SHORT COMMUNICATIONS

Characterization of Molecular Orientation of Stretched Natural Rubber by Solid-State ^{13}C NMR

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The analysis of the molecular orientation of stretched rubbers is of great importance to understand rubber elasticity. To characterize this orientation, X-ray diffraction[1–3] and AFM[4] data have been reported. Toki *et al.* carried out *in situ* synchrotron X-ray diffraction measurements for natural rubber (NR),[1–3] and reported that 75% of polymer chain segments remain unoriented even at a large strain with extension ratio of $\alpha = 6$. At smaller strains with extension ratios, $\alpha \leq 2$, the wide-angle X-ray diffraction (WAXD) images show only amorphous halo patterns and no oriented segments were found.[3] X-ray diffraction method is very useful to detect oriented crystalline components. However, rubbers are mostly amorphous under small strains, and it is difficult to observe oriented amorphous components by X-ray diffraction method. Moreover, rubbers have high molecular mobility, which makes the X-ray diffraction analysis more difficult.

In this study, solid-state ^{13}C NMR measurements are carried out on stretched vulcanized NR at extension ratio of $\alpha = 2$ to investigate molecular orientation. Solid-state NMR is a powerful method to detect molecular orientations even for mobile amorphous samples, and therefore, it is quite suitable for the study's purpose to detect the molecular orientation of rubber samples.[5]

EXPERIMENTAL

The vulcanized NR sample used in this study has been cured at 170 °C for 10 min. with sulfur of 1.5 phr, ZnO of 3.0 phr, stearic acid of 2.0 phr and an accelerator of 0.5 phr. A vulcanized rubber sample with an inner diameter of 2.5 mm is prepared using this procedure.

NMR measurements are carried out by a Bruker Avance 400 spectrometer, equipped with static probes operating at 100.6 MHz for ^{13}C. Rubber bands without stretching condition are measured by ^{13}C direct polarization (DP) with ^{1}H dipolar decoupling (DD) in the static state at 25 and −55 °C. The S/N ratio of the ^{13}C spectrum at −55 °C was not excellent, therefore, the spectrum with cross polarization (CP) at −55 °C is also measured. The DP and CP static spectra under ^{1}H DD condition were essentially equivalent. For a stretched sample, the rubber bands are uniaxially stretched by covering a thin teflon plate, which results in $\alpha = 2$ (see Figure 1a). The angle, θ, of
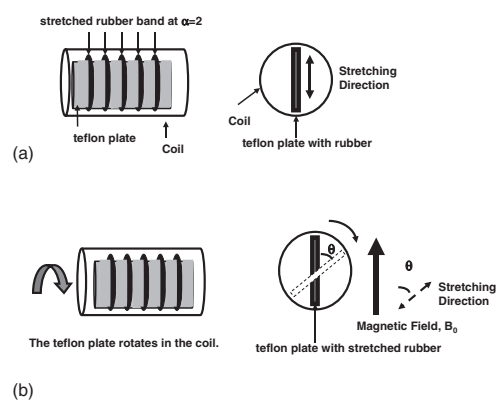

Figure 1. Schematic set-up of stretched vulcanized NR sample. The rubber sample, which was uniaxially stretched by covering the thin Teflon plate with extension ratio of $\alpha = 2$, was inserted into the coil of the static probe (a). The angles, θ, between the stretching direction and the NMR magnetic field, $\boldsymbol{B_0}$ was changed by turning the Teflon plate in the coil (b).

the teflon plate, which corresponds to the stretching direction with respect to the applied static magnetic field, $\boldsymbol{B_0}$, is changed in the static probe, as shown in Figure 1b. The ^{13}C DP/DD spectra are obtained for all the stretched samples at 25 °C. The $\pi/2$ pulse widths were 8.5 and 4.35 μs for the measurements at 25 and −55 °C, respectively. ^{1}H dipolar decoupling field strengths of 29.4 and 57.5 kHz have been applied during the detection of free induction decay at 25 and −55 °C, respectively. All the measurements of stretched rubbers were carried out 10–20 min. after stretching. The delay time was 4–5 s.

RESULTS AND DISCUSSION

Figure 2 shows the ^{13}C dipolar decoupling (DD)-static NMR spectra of unstretched vulcanized NR at −55 (a) and 25 °C (b). The structure of polyisoprene, which is the major constituent of natural rubber, is also shown at the upper-right corner of the figure. Five peaks are assigned to the respective carbons of polyisoprene, according to ref 6. The chemical shift anisotropy (CSA) spectrum at −55 °C is found to be typical powder patterns, with wide CSA spans, $\Delta\delta = |\delta_{11} - \delta_{33}|$, of ∼150–200 ppm and ∼10–50 ppm for sp^2 and sp^3 carbons, respectively, although they are overlapped. This indicates that

