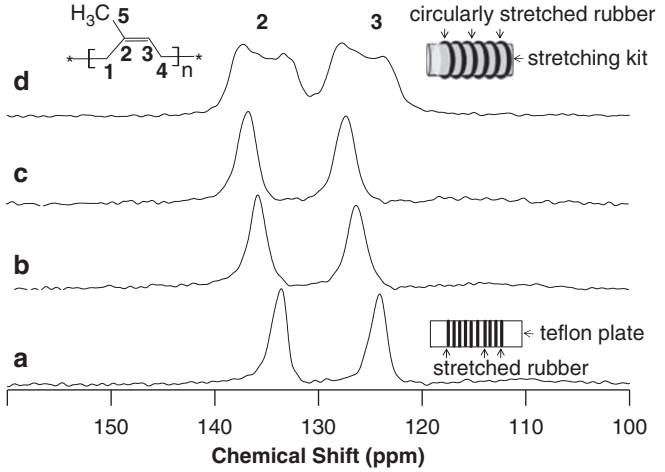

Figure 3 ^{13}C DP-static NMR spectra (C_2 and C_3 in the olefinic region) of uniaxially stretched natural rubber (NR) with $\alpha=2$ observed at various angles, θ, between the stretching direction and the applied NMR magnetic field: $\theta=0^\circ$ (**a**), 45° (**b**) and 90° (**c**). The ^{13}C DP-static NMR spectrum of the circularly stretched NR (Figure 1) is shown as (**d**).

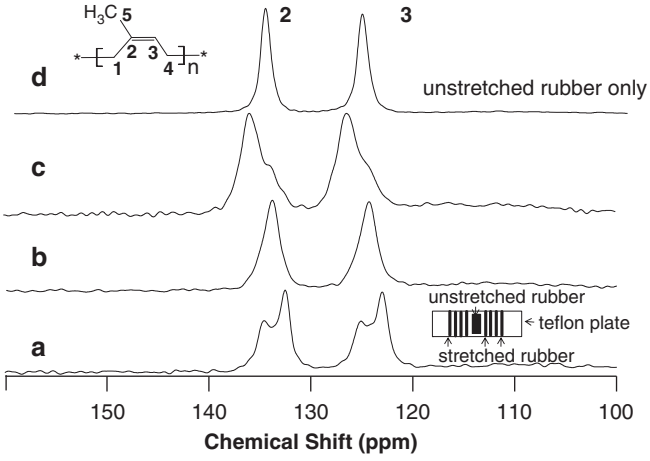

Figure 4 ^{13}C DP-static NMR spectra (C_2 and C_3 in the olefinic region) of a mixture of uniaxially stretched natural rubber (NR) and small amounts of unstretched NR observed at $\theta=0^\circ$ (**a**), 45° (**b**) and 90° (**c**). The spectrum (**d**) of only unstretched NR is also shown.

additional small peak is clearly observed for each C_2 and C_3 carbon. These peaks are almost independent of the angle θ as shown in Figures 4a–c, and peak positions are the same as those observed for the unstretched NR sample (Figure 4d).

Therefore, we have found that the θ-dependent downfield shifts observed in the stretched NR are not artificial and come from the orientation of the rubber chain by stretching as a time average.

Apparently, these findings conflict with the XRD results that only amorphous halo was observed in the stretched NR at $\alpha \leqslant 2$. This conflict must be caused by the dissimilarity of easily observable components using XRD and NMR methods. The XRD method predominantly observes crystalline components in polymer chains. With regard to the characterization of molecular orientation, it seems difficult to observe the oriented components undergoing vigorous molecular motion using the XRD method. On the contrary, NMR measurements in this study can analyze all components in polymer chains, including amorphous components. Observation of orientations is also possible for polymer chains with high molecular mobility. Considering both views of NMR and XRD, it is suggested that NR is oriented by stretching at $\alpha=2$, whereas the degree of orientation is small and oriented crystals are not formed.

