^{29}Si nuclear magnetic resonance studies of oligomeric and polymeric siloxanes: 4. Chemical shift effects of end-groups

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^{29}Si n.m.r. spectra have been obtained for mixtures of polysiloxane oligomers in four cases, viz. MD_nM, $M^HD_nM^H$, $M^{OH}D_nM^{OH}$ and MD^H_nM. Spectral dispersion is best (under the conditions studied) for the $M^{OH}D_nM^{OH}$ series, where signals due to oligomers up to $n = 9$ have been separately detected. The spectra have been fully assigned, and shift effects due to the end-groups (equivalent to shifts expected in long chain polymers) have been derived. The significance of the data is discussed.

INTRODUCTION

The technique of Fourier Transform (*FT*) n.m.r. has now become well established as a powerful method for the characterization of polymeric systems. The majority of the literature focusses, in particular, on the use of ^{13}C *FT* n.m.r. as an aid to the analysis of organic polymers and copolymers. The direct observation of ^{13}C resonances from the backbone of polymer chains has proved to be a highly informative source of structural information.

By far the most important area of organosilicon chemistry involves the study of polymers based on the Si–O–Si linkage, and nearly all of the commercially important silicon polymers contain this linkage as the polymeric backbone. Polymers of this type are known as silicones or polysiloxanes. The ^{29}Si nucleus is magnetically active, with a spin of ½ and a natural abundance of 4.7%. Despite this low natural abundance the inherent sensitivity and accumulation advantages associated with *FT* n.m.r. mean that the nucleus is amenable to study[2]. It is this fact, coupled with the presence of silicon in the polymeric backbone, which has led to several studies of silicones using *FT* n.m.r. techniques[3].

In part 1 of this series[4] ^{29}Si chemical shifts were reported for dimethylsiloxy groups, $Me_2Si(O_{0.5})_2$ (D units[5]), and trimethylsiloxy groups, $Me_3SiO_{0.5}$ (M units[5]) in several short-chain linear poly(dimethyl siloxanes), MD_nM($n = 1$ to 6). Other workers have also reported ^{29}Si chemical shifts for the same series of oligomers[6–9] and for others[1,9]. Common to all of these studies is the determination of ^{29}Si chemical shifts from measurements on individual oligomers, i.e. not using mixtures of oligomers. However, most silicones are prepared by equilibration techniques, so a typical polymeric silicone will contain a whole range of oligomers (in which case we can define $\bar{n}$ as the average number of internal units).

We have therefore studied some equilibrated mixtures of homo-oligomers of general formula $M^xD^y_nM^x$, where x and y designate substituents replacing methyl groups in M and D units, using ^{29}Si n.m.r. We have assigned the resonances to the individual units present in the various oligomers, and are therefore able to tabulate the chemical shifts and discuss them in terms of the length of the chains and the position of the units in the chains. The nature of the end stopper units clearly affects the shifts; we have studied systems with M or M^{OH} ($\equiv HOMe_2SiO_{0.5}$) or M^H ($\equiv HMe_2Si_{0.5}$) as end stoppers. One advantage of studying *mixtures* of oligomers is that differential medium effects (including those due to interactions between silicone molecules) on the resonances are minimized. It is hoped that the results presented will (a) enable the constituents of mixtures of such oligomers to be clearly identified via measurement of ^{29}Si n.m.r. spectra, and (b) further the understanding of the factors affecting the shifts. The data are also of clear relevance to the evaluation of chain lengths for mixtures of medium- or long-chain silicones, such as are of commercial importance, via direct observation of ^{29}Si n.m.r. resonances of units near the chain ends (as illustrated in part 2 of this series[10]).

In all we have examined four series of mixed oligomers, viz. MD_nM, $M^HD_nM^H$, $M^{OH}D_nM^{OH}$ and MD^H_nM. For some of these series samples with different $\bar{n}$ have been studied, but the results were very similar. In order to facilitate the discussion it is essential to define the terms to be used and the situations investigated, as in the next section.

NOMENCLATURE, DEFINITIONS AND INITIAL CONSIDERATIONS

Firstly we shall consider intra-series shifts. The parent series MD_nM will be taken as an example. The main-chain units will be numbered in accordance with their position from the nearest end-group, thus:

MD(1)D(2)D(3) ....

The unit whose resonance is under discussion will be indicated by underlining, for instance the oligomer MD_3M will be written $MD\underline{D}DM$ when the D(2) resonance is referred to. Comparison of the shift for a given unit in oligomers of length differing by one siloxane linkage implies examination of a substituent shift. For the MD_nM series this substitution is of the type $Me \rightarrow Me_3SiO$. Clearly a major influence on such shifts will be the distance of the substitution from the group examined. The effect on the silicon of the group neighbouring that at which substitution takes place is defined as a '*b*' shift, e.g.:

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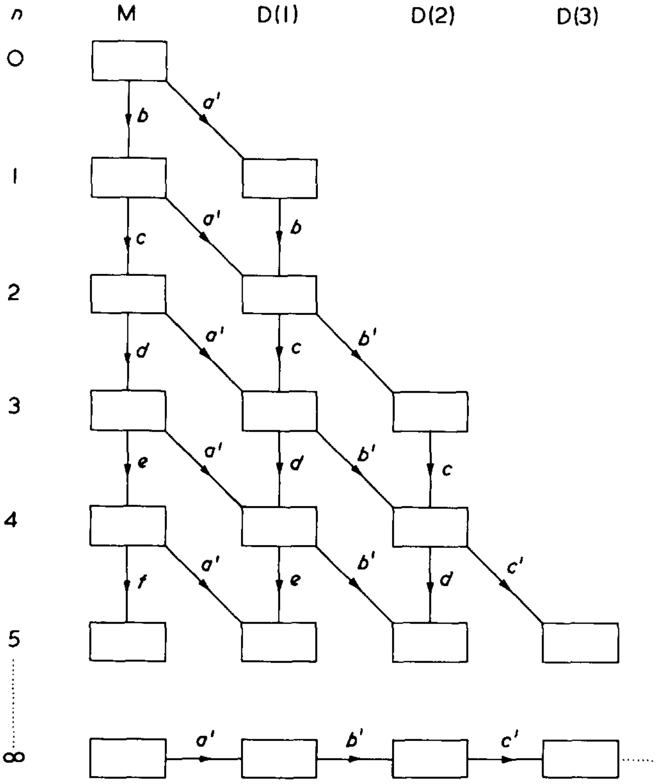

Figure 1 Scheme of designation for ^{29}Si n.m.r. substituent shifts in linear polysiloxanes of type $\mathrm{MD}_n\mathrm{M}$ (and analogous series)

$$\delta(\mathrm{M\underline{D}DM}) - \delta(\mathrm{M\underline{D}M}) \qquad b \text{ for unit D(1)}$$

Shifts at groups further removed from the substitution site are designated *c*, *d*, etc., e.g.

$$\delta(\mathrm{MD\underline{D}DDM}) - \delta(\mathrm{MD\underline{D}DM}) \qquad c \text{ for unit D(2)}$$

$$\delta(\mathrm{M\underline{D}DDDM}) - \delta(\mathrm{M\underline{D}DDM}) \qquad d \text{ for unit D(1)}$$

Resonances of end-groups can be used for a similar description of substituent effects:

$$\delta(\mathrm{\underline{M}DDM}) - \delta(\mathrm{\underline{M}DM}) \qquad c \text{ for unit M}$$

However, it might be generally anticipated that such shifts will not equal those found from D unit resonances alone because of the known[2,11] non-addivity of ^{29}Si shifts, together with the fact that M and D silicons differ in the nature of the atoms directly bonded to them.

If resonances of *different* units are compared, similar substitution effects can be defined, which we shall distinguish by a prime, e.g.:

$$\delta(\mathrm{MD\underline{D}DM}) - \delta(\mathrm{M\underline{D}DM}) \qquad b'$$

When such shifts involve an end-group an 'a' substitution effect is defined, since the group directly bonded to the observed silicon changes, e.g.:

$$\delta(\mathrm{M\underline{D}DM}) - \delta(\mathrm{\underline{M}DM}) \qquad a'$$

Analogous shifts involving direct substitution have been described for many classes of silicon compounds[2,11]. It is established that such effects are in general non-additive, so that the changes in the series $\mathrm{Me_4\underline{Si}} \rightarrow \mathrm{\underline{M}M} \rightarrow \mathrm{M\underline{D}M}$ are not expected to be equal. It is of interest to see whether a similar situation holds for *b* and *c* shifts, for instance in the series $\mathrm{M\underline{D}M} \xrightarrow{b} \mathrm{M\underline{D}DM} \xrightarrow{b'} \mathrm{MD\underline{D}DM}$.

