

The Use of ^{29}Si Fourier Transform Nuclear Magnetic Resonance Spectroscopy for the Characterisation of Polymers and Paints*

Gregory L. Marshall

A range of commercial paint binders and two-pack elastomers containing silicone materials have been investigated by ^{29}Si Fourier transform nuclear magnetic resonance spectroscopy at 17.76MHz. In order to obtain good quality spectra within a minimum of time period, a relaxation agent was used to suppress nuclear Overhauser effects, and to improve the relaxation times of the silicon nuclei.

1. INTRODUCTION

Silicones with a high phenyl content are compatible with organic binders, such as alkyds, oil-soluble phenolic resins, amino resins, epoxide resins, ethyl cellulose and some acrylic resins.¹ Organic polymers with hydroxyl or alkoxy groups can be copolymerised with silicones that contain the $-\text{Si}-\text{O}-\text{C}<$ link. To produce silicone alkyds, for example, methoxy or hydroxy groups present in a silicone are reacted with a polyol, and the product converted into an alkyd by normal methods. This alkyd may be air-drying or it may require stoving to cure, depending on the acids used to form the polyester. The durability of an alkyd can be substantially increased by the incorporation of a silicone.²

Two pack silicone rubber compositions are based on polydimethylsiloxanes. In a typical material there are free silane groups in one component and free vinyl groups in the other.³ These groups can react in the presence of a catalyst to form a cross-linked material.

Two-pack silicone rubbers and silicone alkyds have been investigated by ^1H nuclear magnetic resonance (n.m.r.) spectroscopy.^{4, 5} With the former, the modifying groups can be detected but the technique is unable to distinguish between terminal and pendant groups. The positions of these groups can affect the physical properties of the cured products. ^1H n.m.r. has also been used to investigate the properties of silicone alkyds, but the exact functionality of the silicon cannot be established.⁶ The amount of silicone modification may be quite small and the signals of interest can be masked by signals from the binder and its solvents.

In this work, a series of silicone alkyds and two-pack silicone elastomers have been investigated by ^{29}Si Fourier transform (FT) n.m.r.⁷ The ^{29}Si isotope has a nuclear spin of $I = \frac{1}{2}$, and has a natural abundance of 4.7 per cent. The relative sensitivity of ^{29}Si to ^1H by the n.m.r. technique is 3.69×10^{-4} .⁸ In order to obtain good ^{29}Si n.m.r. spectra a signal-averaging technique must be used. FT n.m.r. will produce ^{29}Si n.m.r. spectra within a few hours for moderately concentrated solutions. ^{29}Si nuclei generally have long spin-lattice relaxation times, which can affect

the signal-to-noise ratios of the spectra. In some cases, negative signals can be obtained by an effect known as nuclear Overhauser enhancement. These problems can be overcome by the use of a paramagnetic relaxation agent, such as chromium (III) tris-penta-dionate, which is moderately soluble in organic solvents. The negative signals can also be made positive by the use of a technique known as gated decoupling.⁹ In view of the difficulties involved in the determination of the silicon content of paints on polymers, quantitative ^{29}Si FT n.m.r. has been attempted in this work on a silicone paint intermediate that is used for making certain silicone alkyds.

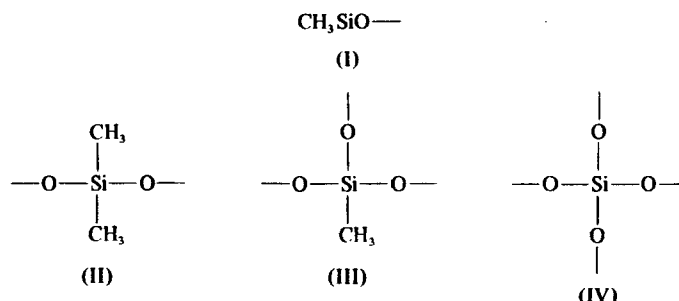
2. EXPERIMENTAL

The high temperature paint resins, the two-pack silicone elastomers, and the silicone paint intermediate were commercial products that were examined as supplied. The air-drying alkyd and the stoving alkyd studied were SC 600 and SC 28 materials, supplied by Croda Resins Limited.

All ^{29}Si FT n.m.r. spectra were recorded using a Jeol FX 90 Q spectrometer operating at 17.76MHz, in the gated decoupling mode, using hexadeuterobenzene solvent to provide a lock signal for the instrument. Tetramethylsilane (TMS) was used as an internal reference from which the chemical shifts of all peaks were measured using the parts per million (ppm) scale. The following instrumental settings were used throughout: 5000Hz sweep width; 90° pulse width. A six seconds scan cycle time was used for quantitative analysis. All spectra were obtained within 2–3 hours, and show a broad peak at ca -105 ppm which is due to silicon in the n.m.r. tubes used throughout.

