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STRUCTURE INVESTIGATIONS OF SOLID ORGANOSILICON POLYMERS BY HIGH RESOLUTION SOLID STATE ^{29}Si NMR

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Summary

The high resolution ^{29}Si NMR spectra of five solid silicon polymers of different structure have been studied and the ^{29}Si chemical shifts of characteristic structure units determined. ^{29}Si—^{1}H cross-polarization in combination with high speed magic angle sample spinning and high power proton decoupling was used to achieve high resolution in the solid state spectra. Comparison of the latter with the results obtained in the liquid state clearly indicates that no special solid state effects on ^{29}Si chemical shifts arise and the relations between δ(Si) and the molecular structure, well known from investigations of liquids, can be used for interpretation of the solid state spectra. It is shown that high resolution solid state ^{29}Si NMR spectroscopy offers detailed information about the structural units of the siloxane resin framework, and this opens up new possibilities for structural determinations of solid organosilicon polymers.

Introduction

High resolution ^{29}Si NMR has proved to be a powerful method for structure elucidation of liquids or solutions of oligomeric and polymeric organosiloxanes [1—7]. The information available from this method ranges from a detailed characterization of the different structural units to the determination of average chain lengths or the degree of condensation of the siloxane framework. In the case of linear siloxane copolymers, consisting of siloxy groups with different substituents, the estimation of sequence distribution up to the pentad and heptad level is possible [6,7]. For solid organosilicon resins or other types of

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TABLE 1

^{29}Si CHEMICAL SHIFTS IN SILICONE POLYMERS (ppm from TMS)

No.	Sample		Me MeSiO— Me	Me —OSiO— Me	Ph HOSiO— Ph	OH —OSiO— Me	Me —OSiO— O	OH —OSiO— Ph	Ph —OSiO— O	H —OSiO— O	OH —OSiO— O	O —OSiO— O
			M	D	$M^{Ph_2,OH}$	D^{OH}	T	$D^{Ph,OH}$	T^{Ph}	T^{H}	T^{OH}	Q
I	Methyl-silicone	*a*		−19,4			−65,6/−55,8 [c]					
	resin	*b*		−19,3			−65,3/−55,9 [c]					
II	Methyl-phenyl-	*a*		−17,9	−37.5	−55.2	−64.3	−70.0	−79.3			
	silicone resin	*b*		−17,8/−21,9	−37.0	−54.6	−64.2	−69.7	−78.7			
III	QT-Polymer	*a*					−67,3					
IV	Trimethylsilylated	*a*	12,5									−111/−113
	polysilicic acid										−100.0	−109.6
V	Dioxodisiloxane	*a*								−85.0		

[a] Powder sample at 20°C. [b] Solution in CCl_4. [c] T units in trisiloxane rings (see text).

insoluble organosilicon polymers, dipolar interactions between nuclear spins and anisotropy of the ^{29}Si chemical shift lead to strong line broadening and overlapping and poor signal to noise ratios of the NMR signals, if conventional FT- or CW-NMR methods are used. This makes it impossible to resolve the signals of silicon atoms in different structural units. Recent progress in the application of ^{29}Si—^{1}H cross-polarization techniques in combination with high power proton decoupling and rapid sample spinning at the magic angle has opened the possibility to obtain ^{29}Si NMR spectra with narrow and well resolved lines of solids as well [8,9].

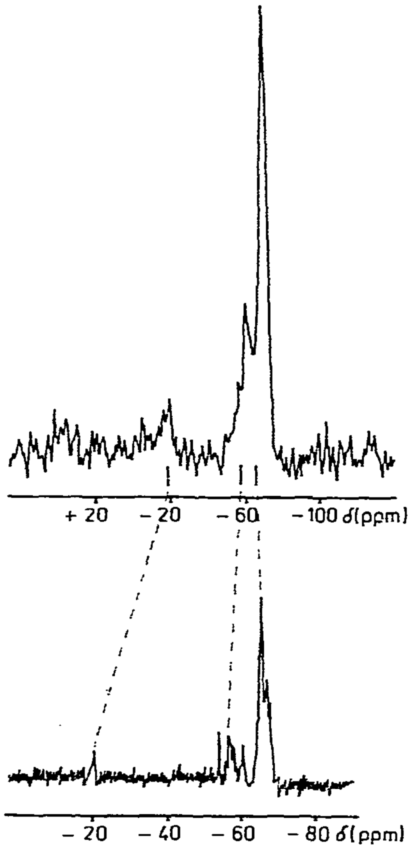
For a general application of this new technique it is of importance to know whether the correlations between ^{29}Si chemical shifts, δ(Si), and the molecular structure derived from investigations in the liquid state are applicable in the case of solid samples, or whether in the latter case some special solid state effects operate, which may lead to specific changes of the δ(Si) values. We have investigated the high resolution ^{29}Si NMR spectra of five representative silicon polymer powders with different structures and have compared the solid state spectra with the NMR results obtained from liquids, either by direct comparison of the spectra or through the use of δ(Si) values of the structural units present in the polymers.

