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^{29}Si N.M.R. investigations of polysiloxanes

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^{29}Si N.M.R. investigations of polysiloxanes

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A number of side chain liquid crystal polysiloxanes prepared from both homo- and co-polymeric backbones have been studied by ^{29}Si N.M.R. and the chemical shifts assigned. Partly mesogenated poly(hydrogenmethylsiloxanes) have been similarly studied and chemical shift assignments made for sequence distributions. The data should prove helpful in studies of compositional variation in preparations of side chain copolymeric polysiloxanes.

1. Introduction

Side-chain liquid crystal polymers, particularly those based upon a polysiloxane main-chain, have become of increasing interest because of their unique properties. Polymeric materials which show reversible thermotropic mesophases combine the viscoelastic properties associated with macromolecules with the electro-optic properties which are characteristic of low molar mass liquid crystals. This combination has led to the possibility of new display and/or data storage devices which utilize these materials [1-3].

Polysiloxanes which exhibit liquid-crystalline properties are prepared by the chemical modification of a non-mesogenic polymer by the addition of an appropriate mesogenic unit. Most commonly this is achieved by the polyhydrosilylation of a mesogenic terminal alkene [4-6] with a polymer containing hydrogenmethylsiloxy groups. Three different kinds of liquid crystal polysiloxane have been reported: homopolymers, random copolymers containing two or more mesogenic units, and random copolymers prepared using poly(hydrogenmethyl-dimethylsiloxane) copolymers as the precursor backbone.

There have been a number of publications concerning the properties and applications of polysiloxanes which show liquid-crystalline properties [7]. However, there has been much less information published about the reproducible synthesis and characterization of these materials [8, 9]. In this report, ^{29}Si N.M.R. spectra are presented and the chemical shifts assigned for a number of polysiloxanes of forms I and II which show liquid-crystalline properties, and a series of chemical shift assignments have been made for sequence distributions for partly mesogenated polysiloxanes of the form III which are precursors to liquid-crystalline polysiloxane copolymers. These are the first reported ^{29}Si N.M.R. studies of materials of these forms.

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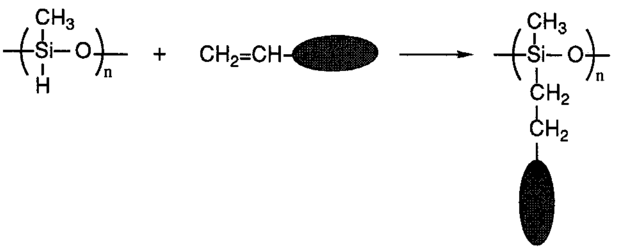
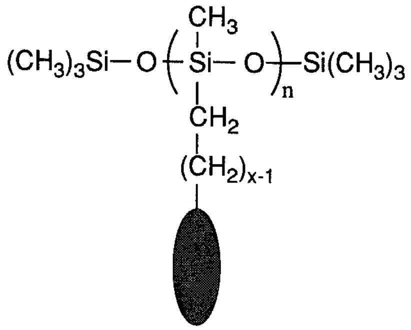
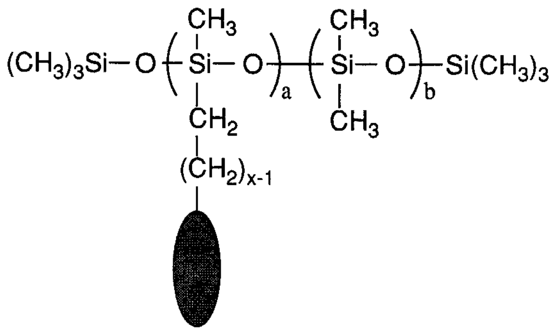


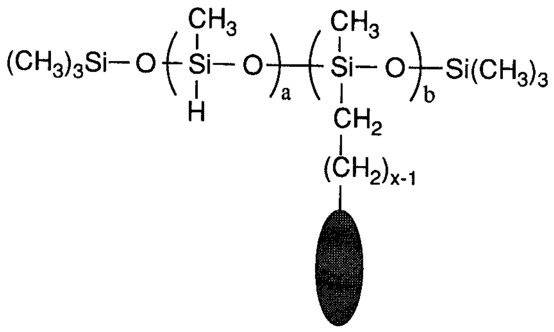
Figure 1. Preparation of liquid crystal polysiloxanes by poly(hydrosilylation); ● ≡ mesogenic unit.