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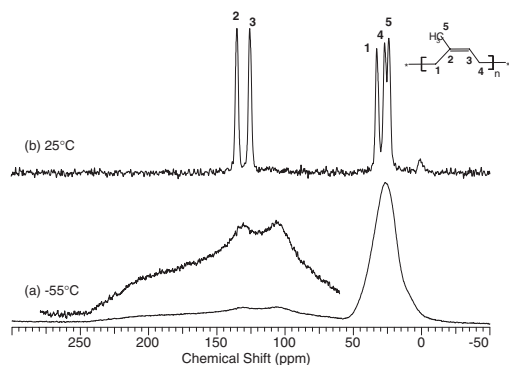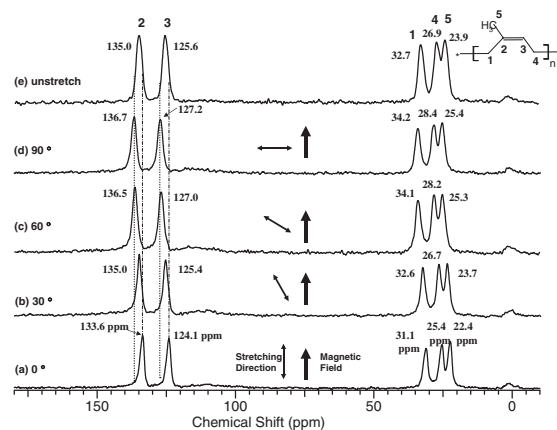
Figure 2. ^{13}C DD-static NMR spectra of unstretched vulcanized NR at $-55\,°C$ (a) and $25\,°C$ (b), respectively. The structure of polyisoprene, which is the major constituent of natural rubber, is also shown.

Figure 3. ^{13}C DD-static NMR spectra of uniaxially stretched vulcanized NR at $\alpha = 2$. The angles, θ, are set to be 0° (a), 30° (b), 60° (c), and 90° (d), respectively. The ^{13}C DD-static NMR spectrum of the vulcanized NR without stretching is also shown in (e) for reference. The ^{13}C chemical shifts are shown for respective resonance lines.

the molecular motion is mostly frozen in the order of kHz.[7,8] With increasing temperature, so-called motional broadening occurs; the resonance lines become too broad to be detected (not shown here). The motional broadening in the present case occurs by the interference of molecular motion and the applied ^{1}H dipolar decoupling. ^{1}H dipolar decoupling field strength is 29.4–57.5 kHz as described in the experimental section. Therefore, the molecular motion in the order of several ten kHz is found to occur between 25 and $-55\,°C$. At $25\,°C$, the rate of motion exceeds the decoupling field strength, and thus the line widths turn to be narrow again.[8] Correspondingly, the CSA spectrum at $25\,°C$ is found to become much narrower than that at $-55\,°C$. The CSAs are narrow Lorentzian lineshpes for all the carbons at $25\,°C$, indicating that the motion observed here is almost isotropic main-chain motion.

Even for such a sample undergoing rigorously tumbling motion at $25\,°C$, the molecular orientation can be analyzed. Figure 3 shows the ^{13}C DD-static NMR spectra of uniaxially stretched vulcanized NR at $\alpha = 2$. The angles, θ, between the stretching direction and $\boldsymbol{B_0}$ is set to be 0°, 30°, 60°, and 90°. The spectrum of unstretched vulcanized NR is also shown in (e) for reference. By changing θ from 0° to 90°, the downfield shifts of $\Delta\delta = 3.0$–3.1 ppm are found for the five carbon resonance lines. This finding clearly indicates that rubber polymer chains are oriented along the stretching direction even at $\alpha = 2$. The unstretched NR also shows θ-dependent chemical shifts (data not shown), but the amounts of the downfield shift is very small; $\Delta\delta = 0.5$ ppm and therefore, the θ-dependent chemical shifts observed at $\alpha = 2$ are not artifacts. The small downfield shifts about 3 ppm suggest that the degree of orientation is not so large. Such small degree of orientation observed at $\alpha = 2$ for NR has been also reported by an infrared dichloism study by Amram *et al.*[9]

In Figure 3a–d, all the resonance lines depend on the stretching direction as described above and the components which are independent of the stretching direction, are almost unobservable. The chemical shift range that is $\Delta\delta$ values of 3–4 ppm for $\theta = 0$–90°, is not as wide as CSA span of unstretched vulcanized NR at $-55\,°C$ in Figure 2a but is similar to that at $25\,°C$ in Figure 2b. This indicates that the large amplitude mobilities of the chain segments, which affect the CSA spans, are almost independent of the sample stretching at least for $\alpha \leq 2$.

Seemingly, the present NMR results are contradictory to the WAXD results that only amorphous halos were observed in the stretched vulcanized NR at $\alpha \leq 2$.[3] The conflict originates from

the difference of easily observable components between X-ray diffraction and NMR. X-Ray measurements predominantly detect crystalline components in polymer chains. With regard to the characterization of molecular orientations, X-ray diffraction would be difficult to observe oriented components when they are mobile and disordered. In contrast, static NMR measurements in this study can analyze all the components in polymer chains including amorphous components. Considering both the NMR and X-ray diffraction results, we can conclude that rubber polymer chains are likely oriented by stretching even at $\alpha = 2$, whereas oriented crystals are not formed.

In conclusion, the molecular orientation behaviour of the highly mobile uniaxially stretched vulcanized NR is analyzed by ^{13}C static NMR. Compared with the wide-span CSA spectrum at $-55\,°C$ with $\Delta\delta = |\delta_{11} - \delta_{33}| = 150$–200 ppm for olefinic carbons, the CSA spectrum at $25\,°C$ is mostly averaged ($\Delta\delta = \sim 3.0$–3.1 ppm), revealing that almost isotropic main-chain motion occurs with a rate above 10^3 Hz. Even under such a highly mobile condition, the angular-dependence of the CSA spectra is clearly detected in uniaxially stretched samples.

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