Journal of Organometallic Chemistry, 70 (1974) 43—49

^{29}Si NUCLEAR MAGNETIC RESONANCE STUDIES OF SOME OLIGO- AND POLYMERIC SILOXANES

ROBIN K. HARRIS and BARRY J. KIMBER
School of Chemical Sciences, University of East Anglia, Norwich, NOR 88C (Great Britain)
(Received September 21st, 1973)

Summary

^{29}Si chemical shift data are reported for the lower members of two series of simple silicone polymers containing dimethylsiloxy (D) units and methylsiloxy (D′) units respectively. With this information as a basis it proved possible to assign spectra due to longer-chain mixed (D/D′) silicone polymers. Details of the microstructure were obtained.

Introduction

Relatively little attention has been given to the study of silicone polymers by ^{29}Si nuclear magnetic resonance (NMR) spectroscopy, although it was initially shown that much information could be obtained [1]. The reason for this lack of interest was that ^{29}Si NMR spectra were experimentally difficult to acquire by direct observation, since the ^{29}Si nucleus has both a low natural abundance (4.7%) and a low magnetogyric ratio (-5.314×10^7 rad T^{-1} s^{-1}). Recent technical developments, particularly the introduction of Fourier Transform (FT) NMR spectrometers [2], have overcome to a large extent many of the sensitivity difficulties, so that ^{29}Si spectra may now be obtained routinely [3—6].

We are carrying out an investigation into the distribution of methyl hydrogen siloxy groups, $HMeSi(O_{0.5})_2$ (D′ units), and of dimethylsiloxy groups, $Me_2Si(O_{0.5})_2$ (D units [7]), within trimethylsiloxy, $Me_3SiO_{0.5}$ (M units [7]) end-stopped polymers of general composition $M(D_xD'_y)M$, which are formed by equilibration [8]. Since a wide molecular weight distribution is obtained from an equilibration mixture [9], no exact chemical formula may be used; however the average expected content may be represented by $Si_{(x+y+2)}H_y$. (This is not, of course, a chemical formula; $(x+y+2)$ is the average chain length, so that x and y need not be integers.) The present paper deals with results which have been obtained for some low molecular weight linear polysiloxanes.

TABLE 1

^{29}Si CHEMICAL SHIFTS (in ppm) FOR POLYMERS OF THE TYPE MD$_x$M [a,b]

	M	D^1	D^2	D^3
MD$_1$M	6.61	−21.46		
MD$_2$M	6.78	−22.08		
MD$_3$M	6.86	−21.91	−22.67	
MD$_4$M	6.86	−21.86	−22.50	
MD$_5$M	7.06	−21.80	−22.27 [c]	
MD$_6$M	6.91	−21.81	−22.41 [c]	

[a] The D or D′ units are numbered from the ends of the compounds, e.g. MD^{1}D^{2}D^{1}M. [b] The results are estimated to be accurate to ±0.05 ppm. [c] D^2 and D^3 resonances not resolved.

Results

When this work was started there was very little chemical shift data in the literature [10], so that it was necessary to study some simple systems prior to investigating the mixed polymers. The chemical shifts for the series MD$_x$M (x = 1—6) and MD$'_y$M (y = 1—6) are reported in Tables 1 and 2 respectively, relative to tetramethylsilane, with positive values when the sample resonates to high frequency of the reference.

These results are in substantial agreement (within 0.15 ppm) with those of Levy and Cargioli [11] in the case of the MD$_x$M system (there are no published values for the MD$'_y$M system to our knowledge). It is clear that M, D and D′ give resonances in greatly differing regions of the spectrum.

The ^{29}Si—{^{1}H} spectra obtained for the D′ region of MD$'_y$M (y = 4, 5, 6) are shown in Fig. 1; the intensities are inverted because of the Nuclear Overhauser Effect (NOE) [12—14], which is strong for the D′ units since they contain a direct Si—H bond. The existence of the NOE causes difficulties in the quantitative use of ^{29}Si NMR. This problem may be circumvented by the addition of a shiftless relaxation reagent, such as Cr(acac)$_3$, which provides a more efficient relaxation mechanism than the (Si, H) dipolar interaction mechanism which is responsible for the NOE. Actually the effect of Cr(acac)$_3$ is two-fold: firstly, it quenches the NOE, secondly it reduces all spin-lattice relaxation times (T_1's) to approximately the same value, thus allowing quantitative intensity measurements, even when the FT pulse repetition rate is significantly shorter than $5T_1$ for the nucleus relaxing most slowly [15]. We have found,

TABLE 2

^{29}Si CHEMICAL SHIFTS FOR POLYMERS OF THE TYPE MD$'_y$M [a]

	M	D$'^1$	D$'^2$	D$'^3$
MD$'_1$M	8.72	−36.86		
MD$'_2$M	9.32	−36.41		
MD$'_3$M	9.52	−36.00	−35.15	
MD$'_4$M	9.57	−35.90	−35.55	
MD$'_5$M	9.63	−35.90	−35.40	−35.09
MD$'_6$M	9.63	−35.85	−35.40	−34.99

[a] See the footnotes to Table 1.

