Chapter 4

Hydrogenated and Deuterated Cyclic Poly(dimethylsiloxanes)

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Poly(dimethylsiloxanes) (PDMS) based on the repeat unit $[(CH_3)_2SiO]$ are important commercial polymers with a wide range of applications, for example as adhesives, surfactants, lubricants, sealants, release agents etc. The polymers may be linear, branched or cross-linked into network structures when based on long chain molecules (see Figure 2).

At York, we prepared sharp fractions of the first synthetic cyclic polymers over twenty years ago, following the preparative investigations of Scott [1], Carmichael and his coworkers [2],[3] and Brown and Slusarczuk [4] in cyclic poly(dimethylsiloxane) chemistry. The cyclic polymers that we obtained using preparative gel permeation chromatography (GPC) [5] were narrow molar mass fractions of cyclic PDMS $[(CH_3)_2SiO]_x$ with number average numbers of skeletal bonds up to and beyond 1000. The fractions were obtained from macrocyclic populations recovered from ring-chain equilibration reactions carried out under high dilution conditions. The dispersities of the fractions (as expressed by the ratio of the mass average and number average molar masses, M_w/M_n) were typically about 1.05. The scale of the preparations is illustrated by the fact that a narrow molar mass fraction of cyclics with an average of more than 100 skeletal bonds was obtained on a 30 g scale.

The properties of the novel cyclic PDMS fractions were investigated in joint collaborative work with twenty other University research groups. They included, for example, small angle neutron scattering (SANS) studies (with Imperial College and Bristol), laser light scattering investigations (with Freiburg) and ultrasonic relaxation measurements (with Strathclyde). All these investigations led to a complete characterisation of the cyclic polymers. A further demonstration of their cyclic nature was obtained by entrapping the rings into networks giving the first topological

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polymers. For example, cyclics with 500 skeletal bonds were entrapped in over 90 % yield (see, for example, Ref [6], [7]).

The corresponding cyclic oligomers and polymers from other polysiloxane systems were also prepared and characterised by our group at York including [R(CH$_3$)SiO]$_x$, where R = H [8], CH$_2$=CH [9] and C$_6$H$_5$ [10],[11]. We then went on to prepare the first cyclic polymer liquid crystals starting with the cyclic [H(CH$_3$)SiO]$_x$ materials. For all these studies the corresponding linear PDMS materials or fractions were prepared for purposes of comparison.

In this chapter we show how hydrogenated cyclic PDMS is prepared, characterised and investigated. These studies form the basis of our preparation and characterisation of the first deuterated cyclic polymers [12] [13] [14]. These are per-deuterated PDMS [(CD$_3$)$_2$SiO]$_x$ and they were obtained by a modification of the method described by Beltzung and coworkers [15]. Preparative GPC was used to prepare sharp fractions in a similar way to the hydrogenated materials.

Hydrogenated Cyclic PDMS.

When PDMS is produced by acid or base catalysed polymerisation from octamethylcyclotetrasiloxane (D$_4$) a thermodynamic equilibrium between ring and chain molecules results:

$$-M_y- \;\rightleftharpoons\; -M_{y-x}- \;+\; M_x \tag{1}$$
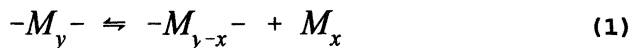
-where $-M_y-$ and $-M_{y-x}-$ represent linear species, M_x represents an x-meric ring species and M represents one monomer unit.

The ring-chain equilibration in PDMS was first investigated by Scott [1] who obtained data giving information on the molecular size distribution of ring and chain species in solution and the undiluted state. This has been followed by the work of Hartung and Camiolo [16] and co-workers [17] [18] [19] [20] extending the investigations to other solvent systems. At this time, kinetic studies of the base-catalysed polymerisation of D$_4$ by Grubb and Osthoff [21], and Morton and Bostick [22] confirmed that the active species was in fact the silanoate ion (Si-O$^-$ K$^+$).

The understanding of PDMS ring-chain equilibria was much advanced when Brown and Sluzarczuk [4] obtained evidence for the presence of macrocyclic species in the base catalysed reaction. They attempted to characterise their distribution and demonstrated the existence of a continuous macrocyclic population extending to at least D$_{400}$. The work of Wright and Semlyen [8] [23] [24] has since extended the investigations further, obtaining accurate molar cyclisation equilibrium constants from the concentrations of the cyclic species over a large range of ring sizes through calculations based on the cyclisation theory of Jacobson and Stockmayer [25].

Jacobson And Stockmayer Cyclisation Theory. The cyclic populations in ring-chain equilibrates may be expressed in terms of the molar cyclisation equilibrium constants K_x for the x-meric ring molecules M_x as follows [26]:

$$K_x = \frac{[-M_{y-x}-][M_x]}{[-M_y-]} \qquad (2)$$

For a most probable distribution of chain lengths in the linear part of the equilibrate then:

$$K_x = \frac{[M_x]}{p^x} \qquad (3)$$

-where p is the extent of reaction of functional groups in the linear polymer. As p is usually close to unity, the K_x values for all but the largest cyclic species may be taken to be equal to the molar concentrations of the cyclic species (in mol dm^{-3}).

A chain undergoing cyclisation must be long enough and flexible enough to obey Gaussian statistics. Kuhn [27] was the first to state that random coil polymer chains would obey the Gaussian expression:

$$W_x(\underline{r}) = (3/2\pi<r_x^2>)^{3/2}\exp(-3r^2/2<r_x^2>) \qquad (4)$$

-for the density $W_x(\underline{r})$ of their end-to-end vectors $\underline{r}$, and where $<r_x^2>$ is the mean-square end-to-end distance of an x-meric chain.

Having calculated the fraction of conformations which are suitable for ring formation using Kuhn's Gaussian expression [27], the cyclisation process is then considered as the fixing of one of the chain ends and calculating the density of the distribution that the other end will be at a distance from the fixed atom such that a ring-forming conformation is assumed, i.e. $r = 0$ for the long chain molecule obeying Gaussian statistics:

$$W_x(\underline{0}) = (3/2\pi<r_x^2>)^{3/2} \qquad (5)$$

In the Jacobson and Stockmayer cyclisation theory [25] the molar cyclisation equilibrium constants are given by:

$$K_x = (3/2\pi<r_x^2>)^{3/2}(1/N_A\sigma_x) \qquad (6)$$

-where N_A is the Avogadro number and σ_x is a symmetry number that represents the number of skeletal bonds of the cyclic that can be opened by the catalyst (2x in the case of PDMS).

The Jacobson and Stockmayer theory [25] gives a simple theoretical expression for the molar cyclisation equilibrium constants for macrocyclics in ring-chain equilibrates. Thus Equation (6) can be used to calculate K_x values provided the corresponding $<r_x^2>$ values are known. Conversely, $<r_x^2>$ values can be obtained by simply measuring K_x values (shown to be equal to molar concentrations).

Figure 1 shows a comparison between the theoretical and experimental data for the macrocyclisation equilibrium constants for PDMS.

Deviations from the theoretical values are observed with the enhanced production of the small cyclics (particularly the tetramer) due to the increased probability of the termini being close together with the correct orientation caused by the favourable conformation of the small molecules [28]. Deviation at high values of x are observed for PDMS in toluene and this has been attributed to excluded volume effects.

Reasons For Studying Ring Macromolecules.

Apart from demonstrating the simple fact that cyclic polymers can be synthesised and isolated, physical studies of such systems allow fundamental investigations into the properties of cyclic macromolecules. Many theoretical predictions have been made with regards to the physical behaviour of a ring compared to that of a corresponding chain. Since PDMS ring-chain equilibrations offer a means of preparing a range of
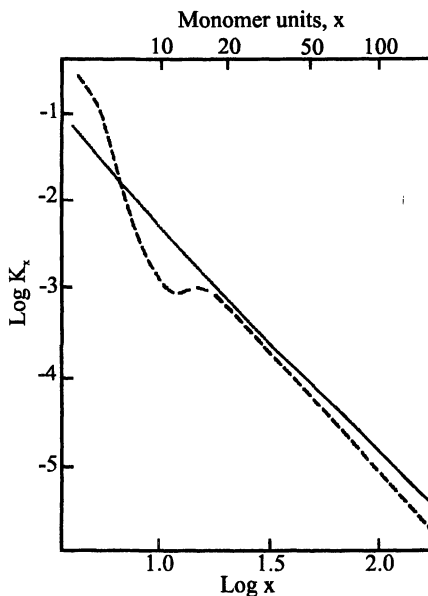

Figure 1: Molar cyclisation equilibrium constants K_x (in mol dm^{-3}) for cyclics $[(CH_3)_2SiO]_x$ in a ring-chain equilibrate in toluene solution (broken line) compared with theoretical values calculated by Flory and Semlyen [28] (solid line). (Reproduced from ref. [28]).

ring macromolecules, it is possible to obtain physical experimental data which can be used to determine the validity of these predictions.

It is of interest to note that many natural forms of deoxyribonucleic acid (DNA) have been shown to be circular macromolecules [29]. Furthermore, a detailed knowledge of the properties and molecular conformations of cyclic polymers should lead to a better understanding of the behaviour of linear polymers, as well as giving new insights into the properties of rubbers, gels and other systems where closed loops are known to exist.

Cyclic polymers offer routes to many more different topologies than linear polymers. The number of different architectural structures possible with cyclic polymers are shown in Figure 2 in comparison to those possible with linear polymers.
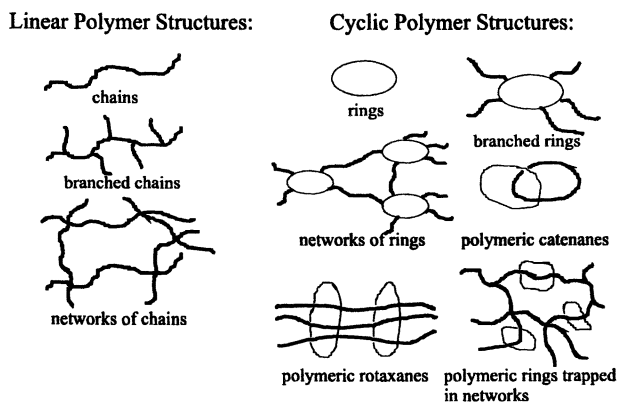

Figure 2: Structural comparison of linear and cyclic polymers.

