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Structure Investigation of Organosilicon Polymers by Silicon-29 NMR

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Summary High resolution silicon-29 NMR is used to study the microstructure of organosiloxane chain copolymers and three-dimensional cross-linked silicone resins. The signal splittings of the Si-29 NMR spectra of methyl-phenyl siloxane copolymers have been assigned to monomer sequences up to the pentad level and the quantitative microstructure parameters have been estimated. It is shown that Si-29 NMR offers valuable information on the polymer framework of silicone resins both in the liquid and in the solid state.

High resolution Silicon-29 NMR has proved to be a powerful tool for structural elucidation of organic and inorganic silicon compounds (for a recent review see HARRIS 1979). Because of the high structural sensitivity of Si-29 chemical shifts, detailed information can be obtained on the structural surroundings of a given silicon atom in a complex molecular framework. This can be used to study microstructural details of organosilicon polymers consisting of a network of SiOSi linkages connected in chains or branched and crosslinked structures.Some earlier work in this field have been reported by ENGELHARDT et al. (1973) and by HARRIS and KIMBER (1974,1975), and more recently by HARRIS and ROBINS (1978) and JANCKE et al. (1979). In this paper some new results on the quantitative microstructure analysis of linear methyl-phenyl siloxane copolymers (silicone oils) and structure investigation of three-dimensional crosslinked silicon resins will be reported.

Depending on the number of OSi-bonds connected with a given

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Si atom, the basic monomer units of methyl polysiloxanes can be divided into four different groupings denoted conventionally by the symbols M, D, T and Q which stand for $me_3SiO_{0.5}$, $me_2Si(O_{0.5})_2$, $meSi(O_{0.5})_3$, and $Si(O_{0.5})_4$ units, respectively. The replacement of one or more methyl groups at the silicon atom by other substituents X is indicated by a superscript, e.g. M^X, $M^{X}2$, D^X and T^X stand for $me_2XSiO_{0.5}$, $meX_2SiO_{0.5}$, $meXSi(O_{0.5})_2$, and $XSi(O_{0.5})_3$ units, respectively.

In Figure 1 the typical silicon-29 chemical shift ranges for the four basic units M, D, T, and Q are summarized together with a series of X-substituted groups commonly used in silicone polymers of practical interest. As can be seen from the Figure, well separated ranges of chemical shifts appear which gives the possibility to determine the type and - by means of signal intensities - the quantitative distribution of the different mono mer units present in a polymer sample. From the quantitative ratio of M and D groups the main chain length and from the D/T ratio the degree of branching of the polymer can be estimated.

In the lower part of Figure 1 some second order effects on chemical shifts of M, D, T and Q units are shown caused by neighbour groups and cyclisation. Similar effects can be observed for the X-substituted units. These relations offer valuable insights in subtle details of the polymer structure.

In organosiloxane chain copolymers consisting of D and D^X units (and possibly some M groups as end stoppers), the chemical shift of a given Si atom is affected by the type of the first neighbour groups and the triad structure of the copolymeric chain can be recognised by characteristic triplet splittings in the Si-29 NMR spectra. Moreover, the influence of the second neighb-ouring group can cause a further triplet splitting of each of the triad lines, i.e. pentad structures are represented in the spectra by a triplet of triplets. This is shown schematically in Figure 2 under the assumption of equal amounts and random distribution of D (denoted by A) and D^X (denoted by B) units in the copolymeric chain.

