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Synthesis of silicon oxynitride from a polymeric precursor

Part III *Polymerization and copolymerization of methylcyclosiloxanes and methylcyclosilazanes*

GA-ER YU*‡, J. PARRICK*, M. EDIRISINGHE‡, D. FINCH‡, B. RALPH‡
*Departments of *Chemistry and ‡Materials Technology, Brunel University, Uxbridge, Middlesex UB8 3PH, UK*

In the present work, homopolymerization and copolymerization of methylcyclosiloxanes and methylcyclosilazanes are investigated. Homopolymers and copolymers produced are characterized using ^{1}H NMR and Fourier transform infrared spectroscopy. It is found that the reactivity of methylcyclosiloxanes is much lower than that of methylcyclosilazanes. The structures of the homopolymers and copolymers produced are discussed and it is suggested that the latter consists of a block structure containing siloxanes and silazanes in which the siloxane units are the smaller.

1. Introduction

Methylcyclosiloxanes (MCSXs) and methylcyclosilazanes (MCSZs), prepared according to the methods described in Parts I and II [1, 2] are copolymerized in order to produce precursors which on pyrolysis are converted into ceramics. Homopolymerization of MCSXs and MCSZs has also been carried out in order to understand the copolymerization process. Both homopolymerization and copolymerization were initiated/catalysed using KH.

1.1. Homopolymerization

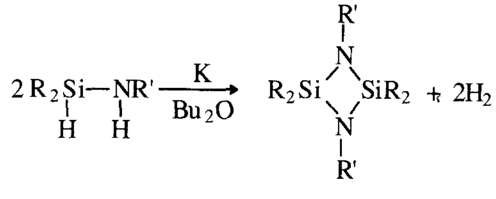
1.1.1. Homopolymerization of methylcyclosiloxanes

Unlike anionic and cationic polymerization of diorganocyclosiloxanes (e.g. polymerization of $[\mathrm{Si(R)(CH_3)O}]_n$, where R $> C_1$), which have been investigated over a long period of time [3–6], there have been relatively few studies on the polymerization of MCSXs, $[\mathrm{Si(CH_3)\,(H)\,O}]_n$ (usually $n > 4$). Recently, linear polymers of MCSXs with molecular weights ($\bar{M}_w$) $> 10^5$ have been prepared by cationic polymerization [7]. In contrast, anionic polymerization of MCSXs gave crosslinked products in either a gel form or a solid polymer when the reaction was initiated using sodium phenylsilanolate and sodium/potassium α-methylstyrene living polymer [8] or KOH [9], respectively.

1.1.2. Homopolymerization of methylcyclosilazanes

Recently, there has been renewed interest in the polymerization of organocyclosilazanes to produce preceramic polymers [10–14]. Several preceramic polymers leading to Si–N–C ceramics have been prepared using mainly dichloromethylsilane, $\mathrm{CH_3SiHCl_2}$ [15–18].

Seyferth and Wiseman [16–18], on the basis of Reaction 1 below [19], used KH as an initiator/catalyst to polymerize methylcyclosilazanes, $[\mathrm{Si(CH_3)(H)N(H)}]_n$ (n = 3, 4, 5) as shown in Reaction 2. They suggest that the resulting polymers are "sheet-like".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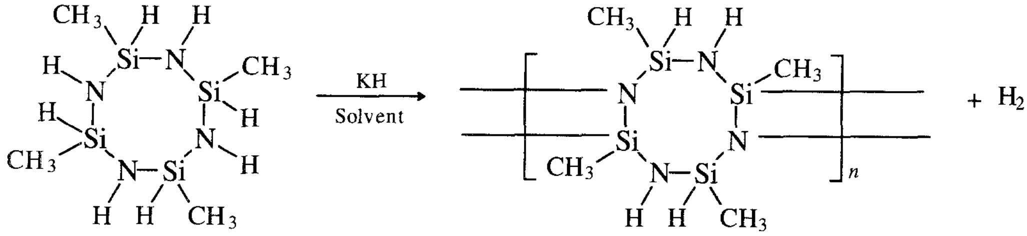
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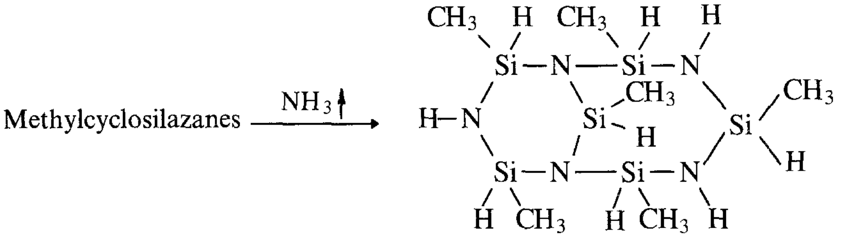
However, subsequent investigations [20] indicated that ring fusion polymerization via cyclodisilazane formation was not the principal polymerization process since ^{29}Si NMR studies of the polymerized products of the KH-catalysed methylcyclosilazanes did not indicate the presence of the Si_2N_2 ring structure. In fact, the polymers produced consisted mainly of larger silazane rings.

