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Spinning Effect on Magic-Angle-Spinning NMR Spectra of Silicone Rubber

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Synopsis. High-resolution solid-state ^{13}C, ^{29}Si, and ^{1}H NMR spectra of silicone rubber have been measured using the magic-angle spinning of the sample. The spectra of the three nuclei split into two or three components in the range of the spinning rate between 1.4 and 2.0 kHz. Below 1.4 kHz and above 2.0 kHz, the spectra consist of only one component. Stress caused by the fast spinning is considered to cause conformational changes in the polydimethylsiloxane chains.

Silicone rubber is a very popular material which is widely used in a daily life as well as in chemical laboratories. It is very flexible, and is usually composed of polydimethylsiloxane. Molecular motions are very rapid in silicone rubber as if they were in liquid state from the standpoint of NMR. The dipolar interactions between the nuclei are weak, and they can be easily averaged out by the magic-angle spinning (MAS) of the sample. Thus, one can get high-resolution spectra of ^{13}C, ^{29}Si, and ^{1}H nuclei in silicone rubber only by MAS. Due to this favorable property, silicone rubber has been used as the shift reference frequently.1) Cross polarization (CP) is not at all effective in this material.

Recently we have measured the NMR spectra of silicone rubber with very high resolution to determine the chemical shift precisely. In the course of the measurement we have found that the line shape changes in a certain range of the spinning rate.2) In other words, the spinning induces a change in the NMR spectra. We have recently reported spinning-rate dependent phenomena; one is Cu and halogen NMR signals in copper (I) halides,3) and the other is ^{31}P MAS NMR spectra of inorganic pyrophosphates.4) In the former case, the Lorentz force working on the charged particles excites the ion motion, resulting in the frequency shift. In the latter, the homonuclear dipole-dipole interaction is not averaged out by MAS.5) Bjorholm and Jakobsen6) have reported a crystalline-to-plastic phase transition induced by MAS in ^{31}P NMR in P_4S_3, although the true origin is the temperature rise induced by the spinning. In the present case, the stress caused by the spinning is considered to influence the conformation of silicone rubber. In this note, we present the spinning-induced changes in the ^{13}C, ^{29}Si, and ^{1}H MAS NMR spectra of silicone rubber. To our knowledge, this is the first observation of the conformational change induced by the stress in MAS NMR.

Experimental

The instrument used for the NMR measurements was a Bruker MSL400 pulsed spectrometer, whose magnetic field strength was 9.4 T. The resonance frequencies were 100.614, 79.496, and 400.136 MHz for ^{13}C, ^{29}Si, and ^{1}H, respectively. The details of the high-resolution measurements were described previously.2) Chemical shifts were referenced directly to pure tetramethylsilane under MAS, being expressed the higher frequency side as positive. The experimental errors in the shift values was about ±0.004 ppm, and the relative shifts in the same sample had the better accuracies with errors less than ±0.002 ppm. Temperature was 294 K. Two kinds of pulse sequences were used; single pulse, and single pulse with ^{1}H decoupling only during the data aquisition. Simulation of the spectra was carried out using the CLINFIT program supplied by Bruker.

Materials were available commercially. Although there were many kinds of silicone rubber, we have characterized the sample by NMR, as described below.

