Molecular Motion in Cyclic Siloxanes Studied by ^{17}O, ^{29}Si, and ^{13}C Nuclear Magnetic Resonance Spectroscopy

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NMR studies of nine cyclosiloxanes, D_n, have been carried out, and measurements made of ^{17}O NMR line-widths and chemical shifts, and ^{29}Si and ^{13}C NMR relaxation parameters. The results obtained give information on the changes in molecular motion with increasing ring size. It is proposed that the smaller D_n compounds, up to D_8, can be assumed to be undergoing isotropic motion as neat liquids and in solution in C_6D_6. At $\sim D_8$, in 1 mol dm^{-3} solution, isotropic motion is no longer sufficient to describe the relaxation parameters, and for the larger rings a novel conformational process involving $SiMe_2$ groups passing through the D_n ring is proposed to account for the results.

The cyclic dimethylsiloxanes, $(Me_2SiO)_n$, usually referred to as D_n, provide a unique series of well characterised cyclic ethers, suitable for study by NMR spectroscopy. In particular the D_n series allows the effect of ring size on molecular motion to be studied for closely related compounds. This topic, of considerable interest, has received scant attention although some information is available for crown ethers,[1] particularly from ^{13}C NMR spectroscopy. To our knowledge there is no report of a systematic study of relaxation phenomena for each atom in related rings of varying sizes.

Our aim, in this initial study, was to measure the ^{29}Si and ^{13}C NMR relaxation parameters, and ^{17}O NMR chemical shifts and line-widths, of a series of medium-to-large-ring D_n compounds. As these data contain much information on molecular dynamics a further aim was to combine the information from each nucleus to provide a model for the overall motion in cyclic siloxanes. The combination of ^{29}Si and ^{17}O NMR spectroscopy allows for the examination of all atoms in the D_n rings. The high symmetry of each compound, through which the sets of silicon and oxygen nuclei are isochronous, simplifies the interpretation significantly.

Oxygen-17 is a quadrupolar nucleus, $I\,\frac{5}{2}$, and has not been widely used in the analysis of silicones.[2,3] For a quadrupolar nucleus the line-width, $\Delta\nu_{\frac{1}{2}}$, carries motional information, and is related to the transverse relaxation time, T_2, through equation (1).

$$\Delta\nu_{\frac{1}{2}} = 1/\pi T_2 \qquad (1)$$

In the condition of extreme narrowing, generally held to obtain for non-polymeric materials, the relationship shown in equation (2) is accepted[2] for O^{17} NMR spectroscopy, where T_1

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{12\pi^2}{125}\cdot\left(1 + \frac{\eta^2}{3}\right)\chi^2\tau_c \qquad (2)$$

is the longitudinal relaxation time; η in this case is an electrical field gradient asymmetry parameter; χ is the nuclear quadruple coupling constant; and τ_c is the molecular correlation time, taken to be the time for the molecule to describe an arc of one radian. Combination of equations (1) and (2) gives equation (3).

$$\Delta\nu_{\frac{1}{2}} = \frac{12}{125}\pi\cdot\left(1 + \frac{\eta^2}{3}\right)\chi^2\tau_c \qquad (3)$$

Furthermore, for isotropic motion the molecular correlation time τ_c is related to viscosity, η, through equation (4) where a is

$$\tau_c = \frac{4\pi\eta a^3}{3kT} \qquad (4)$$

the radius of the isotropic body, k is the Boltzmann constant, and T is temperature.

For D_n molecules it is reasonable to assume that for such similar oxygen environments the parameters χ and η (the asymmetry parameter) are similar across the series. From equations (3) and (4) it is apparent that the ^{17}O NMR line-widths should be linearly related to viscosity, η, for isotropic motion. For non-isotropic motion the equations become very complicated, and *inter alia* the viscosity term η is substituted by a microviscosity term which describes motion in the vicinity of the nucleus under study and is not necessarily related to the macroscopic viscosity, η.