The polymerization of diorganocyclosilazanes by KOH has been studied by Andrianov and Kotrelev [21] who suggest that the reaction products consist of a complicated structure because of the loss of NH_3. Semenova *et al.* [22] describe the structure of the polymerized product as a "condensed hydride methylsilazane" (see Reaction 3 below) which arises due to the elimination of NH_3 from the cyclosilazanes formed with subsequent condensation of the decomposition products.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Laine and co-workers [23–26] used a transition metal catalyst, $Ru_3(CO)_{12}$, to polymerize cyclosilazanes as preceramic precursors. Transition metal catalysed reactions are not discussed in the present paper.

1.2. Copolymerization of methylcyclosiloxanes and methylcyclosilazanes

Copolymerization of methylcyclosiloxanes and methylcyclosilazanes has been investigated previously [27, 28] as a route to synthesize ceramics but the characteristics of the process and products have not been reported. Seyferth *et al.* [27] prepared several copolymers using KH as an initiator/catalyst and pyrolysed the polymers to Si–O–N ceramics. Yu and Mah [28] investigated the pyrolytic properties of copolymers described as "graft" and "in-situ" to prepare silicon oxynitride, but the structures and properties of the copolymers were not discussed.

2. Experimental procedure

2.1. Monomers

2.1.1. *Methylcyclosiloxanes*

The method of preparation of methylcyclosiloxanes has been described previously [1]. Methylcyclosiloxanes prepared were dried using CaH_2 powder and distilled under a vacuum of 10^{-2} mm Hg in the temperature range 20–100 °C to a liquid nitrogen trap before use in all the polymerization experiments described below, except where indicated otherwise.

2.1.2. Methylcyclosilazanes

The method of preparation of methylcyclosilazanes has also been described previously [2]. The products from the ammonolysis reaction were kept in solution in tetrahydrofuran (THF) before use in polymerization experiments. The concentration of products in such a solution was checked by withdrawing an aliquot and weighing the polymer formed after polymerizing the cyclosilazanes remaining upon evaporation of the solvent under vacuum.

2.2. Homopolymerization experiments

2.2.1. *Homopolymerization of methylcyclosiloxanes*

Distilled methylcyclosiloxanes were added to a flask with THF (freshly distilled from Na/benzophenone). The mixture was stirred and air was excluded by flushing with dry N_2. KH powder (washed using dry THF) was added to the system to initiate the polymerization. The final product was separated by evaporating the THF under vacuum for 15 h. Reaction conditions are given in Table I.

2.2.2. *Homopolymerization of methylcyclosilazanes*

The clear solution resulting directly from the ammonolysis reaction was injected into a flask under dry N_2. KH powder was then added to the stirred mixture. A large amount of gas was released during the first 1.5 h. Thereafter, the evolution of gas reduced gradually and was complete after 3 h. Polymerization was carried out over 3 h and a white solid (polymer) was produced. This polymer was dissolved in THF (other common organic solvents could also be used) and was separated subsequently by evaporation of the solvent. Reaction conditions are given in Table II.

2.3. Copolymerization

Copolymerization experiments were carried out at several temperatures with different starting molar ratios of N to O in the monomers. Methylcyclosilazane solution was injected into a flask and where necessary heated to the reaction temperature (see Table 3). Subsequently, methylcyclosiloxanes were injected into the flask under dry N_2 and KH powder was added to the stirred mixture. The rate of reaction appeared faster at higher temperatures and in all cases described in Table 3 a large amount of gas was released when KH was added. The reaction was carried out for at least 10 h. Polymerization was ended by adding CH_3I or $(CH)_3SiCl$ into the system. The polymers produced were obtained by evaporating the solvent under vacuum over 10 h.

2.4. Proton nuclear magnetic resonance spectroscopy (^{1}H NMR)

^{1}H NMR spectra were obtained using a Jeol FX200 spectrometer. Solutions (5–10 % wt/vol) of polymers, copolymers or other samples (as described in section 3 below) in $CDCl_3$ or C_6D_6 were studied at 200 MHz. Usually, tetramethylsilane (TMS) was used as the internal reference, otherwise the resonance from residual $CHCl_3$ or C_6H_6 was used as the reference. A delay time of 6–10 s was used to ensure full relaxation of the protons between pulses.

