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N.m.r. analysis of poly(1,1,1-trifluoropropylmethylsiloxane-*co*-dimethylsiloxanes)

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Oligomeric copolymers of dimethyl siloxane and 1,1,1-trifluoropropylmethyl siloxane having functional amine groups at both ends were prepared and their microstructures were analysed by n.m.r. spectroscopic techniques. The compositions of these polymers were obtained by integration of the corresponding peaks of ^{1}H n.m.r. spectra, while the monomer triad sequences were calculated from the $SiC\underline{H}_3$ regions with the aid of curve fitting. Being oligomers, the polymers contain a significant amount of end groups, and the peak positions corresponding to the end $SiC\underline{H}_3$ units that are contributing to the $SiC\underline{H}_3$ regions were determined by two-dimensional ^{1}H COSY spectroscopy. The compositions of the polymers were found to be almost equal to the feed ratios, and the monomer sequence distributions appeared to follow the Bernoullian statistics. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: siloxane copolymer; end group functionalisation; n.m.r.)

INTRODUCTION

Polyorganosiloxanes have received widespread attention as inorganic backbone polymers having useful properties. Polyorganosiloxanes have outstanding physico-chemical properties such as excellent thermal stability, extremely low glass transition temperature, low surface tension, low solubility parameter, high stability against oxygen plasma, high permeability to various gases, chemical and physiological inertness, and so on. Applications utilising these properties range from medical devices to gas separation membranes, and from protective coatings to water repellents[1,2].

However, when polyorganosiloxanes are used alone, they usually exhibit very weak rubbery properties. Therefore, many studies have focused on how to improve the mechanical properties of polyorganosiloxanes while maintaining processability. A very effective way of achieving this goal is the controlled synthesis of block or segmented copolymers in which the rubbery polyorganosiloxanes and glassy or crystalline segments are used as the soft and hard components, respectively[2]. In this case, the preparation of functionalised siloxane oligomers with well-defined reactive end groups becomes important.

In general, siloxane copolymers of monomeric units with different organic substituents on the silicon atoms can be synthesised by the ring-opening polymerisation of cyclic siloxane monomers[3–5]. For these copolymers, the composition and the sequence distribution are the most important microstructural variables that are directly correlated with the physico-chemical properties.

In this study, aminopropyl-terminated poly(1,1,1-trifluoropropyl-methylsiloxane-*co*-dimethylsiloxanes) (TFPMS-DMS) were synthesised, and their compositions and sequence distributions analysed using n.m.r. spectroscopy. These results were used to characterise the copolymerisation statistics, hence the reversibility involved in the siloxane copolymerisation reaction. Note that while ^{29}Si n.m.r. spectroscopy is successfully applied for the analysis of such siloxane copolymers as poly(dimethylsiloxane-*co*-methylvinylsiloxanes)[6,7] and poly(dimethylsiloxane-*co*-diphenylsiloxanes)[8], we found that ^{29}Si n.m.r. spectra were not readily tractable for the microstructure analysis of the copolymers under study, mainly because of complicated peak overlaps.

EXPERIMENTAL

Tetramethyl ammonium hydroxide pentahydrate ($(CH_3)_4NOH{\cdot}5H_2O$, TMAH, Aldrich) was used as received. Octamethylcyclotetrasiloxane (D_4, Petrach Inc.), (1,1,1-trifluoropropyl)methylcyclopolysiloxane (3 mer/4 mer ratio 1/1, $F_{3\text{-}4}$, Petrach Inc.), and 1,3-bis(γ-aminopropyltetramethyl)disiloxane (DSX, Petrach Inc.) were dried over calcium hydride and then distilled under vacuum before use.

First, the catalyst tetramethyl ammonium siloxanolate base was prepared according to the method proposed by McGrath *et al.*[9]. The calculated amounts of DSX, D_4, and $F_{3\text{-}4}$ for the controlled molecular weight ($\approx$ 2000) and compositions were charged into a round bottomed flask along with the base catalyst (0.1 mol% to monomers). Polymerisation was carried out at 80°C for 24 hrs under N_2 gas. Then the reaction mixture was heated to 150°C and kept at that temperature in order to allow the catalyst to

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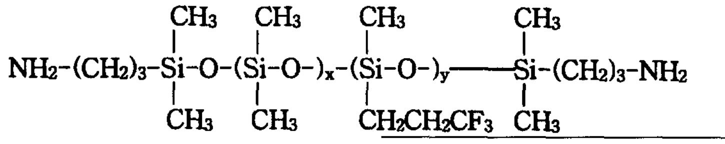
decompose. Volatiles and unreacted monomers were removed by further vacuum distillation.