Silicon-29 NMR spectroscopy has been widely used in analysis of silicones[4,5] mainly through chemical-shift data. Levy[5] reported a major study on relaxation in silicon compounds, including some silicones. Harris and Kimber studied medium effects on the relaxation time of hexamethyldisiloxane.[6]

The appropriate equations for ^{29}Si relaxation are well established.[5] By contrast to ^{17}O, ^{29}Si is not quadrupolar, being of spin $\frac{1}{2}$. For silicon nuclei the longitudinal relaxation time, T_1, contains information on molecular dynamics. For silicon nuclei with no directly bonded protons, relaxation times are frequently rather long, typically 20–200s, compared with protonated carbon nuclei relaxation times of a few seconds. This can, however, be turned to advantage as T_1^{DD}, the relaxation time from dipole–dipole interactions, is very sensitive to molecular correlation times, τ_c, as shown by equation (5) where

$$\frac{1}{T_1^{DD}} = \pi^2\tau_c\Sigma_S\gamma_I^{\,1}\cdot\gamma_S^{\,2}\cdot r_{IS}^{-6} \qquad (5)$$

γ_X is the gyromagnetic ratio of nucleus X, and r_{IS} is the distance separating the nuclei I and S. Equation (5) only holds strictly for isotropic motion in rigid molecules. For flexible molecules undergoing conformational change, τ_c is replaced by an effective correlation time, τ_{eff}.

The dipole–dipole relaxation time, T_1^{DD} for ^{29}Si nuclei is

Table 1. ^{17}O NMR parameters for siloxanes D_n.

Compound	δ_O (ppm)[a]	$\Delta\nu_{\frac{1}{2}}$/Hz[b]
D_3[c]	73	50
D_4 (neat)	73	140
(90% w/w in C_6D_6)	73	125
(80% w/w in C_6D_6)	73	120
D_5	73	190
D_6	74	210
D_7	73	260
D_8[c]	73	290
D_9	73	360
D_{12}	*ca.* 73	450

[a] Relative to external water. [b] Measured line-width at half height. [c] *ca.* 80% w/w in C_6D_6.

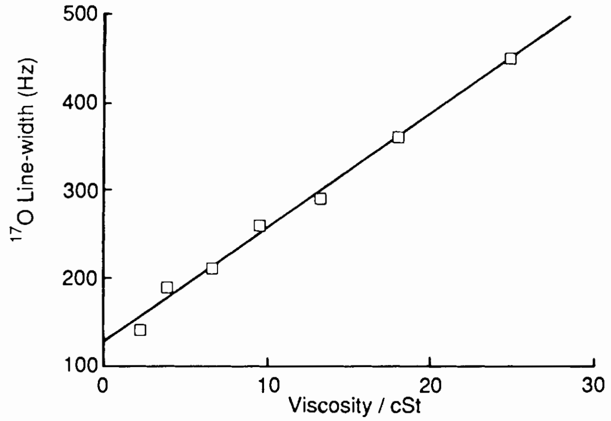

Figure 1. Oxygen-17 line-widths *versus* viscosity for a series of cyclic siloxanes, D_4–D_9 and D_{12} measured as neat liquids.

Table 2. Viscosities of siloxanes D_n.[7]

	Viscosity/cSt		Viscosity/cSt
D_3		D_9	17.98
D_4	2.3	D_{12}	24.75
D_5	3.87	D_{15}	24.56
D_6	6.62	D_{18}	24.82
D_7	9.47	D_{21}	24.65
D_8	13.23		