Results and Discussion

^{1}H and ^{13}C MAS NMR spectra have only one signal,

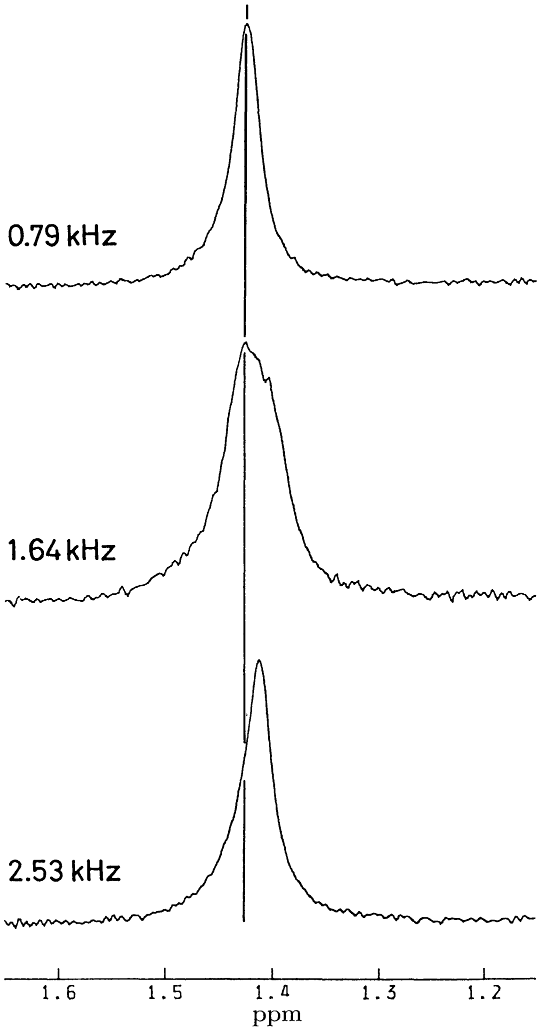

Fig. 1. ^{13}C MAS NMR spectra of silicone rubber with ^{1}H decoupling (ν_0=100.614 MHz). Numbers in the figure are the spinning rates.

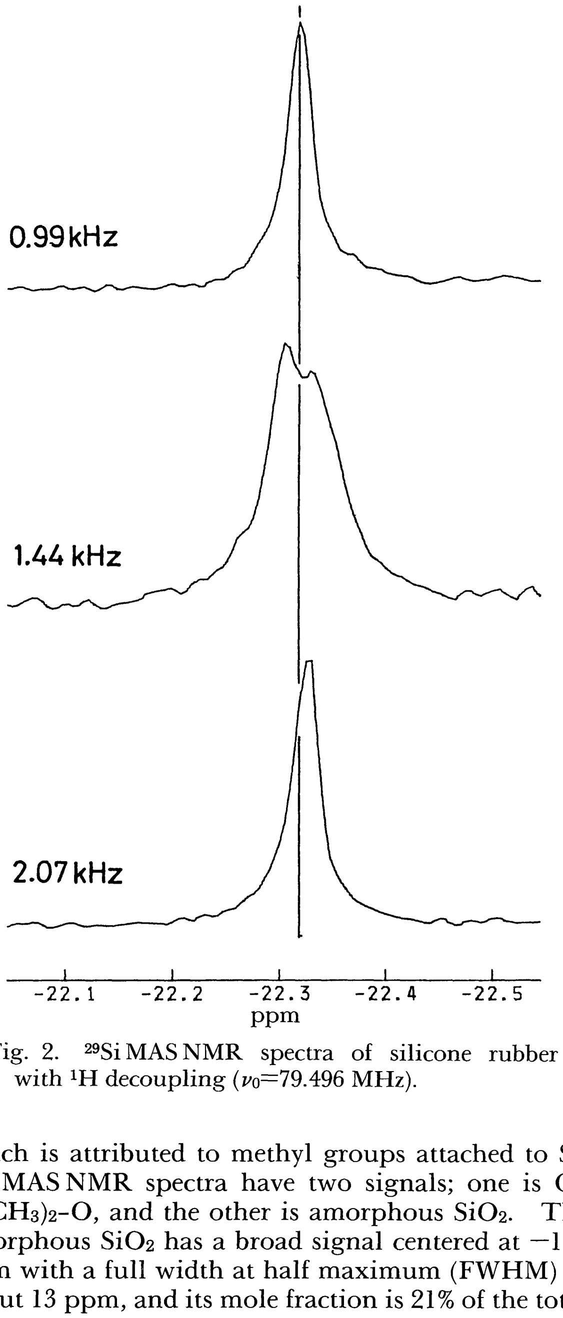

Fig. 2. ^{29}Si MAS NMR spectra of silicone rubber with ^{1}H decoupling (ν_0=79.496 MHz).