The above considerations apply to examination of the effects of chain extension on the ^{29}Si n.m.r. shifts of oligomeric siloxanes. Clearly the same influences cause the end-group effects for long-chain homopolymers (though logically 'end-group effects' should be measured from the main-chain resonance–thus having opposite signs to effects of chain extension). For instance, the $\mathrm{\underline{M}} \rightarrow \mathrm{\underline{D}(1)}$, $\mathrm{\underline{D}(1)} \rightarrow \mathrm{\underline{D}(2)}$ and $\mathrm{\underline{D}(2)} \rightarrow \mathrm{\underline{D}(3)}$ changes for such a polymer represent *a'*, *b'* and *c'* substituent effects, respectively.

Schematically, then, *Figure 1* shows how a table of ^{29}Si shifts for systems of the type we are considering yields substituent effects as described above. Clearly, the consistency or otherwise of the shift changes is of some importance for the assignment of spectra for mixtures of oligomers, and also for any physical or theoretical interpretation of the changes. Of course, not all the values of the shift changes are independent, since cyclic relationships are involved, e.g. $\mathrm{\underline{M}M} \xrightarrow{b} \mathrm{\underline{M}DM}$ plus $\mathrm{\underline{M}DM} \xrightarrow{a'} \mathrm{M\underline{D}DM}$ necessarily equals $\mathrm{\underline{M}M} \xrightarrow{a'} \mathrm{M\underline{D}M}$ plus $\mathrm{M\underline{D}M} \xrightarrow{b} \mathrm{M\underline{D}DM}$. *Figure 1* also makes it clear that shift differences between adjacent units of the same oligomer may be expressed as combinations of the parameters defined here, for instance.

$$\delta(\mathrm{MD\underline{D}DM}) - \delta(\mathrm{M\underline{D}DDM}) = b' - c$$

If the substituent shift parameters have consistent values for a given oligomer series, the spectrum of a mixture of such oligomers takes on a predictable appearance. The number of distinguishable resonances for a given unit is clearly of some importance; it depends on the magnitude of the end-group effects, the resolution of the spectrometer and the distribution of the oligomers. This number of peaks for unit D(*m*) will be one less than for the neighbouring unit nearer the end-group, D(*m* – 1). The line spacings for the different units should be the same, though clearly the relative intensities will depend on the concentration distribution of the oligomers. The first member for any series of lines will tend to be half the intensity of other members because it corresponds to the central unit for an oligomer with *n* odd. It is possible that a consistent pattern of resonances will extend to the end-group itself, though this is not very likely in view of non-additivity effects. If *n* is sufficiently large (long-chain oligomers present), the lines due to D(*m*) for a range of *m* will merge and an intense peak will result.

For the $\mathrm{M^HD}_n\mathrm{M^H}$ series the relevant substitution is $\mathrm{H} \rightarrow \mathrm{Me_2HSiO}$, whereas for the $\mathrm{M^{OH}D}_n\mathrm{M^{OH}}$ series it is $\mathrm{HO} \rightarrow \mathrm{HOMe_2SiO}$. In the case of the $\mathrm{MD}_n^{\mathrm{H}}\mathrm{M}$ series the substitution is not so simple since it involves both $\mathrm{Me} \rightarrow \mathrm{Me_3SiO}$ and $\mathrm{Me} \rightarrow \mathrm{H}$.

It may also be of interest to describe inter-series shifts. These are also, of course, substituent effects. The situation is straightforward when comparing oligomer series with common chain units but different end-groups, e.g. $\mathrm{MD}_n\mathrm{M}$ and $\mathrm{M^HD}_n\mathrm{M^H}$. The shift effects are then comparable in type to the intra-series ones. The only problem is that of ensuring that the referencing procedures are comparable. One way to overcome such difficulties is to use the signal from the main-chain units with *n* large as the reference, since this peak should not be greatly affected by the nature of the end-groups. However, solvent effects may still be a problem, and differences in end group can, in practice, contribute to these. Comparison of series with common end-groups and differing main-chain units is of little value, except in limited circumstances.

Table 1 ^{29}Si chemical shifts[a] of cyclic poly(dimethyl siloxanes)[b] present in the oligomer mixtures

Mixture	D_4	D_5	D_6
MD_nM ($\bar{n} \approx 4$)	−19.69	−22.04	−22.66
MD_nM ($\bar{n} \approx 8$)	−19.71	−22.05	−22.67
$M^HD_nM^H$ ($\bar{n} \approx 3.6$)	−19.73	−22.08	−22.69
$M^HD_nM^H$ ($\bar{n} \approx 4.8$)	−19.75	−22.10	–
$M^{OH}D_nM^{OH}$ ($\bar{n} \approx 3$)	−19.17	−21.56	−22.21

[a] Data given as δ_{Si} (ppm)
[b] Shifts measured after deliberate addition of cyclics, except in the case of $M^HD_nM^H$ ($\bar{n} \approx 4.8$)

When comparing inter-series shifts it becomes valid to speak of substituent effects of types commonly discussed in other n.m.r. situations. The normal substituent effect notation α, β, etc, which will be used here, relates to the number of bonds separating the substituent and the test nucleus. Thus the replacement $HMe_2SiO\underline{Si} \rightarrow Me_3SiO\underline{Si}$ is a γ effect of H → Me. Such a replacement has been shown generally[12–14] to give a shielding effect (whether the test nucleus is ^{13}C, ^{15}N, ^{31}P or, as here ^{29}Si), the causes of which have been extensively debated[12,14]. It should be noted that our notation *a*, *b* etc for substituent effects which is more convenient for discussing intra-series shifts for polysiloxanes, relates to the number of intervening *siloxane bridges* rather than bonds, except for shifts of the *a* type, which are equivalent to α.

EXPERIMENTAL

The MD_nM ($\bar{n} \simeq 4$ and $\bar{n} \simeq 8$), $M^{OH}D_nM^{OH}$ ($\bar{n} \simeq 3$) and MD_n^HM ($\bar{n} \simeq 2$ and $\bar{n} \simeq 6$) equilibrates were obtained from the Silicones Operations Group of ICI Organics Division. The MD_nM systems were prepared by equilibration of octamethyl cyclotetrasiloxane (cyclic D_4) with hexamethyl disiloxane (MM) (a source of end-stopper units), and the $M^{OH}D_nM^{OH}$ system (*not* an equilibrate) was prepared by a cohydrolysis/condensation process using $SiMe_2Cl_2$. The MD_n^HM equilibrates were prepared by equilibrating MD_n^HM ($\bar{n} \simeq 50$) and M_2.

The $M^HD_nM^H$ equilibrates ($n \simeq 3.6$ and $n \simeq 4.8$) used in this study were prepared by equilibrating cyclic D_4 with a mixture of M^HDM^H and M^HDDM^H. These equilibrations were performed by simple mechanical stirring of the starting materials at room temperature in the presence of concentrated sulphuric acid as a catalyst. Equilibration was allowed to proceed for at least 5 days to ensure a good range of oligomers in the final equilibrates, and after the equilibration period the resulting solutions were washed 6 times with saturated NaCl solution and then twice with saturated $NaHCO_3$ solution before drying the products over molecular sieves.

Impurity peaks were observed in several of the spectra for the equilibrated mixtures. In most cases these proved to be cyclic oligomers of the type D_n. In order to check this assignment cyclics were deliberately added to the MD_nM (both solutions), $M^HD_nM^H$ ($\bar{n} \simeq 3.6$) and $M^{OH}D_nM^{OH}$ samples. The measured chemical shifts of these cyclic species are given in *Table 1* since they can be used as internal reference guides or as indicators of medium effects (the latter are suggested by *Table 1* for the $M^{OH}D_nM^{OH}$ case). Hexamethyl disiloxane or tetramethyl disiloxane were also added to some samples to clarify assignment. In all cases our tabulated data are for the solutions *after* the addition of the extra species, except for the value of δ for M_2 in the MD_nM ($\bar{n} \simeq 4$) mixture. The sample of MD_n^HM ($\bar{n} \simeq 6$) showed impurity peaks at $\delta_{Si} = -5.18$ and -7.19 due to M^HM^H and $\underline{M}^HD\underline{M}^H$ respectively. The sample of $M^{OH}D_nM^{OH}$ gave a peak assigned to cyclic D_3 at $\delta_{Si} = -8.75$.

