

End-groups and Tacticity in Polymeric Silicones Detected by ^{29}Si Nuclear Magnetic Resonance

By ROBIN K. HARRIS* and BARRY J. KIMBER

(School of Chemical Sciences, University of East Anglia, Norwich NOR 88C)

Summary It is shown that for a polymeric silicone of average chain-length 50 units (excluding the end-stopping groups) separate $^{29}\text{Si}\{^1\text{H}\}$ resonances can be seen for the three units at each end, and tacticity effects can also be observed when asymmetric units are involved (in the case investigated the silicone is probably atactic); tacticity effects on ^{29}Si spectra are also demonstrated for a short-chain silicone.

RECENT improvements in n.m.r. techniques, particularly the advent of the Fourier transformation method,¹ have given a fillip to the study of polymers. In most instances such studies have used ^{13}C n.m.r.,² but in the case of silicones ^{29}Si spectra may be used in much the same way. Some ^{29}Si n.m.r. studies of silicones have already been published,^{3,4} and we have been able to show that extensive information about the microstructure of copolymers may be obtained.⁴ Thus, for polymers containing both D and D' units we have



detected chemical shift effects at the pentad level, and have shown that D and D' units are distributed at random. However, the influence of the terminal trimethylsiloxy (M), $\text{Me}_3\text{SiO}_{0.5}$, units on the shifts of nearby D and D' ^{29}Si nuclei was not clear, nor were tacticity effects seen.⁴ Indeed, we believe that influences arising from asymmetry in silicone units have not been reported previously by any physical technique, with the exception of a brief mention (involving ^1H n.m.r.) in the patent literature.⁵

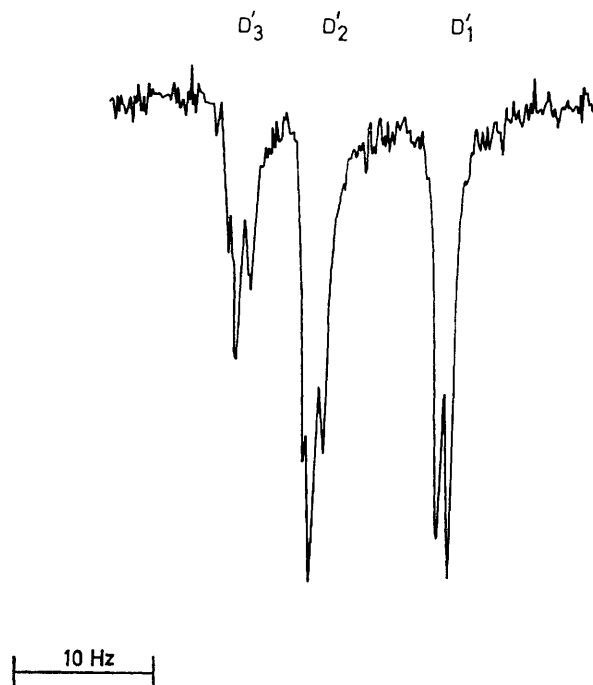
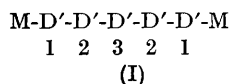


FIGURE 1. $^{29}\text{Si}\{-^1\text{H}\}$ n.m.r. spectrum (D' region) of MD_5M . 600 pulses were used to accumulate the free induction decay.

We have now succeeded in obtaining higher-resolution noise-decoupled $^{29}\text{Si}\{-^1\text{H}\}$ spectra that demonstrate the existence of both tacticity and end-group effects in polymeric silicones involving the D' unit. Figure 1 shows the spectrum of the compound $\text{MD}'_5\text{M}$ (this is similar to Figure 1B of ref. 4 but recorded with higher resolution under slightly differing conditions). The three groups of lines, centred at $\delta_{\text{Si}} = -36.00$, -35.52 , and -35.22 , are due to the three types of D' unit 1, 2, and 3 [see (I)], in order from low to high frequency.



The fine splittings which can be seen must be due to asymmetry effects. The spectrum is consistent with the supposition that only nearest-neighbour influences can be resolved. Thus the resonance of the 1 unit is split into two because

group 2 may be either *d* or *l*, whereas the 2 and 3 resonances are each split into triplets because each group has two asymmetric neighbours (leading to sequences $ddd \equiv ll$, $ddl \equiv ldd \equiv lld \equiv dll$, and $ldl \equiv dld$).