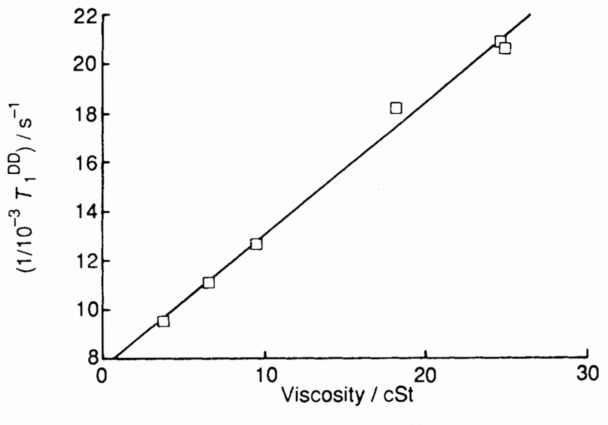

Figure 2. $1/10^{-3}\ T_1^{DD}$ *versus* viscosity for the ^{29}Si nuclei in a series of neat cyclic siloxanes, D_5–D_7, D_9, D_{12}, and D_{15}.

obtained from the overall relaxation time T_1, and the nuclear Overhauser enhancement, η, through equation (6).

$$T_1^{DD} = \frac{-2.52}{\eta} T_1 \qquad (6)$$

The contribution from other relaxation mechanisms, T_1^{other}, can be obtained easily from equation (7). T_1^{other} contains, for

$$\frac{1}{T_1} = \frac{1}{T_1^{DD}} + \frac{1}{T_1^{other}} \qquad (7)$$

silicon nuclei, contributions from spin-rotation relaxation, SR, and possibly from chemical-shift anisotropy, CSA, although SR is the dominant 'other' mechanism for relaxation.[5]

For the D_n series the major difference between homologues, reflected in T_1^{DD}, can be seen to be τ_c. The other terms will be very similar for each homologue as near-neighbour contributions dominate, as shown by the r_{IS}^6 term. This statement does need to be tempered by the knowledge that intermolecular dipole–dipole relaxation can contribute quite strongly to ^{29}Si NMR relaxation.[5]

We have therefore measured ^{17}O NMR line-widths and ^{29}Si and ^{13}C NMR relaxation times to determine, as far as possible, the factors affecting molecular motion in cyclic silicones D_n.

Results and Discussion

The oxygen-17 NMR spectra for eight D_n siloxanes were obtained from neat liquids where possible. D_3 and D_8 are solids at ambient temperature and were investigated as concentrated solutions (*ca.* 80% w/w). The chemical shifts and line-widths are given in Table 1.

The ^{17}O chemical shifts of the D_n compounds are identical within experimental error, which suggests that the magnetic environments of the oxygen nuclei are similar for each compound.

The ^{17}O NMR line-widths do exhibit the expected increase as viscosity η increases, and the viscosities of D_n are plotted against ^{17}O NMR line-widths in Figure 1. The line-width for D_8 is that measured in 80% w/w C_6D_6. Dilution studies on D_4 show that the absolute value of the D_n line-width, in the absence of added solvent, would be rather greater than the 290 Hz measured. Although the correlation between ^{17}O NMR line-widths and viscosity is not perfectly linear it is apparent from Figure 1 that there is no discernible trend to curvature, and that within reasonable limits the line-width is directly related to the viscosity of the medium for D_n. (Viscosities for siloxanes are given in Table 2.) This is interesting as it suggests that, for the oxygen nuclei, the model of isotropic tumbling is sufficient to describe the molecular motion, even for D_{12}. In view of the large size of the twenty-four-membered D_{12} ring, in particular, it would not have been surprising to find that the line-widths of the larger D_n compounds were somewhat smaller than those predicted by extrapolation from the smaller-ring D_n compounds. However, any contribution to τ_{eff} from internal conformational changes is smaller than the experimental error in measuring line-widths.

Two significant conclusions can be drawn from this study of the ^{17}O NMR spectra of D_n compounds. The first is that viscosity is a reliable indicator of expected ^{17}O line-widths for small silicones; conversely, ^{17}O NMR spectroscopy may find use as a simple method for estimating the viscosities of small silicones. The second conclusion is that any conformational changes in these D_n silicones have essentially no effect on the ^{17}O NMR line-widths.

In view of the unexpected findings from ^{17}O NMR spectroscopy for the neat liquids, the ^{29}Si NMR relaxation times are

Table 3. ^{29}Si NMR chemical shift and relaxation parameters for siloxanes D_n.