The ^{29}Si n.m.r. spectra were obtained using a Varian XL100–15 n.m.r. spectrometer operating in the Fourier transform mode at 19.87 MHz, with broad-band proton decoupling to remove all (Si, H) scalar couplings. The spectrometer probe operating temperature is 37° ± 1°C. The $M^{OH}D_nM^{OH}$ sample was run as a 50% v/v solution in a mixture of C_6H_6/C_6D_6 whereas the MD_nM, $M^HD_nM^H$ and MD_n^HM equilibrates were run after the addition of 12.5% by volume of C_6D_6. In all cases the C_6D_6 was used to provide a ^2H signal for field/frequency locking as well as to provide a reference for the calculation of ^{29}Si chemical shifts by the indirect method described previously[15] [using $\Xi_D(C_6D_6) = 15\,350\,721$ Hz and $\Xi_{Si}(TMS) = 19\,867\,184$ Hz]. The n.m.r. tubes were of 12 mm o.d. The samples were not degassed nor were the tubes sealed. However in the case of the MD^HM equilibrates the samples were bubbled with nitrogen prior to use since D^H units have a large *NOE* which if utilized can lead to improved *S/N*. Most of the spectra were obtained using 90° pulse flip angles and pulse delays of 30 sec, with the decoupler gated off during the pulse delay in order to allow relaxation of the nuclear spins and to supress build up of the *NOE* (which is negative for ^{29}Si as a result of its negative magnetic moment). However, it is unlikely that the conditions were adequate for intensities to give true quantitative estimates of molecular concentrations. In the case of the MD_n^HM samples flip angles of 45° were used with no pulse delays, since the *NOE* was wanted. All spectra were arbitrarily phased to give positive intensities. The number of pulses used to obtain the spectra varied according to the sample, although generally at least 250 pulses were required in order to obtain an acceptable signal-to-noise ratio. Exponential weighting of accumulated *FID*s to increase the signal-to-noise ratio in the resultant spectra was not employed (except for *Figure 5*) as this tends to lower the resolution attainable. The sweep widths varied from 250 Hz to 1250 Hz, with acquisition times appropriate for filling 8192 words of memory in the Varian 620/1 computer, except in the case of *Figure 4*.

All chemical shifts are quoted with respect to the ^{29}Si signal of TMS, with a positive value indicating resonance to higher frequency of the reference.

RESULTS

MD_nM equilibrates

Figure 2 shows the ^{29}Si n.m.r. spectrum of the equilibrated polymeric siloxane MD_nM ($\bar{n} \simeq 4$). The D region only is shown although all chemical shift values are listed in *Table 2*. A small amount (approximately 0.4 ml) of a 1:1:1 v/v mixture of the cyclics D_4, D_5 and D_6 was added to the mixture, as well as a small volume of hexamethyl disiloxane. Comparison of the spectra before and after these additions indicated that D_4 and D_5 were present in the original sample but that neither D_6 nor hexamethyl disiloxane were present. The spectrum shown in *Figure 2* and the data presented in *Table 2* are those obtained after these additions were made. Assignments were made on a

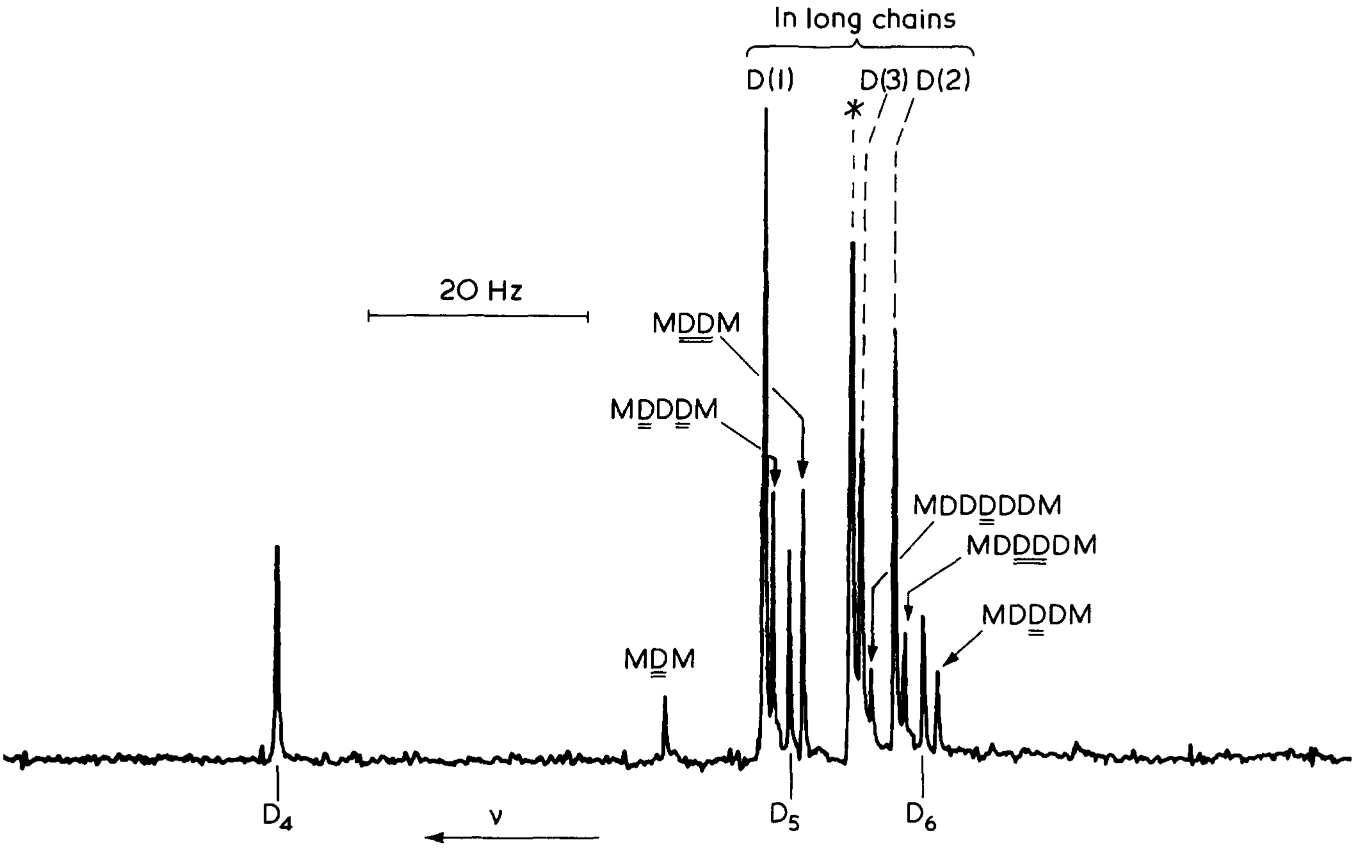

Figure 2 ^{29}Si- $\{^1H\}$ n.m.r. spectrum (D region only) of a mixture of oligomeric siloxanes MD_nM ($\bar{n} \approx 4$), plus cyclic siloxanes D_4, D_5 and D_6. The peak marked with an asterisk is due to D(m) with $m \geqslant 4$. The acquisition time was 8 sec. The spectrum results from the accumulation of 251 free induction decays

Table 2 ^{29}Si chemical shifts[a] for MD_nM oligomers, obtained using a mixture with $\bar{n} \approx 4$

n	M	D(1)	D(2)	D(3)	D(4)[b]
0	6.73[c]				
1	6.58	−21.47			
2	6.77	−22.10			
3	6.82	−21.97	−22.73		
4	(6.82)[d]	−21.93	−22.58		
5	(6.82)[d]	(−21.93)[d]	−22.52	−22.42	
6	(6.82)[d]	(−21.93)[d]	(−22.52)[d]	−22.37	
7	(6.82)[d]	(−21.93)[d]	(−22.52)[d]	(−22.37)[d]	−22.32
≈26[e]	7.26	−21.46	−22.05	−21.90	−21.86[f]
≈64[e]	7.22	−21.50	−22.10	−21.94	−21.90[g]

[a] Data given as δ_{Si} (ppm)

[b] D($m > 4$) in higher oligomers contributes to the signal at −22.32

[c] This value refers to a solution after addition of M_2. The remaining data relate to a solution before such addition

[d] Values in parentheses indicate the signal is indistinguishable from the one listed immediately above

[e] Recorded[16] for separate solutions of longer-chain systems ($\bar{n} \approx 26$ and 64). Attention should be directed to the shift differences between units rather than the absolute values since the latter are influenced by the medium conditions.