^1H n.m.r. spectra were obtained using a Perkin Elmer R32 spectrometer operating at 90MHz using deuteriochloroform as solvent and TMS as internal reference

The functionality of the silicon nuclei in the n.m.r. spectra is represented as M (I), D (II), T (III) or Q (IV).



Materials Quality Assurance Directorate, Royal Arsenal East,
London SE18 6TD
(Manuscript received 25 September 1981)

* Presented as a poster at the 'Advances in Polymer
characterisation' Meeting, Durham, England, July 1981.
Manuscript received 25 September 1981

This shows the number of oxygen atoms bonded to methylated silicon. Substitution of methyl by other functional groups is indicated by a superscript, ie M^{Ph} is equivalent to $(CH_3)_2 Ph Si-O$.

3. RESULTS AND DISCUSSION

A wide range of polysiloxanes has been studied by ^{29}Si n.m.r.¹⁰ Some results of interest are shown in Table 1. Using the nomenclature described above, the effects of hydroxyl, alkoxy, phenyl, vinyl and hydride groups on the chemical shifts of polydimethylsiloxanes are shown. These data are used to help assign the different signals in the n.m.r. spectra below.

Table 1 ^{29}Si n.m.r. chemical shift ranges of some substituted polydimethylsiloxanes, relative to tetramethylsilane.¹⁰

X	M^x	D^x	T^x
—	+10 to +4	−17 to −24	−65 to −69
Ph	~ −3	−30 to −35	−77 to −80
Vi	−4 to −6	−32 to −35	—
H	−5 to −8	−32 to −37	—
OH	−10 to −14	ca −57	−95 to −100
OR	ca −12	−57 to −61	−102 to −104
Q = −104 to −110			

3.1 High Temperature Paint Resins

The ^{29}Si FT n.m.r. spectrum of high temperature paint, Resin A, is shown in Fig. 1. It shows five major silicon resonances at −17, −55, −64, −69 and −78ppm. From the Table the peaks at −17 and −64 can be assigned as D and T silicon nuclei respectively. Only methyl substituents are present. The signals at −55 and −78ppm can be assigned as D^{OR} and T^{Ph} species, respectively. The peak at −69ppm is assigned as $D^{Ph, OR}$ by extrapolating between the values of D^{Ph} and D^{OR} shown in the Table. Smaller peaks in the spectrum are not assigned, although they are thought to reflect genuine small modifications in the structure of the silicone polymer.

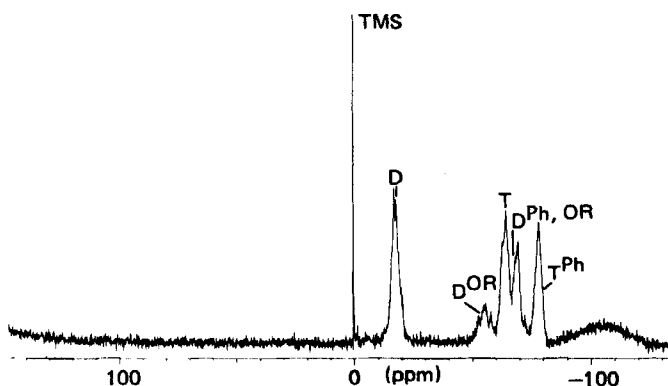


Fig.1 ^{29}Si FT n.m.r. spectrum of resin A

The ^{29}Si FT n.m.r. spectrum of another high temperature paint resin is shown as Resin B in Fig. 2. This sample has many features in common with Resin A; D, D^{OR} , T, $D^{Ph, OR}$ and T^{Ph} units can be identified. However, there is

noticeably more detail in the −30 to −60ppm region of the spectrum. These signals are probably due to the presence of D^{Ph} and D^{Ph2} units at −33 and −46ppm respectively. The greater phenyl content at Resin B may be reflected in its higher temperature range than Resin A.