In spite of the molecular orientation of stretched NR, the range of ^{13}C chemical shift change caused by varying the angle θ is surprisingly small (about 3 p.p.m.). The small range of ^{13}C chemical shift anisotropy (CSA) of the stretched NR is expected to be the result of anisotropical motional narrowing, such as a rotation around one axis.[25–27]

Range of chemical shift anisotropy of frozen NR

To determine the original range of ^{13}C CSA of NR when the rubber molecular motion is frozen, ^{13}C spectra of NR were measured at −55 °C. Figure 5 shows ^{13}C CP static (a) and low-speed MAS NMR spectra ((b) and (c)) at −55 °C of the C_2 and C_3 carbons of unstretched NR. Here, the MAS speeds of Figures 5b and c were 3 and 4 kHz, respectively. As the ranges of ^{13}C CSAs ($\Delta\delta=\delta_{11}-\delta_{33}$) are almost unchanged at less than −50 °C, a temperature of −55 °C is adopted.

The ranges of ^{13}C CSAs are considered to be more than 100 p.p.m., as determined from Figure 5a. The exact principal values of CSAs can be determined by spectral fittings to low-speed MAS spectra as shown in Figures 5b and c. As a result, the CSA principal values of the C_2 and C_3 carbons of NR were determined as (δ_{11}, δ_{22}, δ_{33})=(225.0, 133.2, 48.0) and (209.3, 107.0, 61.1), respectively (Table 2).

The simulated static spectrum shown in Figure 5d with these CSA values is very close to its corresponding experimental spectrum in Figure 5a, although the upperfield skirt of the experimental spectrum in Figure 5a overlaps with the downfield skirt of aliphatic carbon peaks. Thus, the ranges of ^{13}C CSAs ($\Delta\delta=\delta_{11}-\delta_{33}$) of olefinic carbons are more than 140 p.p.m. when molecular motion is frozen.

Motional narrowing of CSA by anisotropic motion of stretched NR

Although the CSA ranges ($\Delta\delta=\delta_{11}-\delta_{33}$) of C_2 and C_3 carbons of NR at frozen molecular motion are over 140 p.p.m., the observed ranges of the chemical shift change of stretched NR by varying the angle θ are only 3 p.p.m. This seems to be caused by the rapid molecular rotation around one axis.[25–27]

Figure 6 shows simulated CSA patterns of the C_2 carbon: (a) frozen molecular motion of unstretched NR and (b) stretched NR at room temperature.

The CSA pattern of frozen molecular motion is simulated from the experimental CSA principal values of the C_2 carbon. Conversely, the pattern of stretched NR is simulated from the chemical shift values of stretched NR at $\theta=0^\circ$ and 90°, as seen in Figures 3a and c. The chemical shift of the C_2 carbon of stretched NR at $\theta=0^\circ$ (δ=133.6 p.p.m.) is very close to the δ_{22} value at frozen molecular motion (δ=133.2 p.p.m.). The chemical shift of stretched NR at $\theta=90^\circ$ (δ=136.7 p.p.m.) coincides with the averaged value of δ_{11} and δ_{33} at frozen molecular motion (δ=136.5 p.p.m.). This finding indicates that isoprene units of the rubber chain in the stretched NR rapidly rotate around the δ_{22} direction of the C_2 carbon and therefore the chemical shifts, δ_{11} and δ_{33}, perpendicular to the rotation axis should be averaged. By disclosing the relationship between the rotation axis (δ_{22} direction of the C_2) and the isoprene molecular axis, the

Table 2 Experimental and calculated chemical shifts of the C_1–C_4 carbons of natural rubber (NR)