2.5. Fourier transform infrared spectroscopy (FT-IR)

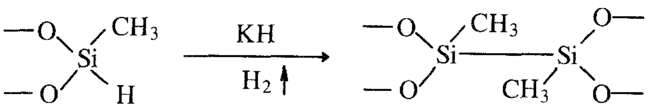
FT-IR spectra of the polymers or copolymers were obtained using a Nicolet 710 FTIR spectrometer. A drop of the polymeric solution was put on a KBr disc and the solvent was left to evaporate under N_2 before spectra were obtained in the range 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Homopolymerization of methylcyclosiloxanes

Results of homopolymerization experiments of MCSXs are summarized in Table I. The yield of homopolymer produced in experiment A was very low. The yield could be increased to 95 wt % (experiment B) but only after increasing the reaction time and temperature significantly (see Table I). This indicated that the reactivity of MCSXs was very low under the polymerization conditions used. Experiment A was stopped by evaporating the solvent in a high-vacuum line. All the solvent and unreacted materials were collected in a liquid nitrogen trap and a viscous polymer was left in the reactor. Later, the solvent was distilled using a vacuum line to a solid CO_2 trap leaving a liquid sample.

A comparison of the ^{1}H NMR spectra of the homopolymer produced, the liquid sample resulting from the distillation of the solvent and the starting materials (a mixture of methylcyclosiloxanes with 52.4 wt % of tetramethylcyclotetrasiloxane, 32.2 wt % of pentamethylcyclopentasiloxane, 11.5 wt % of hexamethylcyclohexasiloxane, 2.8 wt % of heptamethylcycloheptasiloxane and 1.1 wt % of octamethylcyclooctasiloxane as determined by gas chromatography) is shown in Fig. 1. Spectra shown in Fig. 1b and c are almost identical, indicating that the liquid remaining after distillation of the solvent used in Reaction 1 is unreacted starting material. The spectrum shown in Fig. 1a shows a single, uncoupled proton resonance at 0.3 p.p.m. indicating the presence of an isolated methyl group in the polymer. We suggest that the polymerization reaction can be described by Reaction 4 given below:



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3.2. Homopolymerization of methylcyclosilazanes

The results of homopolymerization experiments of MCSZs are summarized in Table II. Comparison with the corresponding results from the homopolymerization of MCSXs (Table I) shows that, in the case of MCSZs, the yields are higher and the reaction times are shorter. It was clear that at the higher temperature of 60 °C (preparation of homopolymer P12 in Table II), the reaction occurred much more vigorously and a larger volume of gas was released as soon as KH powder was introduced into the system. At least three gases, i.e. NH_3, H_2 and CH_4, were identified by test paper and gas chromatography (GC) methods.

Fig. 2 shows the ^{1}H NMR spectrum for sample P12 (P7 and P8 have similar spectra) in Table II. The presence of broad peaks indicates a polymer of complex structure. The discussion below is based on spectral assignments similar to those made for the monomers of methylcyclosilazanes described in Part II [2]. In Fig. 2, the ratio of the intensities for Si-$\underline{H}$, N-$\underline{H}$ and Si-C$\underline{H}_3$ is about 1 : 1.1 : 7.8. This ratio does not rule out the possibility of the structure suggested by Reaction 2. However, considering the types of gas released during polymerization, a more complicated structure could be present in the homopolymers prepared in the present way. The FT-IR spectrum shown in Fig. 3 also supports a more complicated structure for the homopolymer as it contains broad peaks, e.g. the broad bands at 3380 cm^{-1} for N–H stretching and 1173 cm^{-1} for the N–H bending. Compared with the FT-IR spectrum of the monomers [2], the relative intensity of N–H bands shows a decrease and this agrees with the conclusions drawn from the ^{1}H NMR spectrum discussed above. The distorted and broad band for Si–N–Si asymmetric stretching in Fig. 3 at 973 cm^{-1} indicates the disappearance of the uniform cyclic structure present in the monomers. This feature, and the detectable release of NH_3 during the reaction,

TABLE I Reaction conditions and products of homopolymerization of MCSXs

Experiment No.	Mass of MCSXs (g)	Volume of THF (ml)	Mass of KH (g)	Temperature (°C)	Reaction time (h)	Yield (wt %)	Product state
A	2.0	15	0.05	20	24	≃ 5	Liquid
B	4.7	80	0.1	60	120	≃ 95	Liquid