I Homopolymer



II Random copolymer



III Partially substituted copolymer

^{29}Si Fourier transform N.M.R. may be used for the identification and characterisation of polysiloxanes [10–13]. Such spectra of siloxanes can give much information relating to the tacticity of homopolymers and the sequence distribution of copolymers [10, 14]. ^{29}Si (natural abundance = 4·7 per cent; $I = \frac{1}{2}$) is the only naturally occurring silicon isotope with non-zero spin. As there is very little probability of ^{29}Si–^{29}Si or ^{29}Si–^{13}C coupling, fully proton-decoupled spectra give, almost invariably, single line resonances for each silicon environment. Equally favourably, the chemical shift range for organosiloxanes is considerable (greater than 70 ppm for linear polymers) [11]. There have been many ^{29}Si N.M.R. investigations of both linear and cyclic siloxanes. The majority have concentrated on dimethylsiloxane oligomers and polymers [15–17]. Other studies have included phenylmethylsiloxanes [16, 18], hydrogenmethylsiloxanes [14, 19, 20], copolymers of dimethyl- and methylphenylsiloxane [16] and dimethyl-hydrogenmethylsiloxanes [14, 21].

2. Experimental

2.1. *Preparation*

The alkenes used to prepare the liquid crystal polysiloxanes referred to in this study were obtained by standard methods described in the literature [6, 22, 23]. I.R. spectra were obtained on a Perkin Elmer 580B infra-red spectrophotometer. ^{1}H N.M.R. spectroscopy was carried out using a JEOL JNM-PMX-60 spectrometer. The liquid-crystalline polysiloxane homopolymers and random copolymers were prepared by poly-hydrosilylation using boiling toluene as a solvent, as described previously [4, 5, 6, 8, 9]. Homopolymers were prepared using poly(hydrogenmethylsiloxane) (Dow Corning DC1107 fluid) from which low molar mass linear and cyclic species had been removed by fractional precipitation. Random copolymers were prepared using poly(hydrogenmethyl-dimethylsiloxane) copolymers as supplied (Petrarch PS 122·5, MeH : $Me_2 \approx 1:1$ and Petrarch PS 123, MeH : $Me_2 \approx 1:6$). The initiator used for reaction was hexachloroplatinic acid in propan-2-ol at a Pt : alkene ratio in the range $1:10^3$–10^6. A 10 per cent molar excess of alkene to Si–H was used. The progress of the reaction was monitored by I.R. spectroscopy, using an evaporated film of the reaction mixture, by following the loss of the Si–H absorption at *c*.2160 cm^{-1}. For homopolymers and random copolymers, the extent of reaction was greater than 95 per cent occupancy of available Si–H sites. After reaction, the solutions were filtered (Millipore PTFE membrane, 0·5 μm pore size) and the solvent removed by rotary evaporation. No procedures were carried out to remove the excess of alkene impurity as previously described [9], as the only silicon containing species which would be detected by ^{29}Si N.M.R. is the liquid-crystalline polymer.

Partially substituted copolymers were obtained by removal of samples at intervals of time from the hydrosilylation reaction mixtures. In order to obtain polymers of low degree of Si–H substitution, reactions were carried out using boiling benzene. In order to quench the hydrosilylation reaction, samples of the reaction mixture were cooled rapidly to below room temperature subsequent to their removal, filtered, washed with methanol, and the solvent removed by rotary evaporation. The extent of reaction was calculated by integration and comparison of the substituted and unsubstituted regions of the ^{29}Si N.M.R. spectra.

2.2. *^{29}Si N.M.R. methods*

^{29}Si FT-N.M.R. spectra were obtained at the University of York using a JEOL FX-90Q spectrometer, and at the University of Hull using a JEOL JNM GX-270 spectrometer; the experimental conditions are detailed in table 1. Spectra were obtained at a concentration of ca. 20 per cent (weight/volume). The deuterium present in the solvent was used for the internal lock of the spectrometer. N.M.R. tubes of 5 mm or 10 mm o.d. were used for sample containment and the solutions were not degassed prior to analysis.

Table 1. ^{29}Si N.M.R. experimental conditions.