	δ_{iso}[a]	δ_{11}[b]	δ_{22}[b]	δ_{33}[b]	$\Delta\delta=\delta_{11}-\delta_{33}$[c]	$\Delta\delta=\delta\perp-\delta\parallel$[d]	$\Delta\delta$ (θ–changing)[e]
Experimental							
C_1	33.0	—	—	—	—	—	−3.0
C_2	135.4	225.0	133.2	48.0	177.0	−3.5	−3.1
C_3	125.9	209.3	107.0	61.1	148.2	−3.7	−3.1
C_4	27.3	—	—	—	—	—	−3.0
Calculated							
C_1	29.7	46.2	25.4	17.3	28.9	−1.5	—
C_2	147.1	260.2	146.4	34.8	225.4	−1.1	—
C_3	135.8	237.0	110.8	59.5	177.5	−6.0	—
C_4	27.5	41.8	22.2	18.3	23.5	−0.6	—

[a]Isotropic chemical shift in p.p.m. determined from Figure 2.
[b]Principal values of chemical shift anisotropies (CSA) in p.p.m.
[c]Range of CSA ($\Delta\delta=\delta_{11}-\delta_{33}$) in p.p.m.
[d]Motionally narrowed anisotropies. The δ_{22} direction of C_2 carbon is assumed to be the rotation axis.
[e]Range of CSA obtained from θ changing experiment of stretched NR.

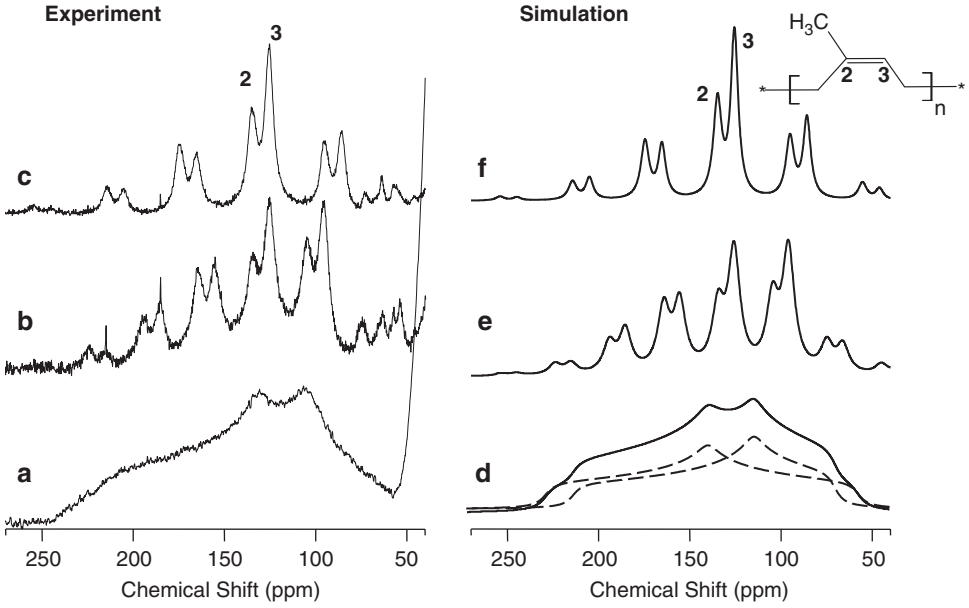

Figure 5 ^{13}C CP static and low-speed MAS NMR spectra of the olefinic region of natural rubber (NR) at −55 °C: static (**a**), 3 kHz magic angle spinning (MAS) (**b**), 4 kHz MAS (**c**). The fitting spectra of 3 and 4 kHz MAS are shown in (**e**) and (**f**), respectively, and the simulated static spectrum is shown in (**d**). Linewidths were set to be 900 Hz for simulated MAS spectra and the line-broadening factor was set to be 1 kHz for the simulated static spectrum. Lorentzian was used as the line-broadening function for spectral simulation.