[f] The signal at −21.86 is for all D(m) with $m \geqslant 4$

[g] The signal at −21.90 is for all D(m) with $m \geqslant 4$

four-fold basis. Firstly it should be noted that all linear oligomers present, with the exception of MM, will contain at least one D(1) unit and therefore the overall intensity of the D(1) group of resonances will be greater than those of the D(2) group of resonances. Similarly the D(2) group of resonances will have an overall intensity which is greater than the D(3) group of resonances, and so on. It should be noted, however, that because an inadequate pulse delay was used for accurate quantitative work (a pulse delay of at least 5 times the longest T_1 would be required for this, and since Levy *et al.*[17] have shown that T_1 for the D(1) resonance of MD_3M is 82 sec this would obviously require prohibitive spectrometer time) the actual intensities of the resonances should be interpreted with some caution. However, as shown by Levy *et al.*[17] the major difference in T_1 values and *NOE*s occurs between the M and D units and hence the intensity data from the D region should serve as a rough guide for assignment. *Figure 1* clearly shows the halving of intensities for the central unit of MD_nM with n odd. Secondly, assignments were checked with reference to the previous data obtained from the individual oligomer studies[4,6,7]. Chemical shift difference agreement with the earlier work was, on the whole, good despite different solution conditions. Thirdly, as $\bar{n}$ was known to be ~4, the expected product distribution provided a clue to relative intensities of D(m) as m increases. Fourthly the end-group effects on the various D(m) units were consistent and gave a characteristic repetitive pattern of splittings, as discussed above. Assignments for the M region of the spectrum were made on a similar basis (omitting the fourth criterion), noting[17] that T_1 and *NOE* values for the M units in the different oligomers are very similar and hence intensity considerations should provide a fairly accurate guide to assignment when coupled with the fact that the maximum concentration for a particular oligomer should be for MD_4M, with individual oligomer concentrations decreasing as the number of D units increases or decreases from 4.

The ^{29}Si n.m.r. spectrum of the equilibrated polymeric siloxane MD_nM ($\bar{n} \simeq 8$) was also obtained. In chemical

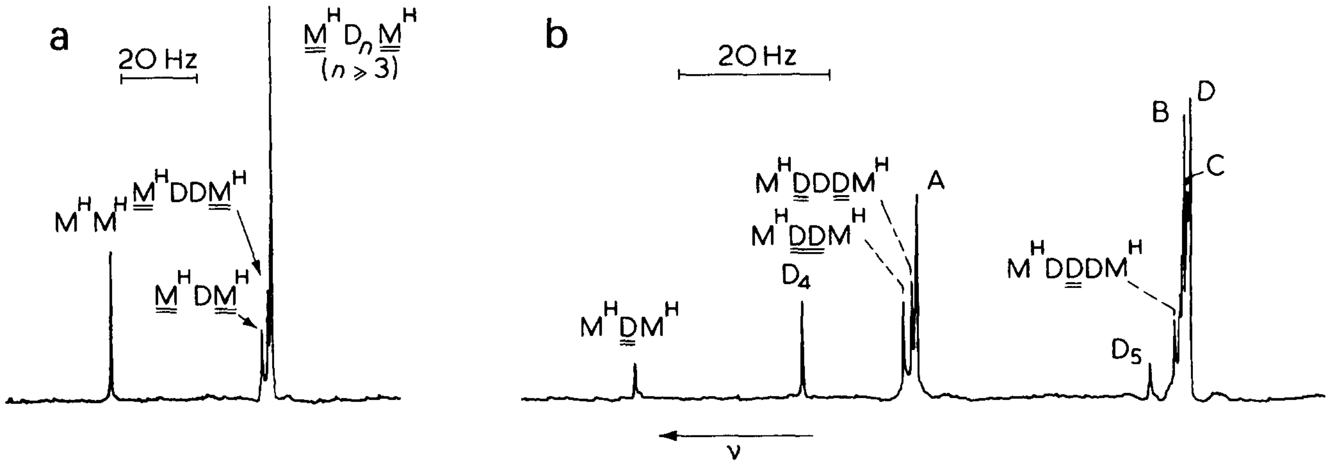

Figure 3 ^{29}Si-$\{^1H\}$ n.m.r. spectrum of an equilibrated mixture of oligomeric siloxanes $M^HD_nM^H$ ($\bar{n} \approx 4.8$), plus added dimer M^HM^H (a) M^H region; (b) D region. The two parts of the Figure differ by a factor of two in the frequency scale. The peaks marked A, B, C and D are due to D(1), D(2), D(3) and D(≥4) in longer chains, respectively. The acquisition time was 8 sec. The spectra result from the accumulation of 357 free induction decays

Table 3 ^{29}Si chemical shifts[a] for $M^HD_nM^H$ oligomers, obtained using a mixture with $\bar{n} \approx 3.6$ (plus additional $M_2{}^H$)

n	M^H	D(1)	D(2)	D(3)[b]
0	−5.25			
1	−7.27	−18.59		
2	−7.35	−20.41		
3	−7.39	−20.47	−22.25	
4	−7.40	−20.51	−22.29	
5	(−7.40)[c]	(−20.51)[c]	−22.31	−22.34

[a] Data given as δ_{Si} (ppm)

[b] D(m > 3) in higher oligomers appears to give a signal at −22.35

[c] Values in parentheses indicate the signal is indistinguishable from the one immediately above

shift terms the spectrum is practically identical to that with $\bar{n} \simeq 4$ and shows the predicted decrease in intensity from the M and D units in the low molecular weight oligomers.

$M^HD_nM^H$ equilibrates

The proton-decoupled ^{29}Si n.m.r. spectrum of the shorter average chain length equilibrate ($\bar{n} \simeq 3.6$) is shown in *Figure 3* and a full listing of chemical shifts in *Table 3*. The results of *Table 3* are for solutions after the addition of extra M_2^H. Assignments were made as for the MD_nM series, as well as by noting the trend to convergence of the resonances in each chain position as the oligomer length increases. To our knowledge no other values for ^{29}Si n.m.r. chemical shifts for the $M^HD_nM^H$ series of oligomers, apart from two values given for tetramethyl disiloxane[13,18], are available in the literature for comparison. The ^{29}Si n.m.r. spectrum of the longer chain ($\bar{n} \simeq 4.8$) $M^HD_nM^H$ equilibrate gives practically identical chemical shift values, with the predicted increase in intensity from the higher molecular weight oligomers as a result of their increased concentration.

$M^{OH}D_nM^{OH}$ system

Figure 4 shows the proton-decoupled ^{29}Si n.m.r. spectrum (D region only) of the $M^{OH}D_nM^{OH}$ ($\bar{n} \simeq 3$) siloxane after addition of a small quantity (~0.4 ml) of a 1:1 v/v mixture of the cyclic species D_5 and D_6. By comparing the spectra before and after this addition we were able to deduce that only cyclic D_4 was present in the original polymeric system. The cyclic mixture added also contains an additional component, possibly cyclic D_7, as indicated by the appearance of an additional, unexpected, resonance at −22.54 ppm. The D region shows no less than 19 resonances from units at different chain positions in the various linear oligomers present, and these were assigned by a combination of intensity considerations (although they are not totally reliable for reasons mentioned previously) and by noting the trend to convergence of the various D(m) series of resonances. The M^{OH} region of the spectrum has also been fully assigned. Considerable effort was required to obtain the extremely high resolution evident in the spectra. Initial attempts at running the spectrum using $Cr(AcAc)_3$ shiftless relaxation reagent tended to obscure detail as a result of line broadening caused by the reagent, and attempts to use lanthanide shift reagents to increase the available dispersion also failed for the same reason.

^{29}Si chemical shifts for certain M^{OH}-ended poly(dimethyl siloxanes) have been reported previously by Horn and Marsmann[8] and LaRochelle *et al.*[19,20]. In refs 8 and 20 only individual oligomers were studied, and although in ref 19 equilibrated M^{OH}-ended siloxanes were studied no attempt was made to make assignments to individual units within the various oligomers since the study was aimed at measuring the average degree of polymerization by comparing the integrated intensity of resonances in the M^{OH} region with those in the D region. Hence, to our knowledge, this is the only study of a short-chain M^{OH}-ended poly(dimethyl siloxane) mixture where a complete assignment has been made.