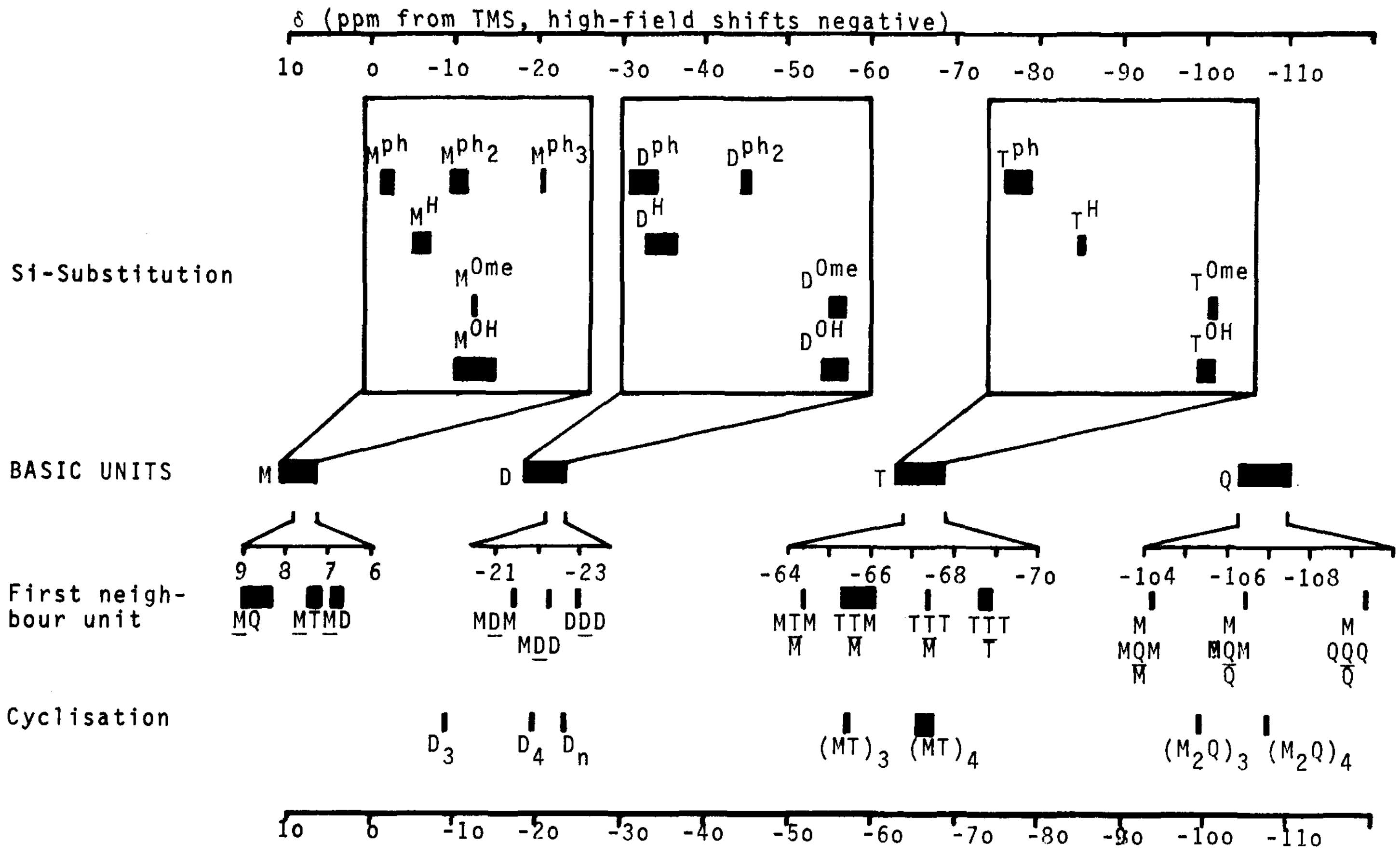

Figure 1. Structure correlations of Si-29 chemical shifts

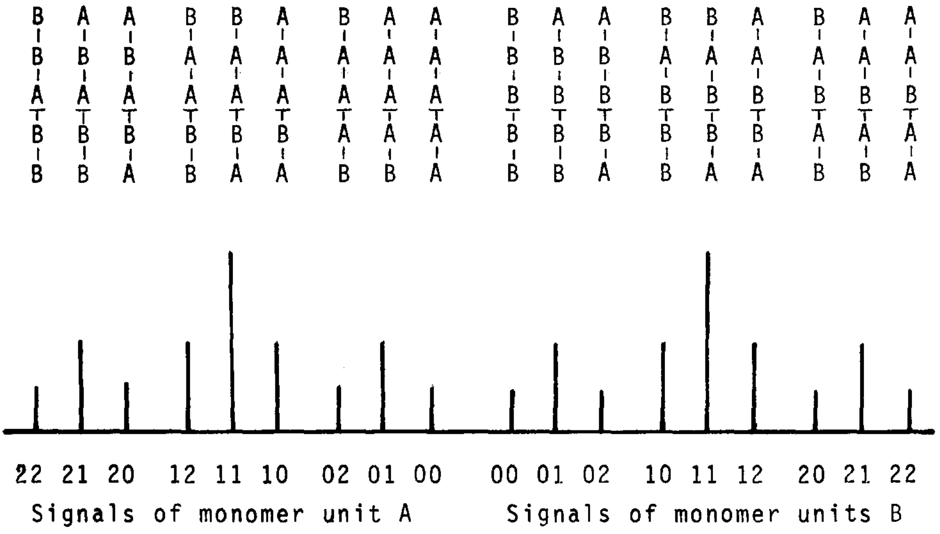

Figure 2. Signal assignment for pentad sequences

The main point for further evaluation of the spectra with respect to the quantitative microstructure analysis is the assignment of the signals to the corresponding triad and pentad sequences. In the case of methyl-phenyl siloxane copolymers investigated in this study, it has been shown by model compounds that increasing numbers of D^{ph} or D^{ph2} units in the neighbourhood of a given D or D^{ph} unit lead to low-field shifts of its Si-29 NMR signal (ENGELHARDT et al. 1973). By means of this regularity a full assignment of all the pentad lines present in the spectra of different types of methyl-phenyl silicone oils could be performed.

As an example the 39.75 MHz Si-29 NMR spectrum of the methyl-phenyl silicone oil OV-7 is shown in Figure 3. The spectrum exhibits three groups of well resolved signals corresponding to the M, D and D^{ph} units present in the polymer chain. The M-group gives four signals according to the four different arrangements of the next two D/D^{ph} units near the chain end (see Fig.3). The D an D^{ph} signal show the expected splittings for the nine different pentad sequences given in Figure 2. The left part of the D^{ph} signal shows line broadening effects probably due to different steric orientations of the closely adjacent phenyl groups.