Figure 2 shows the ^{29}Si n.m.r. spectrum of a polymer of average composition $\text{MD}'_{50}\text{M}$. The predominant feature is a triplet at $\delta_{\text{Si}} = -34.88$ (with 1:2:1 intensity distribution) which may be explained in the same way as the resonances for units 2 and 3 of $\text{MD}'_5\text{M}$. Clearly this triplet is due to the bulk of the D' units in the polymer. It seems clear from the relative intensities of the triplet that the polymer is either atactic or that chains of differing tacticities are produced in nearly equal amounts (probably the former). Moreover, Figure 2 shows that there are several weaker features to low frequency of this triplet. These may be assigned to D' units near the end-groups. The separation of the doublet (centred at $\delta_{\text{Si}} = -35.82$) and the triplet (centred at $\delta_{\text{Si}} = -35.33$) is (within experimental error) equal to the separation found for groups 1 and 2 of $\text{MD}'_5\text{M}$. The triplet centred at $\delta_{\text{Si}} = -34.95$ is slightly shifted from that due to group 3 of the $\text{MD}'_5\text{M}$, as might be anticipated. Only 400 pulses (taking *ca.* 53 min) were required to accumulate the spectrum shown in Figure 2, and it is clear that it will be feasible to observe both end-group effects and tacticity in considerably longer silicone polymers. Similar effects are apparent in ^{13}C spectra of these compounds, but the spread of chemical shifts is not so favourable.

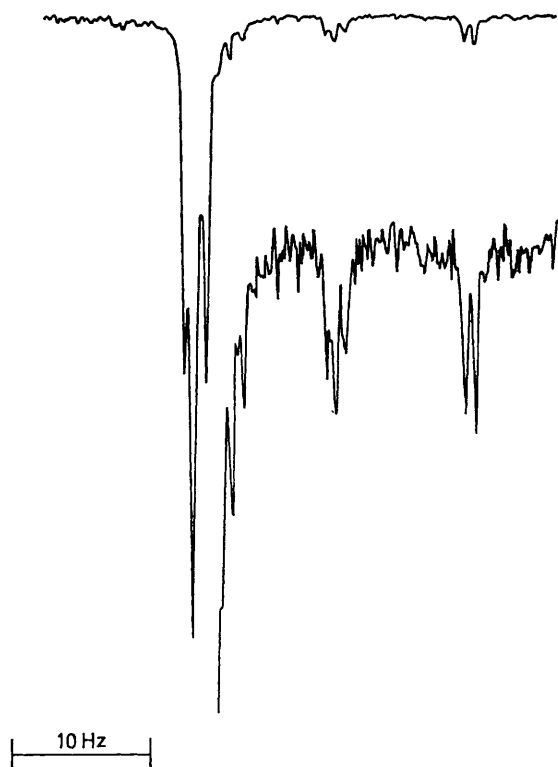


FIGURE 2. $^{29}\text{Si}\{-^1\text{H}\}$ n.m.r. spectrum (D' region) for a polymeric silicone of average composition $\text{MD}'_{50}\text{M}$. A trace expanded in the ordinate is included.

The spectra were recorded at 19.87 MHz using a Varian XL 100 spectrometer in the Fourier transform mode. For both cases the acquisition time was 8 s, and no pulse delay

was used. Both samples were degassed (using the freeze-pump-thaw technique) and sealed into 12 mm n.m.r. tubes. The solution conditions were (a) 75% MD₃M with 25% CD₂Cl₂, and (b) 88% MD₅₀M with 12% C₆D₆, in each case v/v. The ²H signal of the 'solvent' was used for field-frequency locking. The chemical shifts, relative to the Me₄Si resonance, were obtained by measuring the r.f. resonance frequencies and converting to a scale based on the magnetic field at which the ¹H nucleus of Me₄Si resonates

exactly at 100 MHz.⁶ The spectra of Figures 1 and 2 are inverted because of the nuclear Overhauser effect.⁷

One of us (B.J.K.) is grateful to the S.R.C. and to I.C.I. Ltd. (Organics Div.) for a Research Studentship under the C.A.P.S. scheme. We thank members of the Technical Development Department (Silicones Operating Group) of I.C.I. Ltd. Organics Div., for the compounds used and for fruitful discussions.

(Received, 3rd May 1974; Com. 514.)

¹ D. G. Gillies and D. Shaw, *Ann. Report N.M.R. Spectroscopy*, 1972, 5A, 557.

² V. D. Mochel, *J. Macromol. Sci. Macro. Chem.*, 1972, C8, 289.

³ G. Engelhardt, M. Mägi, and E. Lippmaa, *J. Organometallic Chem.*, 1973, 54, 115.

⁴ R. K. Harris and B. J. Kimber, *J. Organometallic Chem.*, 1974, 70, 43.

⁵ U.S.P. 3,337,497, 1967.

⁶ W. McFarlane, *Ann. Rev. N.M.R. Spectroscopy*, 1968, 1, 135.

⁷ J. H. Noggle and R. E. Schirmer, 'The Nuclear Overhauser Effect,' Academic Press, New York, 1971.