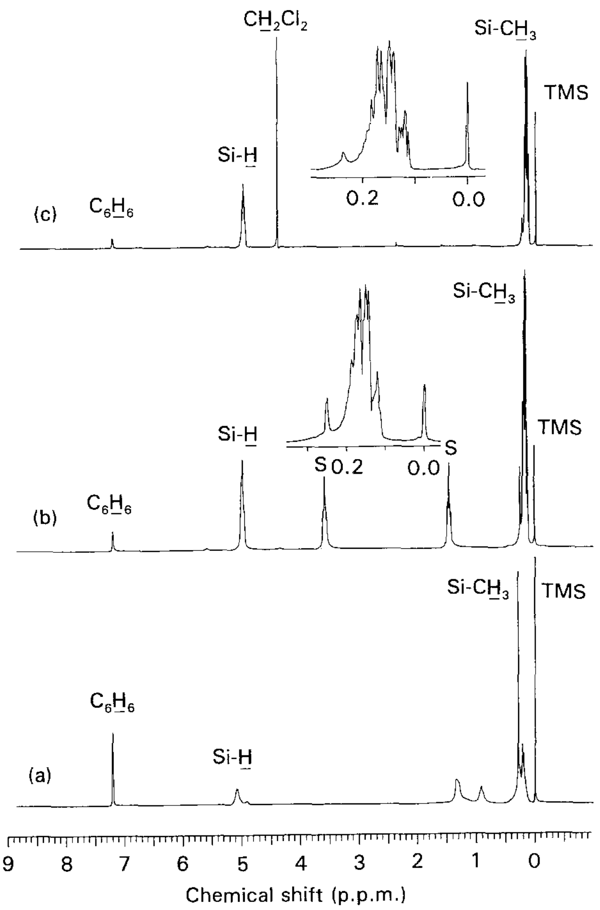

Figure 1 ^{1}H NMR spectra (in C_6D_6) of (a) the homopolymer produced in experiment A (see Table I), (b) the liquid after distillation of the solvent used for polymerization in experiment A, (c) the reactants used in experiment A. The expanded peaks of Si–C$\underline{H}_3$ are shown in (b) and (c). TMS and S refer to tetramethylsilane and solvent, respectively.

TABLE II Reaction conditions and products of homopolymerization of MCSZs

	P7	P8	P12
Mass of MCZ (g)	0.04	3.0	1.5
Volume of THF (ml)	10	60	50
Mass of KH (g)	0.01	0.1	0.03
Reaction temperature (°C)	20	20	60
Reaction time (h)	5	1	20
Volume of CH_3I or $(CH_3)_3$ SiCl (ml)	CH_3I, 0.2	CH_3I, 0.1	$(CH_3)_3SiCl$, 0.02
Yield (wt %)	≃ 95	≃ 95	≃ 95
Product state	Solid (white)	Solid (white)	Solid (white)
Solubility	Soluble	Soluble	Soluble

supports the presence of a structure with large rings similar to that suggested by Semenova *et al.* [22] and illustrated by Reaction 3. The FT-IR spectrum also shows peaks at 3450 and 3300 cm^{-1} for NH_2 stretching and a peak at 1540 cm^{-1} for NH_2 deformation. These peaks indicate the presence of Si–NH_2 in the homopolymer.

3.3. Copolymerization

Details of the copolymers produced are described in Table III. NH_3, H_2 and CH_4 were detected (by test paper and GC) in the released gases during polymerization. Copolymers P4, P6, P11A and P11B listed in Table III have similar ^{1}H NMR and FT-IR spectroscopic properties (those of P11B are used in the