Additionally, one obvious reason for studying ring macromolecules is to determine if PDMS rings have any particular physical properties which might be industrially applicable. This can only be achieved by building up a detailed picture of the physical properties of PDMS over a range of ring sizes, and defining any major differences which appear with respect to linear PDMS which has already been shown to be exceedingly commercially important.

Preparation Of Hydrogenated Linear And Cyclic PDMS.

As mentioned above, linear PDMS may be prepared by the acid or base catalysed polymerisation of octamethylcyclotetrasiloxane (D_4). A controlled amount of $(CH_3)_3Si-O-Si(CH_3)_3$ (hexamethyldisiloxane) is added to cap the reactive end groups resulting in trimethylsilyl end-terminated chains.

Cyclic PDMS is also synthesised by acid or base catalysed polymerisation of D_4, however, the reaction is now carried out at high dilution (and in the absence of any terminating groups). The methods of Brown and Slusarczuk [4] and Chojnowski et al. [30] [31] [32] [33] (see below) have been well established by the group at York and details of both are given below. Both methods establish a ring/chain equilibrium forming both linear and cyclic PDMS. Once equilibrium has been reached the catalyst is neutralised, end groups maybe added to terminate the linear PDMS chains and the cyclics may be separated out.

Brown And Slusarczuk Base Catalysis. The Brown and Slusarczuk [4] method of preparing cyclic PDMS involves an anionic i.e. base catalysed ring-chain equilibrium. The mechanism for the anionic polymerisation of D_4 is shown in Figure 3.
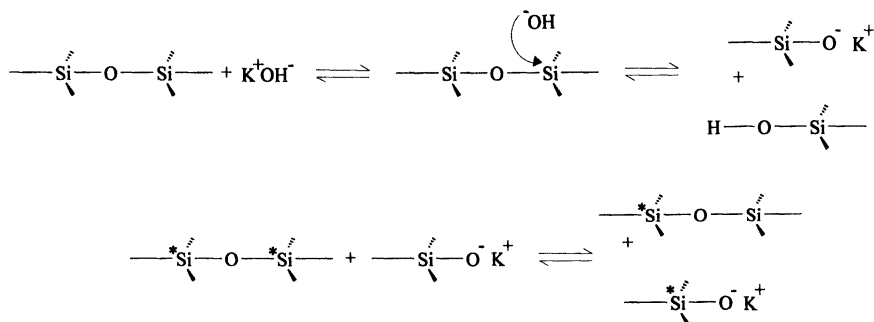

Figure 3: Brown and Slusarczuk reaction mechanism. The * denotes a second siloxane species in the reaction.

Potassium hydroxide is used as the base in the presence of distilled diglyme (2-methoxyethylether). The diglyme complexes the potassium ions and promotes the formation of hydroxide ions. The D_4 starting material must be dried and distilled from calcium hydride prior to use. The reaction is refluxed at 384 K in sodium dried toluene for 14 days under a nitrogen atmosphere. Dry reaction conditions must be maintained since the presence of any water terminates the reaction.

Once the reaction has come to equilibrium, it is quenched by the addition of glacial acetic acid. The cyclic species can then be extracted from the reaction mixture.

Chojnowski Acid Catalysis. The Chojnowksi [30] [31] [32] [33] reaction involves cationic i.e. acid catalysed polymerisation of D_4. The mechanism for the cationic

polymerisation is shown in Figure 4. The acid used for the reaction is trifluoromethanesulphonic (triflic) acid. Trimethylsilyltrifluoromethane sulphonate is added to assist the acid as suggested by Lebrun, Sauvet and Sigwalt [34]. The D_4 is dried as in the Brown and Slusarczuk reaction but the dichloromethane (methylene chloride) solvent is not, as in this case a trace amount of water is required for the reaction to proceed. The reaction is carried out at room temperature under a nitrogen atmosphere (to prevent the introduction of excess water) for up to 48hrs.
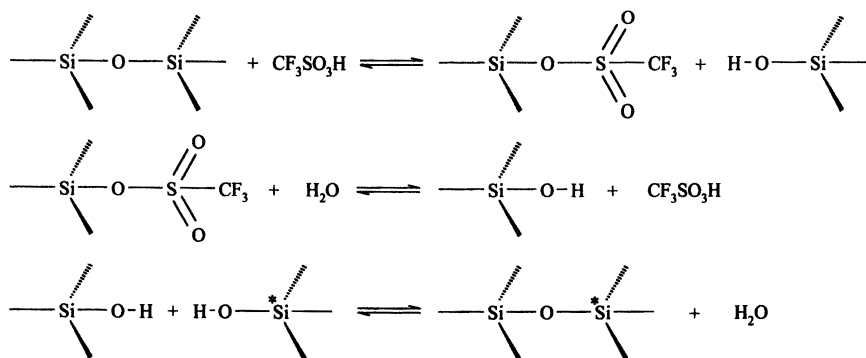

Figure 4: Chojnowski reaction mechanism. Once again, the * denotes a second siloxane species taking part in the reaction.

Again, once equilibrium has been reached the reaction is quenched with copious amounts of sodium carbonate (to neutralise the acid) and the cyclics may then be extracted.

Both of the above mechanisms are complex processes with polymerisation, depolymerisation, repolymerisation and chain transfer all occurring. Since all the siloxane bonds present in the reaction mixture will stand an equal chance of undergoing reaction whether they are present in D_4, oligomers or polymer a ring/chain equilibrium is established.

Separation Of Linear and Cyclic PDMS. The cyclic PDMS was separated from the linear PDMS by three refluxes at 10% weight by volume in acetone. The cyclics are soluble in acetone, the linears are not and so precipitated out on cooling overnight to room temperature and were removed using a separating funnel. The separated cyclics were analysed by GPC and gas liquid chromatography (GLC) and some of the low cyclic oligomers and D_4 starting material were removed by careful vacuum distillation and washing with methanol (methanol is a good solvent for the smaller cyclic species but a poor solvent for the larger cyclics).
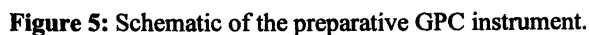
Preparative Gel Permeation Chromatography.

The ability to prepare a series of sharp fractions (i.e. fractions with a dispersity as close to unity as possible) of a variety of molar masses is vital in order to investigate how a number of properties of a polymer scale as a function of chain length [35].

Sharp fractions of cyclic and linear PDMS containing species with up to 100 skeletal bonds can be prepared conveniently by vacuum fractional distillation. Such fractions have dispersities (M_w / M_n) which are typically 1.03 ± 0.02. Larger cyclic and linear PDMS can be fractionated using classical solution fractionation (for example acetone and water mixtures may be used to fractionally precipitate the polymers [36]). This can be very time consuming and broad fractions often result.

GPC may be used to prepare sharp fractions of cyclic and linear PDMS with number average numbers of skeletal bonds in the range $100 < n_n < 1000$. The preparative GPC instrument used for this purpose is described below. The cyclic and linear PDMS fractions obtained this way typically have dispersities (M_w / M_n) of 1.05 ± 0.05, considerably lower than those obtained using conventional fractionation techniques.

Preparative GPC Instrument. Preparative scale GPC units typically involve the use of much larger separation columns, greater solvent volumes and relatively larger amounts of sample than conventional analytical systems. The Preparative GPC instrument used to prepare sharp fractions of polymers was designed and constructed by Mr. D. Sympson at the workshops of the University of York Chemistry Department [5]. A block diagram of the instrument is shown in Figure 5.

Toluene was used as the chromatographic solvent and was delivered from the tank(1) to the still(4) via a constant level device(3). The distilled solvent was pumped through the system by an adjustable pressure pump(5) - the available solvent flow rates being in the range 10 - 180 cm^2 min^{-1} at pressures of up to 100 psi. Adjustable bellows(6) damped the solvent flow and an overpressure release valve(7) was available to control the solvent pressure. The solvent flow was then split into reference and sample streams after passing through a filter(8). The reference stream was only opened at the start of a run and passed through the reference cell of a Waters R4 'Preparative' differential refractometer(12). The sample stream was directed through a 6-port injection valve(9) having a sample loop with nominal capacity of 10 cm^3. The sample loading for each fractionation was 1-2 g of polymer, which was dissolved in ~10 cm^3 toluene. The solution was then filtered using a 0.45 μm filter (Millipore Ltd.) and transferred to the injection loop manually using a 10 cm^3 syringe. The sample stream could then be passed through either column A(10) or column set B(11) or through both in series. Column A was ~120 cm in length and ~5 cm internal diameter. Column set B consisted of two columns each of length ~30 cm and ~5 cm internal diameter in series. All of the columns were packed and supplied by Waters Associates Ltd.. Column A had $^2/_5$ of the column packed with Styragel (cross-linked polystyrene) of nominal porosity 100 nm and the remaining $^3/_5$ was packed with Styragel of nominal porosity 300 nm. Column set B was packed with μ-Styragel 103.

1 Solvent tank	6 Pulsation damper	11 Preparative columns set B
2 Still pump	7 Pressure control valve	12 Differential refractometer with
3 Constant level device	8 Filter	chart recorder
4 Still	9 Sample injection valve	13 Solvent and eluent flow sight glasses
5 Pressure pump	10 Preparative column A	14 Solvent counter and fraction cutter

Figure 5: Schematic of the preparative GPC instrument.

After eluting through the columns, part of the sample flow was directed through the differential refractometer detector, the response being plotted on a Chessell chart recorder. The sample flows were then recombined and the automatic fraction cutter(14) was then used to split the column output volumetrically in to fractions of up to 50 cm^3 (each fraction corresponding to one count) and the fraction cuts were automatically deposited into individual collection containers for subsequent work-up.