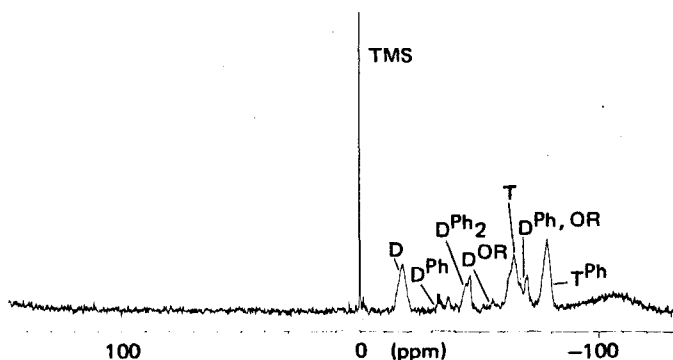


Fig.2 ^{29}Si FT n.m.r. spectrum of resin B

3.2 Intermediate Used for Silicone Alkyds

The ^{29}Si FT n.m.r. spectrum of a silicone paint intermediate is shown as Resin C in Fig. 3. This material contains free hydroxy groups that enable it to participate in the reaction to produce an alkyd.³ Four clearly distinguishable signals are present in the spectrum. The peaks at −64 and −78ppm correspond to the T and T^{Ph} units respectively. The remaining signals are from D^{OH} and $D^{Ph, OR}$ units. It is rather difficult to detect any hydroxyl groups in the 1H n.m.r. spectrum of the material,⁴ yet alone to distinguish between MOH , DOH or TOH hydroxyl groups. This distinction is most important because the materials formed by reaction at these different hydroxyl groups will have different three-dimensional structures and properties. A quantitative silicon analysis of this material is described below.

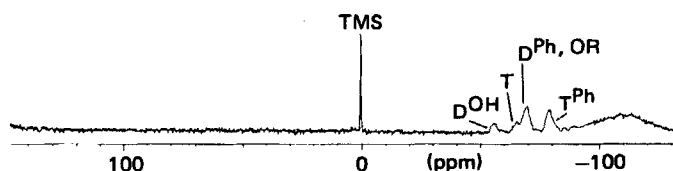


Fig.3 ^{29}Si FT n.m.r. spectrum of resin C

The air-drying alkyd SC 600 (Croda Resins Ltd) is made using the above silicone intermediate. The 1H n.m.r. spectrum of this material is shown in Fig. 4. The sample must be dried carefully to remove all traces of solvent which can interfere with spectral interpretation. The peaks from the silicone modification can only be seen as broad peaks at ca 7.5 and 0.5ppm. The ^{29}Si FT n.m.r. spectrum of SC 600 alkyd can be recorded without the need for time-consuming solvent evaporation. This is shown as Resin D in Fig. 5. It shows many similar features to Resin C. However, there are definite changes in the spectrum due to the presence of D^{OR} and $D^{Ph, OR}$ units which have been produced by the esterification reaction to form the alkyd. Precise analysis of all peaks in the spectrum is difficult but a useful fingerprint of the material is produced which enables it to be distinguished from similar materials.

A material that is similar to SC 600 alkyd is SC 28 alkyd (Croda Resins Ltd). This material is not air-drying and is prepared from the same silicone intermediate but different acids and alcohols. The ^{29}Si FT n.m.r. spectrum is shown

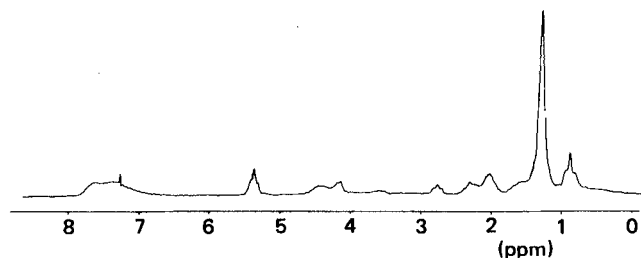


Fig.4 ^1H n.m.r. spectrum of resin D

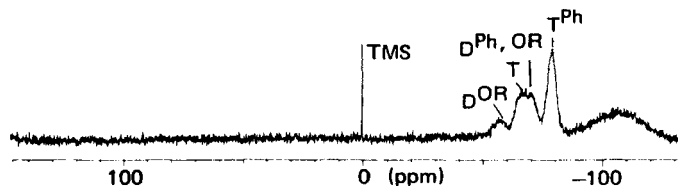


Fig.6 ^{29}Si FT n.m.r. spectrum of resin E

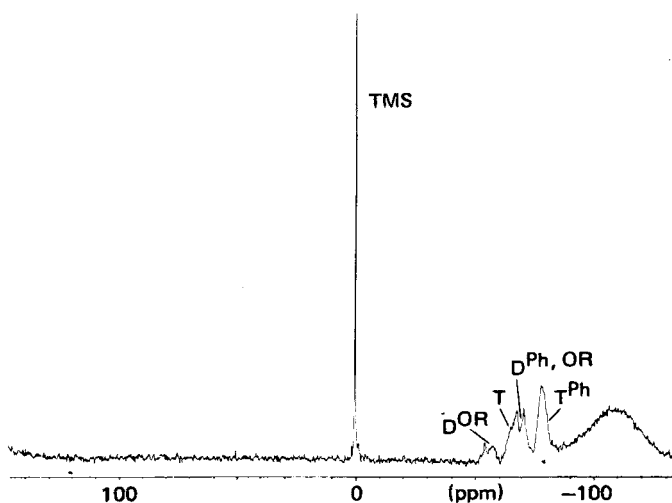


Fig.5 ^{29}Si FT n.m.r. spectrum of resin D

as Resin E in Fig. 6. This fingerprint is noticeably different to that obtained with Resin D, although the functional groups present are very similar.