Results and discussion

The investigated compounds I to V and their δ(Si) values are shown in Table 1 together with the assignments of the lines. The solid state ^{29}Si NMR spectra are shown in Figs. 1—5. In Figs. 1 and 2 the ^{29}Si NMR spectra of solutions in CCl_4 of the samples I and II are included. A direct comparison of these spectra shows that in general the same signals with equal δ(Si) values could be observed for both the solutions and solids, although with increased line widths in the solid state. Only the line at $\delta = -21.9$ ppm in compound II could not be observed in the solid state spectrum. This line corresponds to the very flexible D_n chain of dimethylsiloxy groups which cannot be recorded under the cross-polarization conditions used, but can be detected by direct FT techniques. Because of their insolubility, no solution spectra could be obtained from samples III and V. The solution of sample IV shows, even at a 10% concentration, a rather high viscosity and a spectrum of sufficient quality could not be obtained even after 36 h of accumulation.

In all cases the solid state ^{29}Si NMR spectra provide detailed information about the structural units present in the investigated silicon polymers. The highly cross-linked methyl-silicone resin I consists mainly of T units (for the explanation of the symbols see Table 1) with a small admixture of D units. The weaker line at $\delta = -55.8$ ppm can be assigned to T groups in cyclotrisiloxane fragments, because in such trimeric rings a characteristic low field shift of about 9 to 10 ppm has been observed in liquids ($\delta = -55.2$ ppm in the bicyclic T_2D_3) [1,3]. Using the ^{29}Si shifts alone, it could not be excluded that the relatively broad signal at least in part is caused by D^{OH} groups, for which in M_2D^{OH} $\delta = -57.1$ ppm has been measured [4]. However, in the ^{1}H NMR spectra of sample I in CCl_4 solution SiOH groups could not be found.

The (methyl)(phenyl)silicone resin II has a complex structure, consisting of



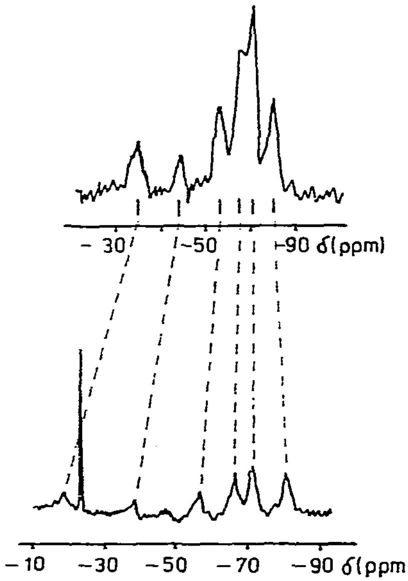


Fig. 1. ^{29}Si NMR spectrum of methyl-silicone resin I; a) solid powder, 1000 scans, pulse repetition rate 1 s, contact time 2.5 ms (total time 17 min). b) 20% solution in CCl_4, 6500 scans, pulse repetition rate 2 s (total time 14.4 h).

Fig. 2. ^{29}Si NMR spectrum of (methyl)(phenyl)silicone resin II; a) solid powder, 1900 scans, pulse repetition rate 1 s, contact time 3 ms (total time 32 min). b) 15% solution in CCl_4, 16100 scans, pulse repetition rate 6 s (total time 26.8 h).

D, T and T^{Ph} units and contains a considerable proportion of unreacted SiOH groups, such as $M^{Ph_2,OH}$, D^{OH} and $D^{Ph,OH}$. Assignment of the D, T and T^{Ph} signals follows unambiguously from investigations of model compounds [2], while the corresponding OH-containing groups can be assigned through the characteristic low field shift of 9 to 10 ppm for SiOH in comparison to SiOSi [4,10,11]. The existence of T and T^{Ph} groups in trisiloxane rings cannot be completely excluded, because of the very similar ^{29}Si shifts.

Sample III consists of a silicon polymer, containing only T and Q groups in a highly cross-linked siloxane framework. In comparison to samples I and II, the signal of the T units is slightly shifted to high field due to the neighbouring Q groups [2]. The position of the Q signal corresponds to that of amorphous silica [9]. This shift confirms the polymeric three-dimensional cross-linked structure of sample III. The observed splittings of the Q signal can be caused by the influence of adjacent T groups, which cause a small low field shift in com-

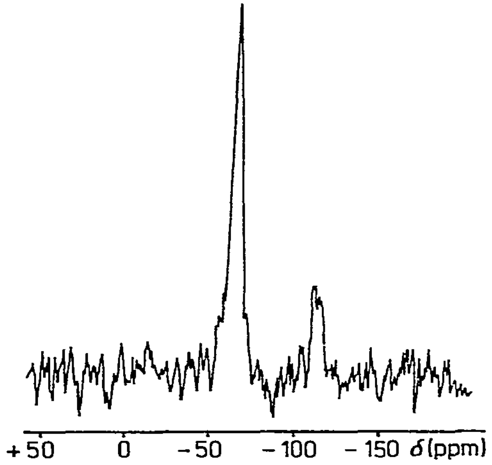
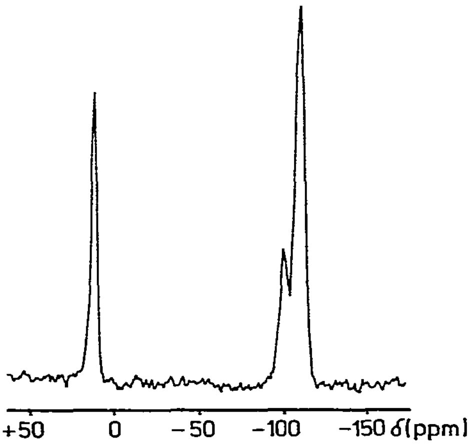