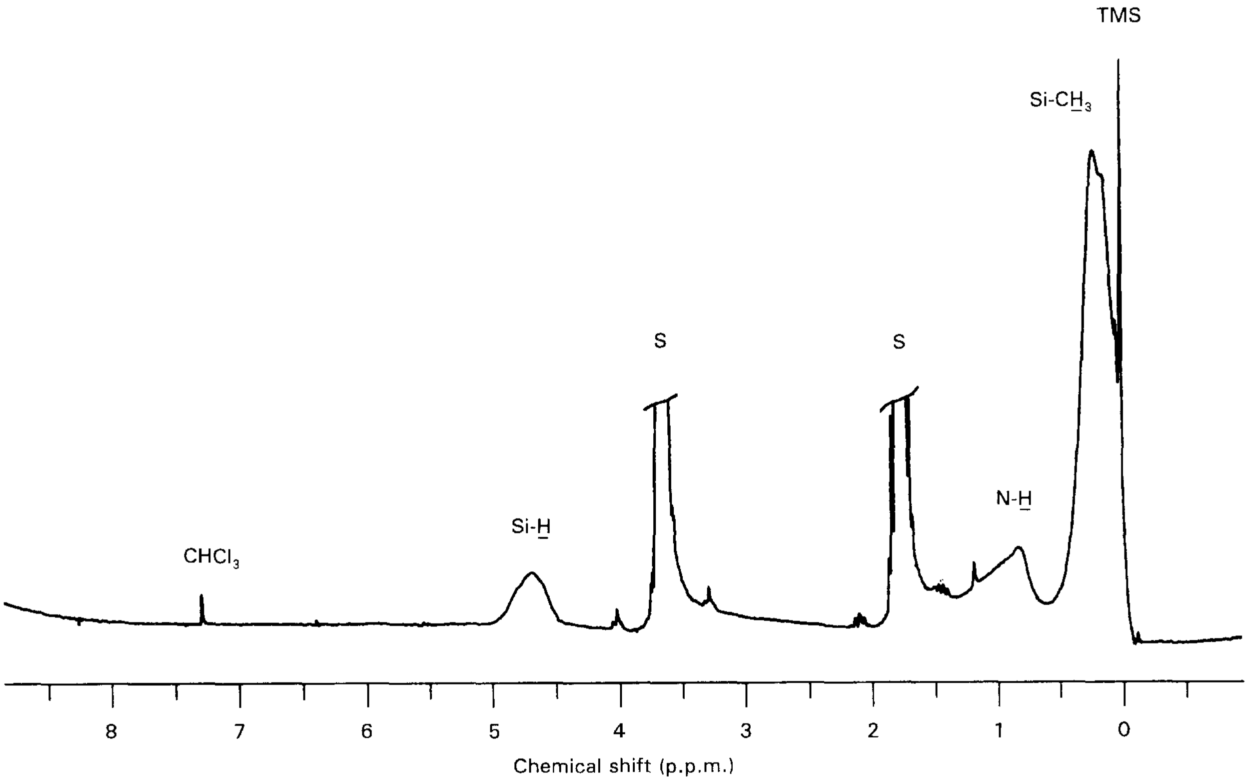

Figure 2 ^{1}H NMR spectrum (in $CDCl_3$) of the homopolymer P12 (see Table II). TMS and S refer to tetramethylsilane and solvent, respectively.

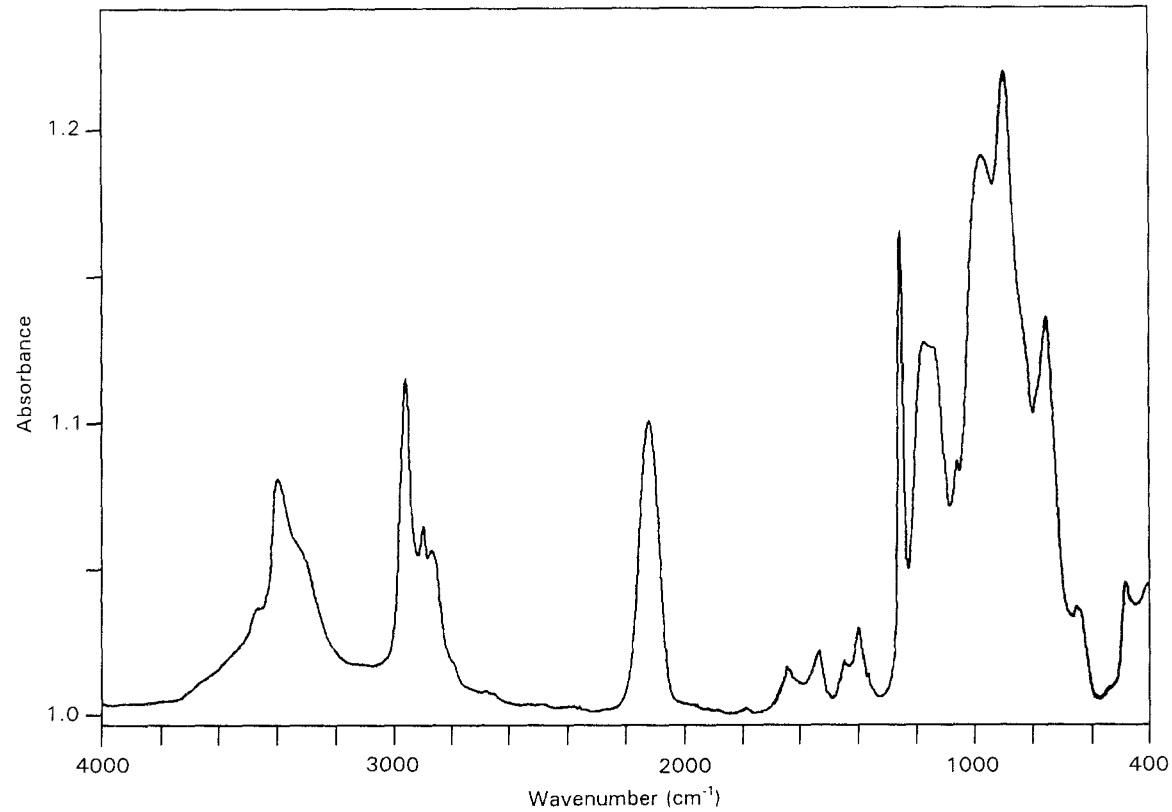

Figure 3 FT-IR spectrum of the homopolymer P12 (see Table II).