One-dimensional ^1H n.m.r. spectra were measured on a Bruker AC-200 (200 MHz) spectrometer, while a two-dimensional ^1H COSY spectrum was recorded on a Jeol GSX-500 (500 MHz) spectrometer. In both cases, $CDCl_3$ was used as the solvent and its chemical shift (7.27 ppm) was used as the internal reference. Curve fitting was carried out by an optimisation method based on the Levenberg–Marquardt algorithm. Bandshapes as defined by weighted sums of Lorentzian and Gaussian curves were used, and the Gaussian fraction was optimised too. Linear background was used. The approximate positions of the peaks were determined first by the second derivative technique and they were used as the initial values for the curve fitting iterations.

RESULTS AND DISCUSSION

Because the peaks corresponding to the trifluoropropyl unit were well separated, the composition analysis of TFPMS-DMS copolymers by ^1H n.m.r. was straightforward. On the other hand, for the analysis of the sequence distribution, curve fitting was necessary due to the presence of several peaks overlapped in the narrow range of about 0.0~0.18 ppm. Although some limitations may be involved in curve fitting as pointed out previously[10], we found out that the ^1H n.m.r. spectra contained sufficient spectral features so that there were few occurrences of resolved peaks which could be fitted in more than one way. On the other hand, a two-dimensional n.m.r. spectroscopic technique was applied to elucidate the peak positions corresponding to the chain end structures. Because the prepared polymer samples in this study have the degree of polymerisation of oligomeric level, the contribution from the end groups to the spectral range under consideration is not negligible and hence should be identified for further structural analysis.

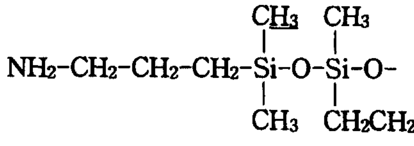
The chemical structure of the siloxane oligomers can be written follows:



$$NH_2-(CH_2)_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-(\overset{CH_3}{\underset{CH_3}{Si}}-O-)_x-(\overset{CH_3}{\underset{CH_2CH_2CF_3}{Si}}-O-)_y-\overset{CH_3}{\underset{CH_3}{Si}}-(CH_2)_3-NH_2$$

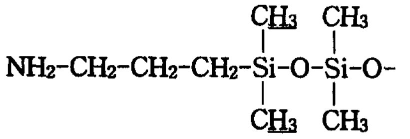
feed mole ratio; for example DF10 and DF82 correspond to the feed ratio of D_4:F_{3-4} of 10:0 and 8:2, respectively. The feed ratios in terms of D and F units as reported in *Table 1* can be calculated based on the fact that four D units and an average of 3.5 F units are obtained from each D_4 and F_{3-4} unit, respectively, in the ring-opening polymerisation.

A typical ^1H n.m.r. spectrum of DF82 is shown in *Figure 1* along with peak assignments. Since the $SiC\underline{H}_3$ (hereafter, underlines will be used to indicate the protons being observed) region of about 0.0~0.18 ppm contains the information on $(D)_x$ and $(F)_y$ as well as E, it was necessary to determine the positions of the peaks corresponding to the E units. For this purpose, a two-dimensional ^1H COSY spectrum was measured using DF46. The region of −0.2~1.0 ppm is shown in *Figure 2* flanked by the projection spectra along both axes. The spectrum is not symmetrised and displays t_1 noise. However, one can clearly notice the two groups of cross peaks that are connected with the $SiC\underline{H}_3$ peaks. On close inspection, it can be found that cross peak I, which crosses peak 1 corresponding to $-C\underline{H}_2CH_2CH_2NH_2$, is split into two subgroups, while cross peak II which crosses peak 5, corresponding to $-C\underline{H}_2CH_2CF_3$ is split into three subgroups. These phenomena were analysed as follows. Considering cross peak I first, the peak corresponding to H^X (peak 5) in $-O-Si(CH_3)_2-C\underline{H}^X_2C\underline{H}^A_2CH_2NH_2$ structure is split into three by H^A (peak 6); moreover, there exist two kinds of such structure, as follows:



$$NH_2-CH_2-CH_2-CH_2-\overset{\underline{CH_3}}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_2CH_2CF_3}{Si}}-O-$$

(I′)



$$NH_2-CH_2-CH_2-CH_2-\overset{\underline{CH_3}}{\underset{\underline{CH_3}}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-$$

(I″)

For the purpose of clarity of the discussion, let's use the symbol R_E for the $-(CH_2)_3NH_2$ end groups, E for the $-Si(CH_3)_2-O-$ units at the chain ends, D for the $-Si(CH_3)_2-O-$ units, and F for the $-Si(CH_3)(CH_2CH_2CF_3)-O-$ units. Now the polymers can be described simply as follows:

$$R_E-E-(D)_x-(F)_y-E-R_E$$

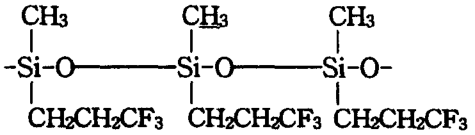
In *Table 1* are summarised the feed ratios of monomers and the yields of the products used in the n.m.r. analysis. The number in the sample name code represents the monomer