Fig. 3. ^{29}Si NMR spectrum of QT polymer III; solid powder, 3600 scans, pulse repetition rate 1 s, contact time 5 ms.

parison to Q-groups surrounded by other Q units [2].

Sample IV, a trimethylsilylated polysilicic acid, can be regarded as a silicon polymer, consisting of Q and M units, which contains some SiOH groups in the T^{OH} units. The signal of the M units shows a characteristic low field shift due to the adjacent Q units [2], just as in MQ groups in Q_8M_8 and $Q_{10}M_{10}$ [8,12]. This leads to the conclusion that each of the Q groups is connected with only one M unit and it can be assumed that before silylation the polysilicic acid did not contain any substantial numbers of geminal $Si(OH)_2$ groups.

Dioxodisiloxane $(HSiO_{3/2})_n$, V, contains only T^H groups which are connected to double chains consisting of tetrameric rings [13]. To our knowledge



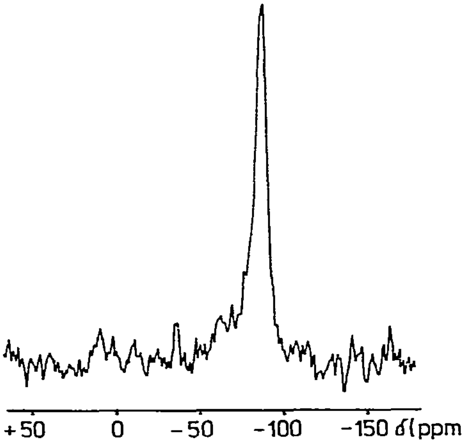


Fig. 4. ^{29}Si NMR spectrum of trimethylsilylated polysilicic acid IV, solid powder, 1800 scans, pulse repetition rate 1 s, contact time 10 ms.

Fig. 5. ^{29}Si NMR spectrum of dioxodisiloxane V, solid powder, 800 scans, pulse repetition rate 1 s, contact time 4 ms.

no compounds with T^H groups have previously been investigated by ^{29}Si NMR, but in a mixture of polysiloxanes obtained by hydrolysis of $HSiCl_3$, one signal at δ = —85.5 ppm was observed [4] which can be assigned to the T^H units in good agreement with our value δ = —85.0 ppm found in the sample V.

The results of our investigations show, in agreement with corresponding investigations of inorganic silicates [9], that in the solid state ^{29}Si NMR spectra of siloxane polymers no additional solid state effects arise. Consequently, the general relationships between ^{29}Si chemical shifts and molecular structure, well known from investigations in the liquid state, can be used for the interpretation of the solid state ^{29}Si spectra. Similar conclusions were reached for the ^{13}C NMR spectra of solid organic compounds [8]. Additional information can be obtained from the solid state spectra if the structure of the solid is different from that in solution (e.g. frozen conformations) or if specific solid-state effects appear (one dimensional conductivity, etc.).

From the experimental point of view the solid state ^{29}Si NMR has the advantage of much shorter measuring times because of the higher sensitivity of the cross-polarization technique, the higher concentration of silicon nuclei in the solid sample and the shorter pulse repetition times. The considerable time saving is clearly demonstrated in the measuring times of the liquid and solid state spectra shown in Figs. 1 and 2.

Experimental

The ^{29}Si NMR spectra of the solutions were measured in the conventional FT-mode with proton noise decoupling at 19.87 MHz using the JEOL PS-100/PFT-180 spectrometer connected to a Nicolet 1085 computer. For shortening of the possibly long T_1 of ^{29}Si, Cr(acac)$_3$ was added to the solution as a relaxation reagent.

The Bruker-Physik CXP-200 solid state high resolution NMR spectrometer was used for the solid state ^{29}Si measurements at 39.75 MHz. The standard ^{13}C Pemas probe, was slightly modified for this purpose. The samples were used as fine powders, placed in the cylindrical cavities of the Andrew-type rotors (total sample volume ca. 0.4 cm^3). The spinning rate used was close to 3 kHz and all measurements were carried out at room temperature with Q_8M_8 as a secondary reference (δ(^{29}Si) of the M groups was taken to equal 11.5 ppm from liquid TMS with no correction for different volume susceptibilities). ^{1}H relaxation times of the polymers are short and only 1 to 2 s time intervals between the r.f. pulse sequences were used. The cross-polarization contact time was varied between 0.5 and 10 ms.

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