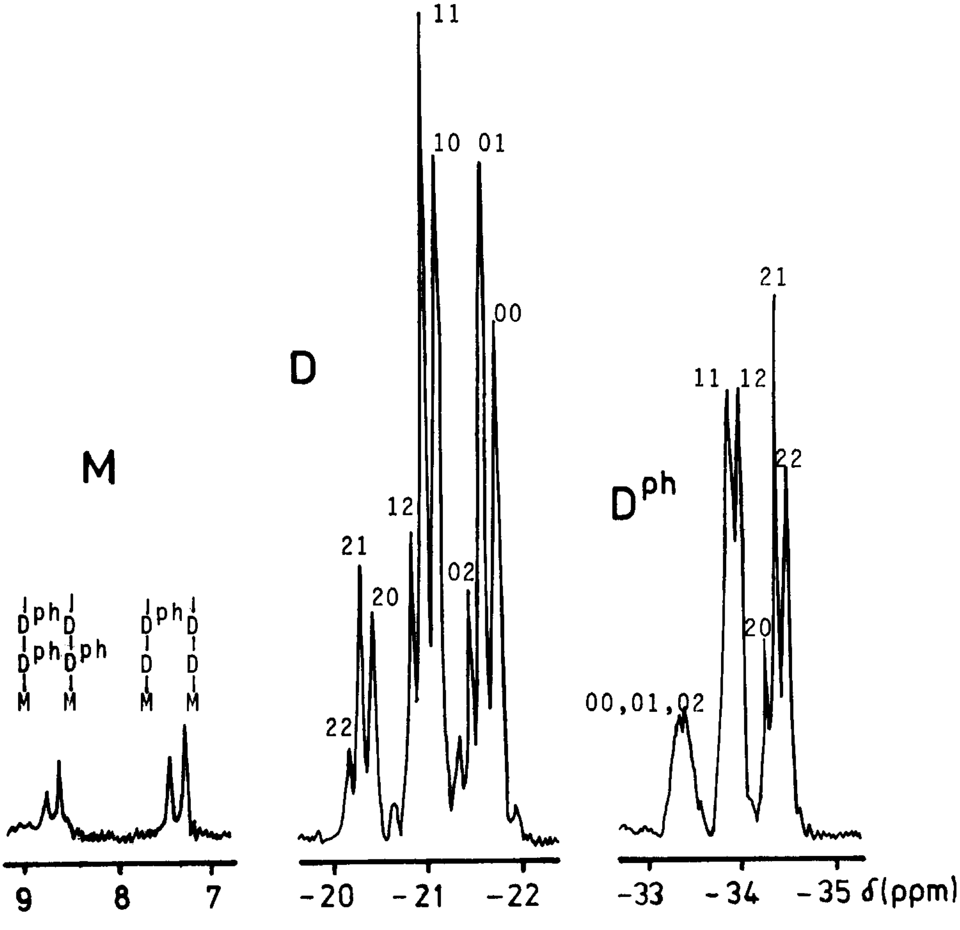

Figure 3. Si-29 NMR spectrum of methyl-phenyl silicone oil OV-7

The signal intensities of the pentad (F_{kl}) or triad (F_k) signals can be used to calculate the quantitative parameters describing the microstructure of the copolymeric chain, i.e.

- Mole fraction of the monomer units, A_M and B_M
- Run number R, giving the average number of monomer sequences (runs) occuring in a polymer per 1oo monomer

units (HARWOOD and RITCHEY 1964)
- Number average sequence length, $\bar{l}_A$ and $\bar{l}_B$
- Linkage probabilities p_{ij}

Using the run number concept according to HARWOOD and RITCHEY (1964), the following equations have been derived (JANCKE et al. 1979):

$$A_M = 100k_B/(k_A + k_B) \qquad B_M = 100 - A_M$$

$$R_{exp} = k_A A_M = k_B B_M \qquad R_{rand} = A_M B_M/50$$

where k_i is given by different combinations of the triad signal intensities $F_k = \Sigma F_{kl}$, e.g.
$k_i = 4F_2/(2F_2 + F_1) = 2F_1/(F_1 + 2F_0) = 2\sqrt{F_2/\Sigma F_k}$ etc.

$$\bar{l}_A = 2A_M/R \qquad \bar{l}_B = 2B_M/R$$

$$p_{AA} = (A_M - R/2)/A_M \qquad p_{BB} = (B_M - R/2)/B_M$$

$$p_{AB} = R/2A_M \qquad p_{BA} = R/2B_M$$

The Table gives the full set of microstructure parameters for six different methyl-phenyl silicone oils of the OV-type (Applied Science Lab.Inc.) and the mean molecular composition derived from the ratio of the signal intensities of the different units present in the polymer chain. In some samples small admixtures of low molecular weight cyclic siloxanes could be detected by characteristic signals well separated from the signals of the copolymer. From the comparison of the estimated run numbers R_{exp} with the run numbers for random distribution R_{rand} it can be concluded that the distribution of the monomer units in the copolymer chain is randomly, except OV-61 where a tendency towards an alternating distribution of the D and D^{Ph_2} units has been observed ($R_{exp} > R_{rand}$).