"Express train" injections were made when quantities of polymer were fractionated. This technique allowed the injection of a second sample into the system before the complete fractionation of the previous sample, so reducing the time required for several fractionations. A minimum time period was chosen between injections so as to avoid the overlapping of peaks. After a number of fractionation runs the solvent was removed from each fraction by rotary evaporation and the polymer sample recovered.

Characterisation of the Hydrogenated Cyclic PDMS Fractions.

The fractions of cyclic PDMS obtained from the preparative GPC have been analysed using a variety of analytical techniques besides GPC. The results of some of these analyses are given below.

Gas Liquid Chromatography. The lower molecular weight cyclic PDMS fractions have been analysed using a PYE series 104 GLC instrument fitted with a heated katharometer detector. The traces obtained for three fractions are shown in Figures 6,7 and 8. The traces show that despite being sharp fractions with dispersities M_w / M_n < 1.05 the fractions consist of a range of individual ring sizes. Also clear from the traces are the lack of linear siloxanes which have slightly different retention times to the cyclic siloxanes and the lack of other volatile impurities.
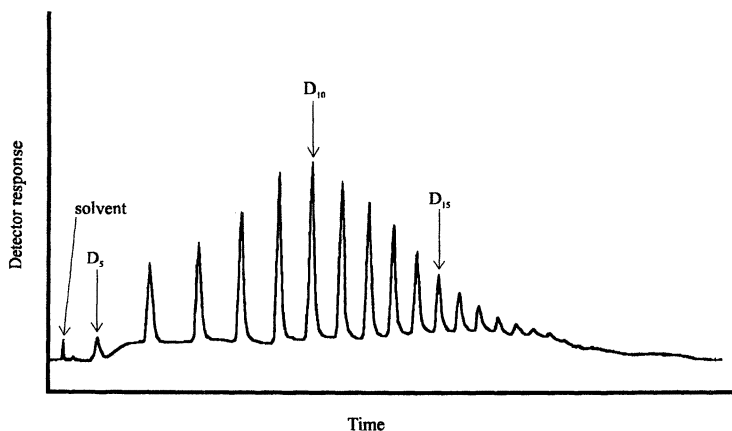

Figure 6: GLC trace of a hydrogenated cyclic PDMS fraction containing rings with 10 to ~42 skeletal bonds.
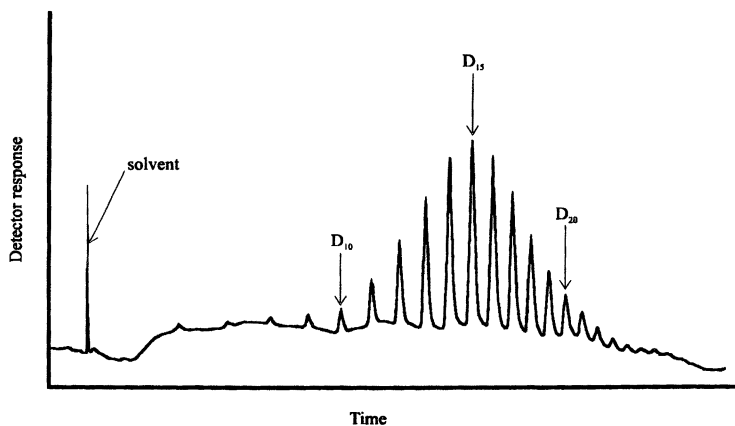
Figure 7: GLC trace of a hydrogenated cyclic PDMS fraction containing rings with 16 to ~52 skeletal bonds.
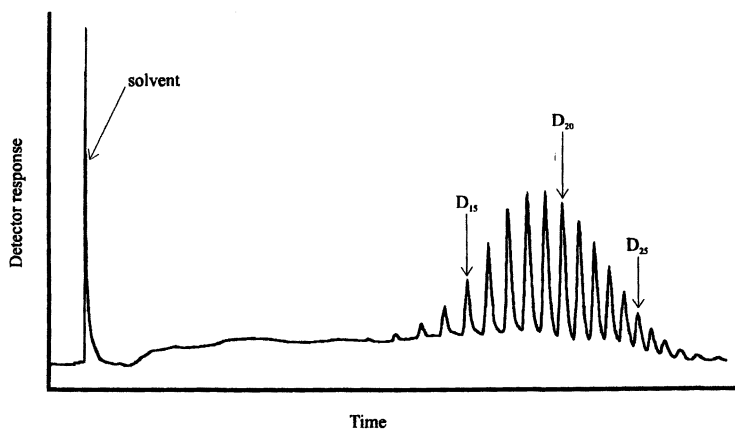

Figure 8: GLC trace of a hydrogenated cyclic PDMS fraction containing rings with 24 to ~60 skeletal bonds.

^{29}Si Nuclear Magnetic Resonance Spectroscopy (NMR). Two of the lower molecular weight cyclic PDMS fractions have been studied using ^{29}Si NMR. The results are shown in Figures 9 and 10. The samples were run in bulk on a Jeol 500 Mhz instrument and show a very interesting effect first observed by Burton et al. [37]. The individual rings can be resolved up to 15 repeat units in a ring. The silicon atoms in a given ring are equivalent, however the different conformations possible in rings of different sizes results in the silicons in the different sized rings experiencing different environments and hence displaying different chemical shifts in the NMR experiment. The minimum chemical shift (σ) occurs for D_8. The peaks then coalesce to the D_{15} peak. Monte-Carlo calculations [38] [39] have shown that marked changes in the shapes of the ring occur up to the D_{15} case, beyond this essentially limiting behaviour has been reached.
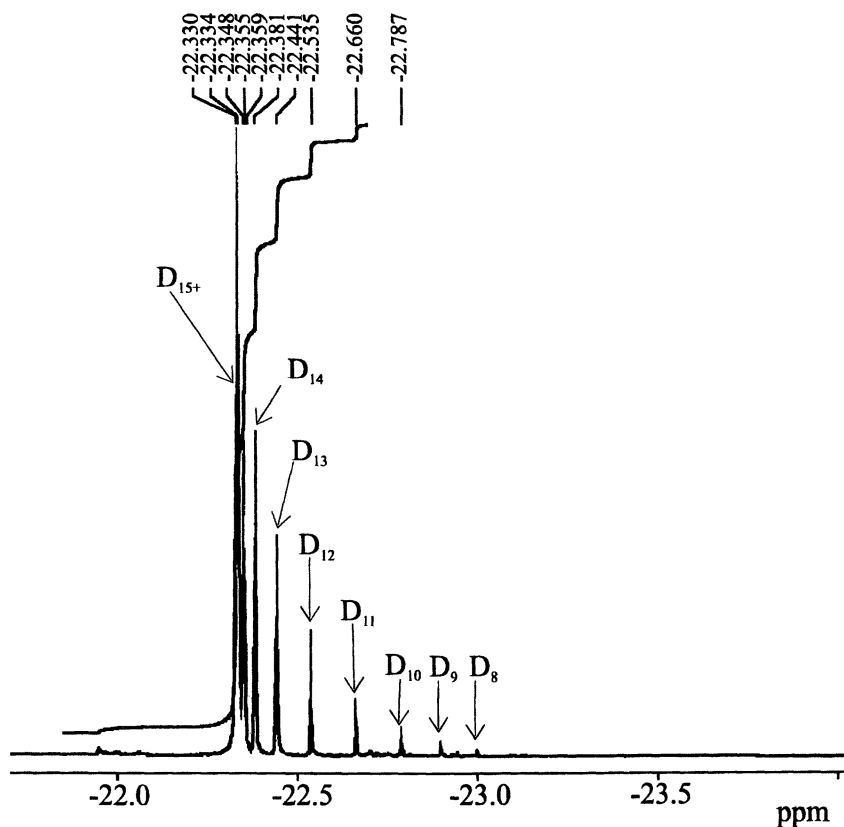

Figure 9: ^{29}Si NMR spectrum of the cyclic PDMS fraction containing rings with 10 to ~42 skeletal bonds.
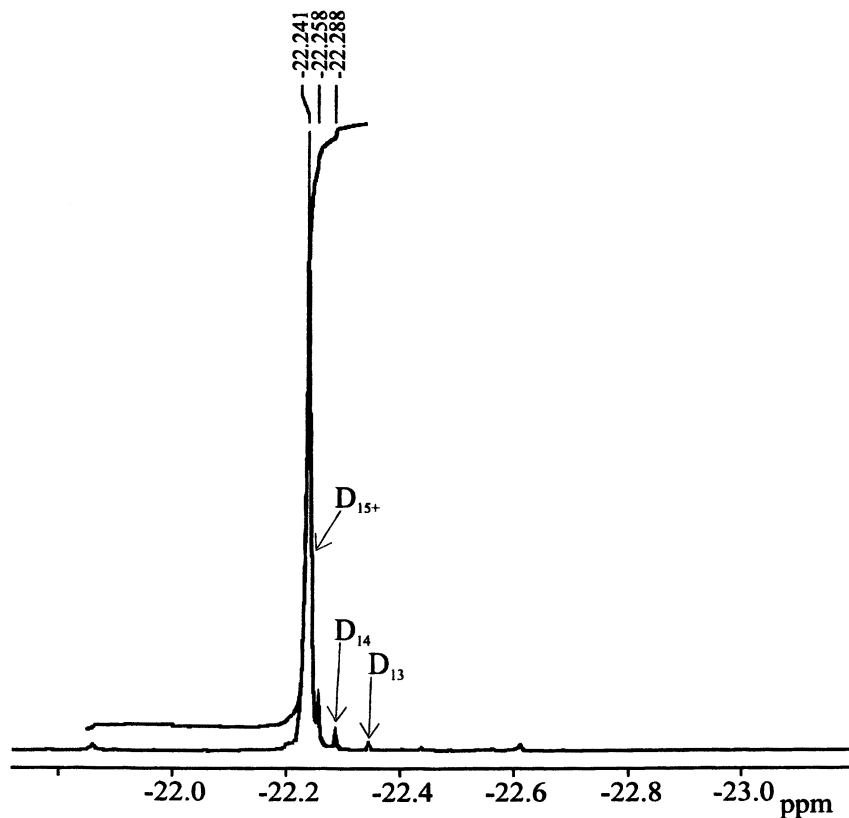
Figure 10: ^{29}Si NMR spectrum of the cyclic PDMS fraction containing ring with 16 to ~52 skeletal bonds.