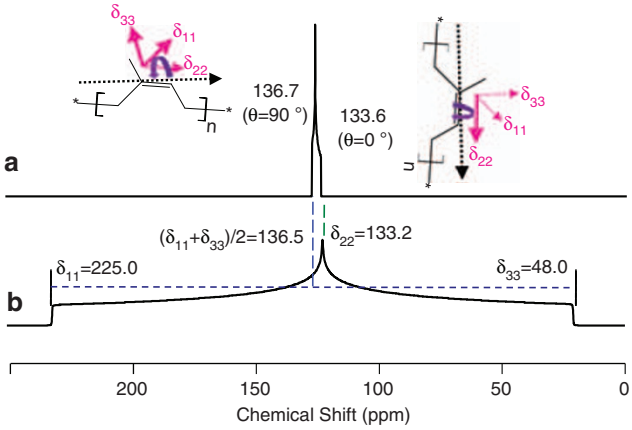

Figure 6 Simulated chemical shift anisotropy (CSA) patterns of C_2 carbon: frozen molecular motion of unstretched natural rubber (NR) (**a**) and stretched NR at room temperature (**b**). The CSA pattern of frozen molecular motion is simulated from the experimental CSA principal values of C_2 carbon. The CSA pattern of stretched NR is simulated from the chemical shift values of stretched NR at θ=0° and 90°. δ_{11} and δ_{33} in spectrum (**b**) correspond to θ=90° and 0°, respectively. δ_{22} was calculated on the basis of the equation $\delta_{iso}=(\delta_{11}+\delta_{22}+\delta_{33})/3$. The line-broadening factor was set to be 10 Hz for simulated static spectra.

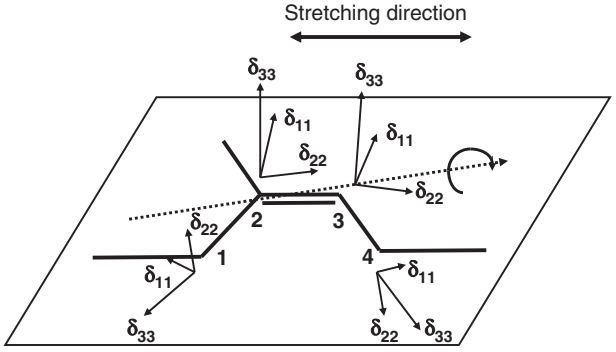

Figure 7 Directions of chemical shift anisotropy principal axes of ^{13}C shielding of a model molecule of polyisoprene with *cis*-conformation determined by density functional theory calculations.

molecular dynamics in stretched NR are clarified. As the CSA directions of NR carbons are impossible to determine experimentally, we performed DFT calculations using a model compound of NR to determine the directions of the CSA principal axes of ^{13}C shielding.

Dynamics of the oriented polymer chain of stretched NR

Figure 7 shows the directions of the CSA principal axes of ^{13}C shieldings of C_1–C_4 carbons of a polyisoprene model molecule with *cis* conformation as determined by DFT calculations.

We found that the δ_{22} component of the C_2 carbon lies approximately along the C=C bond of the isoprene unit of NR, although the δ_{22} direction actually forms an angle of 7° relative to the C=C bond. δ_{11} and δ_{33} components are almost aligned perpendicular to the C=C bond. Therefore, isoprene units of oriented polymer chains in stretched NR rotate rapidly around one axis, which makes an angle of several degrees with respect to the C=C bond direction. This result suggests that isoprene polymer chains are slightly oriented as a time average. We compared the calculated values of motionally narrowed anisotropies with the experimental CSA range observed at the θ changing experiment of stretched NR as seen in Figures 3a–c. The motionally narrowed anisotropy can be expressed by the following equation:[25]

$$\Delta\delta = \tfrac{1}{2}(3\cos^2\beta - 1)[\delta_{33} - \tfrac{1}{2}(\delta_{11}+\delta_{22})] + \tfrac{3}{4}(\delta_{11} - \delta_{22})\sin^2\beta\cos 2\alpha \quad (1)$$