Table 4 shows the full chemical shift listing for this equilibrate.

MD_n^HM equilibrates

The average degrees of polymerization for the samples were $\bar{n} \simeq 2$, and $\bar{n} \simeq 6$. *Figure 5* shows the spectrum (D^H region only) of the $\bar{n} \simeq 2$ mixture and the chemical shifts are given in *Table 5*. Those for the $\bar{n} \simeq 6$ were very similar. The D^H unit is asymmetric and can therefore give rise to tacticity effects. These have been observed in the high resolution ^{29}Si spectra of individual oligomers from this polymeric series[10,21] and are clearly visible in the

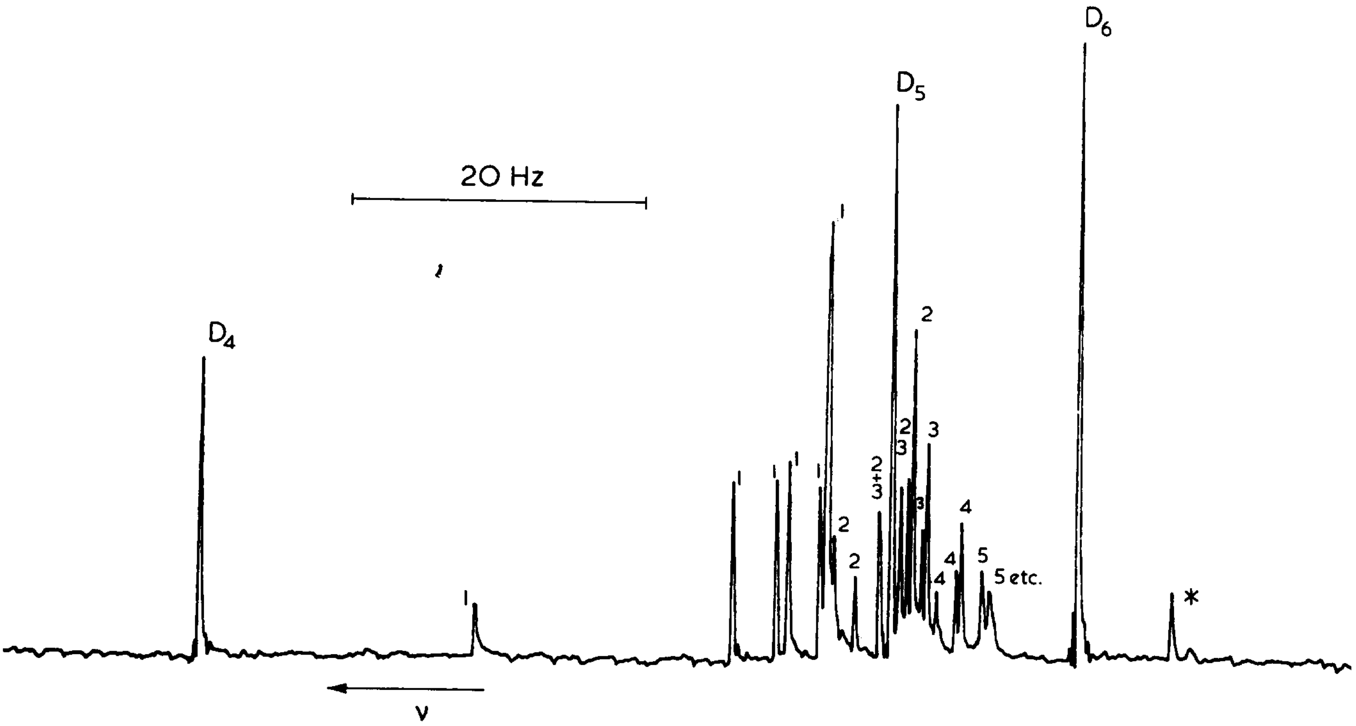

Figure 4 $^{29}Si-\{^1H\}$ n.m.r. spectrum (D region only) of a mixture of oligomeric siloxanes $M^{OH}D_nM^{OH}$ ($\bar{n} \approx 3$), plus cyclic siloxanes D_4, D_5 and D_6. The assignments to cyclic species are indicated. The other numbers refer to the position of the relevant D unit in the chain. The peak marked with an asterisk may be due to D_7

Table 4 ^{29}Si chemical shifts[a] for $M^{OH}D_nM^{OH}$ oligomers, obtained using a mixture with $\bar{n} \approx 3$

n	M^{OH}	D(1)	D(2)	D(3)	D(4)	D(5)[b]
0	−11.11					
1	−11.98	−20.11				
2	−12.14	−21.00				
3	−12.16	−21.15	−21.36			
4	−12.28	−21.20	−21.43			
5	−12.31	−21.30	−21.52	−21.52		
6	(−12.31)[c]	−21.34	−21.62	−21.59		
7	(−12.31)[c]	(−21.34)[c]	−21.63	−21.67	−21.72	
8	(−12.31)[c]	(−21.34)[c]	(−21.63)[c]	−21.68	−21.78	
9	(−12.31)[c]	(−21.34)[c]	(−21.63)[c]	(−21.68)[c]	−21.80	−21.87
10	(−12.31)[c]	(−21.34)[c]	(−21.63)[c]	(−21.68)[c]	(−21.80)[c]	−21.90

[a] Data given as δ_{Si}/ppm

[b] For D($m > 5$) in higher oligomers the signal appears to be at −21.90

[c] Values in parentheses indicate the signal is indistinguishable from the one immediately above it in the Table

$^{29}Si-\{^1H\}$ spectrum of the MD_n^HM ($\bar{n} \simeq 2$) equilibrate where the $D^H(1)$ resonances from the MD_2^HM and MD_3^HM oligomers show a clear doublet splitting. Unfortunately, combination of this asymmetry effect and the frequent similarity of chemical shifts from units in various oligomers leads to an overall broadening of some regions in the spectra, making absolute assignment difficult. However, using the four guidelines mentioned previously, reasonable assignments have been made as to the resonances constituting the broader bands visible. In this procedure, use was made of comparison with published data for MD_5^HM and MD_n^HM with $\bar{n} \simeq 50$. No asymmetry effects are visible for the M region of the spectrum, and assignment is therefore straightforward. The results given in *Table 5* are in reasonable agreement with those reported from studies of pure oligomers (but at lower resolution) in ref 4, once it is recognized that the earlier article contains a misprint, viz. $\delta\,[D^H(2)]$ for MD_3^HM should have been reported at −35.95 not −35.15.

DISCUSSION

There are several points of interest in the data for oligomers presented here. Firstly the number of distinguishable chain units is appreciable and varies with the system. In the cases of MD_nM and $M^HD_nM^H$ separate resonances are observable for D(1), D(2) and D(3), distinct from that of D(m) with $m \geqslant 4$. This implies that signals due to oligomers up to and including $M^XD_5M^X$ can be resolved from all other peaks, and ^{29}Si n.m.r. may therefore prove very useful for the characterization of low molecular weight equilibrated siloxane mixtures, offering an alternative to the usual g.l.c. method of analysing such ranges of oligomers. Earlier