One further point to note is that comparing the NMR results with the GLC traces for the same fractions it is noticed that the NMR peaks appear to agree quantitatively as well as qualitatively with the GLC peaks. This suggests that the high resolution NMR technique may be useful for analysing the smaller cyclic oligomers (up to and including 15 repeat units).

Low Resolution Electron Ionisation Mass Spectroscopy (EIMS). One of the cyclic PDMS fractions has been analysed using EIMS (see Figure 11). The ionisation pattern again agrees well with the GLC and NMR results above. The clean fragmentation pattern (see Table I) shows the purity of the sample obtained and all of the fragments can be accounted for in terms of rearrangements of the cyclic siloxanes which have been observed previously [40] [41].
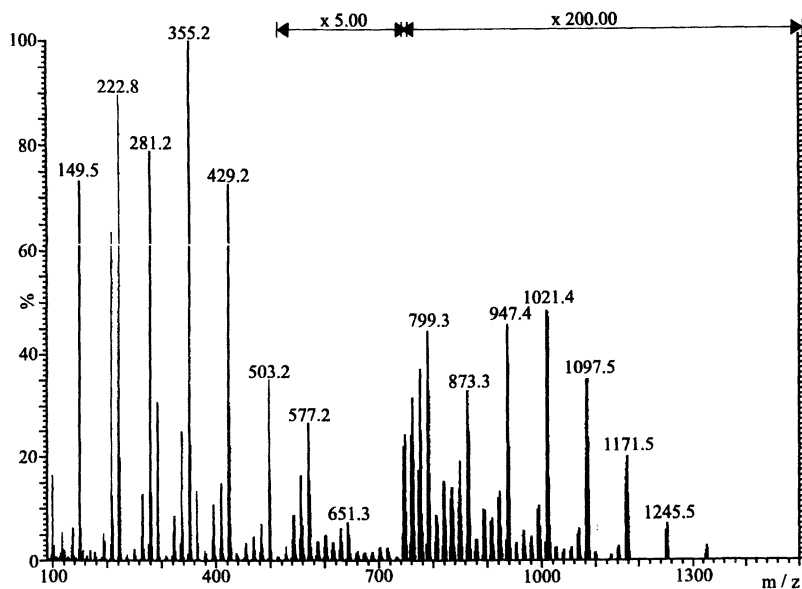
Figure 11: Electron ionisation mass spectrum of a hydrogenated cyclic PDMS fraction.

Table I: Peak assignments for the EIMS spectrum of a hydrogenated cyclic PDMS fraction.

m/z	Composition	Species
281	$Si_4O_4C_7H_{21}$	$(D_4 - CH_3)^+$
355	$Si_5O_5C_9H_{27}$	$(D_5 - CH_3)^+$
429	$Si_6O_6C_{11}H_{33}$	$(D_6 - CH_3)^+$
503	$Si_7O_7C_{13}H_{39}$	$(D_7 - CH_3)^+$
577	$Si_8O_8C_{15}H_{45}$	$(D_8 - CH_3)^+$
651	$Si_9O_9C_{17}H_{51}$	$(D_9 - CH_3)^+$
725	$Si_{10}O_{10}C_{19}H_{57}$	$(D_{10} - CH_3)^+$
799	$Si_{11}O_{11}C_{21}H_{63}$	$(D_{11} - CH_3)^+$
873	$Si_{12}O_{12}C_{23}H_{69}$	$(D_{12} - CH_3)^+$
947	$Si_{13}O_{13}C_{25}H_{75}$	$(D_{13} - CH_3)^+$
1021	$Si_{14}O_{14}C_{27}H_{81}$	$(D_{14} - CH_3)^+$
1095	$Si_{15}O_{15}C_{29}H_{87}$	$(D_{15} - CH_3)^+$
1169	$Si_{16}O_{16}C_{31}H_{93}$	$(D_{16} - CH_3)^+$
1243	$Si_{17}O_{17}C_{33}H_{99}$	$(D_{17} - CH_3)^+$

Investigations of Hydrogenated Cyclic and Linear Poly(dimethylsiloxanes).

As has already been shown, the PDMS ring-chain equilibration provides an excellent route to preparing a wide range of cyclic and linear polymers. To this extent, a large number of studies of both the physical and chemical properties of cyclic PDMS have been carried out and compared with the corresponding linear PDMS. Some examples of these studies are detailed below.

Dimensions Of Rings And Chains In Dilute Solution By Small Angle Neutron Scattering.
Theoretical predictions of the z-average mean-square radii of gyration ($<s^2>_{z,c=0}$) for flexible linear and cyclic polymers with the same number of skeletal bonds in dilute solution at the θ-point, which are unperturbed by excluded volume effects, predict a ratio of $<s_l^2>_{z,c=0} / <s_r^2>_{z,c=0} = 2.0$ [42] [43] [44] (where l refers to linear or chain molecules and r refers to ring or cyclic molecules).

Using small angle neutron scattering (SANS) Higgins et al. [45] measured $<s^2>_{z,c=0}$ for four linear and cyclic PDMS polymers of similar molar masses in dilute benzene-d_6 solution at 292 K. A value for the ratio $<s_l^2>_{z,c=0} / <s_r^2>_{z,c=0}$ of 1.9 ± 0.2 in the region $n_z = 500$ (where n_z is the z-average number of bonds) was obtained in good agreement with the theoretically predicted value.

Bulk Viscosity. The bulk viscosities η of sharp fractions of cyclic and linear PDMS have been measured over a wide molar mass range [46] [47] and are shown in Figure 12.

At low molar masses, the viscosities of the cyclics were found to be considerably higher than those of the corresponding linears. The difference between the values decreased with increasing molar mass until a cross-over was observed at $n_n = 100$ (where n_n is the number-average number of bonds). At higher molar masses the ratio η_r / η_l was found to be approximately 0.5 [46] in agreement with the theory of Bueche [48].
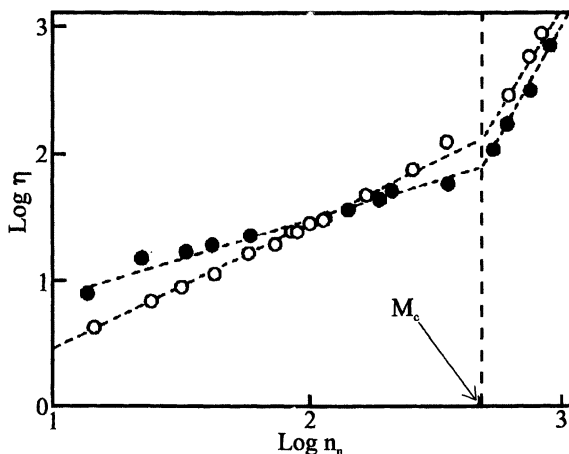

Figure 12: Plot of the logarithm of the viscosity η against the logarithm of the number-average number of skeletal bonds n_n for ring (solid circles) and chain (open circles) PDMS fractions at constant $T - T_g$, where T_g is the glass transition temperature. (Reproduced from ref. [46]).

Values for the critical molar mass for entanglement M_c were found to be ~1.70 x 10^4 g mol^{-1} and ~1.66 x 10^4 g mol^{-1} for ring and chain PDMS respectively. Above this value, the first found for such flexible cyclic molecules, reptation models [49] [50] [51] predict that the motion of linear polymers resemble those of snakes and only the ends of the chains have freedom of motion, moving through 'tubes' created by the entanglements of other molecules. Such models predict that cyclic molecules should be considerably more viscous than the corresponding linear molecules and might even be infinitely viscous. It was found; however, that above M_c the ring polymers are markedly less viscous than the chain polymers [47] and it was concluded that the motion in bulk PDMS does not appear to depend on the movement of chain ends.

Doi [50] has since proposed a tube renewal concept adapted from the melt characteristics of star branched polymers which assumes the motion of rings to be a result of the rearrangement of the tube rather than by the reptation of the polymer down the tube.

Glass Transition Temperature. The thermal behaviour of sharp fractions of linear and cyclic PDMS have been investigated using differential scanning calorimetry [52]. In Figure 13 the glass transition temperatures (Tg) of cyclic and linear PDMS are shown plotted against M_n^{-1}. Linear PDMS shows the expected decrease in Tg with increase in M_n^{-1}. Cyclic PDMS however exhibits the opposite trend. Di Marzio and Guttman [53] have modified the theory of Gibbs and Di Marzio [54] in order to interpret the Tg of these polymers.
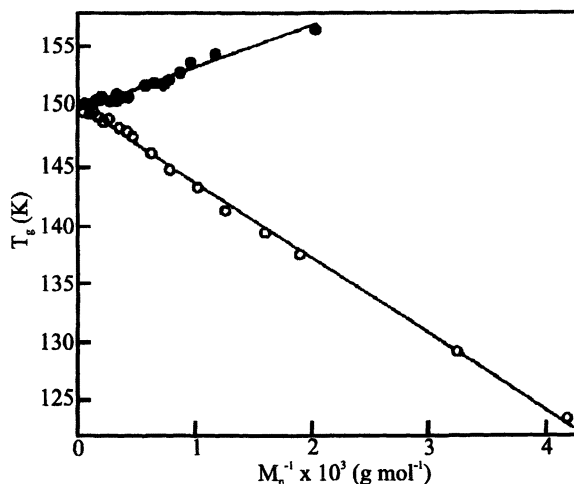

Figure 13: A plot of glass transition temperature (T_g) against reciprocal number-average molar mass (M_n^{-1}) for cyclic (solid circles) and linear (open circles) dimethylsiloxanes. (Reproduced from ref. [52]).

Density and Refractive Index. The densities (ρ) and refractive indices (n_D) of linear and cyclic PDMS have been measured [55] and are shown in Figures 14 and 15 respectively.