where angles α, β are the Euler angles defining the transformation from the principal axis system of (δ_{11}, δ_{22}, δ_{33}) to the molecular rotation frame. In the case of the C_2 carbon, the motionally narrowed anisotropy is calculated at $\Delta\delta$ $(=\delta\perp-\delta_{\parallel})=$ −3.7 p.p.m. The δ_{22} direction of C_2 carbon is assumed to be the rotation axis, and the experimental CSA principal values of (δ_{11}, δ_{22}, δ_{33}) obtained in Figure 5 are used for calculation. The motionally narrowed anisotropy value of −3.7 p.p.m. is very similar to the experimental CSA range of C_2 carbon of $\Delta\delta=$ −3.1 p.p.m., which is obtained from the θ changing experiment of the stretched NR sample as seen in Figures 3a–c. In the case of C_3 carbon, the motionally narrowed anisotropy is calculated at $\Delta\delta$ $(=\delta\perp-\delta_{\parallel})=$ −3.5 p.p.m., which is also very similar to the experimental CSA range of the C_3 carbon of $\Delta\delta=$ −3.1 p.p.m.

Although the CSA principal values of C_3 carbon are different from those of C_2 carbon, the motionally narrowed anisotropy of C_3 carbon becomes almost similar to that of C_2 carbon. This is because of the small difference in CSA principal axes between C_2 and C_3 carbons. The δ_{22} direction of C_3 carbon results in a small difference to the rotation axis. According to DFT calculations, the δ_{22} direction of C_3 carbon forms an angle of about 20°, relative to the δ_{22} direction of C_2 carbon, which is assumed to be the rotation axis. Therefore, the small ranges of θ-dependent chemical shifts of olefinic C_2 and C_3 carbons in stretched NR can be explained as the result of the motionally narrowed anisotropies of C_2 and C_3 carbons. The motionally narrowed anisotropy values of C_2 and C_3 carbons calculated from the experimental CSA principal values are also summarized in Table 2.

Motionally narrowed anisotropies are also calculated from simulated CSA principal values by DFT calculations. Using the simulated values for calculation, the motionally narrowed anisotropies can be calculated not only for olefinic C_2 and C_3 carbons but also for aliphatic C_1 and C_4 carbons. The experimental CSA principal values of aliphatic C_1 and C_4 carbons cannot be determined because of their very small spinning side bands and signal overlapping. The simulated CSA principal values of all C_1–C_4 carbons and the motionally narrowed anisotropies calculated from simulated CSA values are also summarized in Table 2.

CONCLUSION

The molecular dynamics of orientated polymer chains of stretched NR have been successfully studied by solid-state ^{13}C NMR and DFT calculations. From ^{13}C DP-MAS NMR data, we found that ^{13}C linewidths of NR become broader when the extension ratio is raised. This means that the mobility of the polymer chains of NR is restricted by stretching. From the ^{13}C DP-static NMR experiments of uniaxially stretched NR at an extension ratio of α=2 with several stretching directions relative to the magnetic field, we observed that the ^{13}C chemical shifts of two NR olefinic C_2 and C_3 carbons change by varying the stretching directions to the magnetic field. This suggests that isoprene units of rubber polymers become oriented by stretching even at a low extension ratio of α=2. In spite of the molecular orientation of stretched NR, ranges of ^{13}C chemical shift changes caused by varying the stretching direction are small. The small

chemical shift changes are due to rapid molecular rotation around one axis. The motionally narrowed anisotropy of the C_2 carbon of NR suggests that the isoprene units of the rubber polymer chain in stretched NR rapidly rotate around the δ_{22} direction of the C_2 carbon. The DFT calculation shows that the δ_{22} direction of the C_2 carbon lies approximately along the C=C bond of polyisoprene. The motionally narrowed anisotropy of C_3 carbon supports the motional narrowing. Therefore, it is concluded that isoprene units of rubber chains in stretched NR become oriented and undergo rapid molecular rotation around an axis almost aligned with the C=C bond direction of polyisoprene.

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