TABLE III Copolymerization conditions and details of resulting copolymers

	P4	P6	P11A	P11B	P19
Mass of MCSZ (g)	1.2	1.2	1.0	1.0	5.0
Mass of MCSX (g)	1.0	0.6	0.6	0.6	0.7 LR[a]
Molar ratio of N:O in the reactants	1.2: 1	2:1	2:1	2:1	7:1
Volume of THF (ml)	20	40	90	90	100
Mass of KH (g)	0.06	0.05	0.05	0.05	0.06
Reaction temperature (°C)	20	20	60	60	20
Reaction time (h)	24	20	10	24	24
Volume of CH_3I[b] or $(CH_3)_3SiCl$[c] used	2.0[b]	2.0[b]	–	0.2[c]	0.2[c]
Yield (wt %)	> 95	> 95	> 95	> 95	> 95
Details of product	White, soluble solid	White, soluble solid	White, soluble solid	White, soluble solid	Viscous, soluble mass

[a] LR: linear polysiloxanes or large rings of siloxanes.

discussion below). However, the thermal decomposition of these copolymers to produce ceramics is affected by their N: O and this will be discussed in Part IV.

The ^1H NMR spectrum of P11B is shown in Fig. 4. From the spectrum, the copolymer has a molar ratio of Si-$\underline{H}$ (4.3–5.2 p.p.m.) : N-$\underline{H}$ (0.5–1.5 p.p.m.) : $SiC\underline{H}_3$ (0–0.5 p.p.m.) equal to 1 : 1.2: 7.6. The peaks in the spectrum are all broad, supporting the presence of a complicated structure. The FT-IR spectrum for sample P11B is shown in Fig. 5. Compared with the spectrum of methylcyclosilazanes described previously [2], the relative intensities of the Si–CH_3 bands (1258, 898, 764 cm^{-1}) increased compared to those of the Si–H (2160 cm^{-1}) and N–H (3300 cm^{-1}) bands. The FT-IR spectrum also shows minor peaks at 3450 and 1540 cm^{-1} and, as discussed in section 3.2, these indicate the presence of a small amount of Si–NH_2 in the copolymer.

The observed low reactivity of MCSXs compared with MCSZs supports the suggestion that the copolymers obtained under the conditions described in Table III lead to block copolymers, in which the silazane blocks are much larger than those of siloxanes. This also explains why the FT-IR spectrum of P11B is similar to that of the homopolymers of methylcyclosilazanes.

The state of the copolymer from P19 is very interesting. Compared with other copolymers, P19 is different because the starting methylcyclosiloxanes were "large" cyclics ($n \geq 8$) and contained some linear polymethylsiloxanes which corresponded to the mixture left after distillation. Large cyclics or linear polymers are obviously flexible. When these were incorporated in the copolymer they seem to retain their flexibility in the copolymer, in spite of the fact that these blocks are smaller compared to the silazane blocks, and