Comp.	$\delta(^{29}Si)$/ppm	$-\eta$ (NOE)	T_1/s	T_1^{DD}/s	T_1^{other}/s
(a) neat liquid					
D_5	−21.3	1.92	80	105	336
D_6	−21.9	1.98	70.5	90	329
D_7	−22.3	2.00	63	79	311
D_9	−21.8	2.07	45	55	247
D_{12}	−22.0	2.08	40.8	49	234
D_{15}	−22.1	2.06	39	48	213
(b) 0.08 mol fraction in C_6D_6					
D_3	−8.6	1.0	120	302	199
D_4	−18.9	1.2	110	231	210
D_5	−21.3	1.4	103	185	231
D_6	−21.9	1.56	99	160	259
D_7	−22.3	1.85	100	135	372
D_8	−22.5	1.91	83	109	347
D_9	−21.8	1.90	82	111	313
D_{12}	−22.0	1.70	68	100	208
D_{15}	−22.1	1.9	72	95	297

Table 4. ^{13}C NMR chemical shifts and relaxation parameters for siloxanes D_n, 0.08 mole fraction in C_6D_6.

Comp.	$\delta(^{13}C)$/ppm	η (NOE)	T_1/s	T_1^{DD}/s	T_1^{other}/s
D_3	0.98	1.4	7.2	10.2	24.3
D_4	0.91	1.95	7.4	7.54	387
D_5	1.0	1.91	6.8	7.07	173
D_6	1.16	1.86	6.0	6.41	93
D_7	1.2	1.92	5.4	5.60	158
D_8	1.31	1.99	5.1	5.10	∞
D_9	1.16	1.67	5.0	5.95	31.2
D_{12}	1.38	1.17	4.6	7.82	11.2

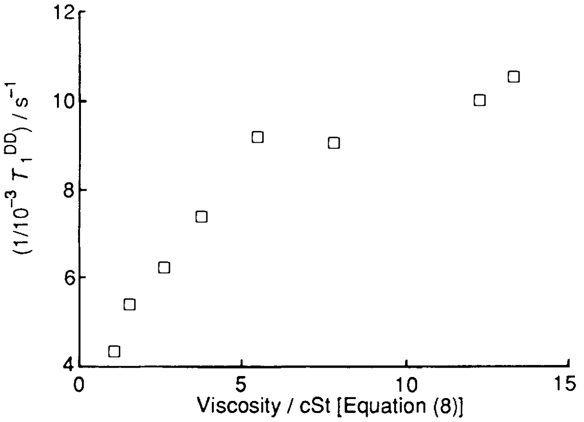

Figure 3. $1/10^{-3}\ T_1^{DD}$ *versus* viscosity as calculated by equation (8) for a series of D_n siloxanes D_4–D_9, D_{12}, and D_{15} in benzene solution.

of interest. A combination of equations (4) and (5) show that $1/T_1^{DD}$ and η (viscosity) are linearly related for isotropic motion. The values for T_1, T_1^{DD}, T_1^{other}, and $-\eta$ (NOE) are given in Table 3 for neat D_5, D_6, D_7, D_9, D_{12}, and D_{15}. A plot of $1/T_1^{DD}$ against η (viscosity) is a reasonable straight line as shown in Figure 2. Again, isotropic motion is suggested for the silicone rings in the neat liquids.

An unusual aspect of the physical properties of cyclic D_n compounds is that D_{12}, D_{15}, D_{18}, and D_{21} all have viscosities very close to 24.5 cSt.* For linear siloxanes there is no such levelling effect;[7] there is a linear relationship between molecular weight $\bar{M}_w$ and viscosity up to molecular weights greater than 10 000. The close similarity in viscosity between the large-ring siloxanes is not understood, but the phenomenon is reflected in the relaxation parameters for D_{12} and D_{15} liquids which are within experimental error (Table 3). Unfortunately, D_{18} and D_{21} are not available in sufficient quantity for NMR measurement.