3.3 Two-pack Silicone Elastomers

^1H n.m.r. can be used to identify the presence of various functional groups present in polydimethylsiloxanes.⁵ However, in order to examine the functionality and the silicon itself, ^{29}Si FT n.m.r. must be used.

The ^{29}Si FT n.m.r. spectrum of one component of a two-pack silicone rubber composition is shown in Fig. 7 as Resin F. The terminal M units of a polydimethylsiloxane can be seen at +10 and +8ppm. The repeating D units of the material give signals at -18, -20, and -22ppm. From these values the chain length of the polymer can be measured.⁸ The remaining signals in the spectrum at ca -36ppm are from D^{H} units, which can be confirmed by the presence of silane protons in the ^1H n.m.r. spectrum. The ^{29}Si n.m.r. result shows quite clearly that this material will not cross-link at the end of the polymer chain, and so will produce a fairly rigid three-dimensional material.

The ^{29}Si FT n.m.r. spectrum from one constituent of another two-pack silicone rubber is shown in Figure 8 as Resin G. The ^1H n.m.r. spectrum of this material in the silane region is very similar in appearance to that obtained in the Resin F above. However, the ^{29}Si n.m.r. spectrum shows obvious differences between these materials. There are no D^{H} units present, but M^{H} units can be seen at ca 1-5ppm. The presence of these terminal silane groups suggests that a linear product could be obtained. Apart from the M or D units from the polydimethylsiloxane, the sample also shows Q signals from a silicate. Another cross-linking mechanism for these materials involves the reaction between a silicate ester in one component with a hydroxy functional group in the other component.³

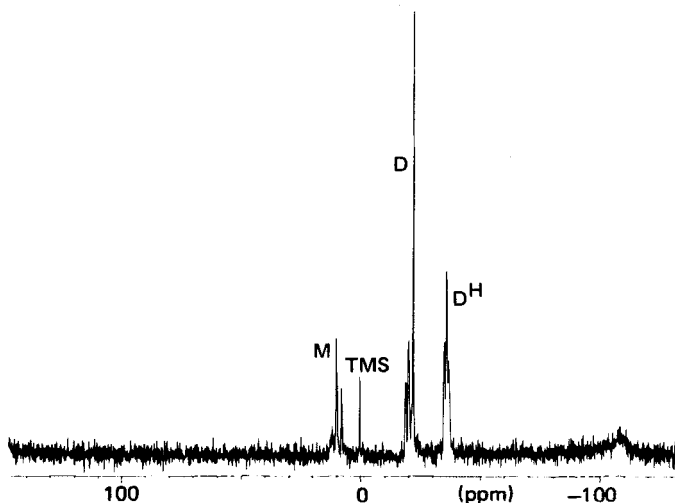


Fig.7 ^{29}Si FT n.m.r. spectrum of resin F

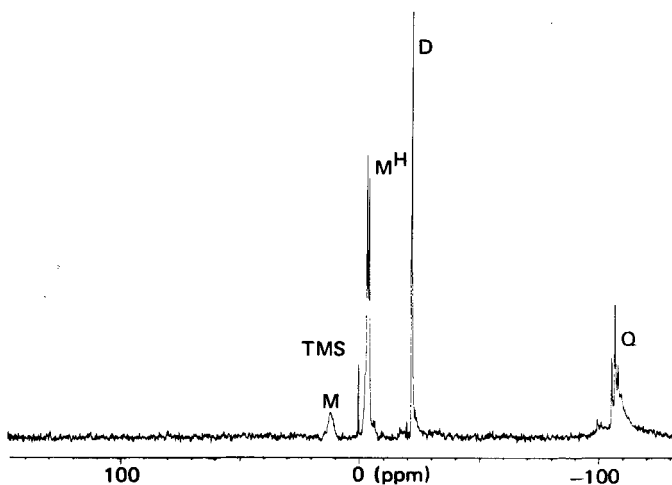


Fig.8 ^{29}Si FT n.m.r. spectrum of resin G

3.4 Quantitative ^{29}Si nmr

In general, silicon nuclei with different chemical environments dissipate absorbed radiofrequency energy at different rates. If this energy is not completely dissipated before further energy is supplied to the nuclei, the resulting signal intensities may not reflect the true relative amounts of the different silicon nuclei.¹¹ The rate at which this dissipation occurs can be found by measuring the spin-lattice relaxation time, T_1 , of all the nuclei. These T_1 values can be shortened by the use of the paramagnetic species chromium (III) tris-pentadionate.