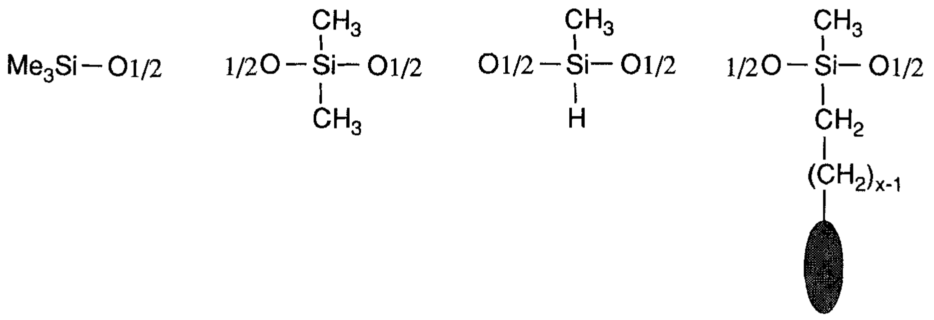
Parameter	Spectra acquired at University of York	University of Hull
Solvent	$CDCl_3$	$CDCl_3$, $CH_2Cl_2 + CDCl_3$
Reference	TMS	TMS
Observing frequency	17·76 MHz	53·54 MHz
^{29}Si–^{1}H decoupling field	89·55 MHz at centre† (of ^{1}H spectrum)	270·2 MHz at centre
Acquisition temperature	ambient (magnet, ~321 K)	294 K
Pulse Width	9–18 μs (5 or 10 mm insert)	7 μs
Pulse delay	60 s	1·5 s
Scans	400–5000	2500–30000

† NNE Decoupler Mode was used (no nuclear Overhauser effect); ^{29}Si can exhibit a negative NOE, so the decoupler is *on* only during spectral acqusition and it is off during the relatively long wait times between each scan. This avoids any build up of NOE.

^{29}Si nuclei, in general, have long spin relaxation times [24], and this necessitates long experimental times. In order to circumvent this, a paramagnetic relaxation agent ($Cr(acac)_3$), at a concentration of *c.*1 per cent (weight/volume) was added to the solutions for spectra acquired at the University of Hull. No discernible shift of the positions of ^{29}Si N.M.R. resonances was observed between spectra recorded for solutions of polymer prior to, and after the addition of the relaxation agent.

3. Results and discussion

The following standard notation commonly used for siloxane units has been applied in the assignment of ^{29}Si N.M.R. spectra of liquid crystal polysiloxanes:



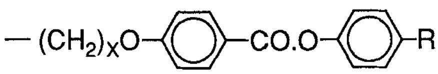
M D D^H D^M

Where sequences are referred to, positions to the left and right of the central nucleus (the nucleus assigned and underlined) are interchangeable. Thus, the pentad sequence $DD^H\underline{D}DD$ is identical to the sequence $DD\underline{D}D^HD$; similarly, $D^HD\underline{D}DD \equiv DD\underline{D}DD^H$.

3.1. *Homopolymers* (*Type I*)

^{29}Si N.M.R. chemical shift assignments for a number of liquid crystal polysiloxane homopolymers are given in table 2. Literature values for other polysiloxane ^{29}Si N.M.R. chemical shift assignments are given for comparison [14, 19]. The D^{M} units have very similar chemical shifts to the D units, although the mesogenic unit appears to shield the Si nucleus more than the methyl group, causing a slight shift of the resonance to lower frequency. The D^{M} resonance was observed to be a triplet in all cases (although total resolution was not achieved for all spectra). This fine splitting is due to asymmetry effects. The parent poly(hydrogenmethylsiloxane) was previously shown to be atactic [21]; thus the liquid crystal polysiloxane will also be atactic. The spectra are consistent with the assumption that nearest-neighbour influences can be resolved sufficiently to be observed. The resonances are split into a 1 : 2 : 1 triplet as each Si nucleus has two asymmetric neighbours (leading to sequences $d\underline{d}d \equiv l\underline{l}l$, $d\underline{d}l \equiv l\underline{d}d \equiv l\underline{l}d \equiv d\underline{l}l$, $l\underline{d}l \equiv d\underline{l}d$).

Table 2. ^{29}Si N.M.R. chemical shift assignments for liquid crystal polysiloxane homopolymers; the mesogenic side chain is of the form.