Table 1 Siloxane oligomers used in the n.m.r. analysis

Sample code	Feed ratio (D:F) (mol%)	Yield (%)
DF10	100:0	85
DF82	82:18	90
DF64	63:37	86
DF46	43:57	94
DF28	22:78	92
DF01	0:100	99

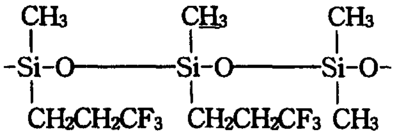
Therefore, two subgroups of triplets appear in the spectrum. The difference in the chemical shifts of I′ and I″ is about 0.02 ppm. In normal COSY spectra, the central peak of triplets usually appears very weak or absent, and the current triplet patterns are consistent with this fact.

Cross peak II can be analysed in a similar fashion. That is, the three subgroups of peaks correspond to the three structures:



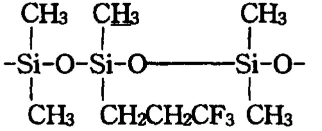
$$-\overset{CH_3}{\underset{CH_2CH_2CF_3}{Si}}-O-\overset{\underline{CH_3}}{\underset{CH_2CH_2CF_3}{Si}}-O-\overset{CH_3}{\underset{CH_2CH_2CF_3}{Si}}-O-$$

$F\underline{F}F$ (II′)



$$-\overset{CH_3}{\underset{CH_2CH_2CF_3}{Si}}-O-\overset{\underline{CH_3}}{\underset{CH_2CH_2CF_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-$$

$F\underline{F}D$ (II″)



$$-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{\underline{CH_3}}{\underset{CH_2CH_2CF_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-$$

$D\underline{F}D$ (II″

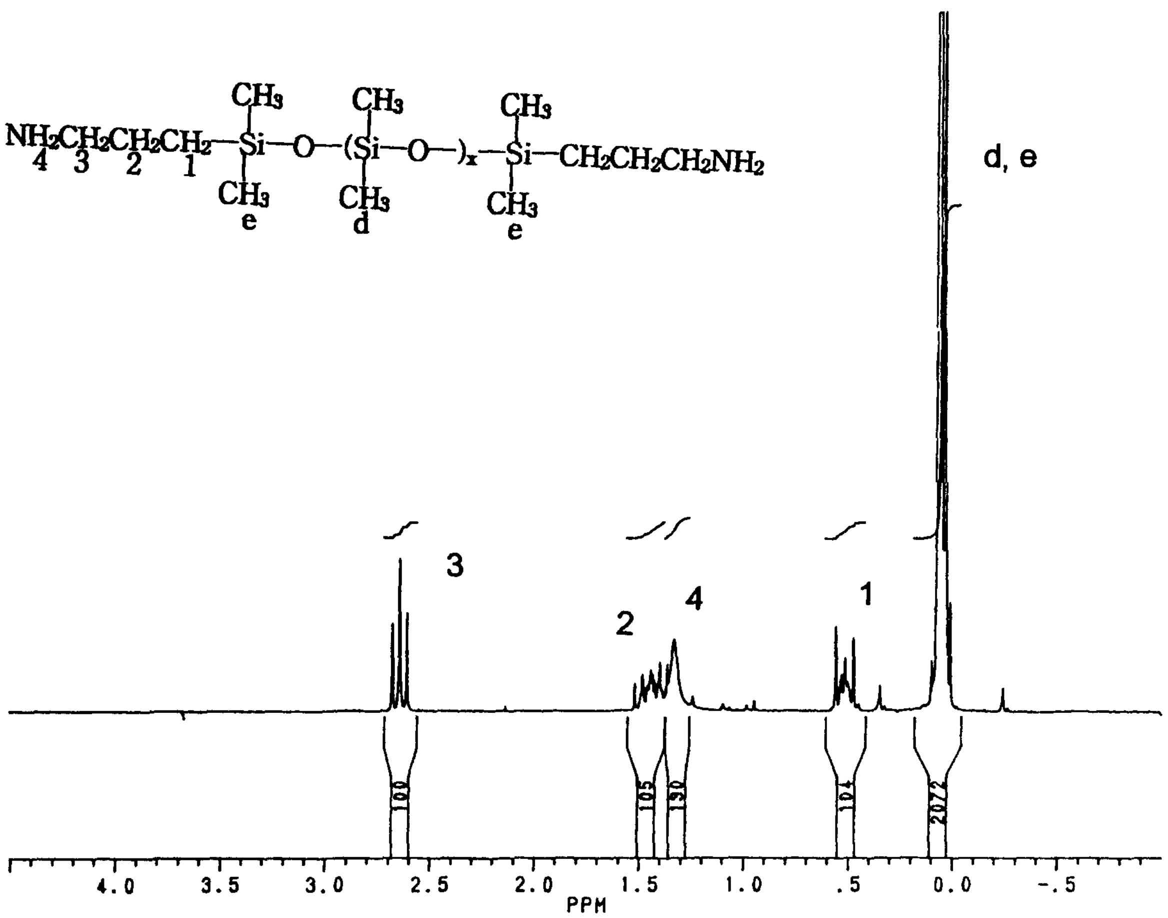
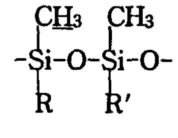