There are well defined maxima for the cyclic polymers in both plots at n_n = 22. No such maxima are shown by the chain molecules. As a results of the different bond angles at the silicon and oxygen atoms of the polysiloxane chain, a cyclic molecule with n_n = 22 can adopt a low energy conformation in the all-trans state. Consequently, the ring has a planar disc-shaped character and such rings can pack more efficiently than spherical molecules, giving rise to the increase in density and refractive index.
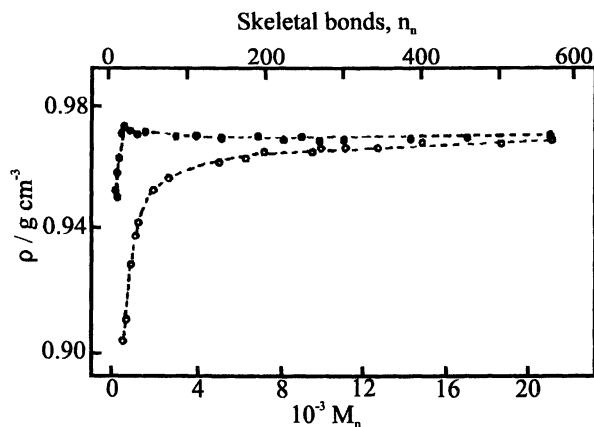
Figure 14: Densities (ρ) of cyclic (solid circles) and linear (open circles) PDMS at 298 K plotted against number-average molar mass. (Reproduced from ref. [55]).
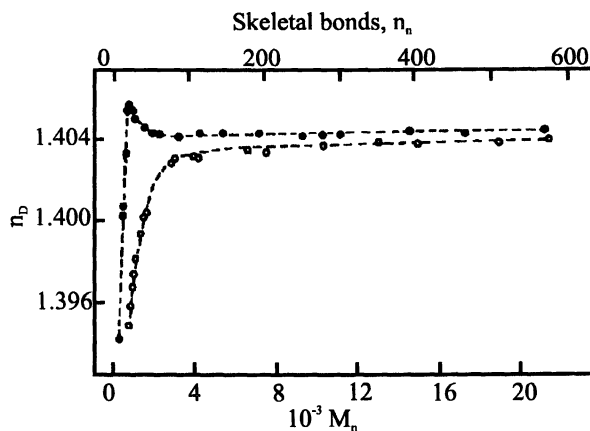

Figure 15: Refractive indices (n_D) of cyclic (solid circles) and linear (open circles) PDMS at 298 K plotted against number-average molar mass. (Reproduced from ref. [55]).

Silicon-29 Nuclear Magnetic Resonance (NMR) Chemical Shift. A Gas Liquid Chromatography (GLC) trace of a cyclic PDMS fraction containing rings - $[(CH_3)_2SiO]_n$- (D_n) with n = 7 - 19 is shown in Figure 16 [37].
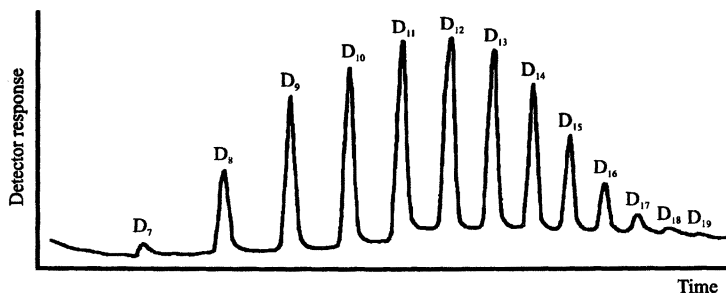

Figure 16: GLC trace for a cyclic fraction containing rings D_x with x = 7-19. (Reproduced from ref. [37]).

The ^{29}Si NMR spectrum for a similar fraction is shown in Figure 17.
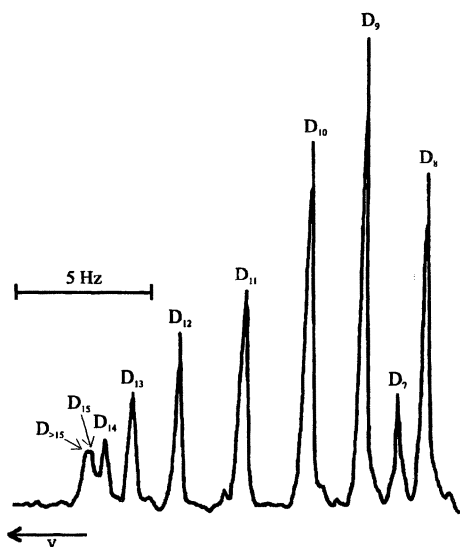

Figure 17: 19.87 MHz ^{29}Si - $\{^1H\}$ NMR spectrum of a cyclic dimethylsiloxane fraction. (Reproduced from ref. [37]).

All silicon atoms in a given ring have the same chemical shift and there are separate resonances for individual rings up to D_{15} where the shifts coalesce to the same value as that for linear PDMS.

Adsorption On Surfaces. The amounts of cyclic and linear PDMS adsorbed on to silica surfaces have been investigated by Fourier transform infrared spectroscopy (FT-IR) [56]. It has been predicted [57] that at low molar masses the adsorption of a cyclic polymer should be greater than that of the corresponding linear polymer, but at high molar masses the reverse should be the case. The predicted crossover was observed (see Figure 18) for PDMS adsorbed onto silica from hexane at ~470 skeletal bonds.
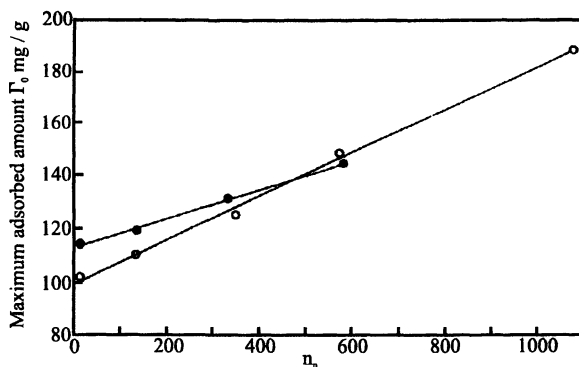

Figure 18: Maximum adsorbed amount Γ_0 plotted as a function of the number average number of skeletal bonds n_n for cyclic (solid circles) and linear (open circles) PDMS adsorbed on silica from hexane. (Reproduced from ref. [56]).

Entrapment Of Rings In To Networks. As discussed earlier, ring molecules are fundamentally different from long chain molecules in that they can form novel topological structures such as catenanes. Investigations have been carried out trapping cyclic polymers into network and rubber structures [58] [59] [60] [61] [62] [63]. The percentage of large rings trapped in to a PDMS network as a function of the number of skeletal bonds n_n is shown in Figure 19.

Deuterated Cyclic PDMS.

Introduction. Deuterated PDMS has previously been obtained from the polymerisation of perdeuterated D_4. This was reported to have been synthesised by Beltzung and co-workers [15] from perdeuterated methanol. The synthesis converts the methanol into methyl iodide via a classical method. The Beltzung reaction scheme is shown in Figure 20:

Figure 19: Percentage of cyclic PDMS trapped in a PDMS network, where n_n represents the number of skeletal bonds. (Reproduced from ref. [60]).

Stage 1: $CD_3I \ + \ Mg \ \xrightarrow{Et_2O} \ CD_3MgI$ *Grignard preparation*

Stage 2: $2\,CD_3MgI \ + \ Ph_2SiCl_2 \xrightarrow{Et_2O} (CD_3)_2SiPh_2 \ + \ 2\,MgICl$ *Grignard reaction*

Stage 3: $(CD_3)_2SiPh_2 \ + HCl \ \xrightarrow[C_6H_6]{AlCl_3} (CD_3)_2SiCl_2 \ + \ 2\,C_6H_6$ *Freidel-Crafts reaction*

Stage 4: $(CD_3)_2SiCl_2 \ + \ nH_2O \xrightarrow{Et_2O} (-Si(CD_3)_2O-)_n$ *Hydrolysis reaction*
linear + cyclic
siloxanes

Stage 5: $(-Si(CD_3)_2O-) + KOH \xrightarrow{heat} D_3 - d_{18} + \ D_4 - d_{24}$ *Thermolysis*

Figure 20: Beltzung outline for per-deuterated D_4 synthesis.

The preparation began by synthesising per-deuterated methyl iodide (CD₃I) from per-deuterated methanol via a classical method. The CD₃I was then reacted with magnesium to produce a Grignard reagent which was subsequently reacted with a dichlorodiphenylsilane to produce bis(trideuteriomethyl)diphenylsilane ((CD₃)₂SiPh₂). Freidel Crafts de-arylation was then performed on the silane with benzene and gaseous hydrochloric acid in the presence of aluminium trichloride to remove the phenyl groups and produce the bis(trideuteriomethyl)dichlorosilane ((CD₃)₂SiCl₂). This was then hydrolysed under acidic conditions to yield a mixture of linear and cyclic per-deuterated siloxanes. Finally a thermal rectification was made using potassium hydroxide to increase the relative amounts of the cyclic tetramer (the starting material for ring-chain equilibration reactions).

Use Of Triflic Acid To Remove The Phenyl Groups From Dimethyldiphenylsilane.

Background.   Investigations into the Beltzung reaction showed that the Friedel-Crafts reaction was not an easy one to achieve under normal laboratory conditions. An alternative method was sought for the removal of the phenyl groups from the dimethyldiphenylsilane intermediate.