IV

X	R	No. of spectra	$\delta(M)$†	$\delta(D^{\mathrm{M}})$†
5	CN	5	+7·3	−22·7
3	OCH_3	4	+8·1	−22·1
6	OC_6H_{13}	2	+8·1	−22·1
3	OC_2H_5	2	+8·1	−21·9
			$\delta(M)$†	$\delta(D)$†
Poly(dimethylsiloxane)			+7·2	−21·9
Poly(hydrogenmethylsiloxane)			+9·6	−34·9

† ppm with respect to TMS; correct to ± 0·1 ppm.

3.2. *Random copolymers* (*Type II*)

^{29}Si N.M.R. chemical shift assignments for random copolymers (type II; $x = 5$, terminal group in mesogenic unit–CN) are given in table 3. A ^{29}Si N.M.R. spectrum is given in figure 2. In order to aid the assignment of the ^{29}Si N.M.R. spectra of random copolymers, two polymers were prepared with varied composition. The chemical shift assignments made for these copolymers are consistent with those observed for the

Table 3. ^{29}Si N.M.R. chemical shifts for random copolymers (II).

		Chemical shift†	
MeMesogen: Me_2	$\delta(M)$‡	$\delta(D)$	$\delta(D^{\mathrm{M}})$
~ 1 : 1	+7·3	−21·9	−22·6
~ 1 : 6	+7·3	−21·8	−22·6

† ppm with respect to TMS; correct to ± 0·1 ppm.
‡ Single resonance observed.

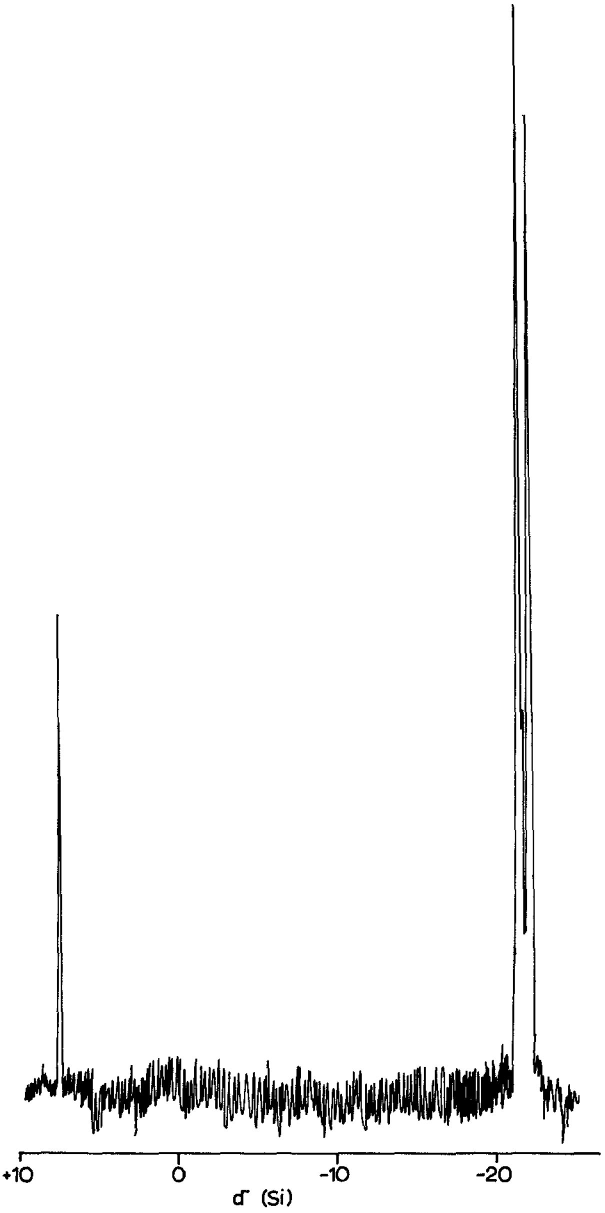


Figure 2. A typical ^{29}Si N.M.R. spectrum for a random copolymer (II).

liquid crystal homopolymers and those reported for poly-(dimethylsiloxane), as given in table 2. Nearest neighbour splittings have not been resolved or assigned due to the proximity of the D and D^{M} resonances.