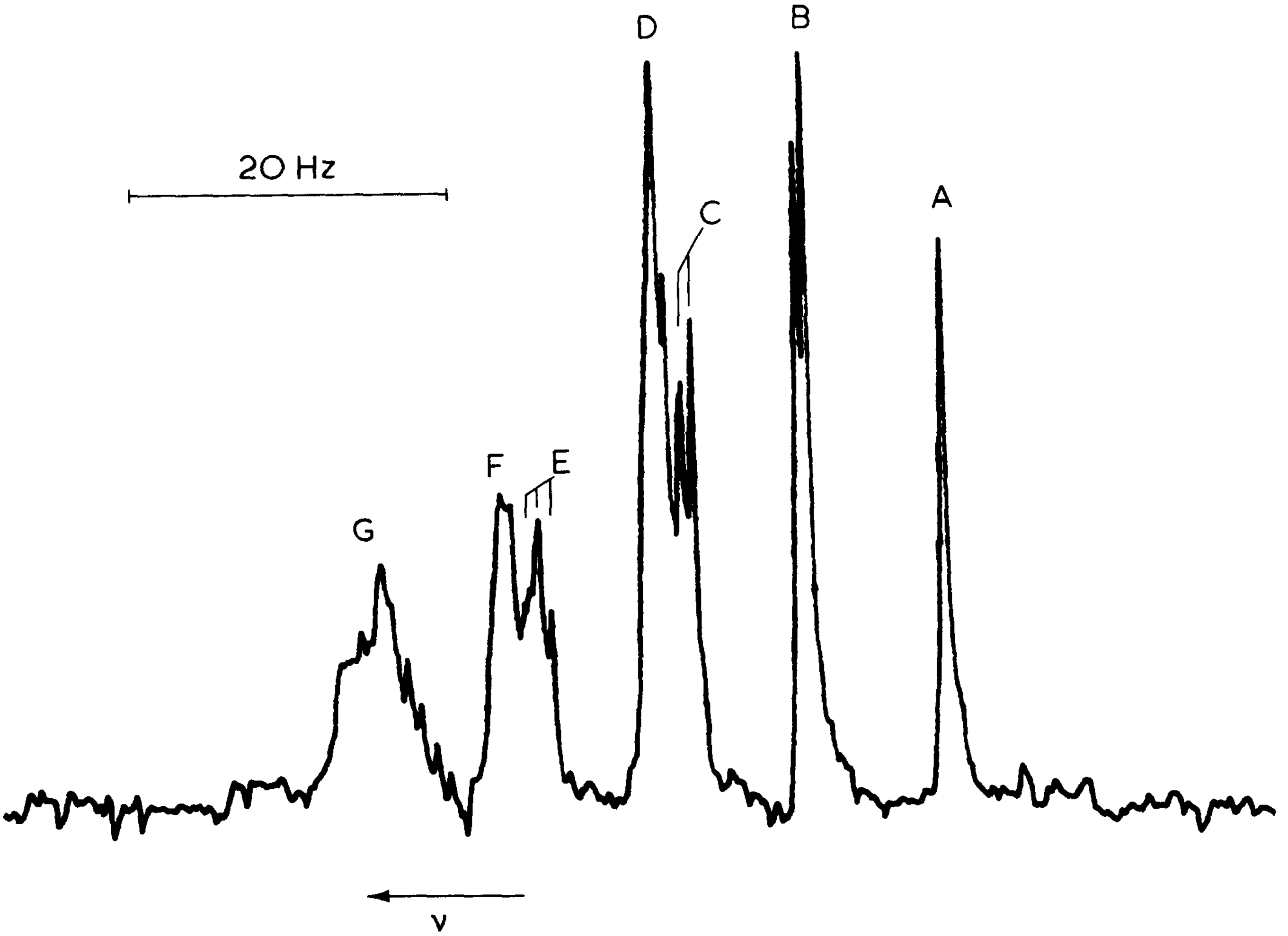

Figure 5 ^{29}Si– $\{^1H\}$ n.m.r. spectrum (D^H region only) of a mixture of oligomeric siloxanes MD_n^HM ($\bar{n} \approx 2$). Bands A, B, C, D, E, F and G are due to $M\underline{D}^HM$; $M\underline{\underline{D^HD}}^HM$; $M\underline{D}^HD^H\underline{D}^HM$; $MD^H\underline{D}^HD^HM$ plus $D^H(1)$ for $n \geqslant 4$; $MD^H\underline{\underline{D^HD}}^HD^HM$; $D^H(2)$ for $n \geqslant 5$; and $D^H(m)$ for $m \geqslant 3$ respectively. The acquisition time was 16 sec, with no pulse delay. The spectrum results from the accumulation of 2539 *FID*, the Fourier transformation being accompanied by a sensitivity enhancement factor of 2.0 sec

Table 5 ^{29}Si chemical shifts[a] for MD_n^HM oligomers, obtained using a mixture with $\bar{n} \approx 2$

n	M	$D^H(1)$	$D^H(2)$	$D^H(3)^b$
0	6.66			
1	8.56	–37.07		
2	9.19	–36.64[c] –36.61[c]		
3	9.35	–36.27[c] –36.24[c]	–36.18[d]	
4	9.39	–36.17[d]	–35.78[d]	
5	9.41	(–36.17)[e]	–35.67	~–35.28[d]
5[f]		–36.00	–35.52	–35.22
≈50[g]		–35.82	–35.33	–34.95

[a] Data given as δ_{Si} (ppm)

[b] $D^H(m > 3)$ in higher oligomers appears to give a signal at ~–35.28

[c] Doublets due to D^H unit asymmetry

[d] Estimated average shift over splitting due to D^H unit asymmetry

[e] Values in parentheses indicate the signal is indistinguishable from the one listed immediately above

[f] Shifts for the isolated oligomers[10]. Attention should be directed to the shift differences between units, rather than the absolute values (which are influenced by the medium)

[g] See ref 10. The units for $m > 3$ give the principal resonance at δ_{Si} = –34.88. The comment under footnote f applies

failure[4] to distinguish D(2) and D(3) units was presumably due to the use of an external lock and the limitations of computer memory to 8 K, as was suggested[21]. It is also clear that for the highest resolution use of shiftless relaxation reagents such as $Cr(AcAc)_3$ must be avoided, though this results in rather severe demands on spectrometer time. Our present results for the MD_nM series are consistent with studies[16] of longer-chain polymer mixtures. In the case of the system $M^{OH}D_nM^{OH}$ the end-group effects are carried further down the chain, at least under the medium conditions used here, so that units up to D(5) may be distinguished from the rest, and signals for oligomers up to and including $M^{OH}D_9M^{OH}$ can be resolved from all other peaks. This is a remarkable situation, particularly since the replacement $OH \rightarrow OSiMe_2OH$ does not change the atoms directly bonded to silicon (in contrast to the situation for the other series), with chemical shift effects transmitted up to 10 bonds removed from the end-group. Presumably intramolecular hydrogen bonding may be associated with this situation. Our observations carry implications about the observability of resonances due to units near the end groups in longer-chain polymers, and indeed we have[16] separately detected signals for units D(1) to D(5) in an OH-ended

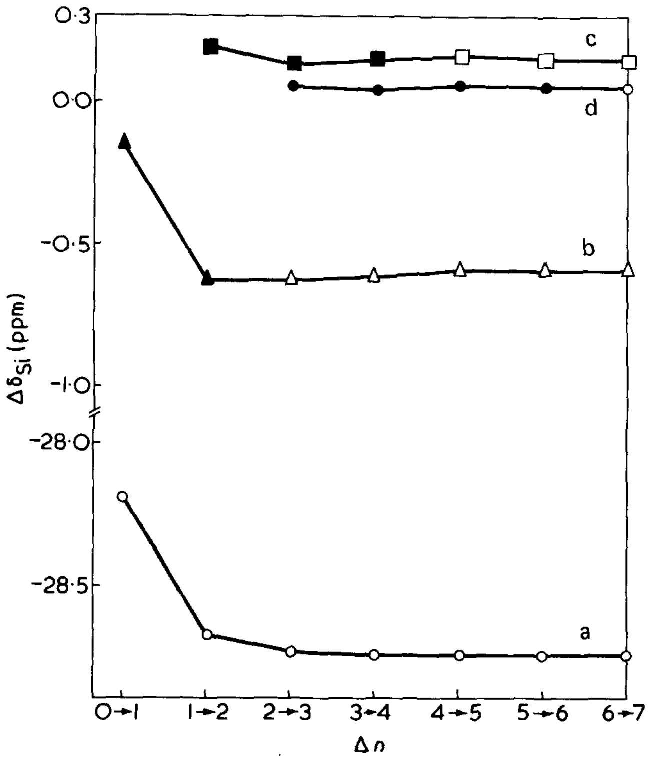

Figure 6 Substituent shift effects for the MD_nM series (using $\bar{n} \approx 4$) (replacement Me → Me_3SiO). The open symbols refer to effects of the types *a'*, *b'* etc., whereas the filled symbols are for *b*, *c* etc. (see *Figure 1*)

poly(dimethyl siloxane) $M^{OH}D_nM^{OH}$ with average composition (determined by ^{29}Si n.m.r.) $n \simeq 24$. In the case of the MD_n^HM series the complications arising from the the asymmetry of the D^H group obscure some of the longer-range substitution shifts. For this series D^H shifts *b* and *c* are of roughly equal magnitude (considerably greater than those of longer range), resulting in a characteristic pattern of five clearly distinguishable bands. The relative intensities of these bands yield information about molecular weight distribution in a relatively simple way.