Figure 1 ^1H n.m.r. spectrum of siloxane oligomer DF82.0

Also the chemical shift differences between II′ and II″ and between II″ and II‴ are about 0.02 ppm.

In summary, the following information could be obtained from the ^1H COSY spectrum: (i) the positions of the two peaks corresponding to the terminal E units, (ii) the positions of the peaks corresponding to the F-centred sequence structures, and (iii) an additive rule which describes that in the structure

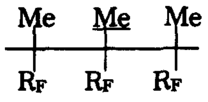


$$-\underset{R}{\overset{CH_3}{Si}}-O-\underset{R'}{\overset{CH_3}{Si}}-O-$$

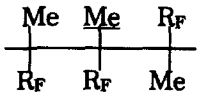
the chemical shift changes by about 0.02 ppm when $R' = -CH_3$ is replaced by $R' = -CH_2CH_2CH_2CF_3$ for each given species of R.

The $SiCH_3$ regions of the ^1H n.m.r. spectra of the samples under investigation are collectively shown in *Figure 3*. The chemical shifts for some peaks appear to change slightly among samples due to the variation in viscosity, etc., but this is known to be a usually observed phenomenon[11]. These spectra were assigned by the following procedure.

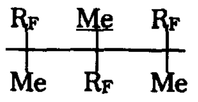
At first, the peaks corresponding to the F-centred sequences were assigned by examining the samples with higher F contents. In the spectrum of DF01 shown in *Figure 3*, in addition to the terminal unit E peak, a group of peaks consisting of the three peaks at 0.126, 0.134, and 0.145 ppm are observed. The latter are assigned as belonging to the FFF sequence, being present in poly(1,1,1-trifluoropropylmethyl) siloxane (PTFPS). Three peaks arise according to the tacticity effect, and could be assigned to the following structures:



mm, 0.126ppm



mr, 0.134ppm



rr, 0.145ppm

Here, Me, R_F, m, and r represent $-CH_3$, $-CH_2CH_2CH_2CF_3$, meso, and racemic, respectively. This assignment was made based on the fact that the Me protons being observed will be deshielded further as more R_F groups are attached nearby in the form of r due to the induction effect.

The result of curve fitting for the spectrum of DF28 is shown in *Figure 4*. Here the FFF structure is readily distinguished as in DF01. Considering the additive rule obtained above, the peaks corresponding to FFD and DFD are expected to appear at 0.02 and 0.04 ppm up-field,