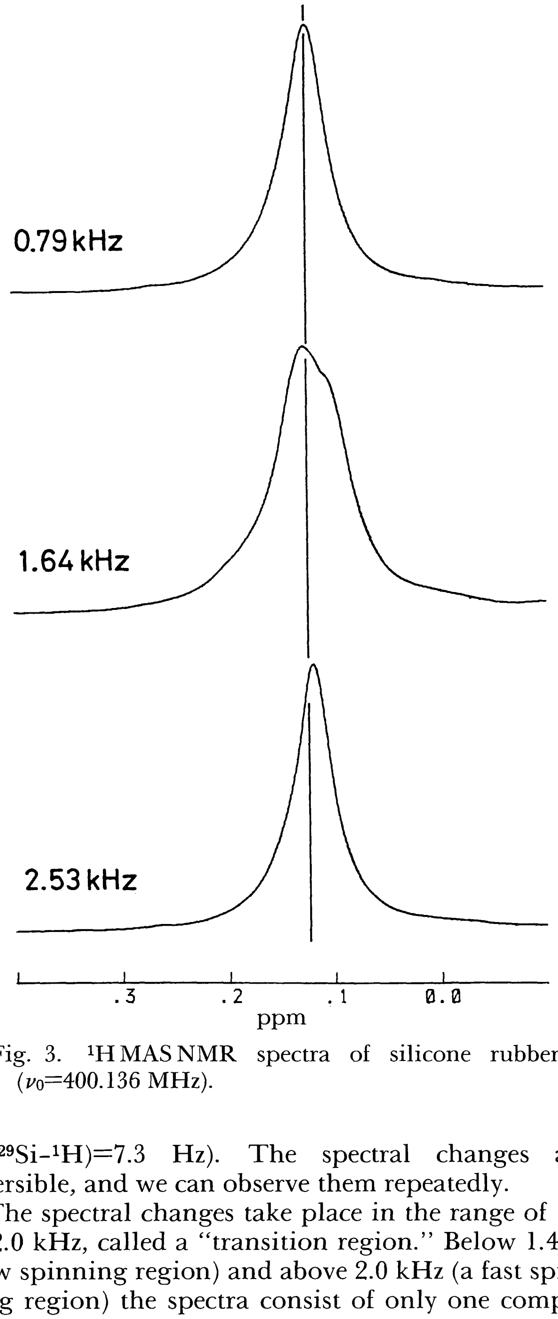

Fig. 3. ^{1}H MAS NMR spectra of silicone rubber (ν_0=400.136 MHz).

which is attributed to methyl groups attached to Si. ^{29}Si MAS NMR spectra have two signals; one is O-Si(CH$_3$)$_2$-O, and the other is amorphous SiO$_2$. The amorphous SiO$_2$ has a broad signal centered at −108 ppm with a full width at half maximum (FWHM) of about 13 ppm, and its mole fraction is 21% of the total Si. The upper limits of the presence of the other species are 2.2, 0.14, and 0.01% for C, Si, and H atoms, respectively, being estimated from the noise levels in the spectra. From these results, it can be concluded that the material is composed of linear polydimethylsiloxane chains and amorphous silica. The density of the sample is 1.17 g cm^{-3}.

Figure 1 shows ^{13}C MAS NMR spectra with ^{1}H decoupling. Note that the spectrum at the spinning rate 1.64 kHz shows line broadening and that the other two spectra have similar narrow linewidths. In the ^{1}H-coupled spectra, the scalar coupling can be observed, whose constant $^{1}J(^{13}\mathrm{C}$-$^{1}\mathrm{H})$ is 118 Hz. The scalar coupling constant does not change with the spinning rate. Similar spectral changes are observed also in ^{29}Si and ^{1}H MAS NMR spectra, as shown in Figs. 2 and 3. The scalar coupling with ^{1}H is observed also in ^{29}Si spectra without decoupling ($^{2}J(^{29}\mathrm{Si}$-$^{1}\mathrm{H})$=7.3 Hz). The spectral changes are reversible, and we can observe them repeatedly.