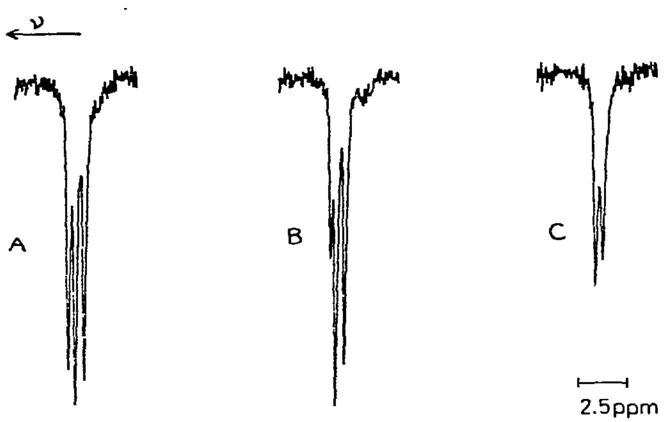

Fig. 1. ^{29}Si—{^{1}H} spectra (D′ region only) of: A. MD′$_6$M, 5*k* pulses. B. MD′$_5$M, 3*k* pulses. C. MD′$_4$M, 2*k* pulses; (All as neat liquids, using a pulse interval of 1.7 s).

in agreement with Levy [16], that a concentration of 0.02—0.04 *M* Cr(acac)$_3$ is sufficient for these purposes.

In principle the D′ units could give rise to tacticity effects, but we have not detected complications from this origin for any of our samples.

Mixed polymers

The silicon-29 NMR spectra have been obtained for several mixed polymers, of differing chain lengths and differing D/D′ ratios, using proton noise-decoupling and Cr(acac)$_3$. The polymers used in this study were 10—50 units long; the distribution of chain lengths within an equilibrated fluid is large and consequently the term chain length should not be thought of as definite. On the basis of the chemical shifts in Tables 1 and 2 we have been able to assign several microstructures within each of the spectral regions. Triad structures have been observed previously for dimethyl- and phenylmethyl-siloxanes [17].

(a). M units

The M units show what we shall call a pseudo-heptad structure, as can be seen in Fig. 2: detectable differences in chemical shift are observed between structures which differ only in the third group from the M unit at resonance. The chemical shifts are reported in Table 3. If the polymer chain is numbered as follows:

$\underline{\mathrm{M}}$—D—D—D
1 2 3

then additivity rules may be drawn up for changes in substitution. If D^{1} is changed to D′, D^{2} to D′, or D^{3} to D′ the M resonance moves to higher frequency by 43, 8 or 2 Hz respectively.

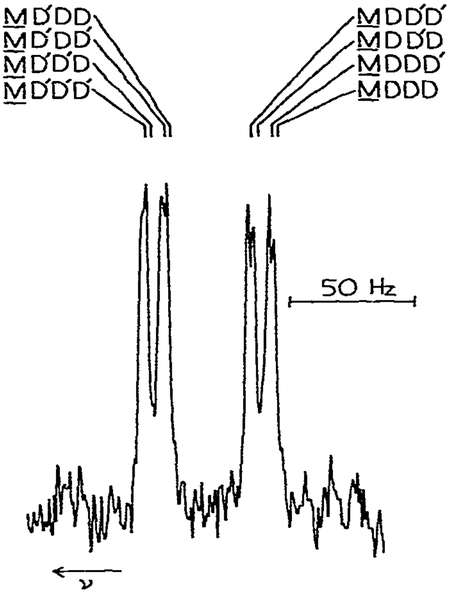

Fig. 2. ^{29}Si—{^{1}H} spectrum of $\mathrm{Si_{18}H_8}$(in $\mathrm{CH_2Cl_2}$ with 0.02 *M* $\mathrm{Cr(acac)_3}$) showing the microstructure for the M units. The ratio of D/D' is 1/1. 21*k* pulses were used, with a pulse interval of 1.8 s and a sensitivity enhancement of 1.0 s.