The silicon content of the silicone paint intermediate, Resin C, was measured by adding a known amount of reference compound, octamethylcyclotetrasiloxane. The T_1 values of all silicon nuclei were measured and from these results the minimum scan cycle time for quantitative results can be found. For the 90° pulse, this was found to

be six seconds. The ^{29}Si FT n.m.r. spectrum shown below in Fig. 9 is the quantitative analysis of the paint intermediate using this scan cycle time of six seconds, which requires 12.5h accumulation. The value of the integral from the intermediate can be compared to that of the internal reference, i.e. A:B. Using the weights of each component, a figure of 21.1 per cent silicon is obtained for the intermediate. This compares favourably with a figure of 22.5 per cent obtained by a gravimetric method using hydrofluoric acid.¹² The experimental error for the integration of the spectrum is of the order of ± 5 per cent, due in part to the presence of the silicon signal from the glass n.m.r. tube. The use of a non-interfering tube may reduce the error of the analysis. However, the n.m.r. method involves far less sample preparation than existing methods of silicon assay.

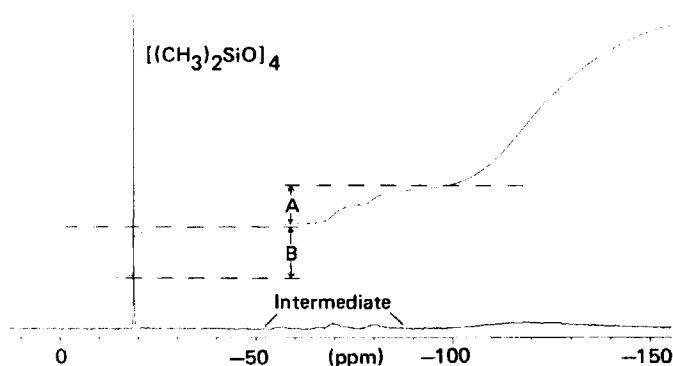


Fig.9 Quantitative ^{29}Si FT n.m.r. spectrum of a paint intermediate

4. CONCLUSIONS

^{29}Si FT n.m.r. is a very useful technique for investigating the structures of silicone paints and polymers. The

technique is far more specific than ^1H n.m.r. Functional groups directly bonded to silicon can be characterised and small differences in complex structures can be detected. The presence of particular silicone intermediates can be observed in modified alkyd materials, and the cross-linking sites of two-pack elastomers can be established. Initial studies suggest that the ^{29}Si FT n.m.r. technique can be used to determine the silicon content of silicones, and that sample preparation is significantly reduced when compared to existing analytical methods.

5. ACKNOWLEDGEMENTS

The author would like to thank: Mr J. Cornish, Croda Resins Ltd, for helpful discussions and the donation of SC 600 and SC 28 alkyds; Mr J.E. Davies and Dr M. Marshall of MQAD for running ^1H n.m.r. spectra; and Mr D. Tucker of MQAD for gravimetric analyses.

References

- 1 Nylén, P., & Sunderland, E., 'Modern Surface Coatings', London: Interscience, 1965, 226.
- 2 Cornish, J., *Polym. Paint Colour J.*, 1981, 171, 278.
- 3 Kookootsedes, G.H., 'Modern Plastics Encyclopaedia', 1979, 10A, 112.
- 4 Coutant, J.E., & Robinson, R.J., 'Analysis of Silicones', London: Interscience, 1974, 287.
- 5 Davies, J.E., MQAD Technical Paper in preparation.
- 6 Marshall, M., MQAD Report No. 261, 1977.
- 7 Shaw, D., 'Fourier Transform n.m.r. Spectroscopy', Amsterdam: Elsevier, 1976, 251.
- 8 Harris, R.K., Kennedy, F.J., & McFarlane, W., 'N.m.r. and the Periodic Table', New York: Academic Press, 1978, 310.
- 9 Martin, M.L., Delpuech, J.-J., & Martin, G.J., 'Practical n.m.r. Spectroscopy', London: Heyden, 1980, 231.
- 10 Reference 9, pp321.
- 11 Reference 9, pp362.
- 12 Newland, B.T.M., MQAD Technical Paper No. 685, 1977.