3.3. *Partially substituted copolymers* (*Type III*)

^{29}Si N.M.R. chemical shift assignments for partially substituted copolymers are given in table 4 and a typical spectrum is shown in figure 3. The chemical shift assignments for the pentad sequences for main-chain Si nuclei and tetrad sequences

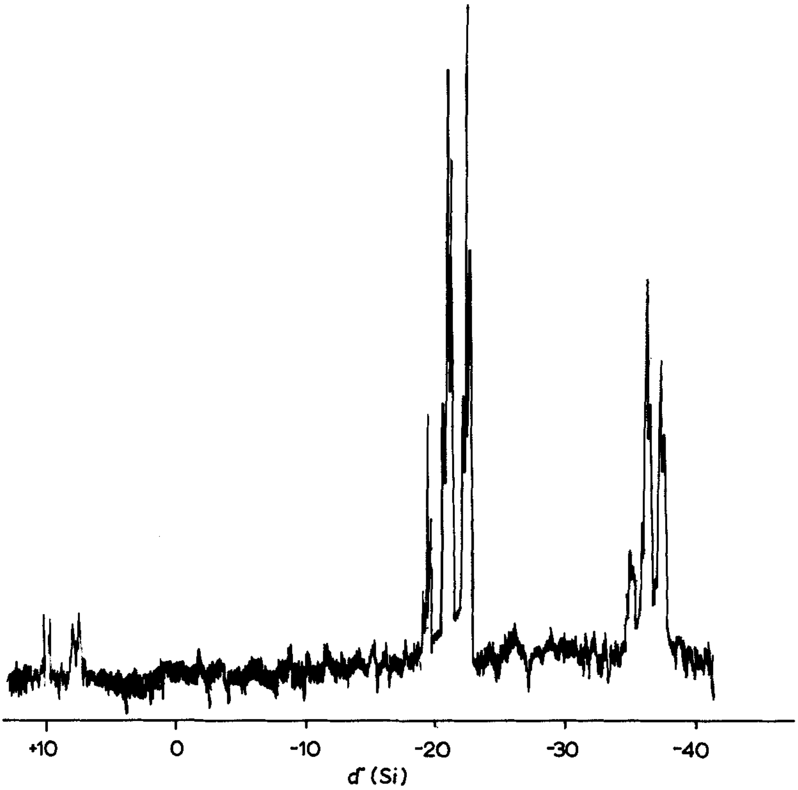


Figure 3. A typical ^{29}Si N.M.R. spectrum for a partially substituted copolymer (III).

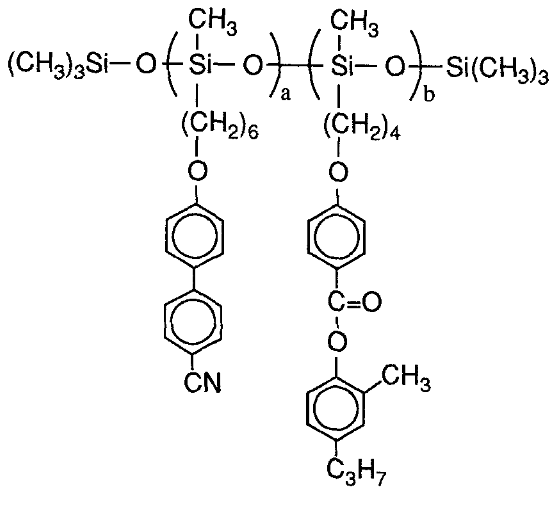
for end-group Si nuclei were based upon previously reported assignments for poly(hydrogenmethyl-dimethylsiloxane)copolymers [14, 21]. In these investigations three broad, but distinct regions of absorption were observed corresponding to *M*, *D* and D^{H} nuclei (see figure 4). Previously reported chemical shift assignments for these random copolymers are given for comparison in table 5 (from [14] and [21]). The chemical shift assignments for the partially substituted copolymers mirror those previously reported for the random copolymers of poly(hydrogenmethyl-dimethyl)-siloxane. For triad sequences the change in sequence $D^{H}\underline{D}D^{H}$ to $D\underline{D}D$ causes a shift in resonance of $-2{\cdot}7$ ppm and we report that the sequence alteration $D^{H}\underline{D}^{M}D^{H}$ to $D^{M}\underline{D}^{M}D^{M}$ gives a shift in resonance of -3 ppm. The change in sequence $D^{H}\underline{D}^{H}D^{H}$ to $D\underline{D}^{H}D^{H}$ is $-2{\cdot}3$ ppm, which is in good agreement with our reported shift for $D^{H}\underline{D}^{H}D^{H}$ to $D^{M}\underline{D}^{H}D^{M}$.