TABLE 3

^{29}Si CHEMICAL SHIFTS FOR THE MIXED POLYMERS [a,b]

Unit	δ(Si) (ppm)[c]
$\mathrm{\underline{M}D'D'D'}$	9.71
$\mathrm{\underline{M}D'D'D}$	9.61
$\mathrm{\underline{M}D'DD'}$	9.33
$\mathrm{\underline{M}D'DD}$	9.18
$\mathrm{\underline{M}DD'D'}$	7.57
$\mathrm{\underline{M}DD'D}$	7.47
$\mathrm{\underline{M}DDD'}$	7.17
$\mathrm{\underline{M}DDD}$	7.07
$\mathrm{D'D'\underline{D}D'D'}$	−18.81
$\mathrm{DD'\underline{D}D'D'}$	−19.02
$\mathrm{DD'\underline{D}D'D}$	−19.28
$\mathrm{D'D\underline{D}D'D'}$	−20.13
$\mathrm{DD\underline{D}D'D'}$ and $\mathrm{D'D\underline{D}D'D}$	−20.41
$\mathrm{DD\underline{D}D'D}$	−20.65
$\mathrm{D'D\underline{D}DD'}$	−21.46
$\mathrm{D'D\underline{D}DD}$	−21.76
$\mathrm{DD\underline{D}DD}$	−22.03
$\mathrm{D'\underline{D}'D'}$	−35.19
$\mathrm{D\underline{D}'D'}$	−36.27
$\mathrm{D\underline{D}'D}$	−37.35

[a] The results are considered to be accurate to ±0.05 ppm [b] The unit observed is underlined. [c] These values are corrected (as described in the text) to be effectively neat liquid data.

(b). D units

The D units show a pentad structure, as can be seen in Fig. 3. If a D adjacent to the group at resonance is changed to D′ there is a shift to higher frequency of 26 Hz. There is a shift of 5 Hz for substitution at position 2 in the structure:

$$\begin{array}{ccccc} \text{D—} & \text{D—} & \underline{\underline{\text{D}}}\text{—} & \text{D—} & \text{D} \\ & & & 1 & 2 \end{array}$$

The chemical shifts are given in Table 3.

(c) D′ units

We have observed a triad structure in the D′ region, together with some extra structure (possibly pentad) which as yet we have been unable to assign (see Fig. 4). The chemical shifts are reported in Table 3. Substitution of D′ for D adjacent to the group at resonance causes a shift of 20 Hz to high frequency.

The intensities for all microstructures are in good agreement with those expected on probability grounds. For example when the D/D′ ratio is 1/1, the probabilities of obtaining each of the end group structures will be equal; this can be seen to be so in Fig. 2. (Some intensity anomalies occur as a result of both the digital nature of the FT spectrum and of the overlapping of resonances.) We therefore suppose that randomization has to a large extent occurred during equilibration. When the D to D′ ratio is high no significant peak is ob-

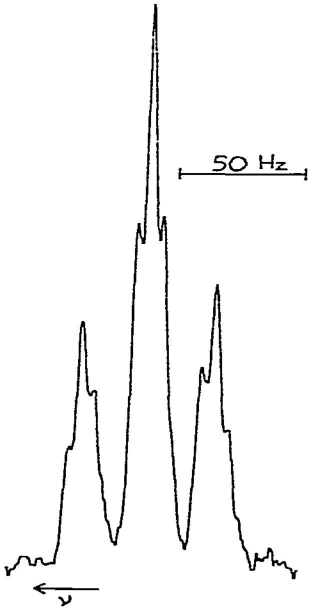

Fig. 3. ^{29}Si—{^{1}H} spectrum of $Si_{18}H_8$ (D region). Same conditions as for Fig. 2, except that the vertical scale has been increased by a factor of 3. For the detailed assignment of the spectrum see Table 3.

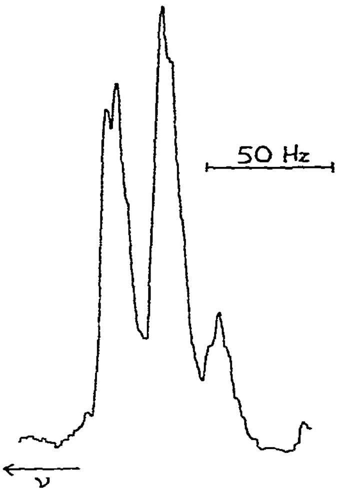

Fig. 4. ^{29}Si—{^{1}H} spectrum of $Si_{18}H_{11}$ (D′ region) for a solution in CH_2Cl_2 containing 0.02 *M* Cr(acac)$_3$. The ratio D/D′ is 5/11. 24*k* pulses were used, with a pulse interval of 1.8 s and a sensitivity enhancement of 1.0 s.

served for D′$\underline{\text{D}}$′D′, and similarly for D$\underline{\text{D}}$′D when the ratio is low. Thus D′ units are not in a block structure within the polymer.