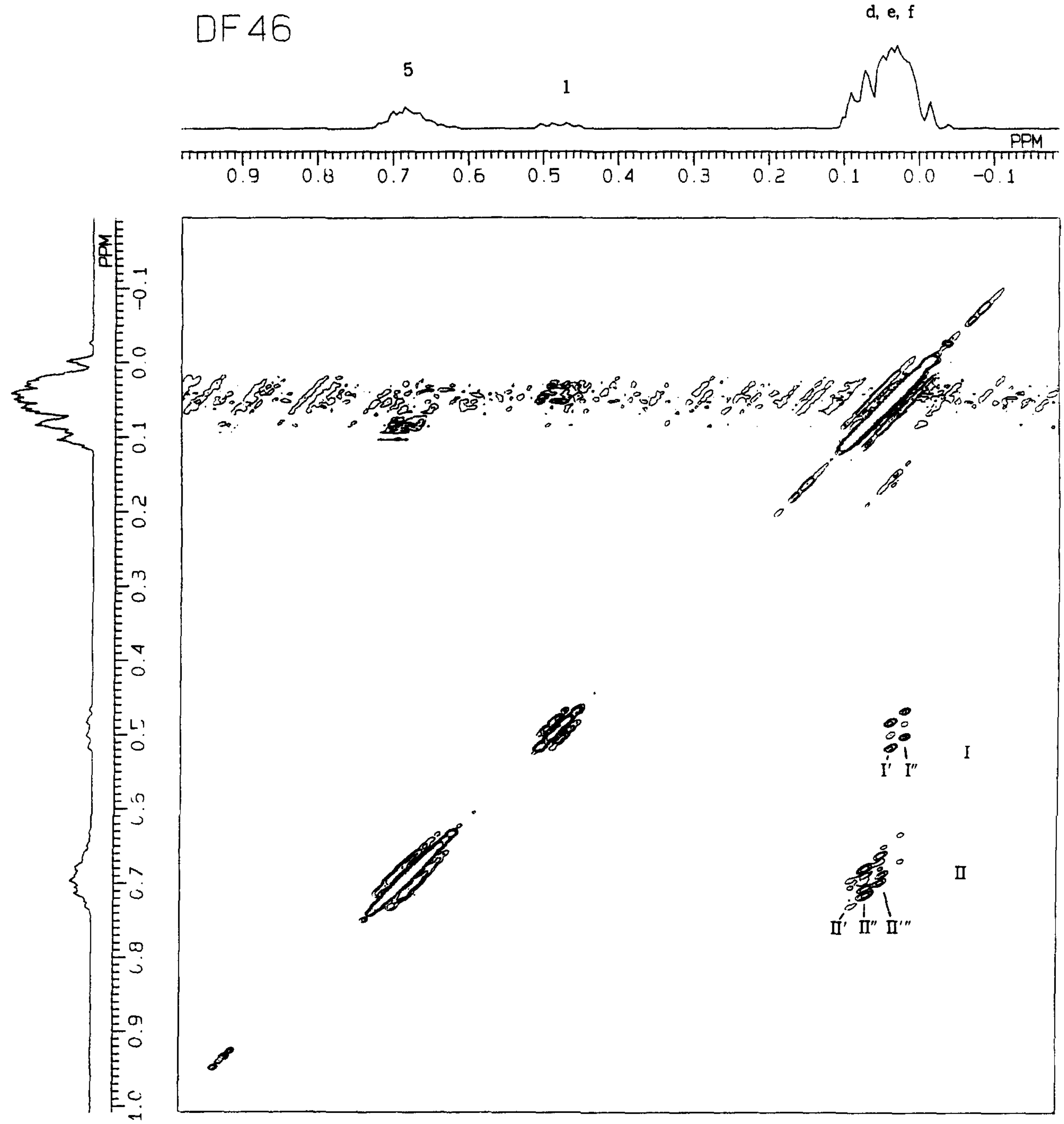


Figure 2 Two-dimensional ^{1}H COSY spectrum of siloxane oligomer DF46 along with projection spectra

respectively, compared with FFF (0.120~0.150 ppm). In fact, the FFD peaks appeared at 0.095~0.115 ppm, while the DFD peaks which appeared at 0.085~0.093 ppm overlapped with FDF (vide infra). These assignments for the F-centred structures are consistent with the results derived from the two-dimensional ^{1}H COSY spectrum shown in *Figure 2*.

Next, for the analysis of the D-centred sequences, the spectra of the samples with higher D contents were examined in a similar way to the F-centred case. From the spectrum of DF10, the peaks corresponding to the DDD structure and the terminal E unit can be immediately assigned. The result of curve fitting for the spectrum of DF82 is shown in *Figure 5*. Two peaks were used for the DDD peak at 0.045 ppm in order to account for the slight asymmetry. Other peaks were observed at 0.054, 0.063, 0.072, 0.084, and 0.105 ppm. Among these, the 0.054 and 0.072 ppm peaks were assigned as the terminal E unit. The 0.063 ppm peak was assigned as DDD since the DDF peak will appear at 0.02 ppm down-field compared with the DDD peak according to the additive rule. Similarly, it is expected that the FDF peak should appear at around 0.083 (= 0.063 + 0.02) ppm, which was actually observed at 0.084 ppm. The chemical shift differences between the D-centred sequence peaks (0.04~0.09 ppm) and the F-centred sequence peaks (0.08~0.15 ppm) were found to be about 0.04 ppm. Based on these assignments all the peaks were assigned as summarised in *Figure 3*.

Area fractions of the peaks were determined using the curve fitting method and the result is shown in *Table 2*. These fractions can be converted into mol% considering the fact that six and three protons are contributing to D and F, respectively, and excluding the contribution by the E units. The result of calculation is summarised in *Table 2*. The sequence distribution of these siloxane copolymers is known to follow the Bernoullian statistics in many cases,