A review of the literature soon revealed what appeared to be an alternative route to obtain siloxane oligomers from dimethyldiphenylsilane as shown in Figure 21:
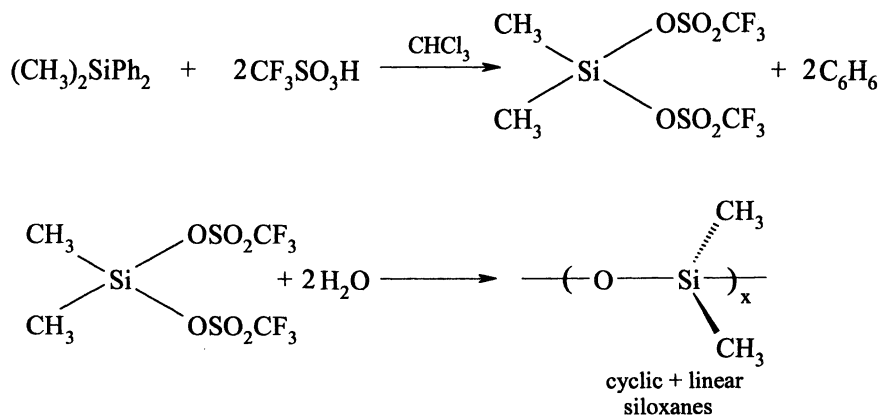

Figure 21: Proposed use of triflic acid to produce siloxane oligomers.

This reaction had not previously been attempted, however, work carried out by Matyazewski and co-workers [64] [65] showed that the removal of the phenyl groups from dimethyldiphenylsilane could be readily achieved at room temperature with two equivalents of triflic acid (Figure 22) and Uhlig [66] had shown that the presence of water leads to siloxane production (Figure 23) - an unwanted side-product in that particular investigation.
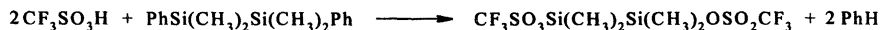
$$2\,CF_3SO_3H + PhSi(CH_3)_2Si(CH_3)_2Ph \longrightarrow CF_3SO_3Si(CH_3)_2Si(CH_3)_2OSO_2CF_3 + 2\,PhH$$

Figure 22: Matyjaszewski and coworkers preparation of silyl triflates from silanes and oligosilanes with phenyl groups.

1/n [(CH$_3$)Si-Si(CH$_3$)Ph-]$_n$ $\xrightarrow[-C_6H_6]{CF_3SO_3H}$ 1/n [(CH$_3$)Si-Si(CH$_3$)Ph-]$_n$ $\xrightarrow[-CF_3SO_3^-]{Nu^-}$ 1/n [(CH$_3$)Si-Si(CH$_3$)Ph-]$_n$
        | | |
        Ph   OSO$_2$CF$_3$ Nu

1/n [(CH$_3$)Si-CH$_2$-]$_n$ 1/n [(CH$_3$)Si-CH$_2$-]$_n$ 1/n [(CH$_3$)Si-CH$_2$-]$_n$
        | | |
        Ph   OSO$_2$CF$_3$ Nu
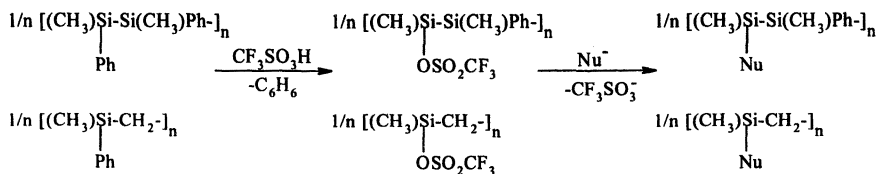
Figure 23: Examples of Uhlig's work with novel organosilicon polymers.

This chemistry was thoroughly investigated in order to produce perdeuterated siloxane materials.

Preparation of Deuterated Cyclic PDMS.

Introduction. The method described here firstly details a route to the per-deuterated small cyclic dimethylsiloxanes from CD_3I [12], and then a route to both linear and cyclic deuterated PDMS [13] [14], based on the investigations in to the use of triflic acid as a means of removing the phenyl groups from the intermediate dimethyldiphenylsilane. Details for the preparation of the deuterated intermediate bis(trideuteriomethyl)diphenylsilane $((CD_3)_2SiPh_2)$ are not given here but may be found elsewhere [12]. The synthesis reported here is more convenient to carry out, requires less purification of reagents and produces per-deuterated dimethylsiloxanes in an improved yield.

Experimental. The first range of per-deuterated cyclics have been achieved in improved yield via the route shown in Figure 24 from per-deuterated methyl iodide [12].
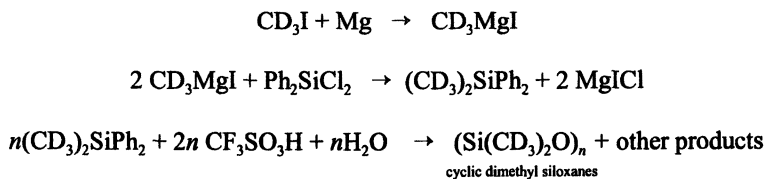
$$CD_3I + Mg \rightarrow CD_3MgI$$

$$2\,CD_3MgI + Ph_2SiCl_2 \rightarrow (CD_3)_2SiPh_2 + 2\,MgICl$$

$$n(CD_3)_2SiPh_2 + 2n\,CF_3SO_3H + nH_2O \rightarrow \underset{\text{cyclic dimethyl siloxanes}}{(Si(CD_3)_2O)_n} + \text{other products}$$

Figure 24: Convenient synthesis of per-deuterated dimethylsiloxanes.

The per-deuterated cyclic dimethylsiloxanes produced in these reactions were to be further polymerised in various ways to yield mixtures of larger cyclic and linear polymers which could be separated and fractionated using preparative GPC in a recognised fashion.

Preparation Of Small Cyclic Per-Deuterated Dimethylsiloxanes. Investigations have shown triflic acid to be capable of removing phenyl groups from dimethyldiphenylsilane and polymerisation of the hydrolysis products is possible in situ. The reaction was now carried out using bis(trideuteriomethyl)diphenylsilane prepared from CD_3I via a Grignard to produce per-deuterated dimethylsiloxanes.

The overall reaction required that 2.66×10^{-1} mol (57.95 g) of $(CD_3)_2SiPh_2$ were reacted with 5.32×10^{-1} mol (79.78 g) of triflic acid in the presence of 2.66×10^{-1} mol (4.79 g) of water.

The silyl triflate intermediates proposed in the reaction mechanism (see below) have been isolated and characterised previously [64] [67] and were reported to be extremely reactive, so for reasons of safety, the reaction was achieved in three stages. The procedure for each stage was as follows: the silane was diluted in dichloromethane at a ratio of 1 : 5 (w : v), one third of the required amount of water was added and the mixture stirred vigorously. One third of the amount of triflic acid was then added extremely cautiously at room temperature and allowed to react for two hours. The reaction was then cooled to <5°C before 200 mls of an approximately 1 M aqueous sodium carbonate solution was added slowly to neutralise the acid. The mixture was allowed to come to room temperature and once clear and colurless, the two layers obtained were separated, the dichloromethane layer was washed with deionised water and evaporated down under reduced pressure to remove the chlorinated solvent.

The progress of the triflic acid reaction was monitored using GLC. This technique is a rapid method of studying the volatile silanes and siloxanes being produced [68]. The product was then reacted further by an identical procedure, analysed again by GLC and the process repeated once more. This resulted in 18.24 g of a clear colourless oil. This was analysed by ^{1}H, ^{13}C and [29]Si Nuclear Magnetic Resonance (NMR) spectroscopy, InfraRed (IR) absorption, Gas Chromatography / Electron Ionisation - Mass Spectometry (GC/EI-MS) and by Gas Chromatography / Chemical Ionisation - Mass Spectrometry (GC/CI-MS)(see below for further details of the analyses).

The traces obtained from the GLC analysis of the reaction (Figure 25) clearly show the production of what have been identified, through the use of GC/EI-MS, as linear phenyl terminated poly(dimethylsiloxane) oligomers (Ph-(Si(CD_3)_2O)_n-Si(CD_3)_2Ph). The subsequent removal of the terminal phenyl groups upon further reaction with triflic acid was seen to result in a rearrangement to small cyclic oligomers of per-deuterated dimethylsiloxane.
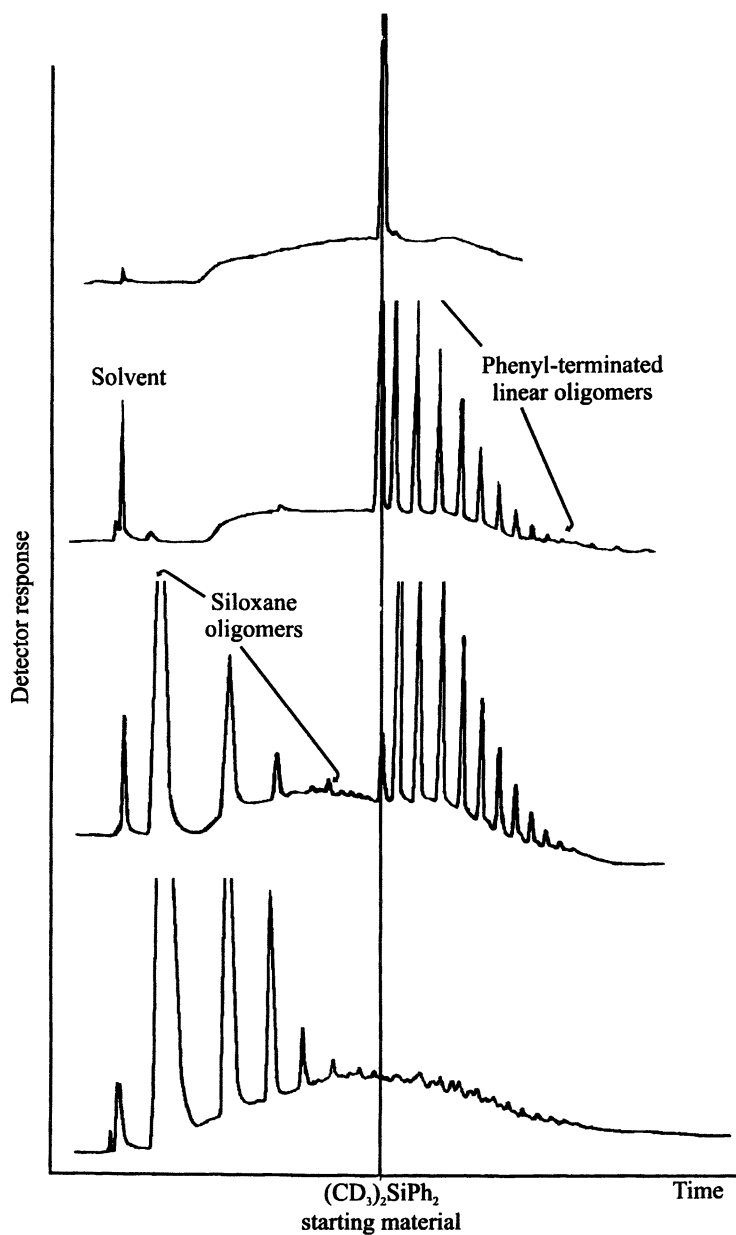
Figure 25: GLC traces recorded during the reaction of bis(trideuteriomethyl)diphenyl silane with triflic acid.