Experimental

The spectra were obtained using a Varian XL100-15 NMR spectrometer operating in the FT mode at 19.87 MHz using 12 mm OD sample tubes with D_2O external lock. The use of an external lock is of particular value where the number of spectra recorded is large and where the addition of a suitable locking compound would limit the solubility of the Cr(acac)$_3$. The external lock arrangement was as follows: a 12 mm Vortex stopper (Wilmad Type 805E) was drilled out so that a sealed 5 mm Microcell (Kontes Glass Co. Catalogue no. K-897025) containing D_2O, could be secured in it. This assembly was inserted into the NMR tube. When the external lock was used it was discovered that the relaxation reagent was not in fact ‘shiftless’; the resonance is shifted to high frequency by the presence of CH_2Cl_2 (ca. 8 Hz) and to low frequency by the Cr(acac)$_3$ (ca. 3 Hz). The shift was corrected by subtracting 5 Hz from the line positions (5 Hz was found to be the difference between neat and doped samples). The chemical shifts were calculated from the line positions in proton noise-decoupled spectra at ambient probe temperature (37°). The MD_xM samples were bubbled with oxygen prior to use since this partially quenches the NOE [16]. The MD'_yM series were bubbled with N_2 since because they have a large NOE this gives better *S*/*N*. For the mixed polymers CH_2Cl_2 was used as solvent and Cr(acac)$_3$ was added to ca. 0.02 *M* concentration. The MD_xM and MD'_yM samples were used as neat liquids.

The mixed polymers were prepared by the equilibration of hexamethyldisiloxane (MM), octamethylcyclotetrasiloxane (D_4), and a polymethylhydrogensiloxane ($MD'_{50}M$) in the presence of slightly acidified Fullers’ earth catalyst. The polymers were stripped under vacuum to remove the low molecular weight monomers, which would otherwise confuse the assignments. The stripping lowers the M content of the polymer, but does not change the D/D′ ratio appreciably.

Conclusions

The results show that the silicon nucleus in a siloxane chain is susceptible to changes in substitution at up to six bonds (in the case of M units) and four bonds (in the case of D units) removed from the silicon nucleus at resonance. This indicates that much information is available, using this technique, about the microstructure of the molecular skeleton, since local pentad and triad patterns may be detected. At present work is being carried out to study the distribution of D′ units within mixed polymers as a function of equilibration time.

Acknowledgements

One of us (BJK) is grateful to the U.K. Science Research Council and to I.C.I. (Organics Division) for the award of a Research Studentship under the C.A.P.S. scheme. The compounds used have all been supplied by the Technical Development Department (Silicones Section) of I.C.I. Organics Division and we thank the members of that group not only for the compounds but also for fruitful discussions.

References

1 P.C. Lauterbur, in F.C. Nachod and W.D. Phillips (eds.), Determination of organic structures by physical methods, Vol. 2, Academic Press, London and New York, 1962, p. 511—515.
2 D.G. Gillies and D. Shaw, Annu. Rep. NMR Spectrosc. A, 5 (1972) 557.
3 G. Engelhardt, H. Jancke, M. Mägi, T. Pehk and E. Lippmaa, J. Organometal. Chem., 28 (1971) 293.
4 G.C. Levy, J. Amer. Chem. Soc., 94 (1972) 4793.
5 R.L. Scholl, G.E. Maciel and W.K. Musker, J. Amer. Chem. Soc., 94 (1972) 6376.
6 H.G. Horn and H.C. Marsmann, Makromol. Chem., 162 (1972) 255.
7 C.B. Hurd, J. Amer. Chem. Soc., 68 (1946) 364.
8 D.W. Scott, J. Amer. Chem. Soc., 68 (1946) 2294.
9 J.B. Carmichael and J. Heffel, J. Phys. Chem., 69 (1965) 2218.
10 B.K. Hunter and L.W. Reeves, Can. J. Chem., 46 (1968) 1399.
11 G.C. Levy and J.D. Cargioli, Proceedings of the N.A.T.O. Advanced Study Institute, Italy, 1972.
12 J.H. Noggle and R.E. Schirmer, The Nuclear Overhauser Effect, Academic Press, New York, 1971.
13 K.F. Kuhlmann, D.M. Grant and R.K. Harris, J. Chem. Phys., 52 (1970) 3439.
14 R.K. Harris and B.J. Kimber, J. Chem. Soc., Chem. Commun., (1973) 255.
15 R. Freeman, K.G.R. Pachler and G.N. La Mar, J. Chem. Phys., 55 (1971) 4586.
16 G.C. Levy, J.D. Cargioli, P.C. Julian and T.D. Mitchell, J. Magn. Resonance, 8 (1972) 399.
17 G. Engelhardt, M. Mägi and E. Lippmaa, J. Organometal. Chem., 54 (1973) 115.