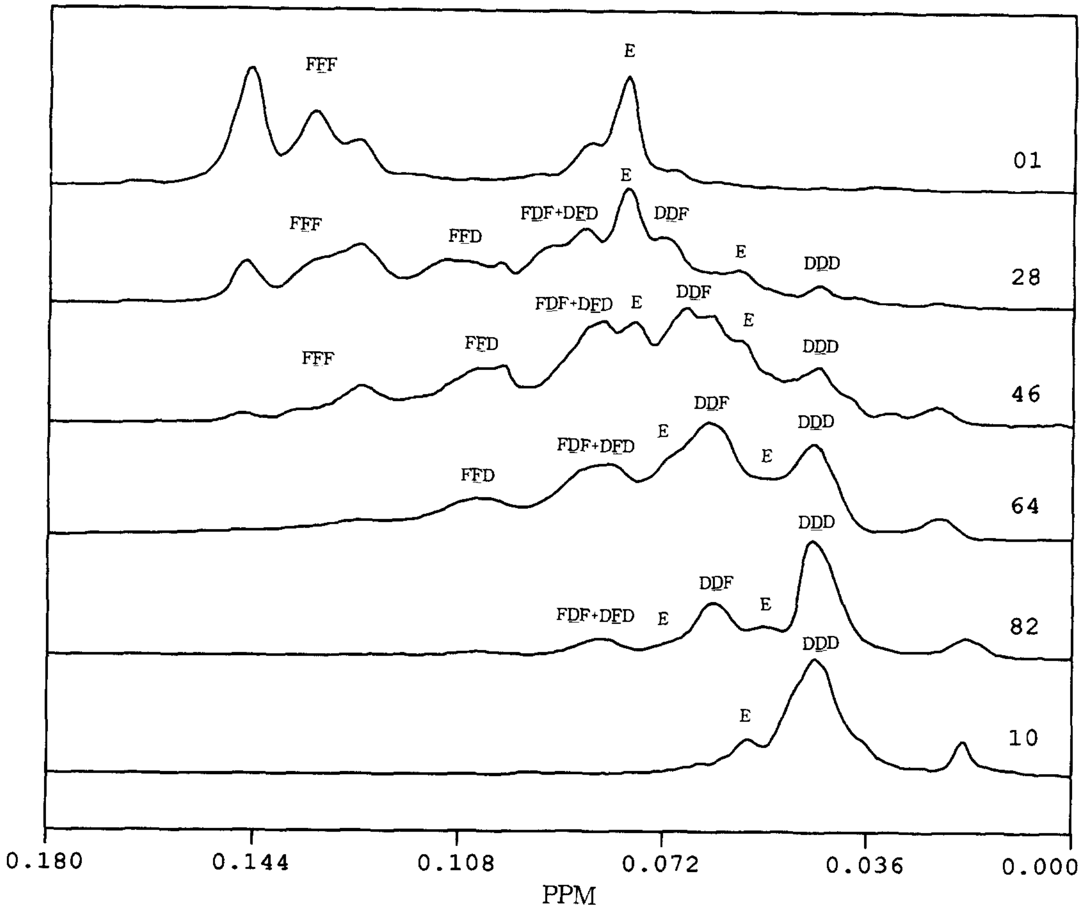


Figure 3 The SiCH$_3$ regions of ^{1}H n.m.r. spectra of siloxane oligomers

Table 2 Results of sequence analysis in the SiCH$_3$ region of ^{1}H n.m.r. spectrum: Mole % of triad sequences (values in parentheses are those calculated assuming Bernoullian statistics)

Sample code	Sequence					
	DDD	DDF	FDF	FFF	FFD	DFD
DF10	100	–	–	–	–	–
	(100)					
DF82	56.1	23.7	1.0	–	3.6	15.6
	(53.1)	(24.9)	(2.9)	(0.7)	(5.9)	(12.5)
DF64	16.3	23.2	22.8	15.8	17.3	4.6
	(23.9)	(29.2)	(8.9)	(5.5)	(17.9)	(14.6)
DF46	9.7	20.6	12.5	14.4	29.3	13.5
	(7.9)	(21.1)	(14.0)	(18.5)	(27.9)	(10.5)
DF28	1.9	12.8	7.9	39.0	22.7	15.7
	(1.2)	(8.1)	(13.6)	(45.6)	(27.2)	(4.1)
DF01	–	–	–	100	–	–
				(100)		

and this is also the case for other types of siloxane copolymers such as poly(dimethylsiloxane-*co*-diphenylsiloxanes)[8]. Therefore, the probability for each sequence was calculated assuming Bernoullian statistics and the result is also shown in *Table 2*. Good agreement exists between the calculated and the observed values for all samples except DF64.

Finally, it was observed that the tacticity distribution in the FFF sequences changed with the copolymer composition. That is, the mole ratios of rr:mr:mm for DF01, DF28, and DF46 were found to be 0.508:0.303:0.189, 0.207:0.326:0.467, and 0.104:0.212:0.684, respectively. In other words, as the F content decreased, the rr content decreased gradually while mm increased. It was speculated that this phenomenon occurred because, when the F content is higher, PTFPS homopolymer being the extreme, rr must be dominant due to the steric effect of the substituents and the interaction between them, but as the F content decreases, the probability for the F unit to meet with the D unit becomes higher, and as a result, the sequence length of the F units decreases and the rr dominance should be diminished accordingly. This fact suggests that, while the mode of addition of TFPMS-DMS copolymers appears to follow the Bernoullian statistics, the tacticity behaviour should be