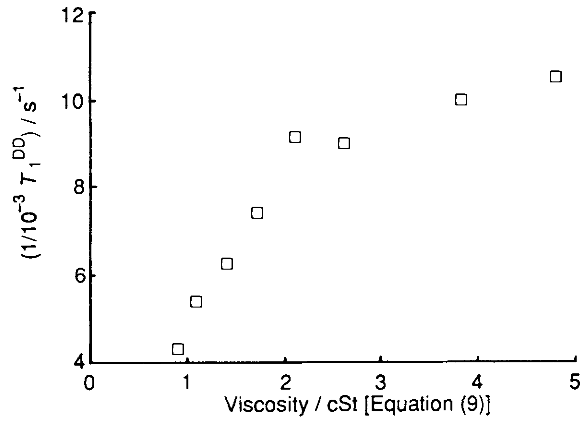

Figure 4. $1/10^{-3}\ T_1^{DD}$ *versus* viscosity as calculated by equation (9) for a series of D_n siloxanes D_4–D_9, D_{12}, and D_{15} in benzene solution.

As the D_n compounds undergo isotropic motion, as neat liquids, even with ring sizes as large as thirty members, we were interested to see whether this behaviour was maintained in more dilute solution. The ^{29}Si NMR and ^{13}C NMR relaxation parameters, of solutions of D_n in C_6D_6, were measured and the results are given in Tables 3 and 4. Each solution contained a constant mole fraction of 0.08 D_n in benzene. The viscosity of binary liquid mixtures is difficult to predict but the relationships given in equations (8) and (9) have both been suggested.[8] Thus

$$\eta = v_1\eta_1 = v_2\eta_2 \qquad (8)$$

$$\log\eta = v_1\log\eta_1 + v_2\log\eta_2 \qquad (9)$$

the viscosity of the mixture, η, is related to the volume fractions v_1 and v_2 and the viscosities, η_1 and η_2, of the two components. A slightly modified version of equation (9) has been applied to mixtures of silicone fluids.[9]

There are two possible effects of dilution on ^{29}Si NMR relaxation times. A decrease in viscosity is accompanied by a decrease in molecular correlation time which, according to equation (5), results in a longer T_1^{DD}. Levy[5] reported that intermolecular dipole–dipole relaxation can contribute up to 15% to dipole–dipole relaxation; dilution with C_6D_6 should diminish this component of relaxation, causing an overall increase in relaxation time. On dilution, both effects will therefore increase T_1^{DD}, which is the major contributor to ^{29}Si NMR relaxation, and the relative increase is predicted to be greater for the small silicones.

Even a superficial examination of Table 3 shows that, although both T_1 and T_1^{DD} are longer for the solutions than for the neat liquids, it is the larger ring systems that are more strongly affected. A closer examination shows a discontinuity in T_1^{DD} ^{29}Si for the 1 mol dm^{-1} solutions at $\sim D_8$. From D_3–D_8 the dipole–dipole relaxation time falls from 302 to 109 s. The larger rings D_8–D_{15} have dipole–dipole relaxation times of 103 ± 8 s. When $1/T_1^{DD}$ for the solutions is plotted against the viscosity, calculated by either of the equations (8) or (9) the

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* 1 St = 10^{-4} m^2 s^{-1}.

relationship is linear for D_4–D_8 with a pronounced discontinuity at D_8 as the points for D_9, D_{12}, and D_{15} converge and lie well below the line for the smaller rings (Figures 3 and 4). The most reasonable explanation for the levelling effect in the larger rings is that conformational mobility increases at $\sim D_8$ so that it is no longer the macroscopic viscosity that dominates dipole–dipole relaxation. For the smaller D_n compounds D_3–D_7, T_1^{DD} falls in a way that is consistent with isotropic motion. Relatively small changes in viscosity therefore allow the larger rings to increase their conformational freedom and begin to behave more like open-chain silicones, whereas the smaller rings undergo isotropic motion even in dilute solution. The values of T_1^{other} in Table 3 do not provide any new insights into the motional behaviour of the D_n compounds. It is usually assumed that the greatest contributor to T_1^{other} is spin-rotation relaxation,[5] although chemical-shift anisotropy may also contribute. The rate of spin-rotation relaxation ($1/T_1^{SR}$) is linearly related to τ_j, the angular momentum correlation time, which is usually taken to be related to the time between molecular collisions and is different from τ_c. In general τ_c and τ_j are related through the Hubbard equation (10),[10] where I_r is the