The second point of interest in the data lies in the consistency or otherwise of the substituent shifts obtained as indicated in *Figure 1*. These shifts are plotted in *Figures 6* to *9*. It is clear that for the MD_nM and $M^HD_nM^H$ series the substituent effects on the D units of the replacements Me → Me_3SiO and H → Me_2HSiO respectively are consistent, though there are minor variations outside the limits of experimental error. There is apparently no discernible difference between, for example, shifts of the *b* type and those of the *b*′ type. For the $M^HD_nM^H$ series all the effects (*a* as well as *b*, *c* and *d*) are negative (progressive shielding of units toward chain centres) whereas for the MD_nM series only the *a* and *b* effects are negative, the *c* and *d* terms causing deshielding. Indeed, this fact complicates the assignment of the resonances for the MD_nM series–monotonic end-group effects on the chain-unit resonances, as for $M^HD_nM^H$, clearly make interpretation easier. However, for both the MD_nM and $M^HD_nM^H$ series the consistency of the substituent shifts leads to easy pattern recognition for the D unit resonances, each unit D(*m*) having one less resonance than the preceding unit D(*m* – 1), but with similar spacings for the corresponding lines, as discussed above. Such patterns are most easily seen for the MD_nM spectrum of *Figure 2*. However, pattern recognition of this type cannot readily be extended to the M region, as becomes clear from the data of *Figures 6* to *9*–the *b* substituent effect on the M^X unit differs from that on the D units. This is particularly noticeable for the MD_nM series, where $b = -0.15$ ppm for the M units whereas *b* and *b*′ range from –0.59 to –0.63 ppm for the D units. Such difference in behaviour of the end-groups and the D units is to be expected in view of the general non-additivity of ^{29}Si shifts, as mentioned above.

The situation for the $M^{OH}D_nM^{OH}$ system is rather different, since the substituent effects are less consistent along the chain (see *Figure 8*). In fact, the plots for *c*, *d* and *e* shifts cross over. Moreover although there is a substantial change at one point in the plots for the *b* and *c* shifts of the $M^{OH}D_nM^{OH}$ series, this occurs not between measurements for the end-group and D(1) but between D(1) and D(2). This situation results in shifts of the *a* type being very consistent in magnitude (–9.00 to - 9.04 ppm) and it is presumably connected with the hydrogen bonding possibilities for this system, as is the solvent dependence of the shifts. We are unable to present a more quantitative explanation for our findings, but it should be noted that our data refer to a specific medium situation. More meaningful results could doubtless be obtained for shifts extrapolated to infinite dilution in an inert solvent, but this is scarcely feasible given the sensitivity of ^{29}Si n.m.r. At all events, perhaps by coincidence, the anomalies result in the pattern of signals for the M^{OH} unit looking very similar to that for the D(1) unit whereas patterns for D(*m*) with $m > 1$ are somewhat different, a fact which inhibited interpretation originally.

The additivity (or otherwise) of *b* and *c* shifts may be tested directly using the present data, by consideration of consecutive shifts of the type $M\underline{\underline{D}}M \xrightarrow{b} M\underline{\underline{D}}DM \xrightarrow{b'} MD\underline{\underline{D}}DM$

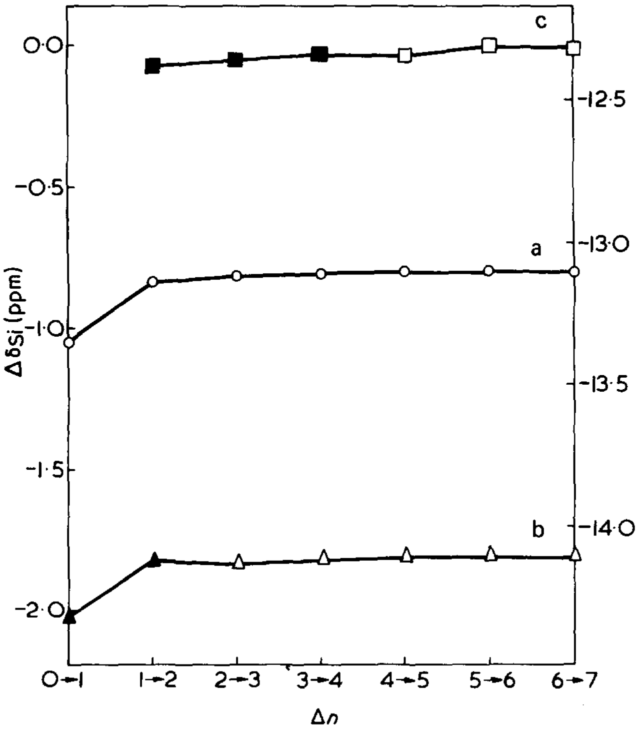

Figure 7 Substituent shift effects for the $M^HD_nM^H$ series (using $\bar{n} \approx 4.8$) (replacement H → Me_2HSiO). The open symbols refer to effects of the types *a'*, *b'* and *c'*, whereas the filled symbols are for *b* and *c* (see *Figure 1*). The scale at the right refers to trace a, whereas that at the left refers to b and c

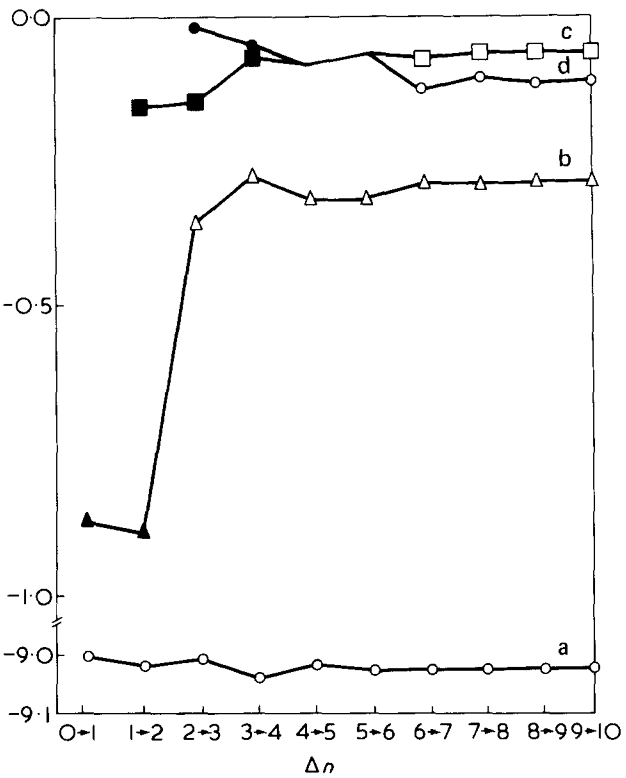

Figure 8 Substituent shift effects for the $M^{OH}D_nM^{OH}$ series (using $\bar{n} \approx 3$) (replacement HO → $HOMe_2SiO$). The open symbols refer to effects of the types *a′*, *b′* etc., whereas the filled symbols are for *b, c* etc. (see *Figure 1*)

and $M D \underline{\underline{D}} D M \xrightarrow{c} M D \underline{\underline{D}} D D M \xrightarrow{c'} M D D \underline{\underline{D}} D D M$ respectively. The results for the MD_nM system with $n \simeq 4$ are $b = -0.63$, $b' = -0.63$ and $c = +0.15$, $c' = +0.16$. For the $M^HD_nM^H$ series the values $b = -1.82$, $b' = -1.84$ and $c = -0.04$, $c' = -0.05$ are found. In both cases for both *b* and *c* shifts, the agreement is excellent i.e. there is a high degree of additivity. However as implied earlier, for the $M^{OH}D_nM^{OH}$ series there is gross departure from additivity for *b* shifts ($b = -0.89$, $b' = -0.36$), and though there is reasonable additivity for *c* ($c = -0.07$, $c' = -0.09$) this is an isolated case, since for the replacement $M^{OH}\underline{\underline{D}}DM^{OH} \rightarrow M^{OH}\underline{\underline{D}}DDM^{OH}$ $c = -0.15$.

Comparison of the shifts for D units remote from the chain ends for the three series (values −22.32, −22.35 and −21.87 ppm for MD_nM, $M^HD_nM^H$ and $M^{OH}D_nM^{OH}$) again show the hydroxyl-ended series is anomalous, though it should be stressed that medium conditions were not standardized. Indeed the apparent deshielding effect for the $M^{OH}D_nM^{OH}$ series may be the result of H-bonding of the end-groups to the central units either within the same molecule or between molecules.