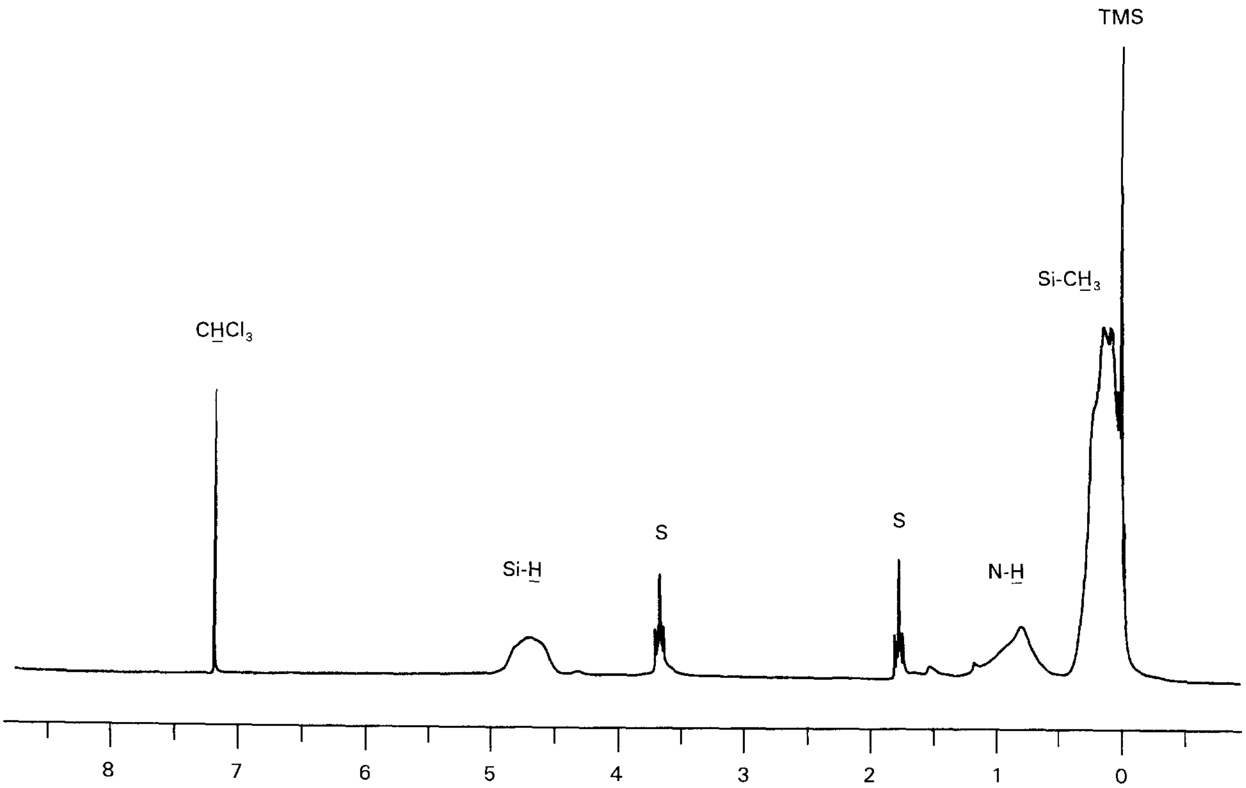

Figure 4 ^{1}H NMR spectrum (in $CDCl_3$) of the copolymer P11B (see Table III). TMS and S refer to tetramethylsilane and solvent, respectively.