The properties of a liquid crystal polysiloxane may be advantageously modified by the incorporation of two or more mesogens. Thus the liquid crystal polysiloxane (V) has been shown to have potential for electrooptical applications [2, 3, 25]. This polymer was prepared by the copolyhydrosilylation of the relevant alkenes with poly(hydrogenmethylsiloxane). A 10 per cent excess of each alkene is used in the reaction mixture. There is no information available concerning the composition of the final polymer (V), a variable which may affect the properties of the material. Preliminary investigations have attributed differences in transition temperatures between batches of polymer V to variations in composition of the copolymers [26]. In addition

Table 4. ^{29}Si N.M.R. chemical shift assignments for partially substituted polymers (III) (x = 5; terminal group in mesogenic unit = CN).

Chemical shift (ppm wrt TMS)	Sequence (nucleus assigned is underlined)†	
+10·2	$\underline{M}D^HD^H$	End group
+9·7	$\underline{M}D^HD^M$	
+7·8	$\underline{M}D^MD^H$	
+7·4	$\underline{M}D^MD^M$	
−19·1	$D^HD^H\underline{D}^MD^HD^H$	
−19·4	$D^MD^H\underline{D}^MD^HD^H$	
−19·7	$D^MD^H\underline{D}^MD^HD^M$	
−20·6	$D^HD^H\underline{D}^MD^MD^H$	
−20·9	$D^HD^H\underline{D}^MD^MD^M$	
−21·2	$D^MD^H\underline{D}^MD^MD^M$	
−22·1	$D^HD^M\underline{D}^MD^MD^H$	
−22·4	$D^HD^M\underline{D}^MD^MD^M$	
−22·7	$D^MD^M\underline{D}^HD^MD^M$	
−34·8	$D^HD^H\underline{D}^HD^HD^H$	
−35·1	$D^MD^H\underline{D}^HD^HD^H$	
−35·3	$D^MD^H\underline{D}^HD^HD^M$	
−35·9	$D^HD^M\underline{D}^HD^HD^H$	
−36·2	$D^MD^M\underline{D}^HD^HD^H$	
−36·4	$D^MD^M\underline{D}^HD^HD^M$	
−37·0	$D^HD^M\underline{D}^HD^MD^H$	
−37·3	$D^MD^M\underline{D}^HD^MD^H$	
−37·6	$D^MD^M\underline{D}^HD^MD^M$	

† Assignments as previously stated.