Analysis Of The Small Per-Deuterated Dimethylsiloxanes.

The structure and purity of the per-deuterated dimethylsiloxanes were confirmed by various analytical techniques described below:

^{1}H NMR. A small sample of the product was analysed in dilute $CDCl_3$ solution spiked with a known amount of dichloromethane using a Jeol 270 MHz NMR instrument (see Figure 26). As expected for a fully deuterated dimethylsiloxane compound, the ^{1}H spectrum showed virtually no signals from the product, however the minute signals at approximately 0 ppm allowed the percentage deuteration to be calculated when the integrations were compared with a similar spectrum recorded with hydrogenated PDMS.
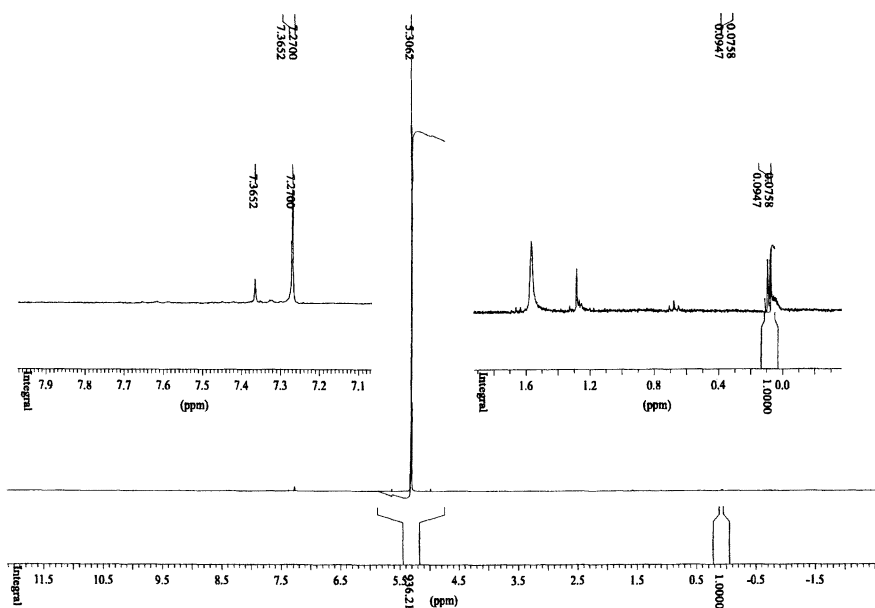
Figure 26: ^{1}H NMR spectrum of the deuterated product spiked with dichloromethane.

The ^{1}H spectrum of the deuterated product shows the almost total deuteration due to the absence of peaks at approximately 0 ppm. All of the phenyl groups have been completely removed from the silane and the hydrolysis has produced deuterated PDMS of high purity. The minute peaks observed at 7.27 and 7.37 ppm are due to residual solvents ($CHCl_3$ and C_6H_6 respectively). The large peak at 5.31 ppm is due to the dichloromethane used as a reference for calculating the percentage deuteration in comparison with a similar spectrum recorded with the hydrogenated cyclic tetramer (D_4).

^{13}C NMR. Again as expected for deuterated dimethylsiloxane compounds virtually no signals were seen to arise from the product in the ^{13}C spectrum.

^{29}Si NMR. ^{29}Si NMR has been identified as another convenient technique for characterising small cyclic poly(dimethylsiloxanes) [37]. The technique allows individual ring species to be identified upto fifteen repeat units in size i.e.D_{15}. A sample of the per-deuterated dimethylsiloxane was analysed undiluted using a Bruker 500 Mhz instrument and the spectrum is shown (Figure 27). Although the spectrum was not locked to any signal as no solvent was present (and so chemical shifts should not be taken as absolute but are shown as a guide), four clearly distinguishable peaks are present. In comparison to the peaks observed with protonated cyclics [37], it is believed that these peaks are due to the tetrameric (-18.6 ppm), pentameric (-21 ppm), hexameric (-21.7 ppm) and septameric (-21. 9 ppm) cyclic species. Higher cyclics may well be present but could not be reliably identified due to the broad peaks observed. The broad peaks (typically with half maximum height peak widths of 10 Hz compared to 0.3 Hz for the protonated cyclics) are a result of silicon/deuterium coupling these may be resolved by running a silicon/deuterium de-coupled spectrum at high resolution to confirm the presence of the higher cyclics.
IR. A small sample of the oil produced from the triflic acid reaction was anlysed as a neat fluid between sodium chloride discs using a Perkin-Elmer FT-1000 Fourier Transform instrument. The resulting spectrum (Figure 28) shows a characteristic broad peak of siloxane asymmetric Si-O-Si stretches at 1076 cm^{-1} [69]. The C-D
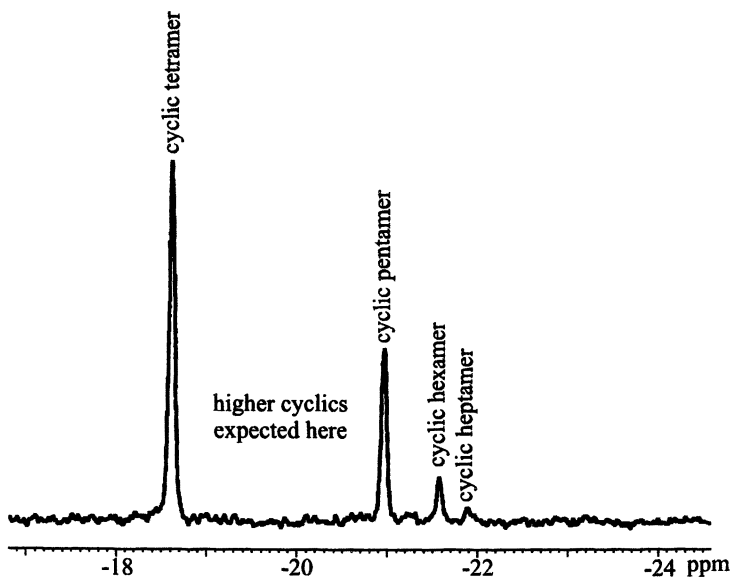

Figure 27: ^{29}Si spectrum of the deuterated small cyclic dimethylsiloxanes.

stretching band is clearly visible at 2217 cm^{-1}, whilst the sharp peak at 1013 cm^{-1} can be assigned to that of the symmetric CD_3 deformation. A spectrum of the hydrogenated cyclic tetramer (D_4) was obtained in the same fashion and is shown in Figure 29 for reference. The siloxane asymmetric stretch is visible at 1070 cm^{-1}. The C-H stretching bands, absent from the deuterated spectrum, are clearly visible at 2905 and 2963 cm^{-1}. Also visible is a sharp band due to the symmetric CH_3 deformation at 1261 cm^{-1} corresponding to the expected shift in frequency of approximately 1.4 times that with deuterium.

Gas Chromatography/Electron Ionisation Mass Spectroscopic Analysis Of The Small Per-Deuterated Dimethylsiloxane Cyclics. A sample of the D-PDMS oil was analysed using GC/EI-MS. This technique separates the volatile siloxane oligomers present and produces a mass spectrum of each component [68] [70]. An Autospec double focussing magnetic sector instrument was used linked to an HP 5890 series II GC fitted with capillary columns. The GC trace obtained (Figure 30) clearly shows the high purity of the sample. Minute peaks observed at 142 and 1009 counts being the only impurities present. The EI-MS spectra were obtained for all of the dimethylsiloxane peaks from the tetramer to the nonamer inclusive (Figures 31 and 32 show those of the hexamer and the nonamer respectively). All of the spectra show a common fragmentation pattern. The most noticeable fragmentation is the facile loss of one CD_3 group leading to a $(M-CD_3)^+$ ion in all cases. Another common loss corresponds to a mass of 100, this corresponds to the loss of $Si(CD_3)_4$ from the cyclic $(M-CD_3)^+$ species and this fragmentation has been accounted for previously in terms of a rearrangement of the cyclic siloxane [40] [41]. A table of the common peaks observed in the EI-MS spectra is given in Table II.
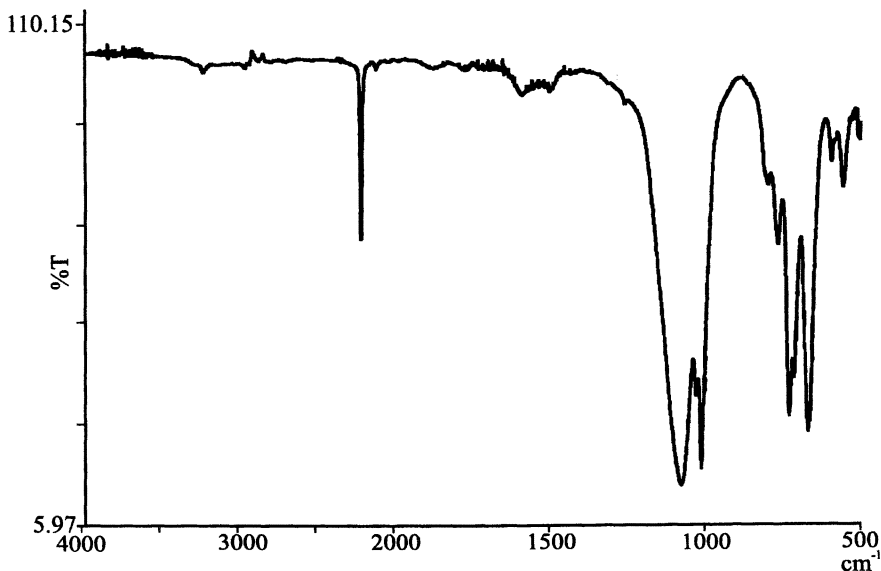