Silicon-29 NMR can also be used for structure investigation of three-dimensional branched and crosslinked silicone polymers in the liquid (solution) and solid state. Figure 4a shows the Si-29 NMR spectrum of a methyl silicone resin in CCl_4 solution. The strong signal at -64 ppm represents T units in the polymeric framework, mainly connected to cyclotetrasiloxane struc-

TABLE

Microstructure parameters of OV-type methyl-phenyl silicone oils

Sample	OV-7	OV-3	OV-22	OV-25	OV-61	OV-17
A	D	D	D^{ph}	D^{ph}	D	D^{ph}
B	D^{ph}	D^{ph}	D^{ph_2}	D^{ph_2}	D^{ph_2}	-
A_M	58.9	83.4	73.1	47.7	64.4	100
B_M	41.1	16.6	26.9	52.3	35.6	-
R_{exp}	48.9	27.5	39.2	48.6	49.5	-
R_{rand}	48.4	27.6	39.3	49.9	45.9	-
$\bar{l}_A$	2.4	6.1	3.7	2.0	1.4	-
$\bar{l}_B$	1.6	1.2	1.4	2.2	0.64	-
p_{AA}	0.585	0.835	0.732	0.491	0.616	-
p_{BB}	0.405	0.172	0.271	0.535	0.305	-
p_{AB}	0.415	0.165	0.268	0.509	0.384	-
p_{BA}	0.595	0.828	0.729	0.465	0.695	-

Mean molecular composition: OV-7: $M_2D_{58}D^{ph}_{42}$, OV-3: $M_2D_{100}D^{ph}_{20}$; OV-22: $M_2D^{ph}_{20}D^{ph_2}_{7}$, OV-25: $M_2D^{ph}_{11}D^{ph_2}_{12}$; OV-61: $(D_9D^{ph_2}_5)_n$, OV-17: $M_2D^{ph}_{11}$.

tures (see Fig.1). The weaker lines shifted to low field can be assigned to T units in cyclotrisiloxane fragments and D^{OR} groups due to incomplete condensation of the reactive sites during the formation process of the resin. In Fig.4b the spectrum of the solid powder of the same silicone resin is shown, measured by cross-polarization (CP) in combination with high speed magic angle spinning (MAS) and high power proton decoupling (DD). Apart from some signal broadening in the solid state spectrum the high similarity of both spectra is evident.

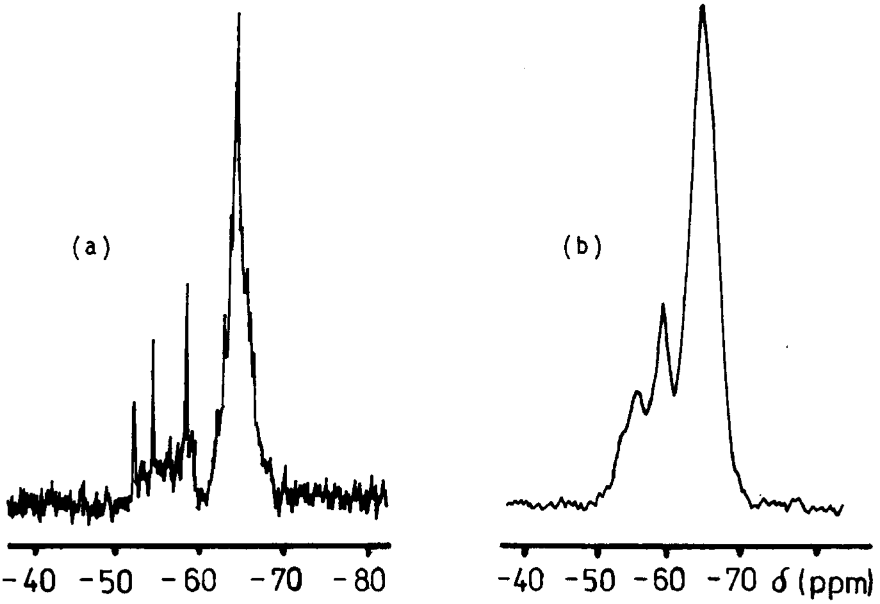

Figure 4. Si-29 NMR spectra of methyl silicone resin in CCl_4-solution (a) and in the solid state (b)

This demonstrates that the structure investigation of silicon polymers by Si-29 NMR is not confined to the liquid state but is likewise well applicable to solid polymers (ENGELHARDT et al. 1981).

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