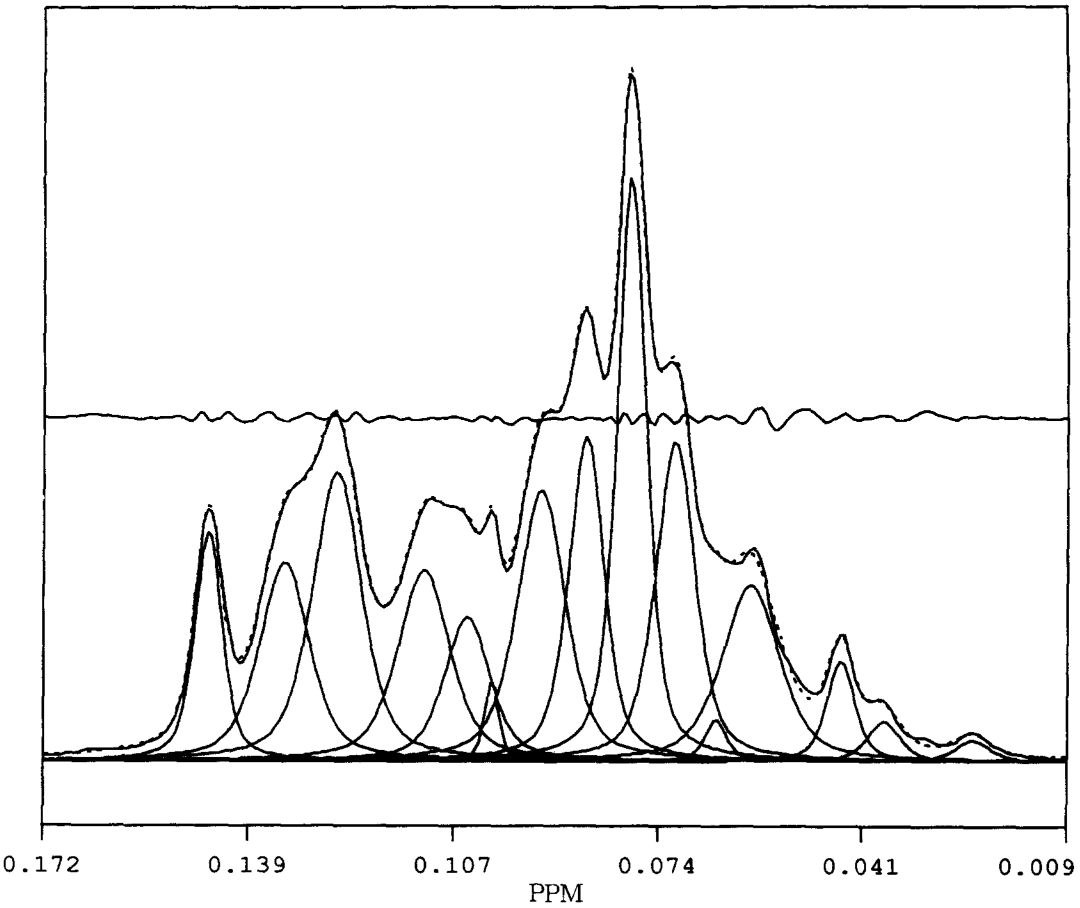


Figure 4 Curve fitting result of ^{1}H spectrum of siloxane oligomer DF28. The dotted line represents the calculated spectrum and the central solid line represents the difference between the calculated and experimental spectra