Polymer V$a \approx b$

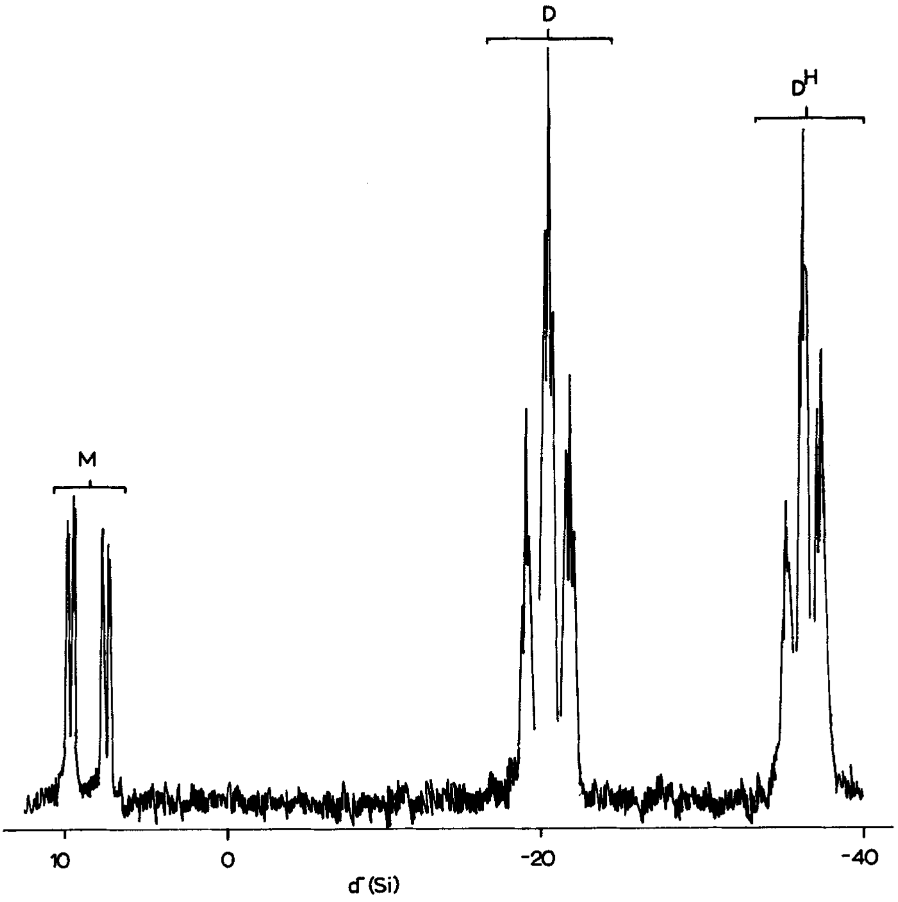


Figure 4. A typical ^{29}Si N.M.R. spectrum of a poly(hydrogenmethyl-dimethylsiloxane) copolymer, showing M, D, and D^H regions.

to this possible variation in composition, there is no indication of the sequence distribution of the mesogenic units, within the copolymer (i.e. is the polymer random or do differences in the reactivity of the alkenes create a pseudo-block or, at the opposite extreme, an alternating copolymer?).

By the preparation of a partially substituted copolymer (up to 50 per cent substitution) from one of the mesogenic alkenes used to make polymer V, a ^{29}Si N.M.R. study of the product, using the chemical shift assignments reported here, would give information upon the sequence distribution and composition of the final copolymer prepared by a subsequent hydrosilylation reaction using the second alkene of polymer V. Comparison of thermal transition temperatures of a copolymer prepared in this way, with those previously investigated, may give information leading to a more rigorous means of reproducible synthesis and of characterization and optimisation of the properties.

Initial data on the sequence distribution of partially substituted copolymers has indicated that, although all expected sequence distributions are observed, at a low degree of substitution, there is a greater than statistically predicted resonance [27] for the triad sequence $D^M\underline{D}^M D^M$. This would imply a tendency for sequential addition of

Table 5. Chemical shift assignments for ^{29}Si N.M.R. spectrum of poly(hydrogenmethyl-dimethylsiloxane).

δSi	Sequence (see text for abbreviations)
−18·7	$D^HD^H\underline{D}D^HD^H$
−19·0	$D^HD^H\underline{D}D^HD$
−19·3	$DD^H\underline{D}D^HD$
−20·1	$D^HD^H\underline{D}DD^H$
−20·4	$D^HD^H\underline{D}DD$
−20·7	$DD^H\underline{D}DD$
−21·4	$D^HD\underline{D}DD^H$
−21·7	$D^HD\underline{D}DD$
−22·0	$DD\underline{D}DD$
−34·8	$D^HD^H\underline{D}^HD^HD^H$
−35·0	$D^HD^H\underline{D}^HD^HD$
−35·3	$DD^H\underline{D}^HD^HD$
−35·9	$D^HD^H\underline{D}^HDD^H$
−36·1	$D^HD^H\underline{D}^HDD$
−36·2	$DD^H\underline{D}^HDD$
−37·1	$D^HD\underline{D}^HDD^H$
−37·3	$D^HD\underline{D}^HDD$
−37·6	$DD\underline{D}^HDD$
9·7	$\underline{M}D^HD^HD^H$
9·6	$\underline{M}D^HD^HD$
9·3	$\underline{M}D^HDD^H$
9·2	$\underline{M}D^HDD$
7·6	$\underline{M}DD^HD^H$
7·5	$\underline{M}DD^HD$
7·2	$\underline{M}DDD^H$
7·1	$\underline{M}DDD$

alkenes. Further studies are required before the reaction selectivity can be elucidated. The interpretation and application of the data reported here offer a simple and efficient method for obtaining this information.

4. Concluding summary

^{29}Si N.M.R. has been used to assign chemical shifts for side chain liquid crystal polysiloxanes prepared from both poly(hydrogenmethylsiloxane) and poly(hydrogenmethyl-dimethylsiloxane) backbones. Chemical shift assignments for sequence distributions in partially mesogenated poly(hydrogenmethylsiloxane)s have also been made. Application of these data to side chain polymers derived from more than one alkene should give information about the composition of the polymer, i.e., whether the side chain distribution is or is not random. This should assist our understanding of cases in which there are batch variations in the properties of such side chain copolymers.

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