Comparison between resonances for different series of compounds gives information about other types of substituent effects. In particular, comparison of the $M^HD_nM^H$ and MD_nM series yields data about the replacement H → Me. The resonances of the end-groups, M^H or M for $n = 4$ or greater gives the α substituent effect as 14.21 ppm. Of course, such comparisons are influenced by medium effects, but it is clear that the α shift is considerably smaller for M units than for alkylsilanes. This may be attributed to the non-additivity of ^{29}Si shifts as expressed by the 'sagging pattern' of shielding[2,11] as a function of substituent electronegativity. Values of a γ shift for the H → Me replacement may be derived in several ways. Thus $\delta(MM) - \delta(M^HM^H) = 11.98$ ppm $= \alpha + \gamma$, giving $\gamma = -2.23$ ppm. Another measure is that of $\delta(M\underline{\underline{D}}M) - \delta(M^H\underline{\underline{D}}M^H) = -2.88 = 2\gamma$ (if additivity holds). For long-chains measurement of $\delta D(1)$ yield $\gamma = -1.42$ ppm. Comparison of $\underline{M}D^HM$ and $\underline{M}DM$ (corrected relative to MM) gives $\gamma = -2.05$ ppm. Although these measures give different numerical values (larger magnitudes for M and M^H units than for D or D^H units), it is clear the γ effect is shielding by 1–3 ppm; this is in line with other results for ^{29}Si and many other nuclei[12–14]. The γ effect is responsible for the marked difference in *b* shifts on the D resonances of the MD_nM and $M^HD_nM^H$ series (and similarly for the M resonances of MD_nM and MD^H_nM). One can also determine an ϵ effect of H → Me replacement, e.g. $\delta(\underline{M}DM) - \delta(\underline{M}^HDM^H) = 13.85$ ppm $= \alpha + \epsilon$, implying $\epsilon = -0.36$ ppm; $\delta(MD\underline{\underline{D}}DM) - \delta(M^HD\underline{\underline{D}}DM^H) = -0.48$ ppm $= 2\epsilon$. Long-chain measurements of D(2) yield $\epsilon = -0.21$. These values are quite large in magnitude, and, indeed, effects are apparently noticeable two bonds further along (especially when corrections are made for the position of the central units). However, medium differences may be responsible for an appreciable part of such apparent long-range effects. Due to the anomalies already noted for the $M^{OH}D_nM^{OH}$ series there is little point in comparing the data with those of the other two series.

Chemical shifts have been reported for other series of siloxane oligomers, though usually using pure oligomers rather than mixtures. Both Engelhardt *et al.*[22] and Harris and Newman[23] report data for trimethylsilylated silicates, which may be classified as $M(QM_2)_nM$. *Table 6* collates the data from these sources. The substitution relevant for this series is 3Me → $3Me_3SiO$. However, the effects are definitely not simply three times those for the MD_nM series, thus illustrating again the non-additivity of silicon shift effects. On the other hand, *within* the $M(QM_2)_nM$ series the *b* shifts are moderately additive, since for $\underline{\underline{Q}}M_4 \rightarrow M_3\underline{\underline{Q}}QM_3 \rightarrow M_3Q.\underline{\underline{Q}}M_2.QM_3$ values are $b = -2.38$ and $b = -2.68$ ppm respectively. The *b* effect on the M(1) units differs in sign from that on the Q units. It might be argued[24]

Table 6 Substitution shifts for the ^{29}Si chemical shifts of trimethylsilylated silicates $M(QM_2)_nM$

Initial *n*	Initial unit	Final *n*	Final unit	Shift type	Value
0	M(1)	1	M(1)	*b*	+1.44[a]
1	M(1)	2	M(1)	*c*	+0.30
2	M(1)	3	M(1)	*d*	−0.07
3	M(1)	4	M(1)	*e*	−0.4[b]
2	M(1)	3	M(2)	*c′*	+0.25
3	M(1)	4	M(2)	*c′*	−0.3[b,c]
0	M(1)	1	Q(1)	*a′*	−111.34
1	M(1)	2	Q(1)	*a′*	−115.16
2	M(1)	3	Q(1)	*a′*	−115.76
3	M(1)	4	Q(1)	*a′*	−116.6[b]
1	Q(1)	2	Q(1)	*b*	−2.38
2	Q(1)	3	Q(1)	*c*	−0.26
3	Q(1)	4	Q(1)	*d*	−0.9[b]
2	Q(1)	3	Q(2)	*b′*	−2.68
3	Q(1)	4	Q(2)	*b′*	−2.7[b]
3	Q(2)	4	Q(2)	*c*	−0.3

[a] This is a new measurement, obtained for a solution of MM and QM_4 with a combined concentration of 40% by volume in C_6H_6/C_6D_6

[b] These values are derived from ref 22; the remaining data are from ref 23

[c] This value appears to be anomalous

Table 7 Summary of *b* and *c* substitution shifts[a] in ^{29}Si n.m.r.

Series	Substitution	*b* on M^X	*b'* on D^Y	*c* on M^X	*c'* on D^Y
MD_nM	Me → Me_3SiO	−0.15	−0.59	+0.19	+0.15
$M^HD_nM^H$	H → Me_2HSiO	−2.02	−1.80	−0.08	−0.05
$M^{OH}D_nM^{OH}$	HO → $HOMe_2SiO$	−0.87	−0.29	−0.16	−0.05
MD_n^HM	Me → Me_3SiO Me → H	+1.90	+0.60	+0.63	+0.38 [*c* on $D^H(1)$]
$M(QM_2)_nM$	3Me → $3Me_3SiO$	+1.44	−2.7	+0.30	−0.3

[a] The shifts on the middle groups D^Y ($\underline{Q}M_2$ for the last series) are those extrapolated to large *n*, where possible

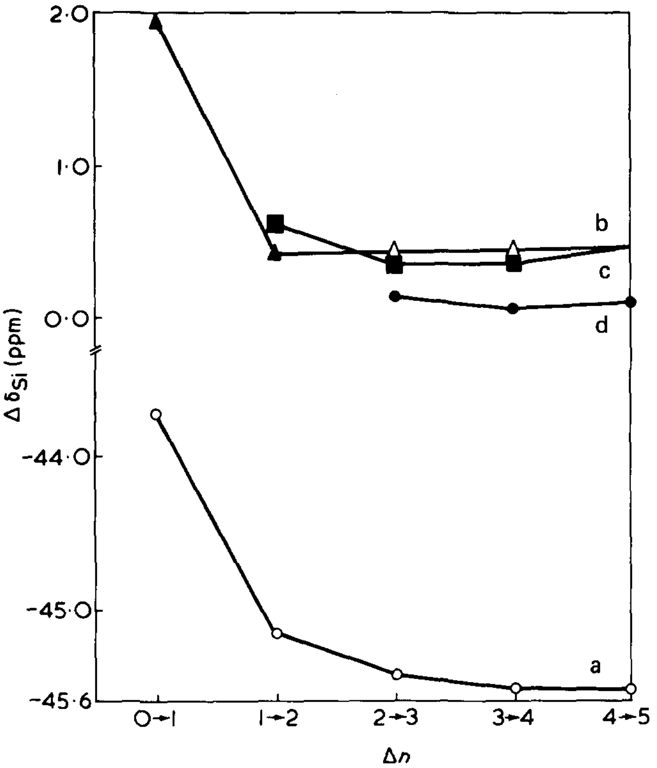

Figure 9 Substituent shift effects for the $MD_n{}^HM$ series (using $\bar{n} \approx 2$) (replacements Me → Me_3SiO and Me → H). The open symbols refer to effects of the types *a'*, *b'* etc., whereas the filled symbols are for *b, c* etc. (see *Figure 1*)

that this is a result of the very different dependence of δ_{Si} on substituent electronegativity in the M and Q regions of the spectrum (the well known 'sagging pattern' for silicon shielding). However, such an hypothesis is scarcely borne out by the results for the other series, summarized in *Table 7*. In particular, the observation of Engelhardt *et al.*[24] that substitution effects of the *a* and *b* types are opposite in sign for molecules of the type $(Me_3SiO)_3SiX$, although in agreement with our data (*Table 6*) for the series $M(QM_2)_nM$, contrasts with the negative value for the *b* effect on M units for the MD_nM series. Clearly the transmission of substituent effects through a siloxane bond to give a *b* type shift depends heavily on the nature of the other substituents at *both* relevant silicon atoms.

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