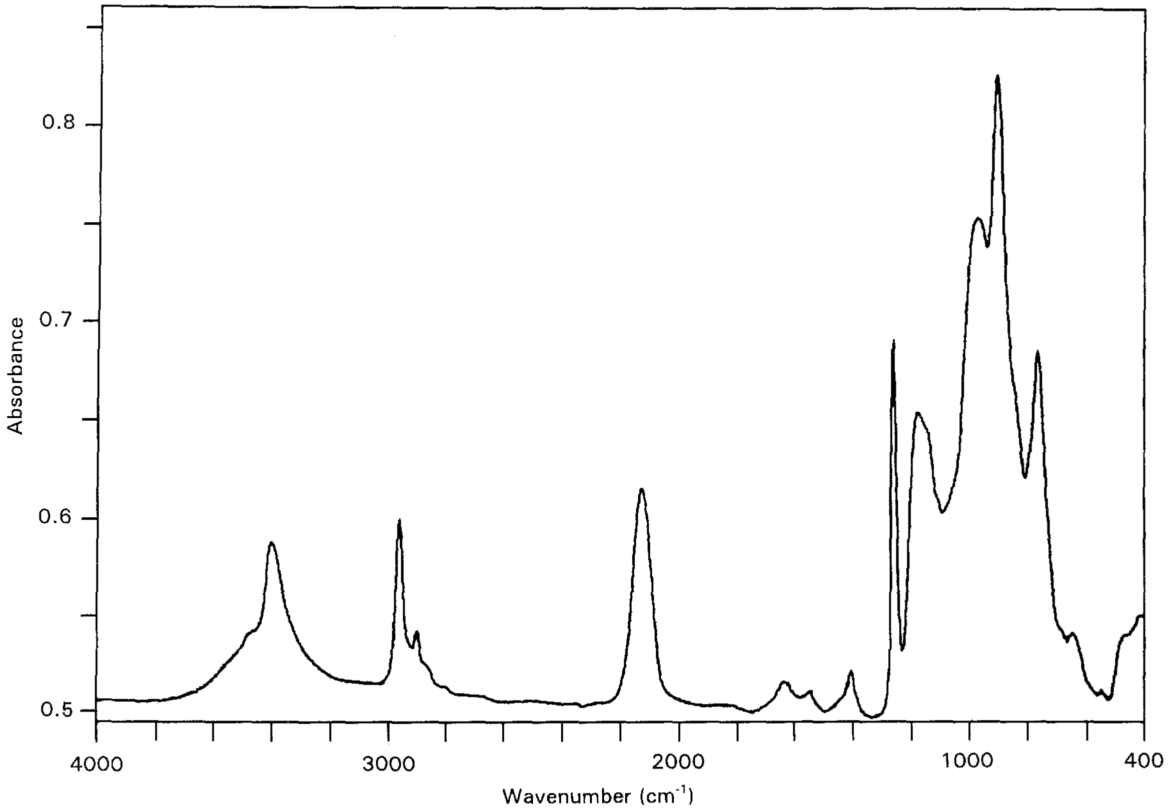

Figure 5 FT-IR spectrum of the copolymer P11B (see Table III).

this causes P19 to exist as a viscous mass rather than a solid (others listed in Table III). The flexibility of the copolymer also gave a slightly better resolved ^{1}H NMR (Fig. 6). In particular, the Si–$\underline{H}$ resonances are better resolved when compared with those in Fig. 4.

4. Conclusions

Homopolymerization studies of methylcyclosiloxanes and methylcyclosilazanes show that the former process is much slower and gives a low yield of product unless the reaction is carried out at higher temperatures over several days. This low reactivity affects the

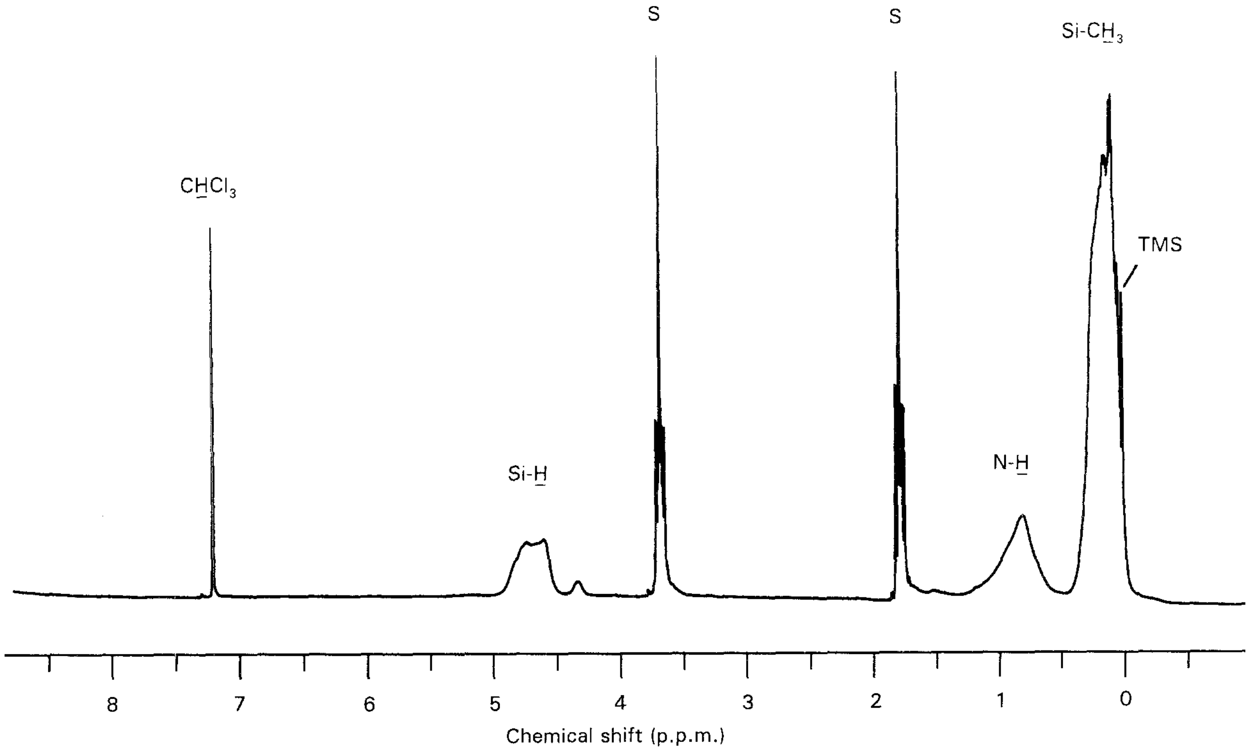

Figure 6 ^{1}H NMR spectrum (in $CDCl_3$) of the copolymer P19 (see Table III). TMS and S refer to tetramethylsilane and solvent, respectively.

structure of the copolymerization product of methylcyclosiloxanes and methylcyclosilazanes, resulting in a block structure where the siloxane units are the smaller.

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