$$\tau_c \,.\, \tau_j = I_r/6kT \qquad (10)$$

molecular moment of inertia. At a given temperature, as τ_c decreases so τ_j increases. As long as T_1^{DD} and T_1^{SR} depend on their respective correlation times, then as T_1^{DD} decreases, T_1^{SR} will increase. Applying this to the D_n series for D_3–D_7 in 1 mol dm^{-3} solution the trend is followed closely, but for D_8–D_{12} T_1^{DD} and T_1^{SR} both decrease simultaneously. For the neat liquids T_1^{DD} and T_1^{SR} both decrease as the ring size increases. We have no explanation for this, but note that Levy[5] gave data for M_2D_{3000} that allowed us to calculate T_1^{DD} as 40.4 s and T_1^{SR} as 83.9 s. In that case, T_1^{SR} is remarkably low for the rather short T_1^{DD}.

The same equations govern ^{29}Si and ^{13}C NMR relaxation. Accordingly we sought confirmation of a quantitative change in motional behaviour at $\sim D_8$ in solution by measuring the ^{13}C NMR relaxation and NOE parameters. These are recorded in Table 4.

The maximum value for η (NOE) in ^{13}C NMR spectroscopy is 1.988, and the large values of η for D_4–D_8 show that dipole–dipole relaxation is the dominant relaxation mechanism. For D_3 and D_{12}, and to a lesser extent D_9, the T_1^{other} mechanisms (dominated by spin rotation) are also major contributors to overall relaxation.

For carbon nuclei in methyl groups, dipole–dipole relaxation is highly efficient[11] and arises from two sources; overall molecular tumbling and methyl-group rotation, about the Si–C bond in the case of D_n compounds. As with ^{29}Si NMR dipole–dipole relaxation, the smaller the correlation time the lower is the rate of relaxation, and hence T_1^{DD} becomes longer. The domination of methyl-group rotation in ^{13}C NMR T_1^{DD} relaxation results in a smaller variation for the D_n series, but the same general trend as for the ^{29}Si NMR spectra is observed. For D_3–D_8 the dipole–dipole relaxation time decreases with increasing viscosity, but again there is a discontinuity at D_8 and T_1^{DD} increases from 5.1 to 7.82 s for D_{12}. This is again consistent with increased motional freedom becoming apparent at $\sim D_8$.

There are too many possible motional processes to enable definite proposals to be made concerning the nature of any motional changes that may occur at $\sim D_8$. Much more detailed information is needed to provide a complete motional picture. We were, however, intrigued to find, by examination of molecular models, that D_8 is the smallest D_n ring for which $SiMe_2$ can pass through the ring in internal conformational changes. That type of motion would increase the number of degrees of motional freedom in rings, but its implications for relaxation are uncertain at present.

Experimental

The D_n compounds were a generous gift from the Dow Corning Corporation, Midland, USA, and were used without further purification.

The ^{17}O NMR spectra were obtained on a JEOL FX90Q NMR spectrometer operating at 12.10 MHz. 4K data points were used and typically 50–100 000 transients were accumulated with a 90° pulse (20 μs), a 5 000 Hz sweep width, and a delay time of 50 μs. The half-height width was taken as the average of three different measurements and the quoted values are generally ± 20 Hz for line-widths >250 Hz and ± 5 Hz for the narrow lines. ^{29}Si and ^{13}C NMR spectra were measured on JEOL FX90Q and Bruker CX200 spectrometers. Relaxation times of the degassed samples were obtained using standard inversion-recovery techniques.

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