The spectral changes take place in the range of 1.4 to 2.0 kHz, called a "transition region." Below 1.4 (a slow spinning region) and above 2.0 kHz (a fast spinning region) the spectra consist of only one component, whose line shape is Lorentzian. The spectra between 1.4 and 2.0 kHz have fine structures, which can be deconvoluted into two or three Lorentzian lines. We present only the ^{1}H NMR results in Table 1. The ^{13}C and ^{29}Si results show similar behavior to ^{1}H, although there are no correlations among the three nuclei. From the table and the figures, several trends common to the three nuclei can be extracted:

(1) The chemical shifts in the fast spinning region deviate slightly towards lower frequency from those in the low spinning region.

(2) In the transition region, one component has a higher frequency than the signal in the slow spinning region, and the other has a lower frequency than that in the fast spinning region. Consequently, the spectra in the transition region are not the superposition of those in the slow and fast spinning regions. Apparently, the signal splitting takes place, keeping

Table 1. ^{1}H MAS NMR Results

Spinning rate kHz	No. of components	δ ppm	FWHM ppm	Fraction %
0.79	1	0.122	0.051	
1.01	1	0.123	0.047	
1.20	1	0.124	0.046	
1.64	2	0.128	0.064	88
		0.097	0.029	12
1.68	3	0.132	0.039	62
		0.113	0.018	9
		0.095	0.027	29
2.00	3	0.130	0.061	91
		0.110	0.006	1
		0.097	0.023	8
2.50	1	0.118	0.044	
2.53	1	0.119	0.045	
3.03	1	0.120	0.047	
3.53	1	0.119	0.050	

the weight point almost constant.

As described above, we have recently reported several spinning-induced phenomena. However, in the present case, the stress caused by the spinning is considered to influence the conformation of silicone rubber. Temperature rise induced by the spinning is negligible in the range of the spinning rate used in this work.

Silicone rubber can be regarded as liquid from the standpoint of the NMR measurement. The high flexibility is considered to make the silicone rubber easily influenced by the spinning. The magnitude of the stress, S, can be estimated using the formula presented previously,[5)]

$$S=(1/3)\,\rho r^2\omega_r^2, \qquad (1)$$

where ρ is the density, r is the distance from the spinning axis, and ω_r is the spinning rate expressed in angular frequency unit. In the present case, $\rho=1.17$ g cm^{-3} and $0\leqq r\leqq 0.28$ cm. The maximum stresses just inside the wall of the rotor are 2.4×10^5 and 5.0×10^5 Pa for $\nu_r=1.4$ and 2.0 kHz, respectively.

The characteristics of the present phenomena is that the conformation changes as if there were a phase transition. No monotonic change is observed with the spinning rate. Conformations in the slow and fast spinning regions are homogeneous. In the slow spinning region the conformation is relaxed, while it is deformed in the fast spinning region. The conformation in the transition region is not a mixture of the relaxed and deformed forms, but a kind of "transition form." Several conformations are considered to coexist inhomogeneously in the transition form.

Recently, spinning rates above 20 kHz are possible.[7)] In those cases, more rigid solids than silicone rubber might undergo the similar transition. The maximum stress at $\nu_r=20$ kHz amounts to 5.0×10^7 Pa.

Aside from the range between 1.4 and 2.0 kHz, silicone rubber is a good shift standard. Even in the range between 1.4 and 2.0 kHz, it can be used as a shift standard, since the spectral change of the order of 0.04 ppm is usually negligible if compared with the larger linewidth in normal solids.

In summary, we have found that the conformation in silicone rubber is influenced by the fast spinning in MAS NMR. This effect might become more general as the spinning rate as high as 20 kHz is applied.

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