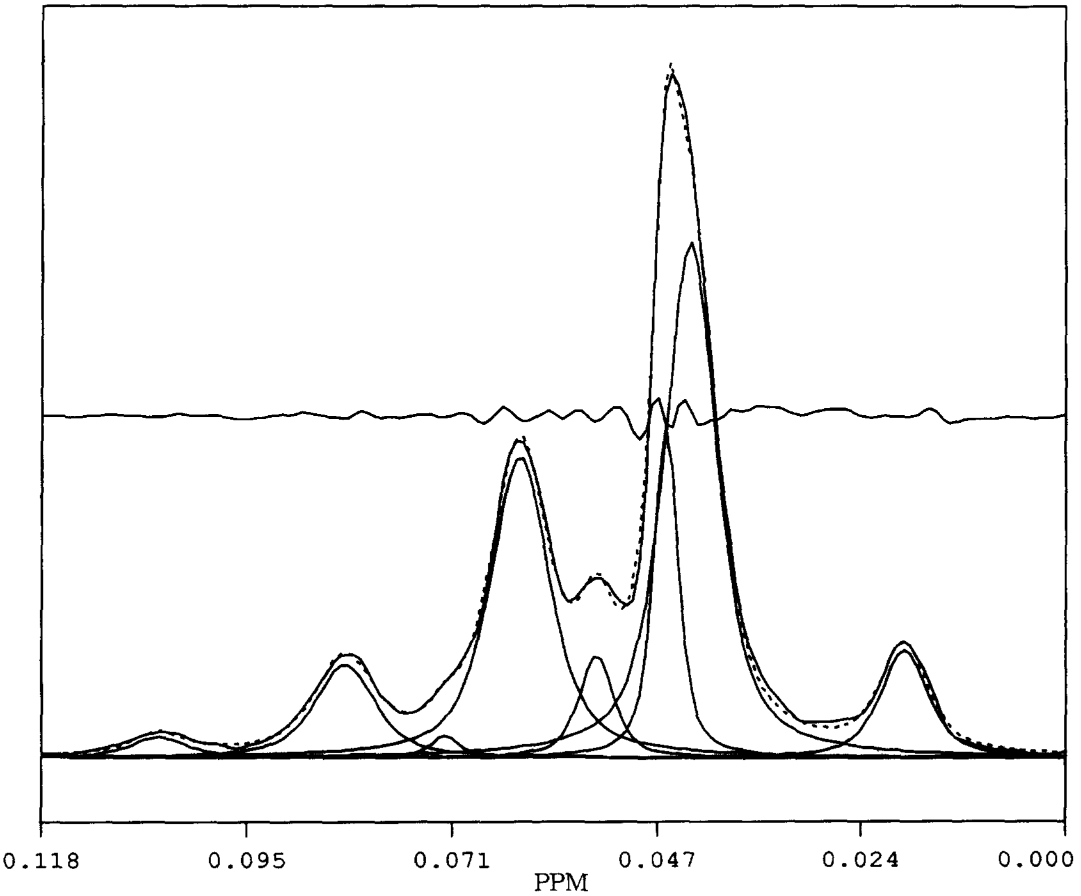


Figure 5 Curve fitting result of ^{1}H spectrum of siloxane oligomer DF82. The dotted line represents the calculated spectrum and the central solid line represents the difference between the calculated and experimental spectra

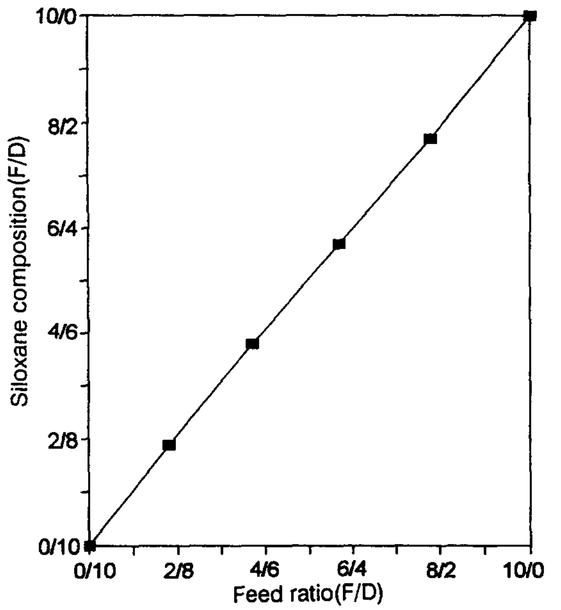


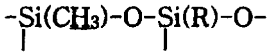
Figure 6 Composition of siloxane polymer as a function of monomer feed ratio

explained in terms of the terminal model at the least. This issue may be elucidated by using some other siloxane copolymers with cotacticity.

The relationship between the feed ratio and the composition is plotted in *Figure 6*. Although the reactivities of D_4 and F_{3-4} are known to be different, the compositions of the copolymers appeared to be almost equal to the feed ratios, respectively. Therefore, it is suggested that the reaction systems reached thermodynamic equilibrium states within the 24 hrs reaction time and the redistribution of the units had proceeded sufficiently.

CONCLUSIONS

A series of TFPMS-DMS copolymers was analysed by ^1H n.m.r. spectroscopic techniques. The peaks in the $SiC\underline{H}_3$ region were well separated up to the triad sequence level. The compositions and sequence distributions were analysed with the aid of curve fitting. The samples were of oligomeric nature, so that the contribution of the terminal units could not be neglected. Two-dimensional ^1H COSY spectroscopy was used to determine the position of the peaks corresponding to the terminal units. Also a useful additive rule was developed in the course of the peak assignment process. In the structure of



$$\text{-Si(C}\underline{\text{H}}_3\text{)-O-Si(R)-O-}$$

the chemical shift of $\underline{H}$ changes by about +0.02 ppm as R = $-CH_3$ is replaced by R = $-CH_2CH_2CF_3$. The composition of each TFPMS-DMS copolymer was found to be almost equal to the feed ratio, and it appeared that the sequence distribution followed the random statistics, that is, the Bernoullian statistics. It is also understood that the ^1H n.m.r.spectroscopic technique can be applied to the microstructural analysis of high molecular weight copolymers based on the results obtained from the oligomeric copolymers.

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