Figure 28: IR spectrum of the deuterated small cyclic dimethylsiloxanes.
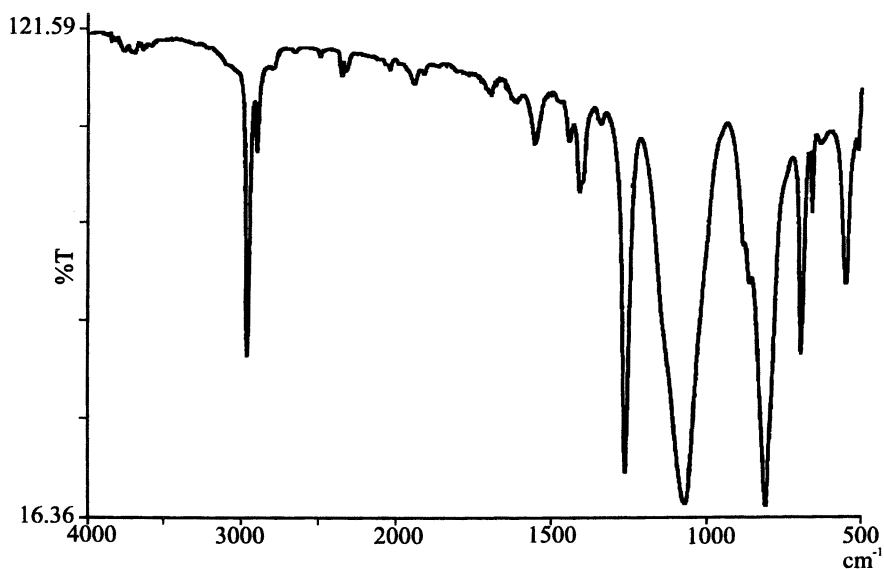
Figure 29: IR spectrum of the hydrogenated cyclic tetramer (D_4) - for reference.
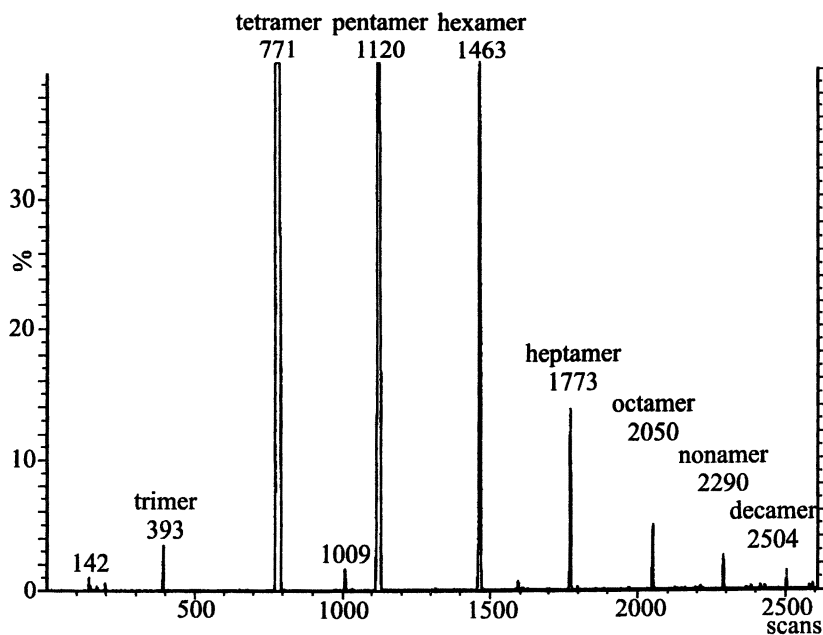

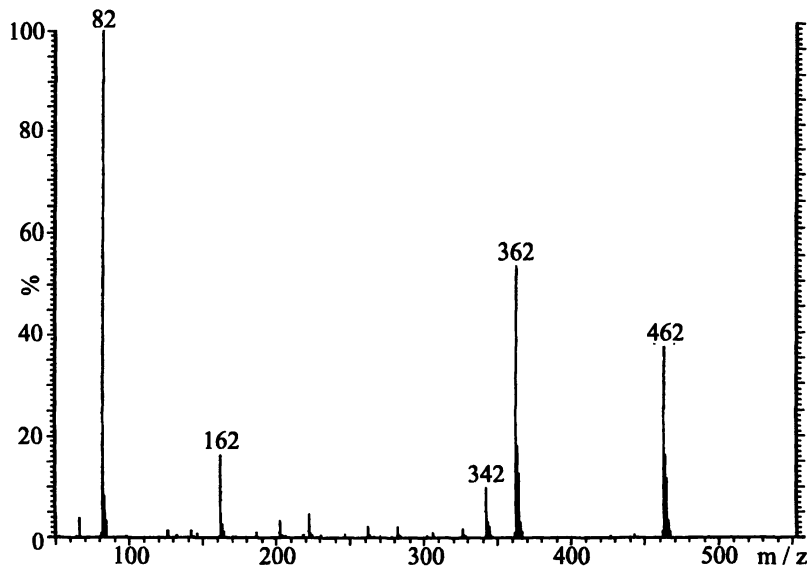**Figure 30:** GC trace of the deuterated small cyclic dimethylsiloxanes.

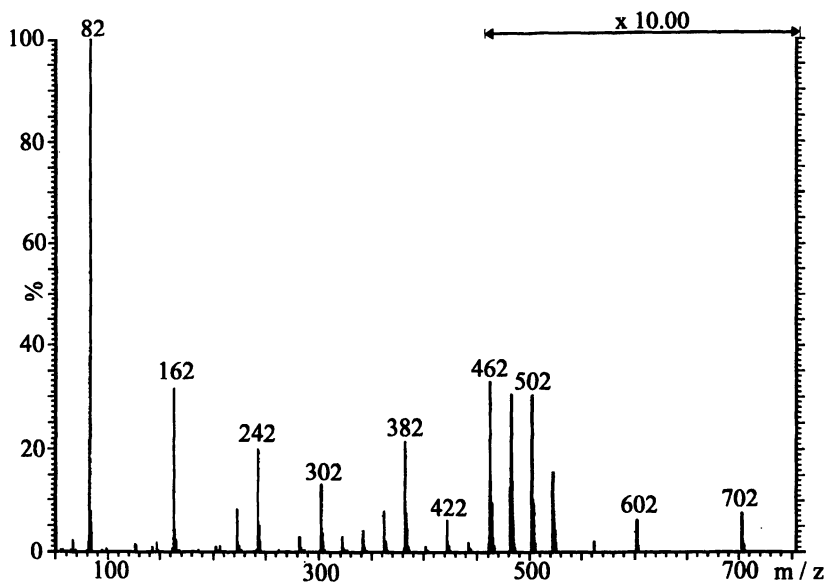**Figure 31:** GC/EI-MS of the per-deuterated cyclic dimethylsiloxane hexamer.

Figure 32: GC/EI-MS of the per-deuterated cyclic dimethylsiloxane nonamer.

Table II: Peak assignments for the GC/EI-MS spectra of the small per-deuterated cyclic dimethylsiloxanes.

m/z	Composition	Species
82	SiC_3D_9	$(Si(CD_3)_3)^+$
142	$Si_2O_2C_3D_9$	$(dimer - CD_3)^+$
162	$Si_2OC_5D_{15}$	$(Si(CD_3)_2OSi(CD_3)_3)^+$
202	$Si_3O_4C_3D_9$	$(tetramer - CD_3 \text{ and } - SiCD_3)_4)^+$
222	$Si_3O_3C_5D_{15}$	$(trimer - CD_3)^+$
242	$Si_3O_2C_7D_{21}$	$(Si(CD_3)_2OSi(CD_3)_2OSi(CD_3)_3)^+$
282	$Si_4O_5C_5D_{15}$	$(pentamer - CD_3 \text{ and } - Si(CD_3)_4)^+$
302	$Si_4O_4C_7D_{21}$	$(tetramer - CD_3)^+$
322	$Si_4O_3C_9D_{27}$	$(Si(CD_3)_2O[Si(CD_3)_2O]_2Si(CD_3)_3)^+$
362	$Si_5O_6C_7D_{21}$	$(hexamer - CD_3 \text{ and } - Si(CD_3)_4)^+$
382	$Si_5O_5C_9D_{27}$	$(pentamer - CD_3)^+$
402	$Si_5O_4C_{11}D_{33}$	$(Si(CD_3)_2O[Si(CD_3)_2O]_3Si(CD_3)_3)^+$
422	$Si_6O_8C_7D_{21}$	$(octamer - CD_3, - Si(CD_3)_4 \text{ and } - Si(CD_3)_4)^+$
442	$Si_6O_7C_9D_{27}$	$(septamer - CD_3 \text{ and } - Si(CD_3)_4)^+$
462	$Si_6O_6C_{11}D_{33}$	$(hexamer - CD_3)^+$
482	$Si_6O_5C_{13}D_{39}$	$(Si(CD_3)_2O[Si(CD_3)_2O]_4Si(CD_3)_3)^+$
502	$Si_7O_9C_9D_{27}$	$(nonamer - CD_3, - Si(CD_3)_4 \text{ and } - Si(CD_3)_4)^+$
522	$Si_7O_8C_{11}D_{33}$	$(octamer - CD_3 \text{ and } - Si(CD_3)_4)^+$
542	$Si_7O_7C_{13}D_{39}$	$(septamer - CD_3)^+$
602	$Si_8O_9C_{13}D_{39}$	$(nonamer - CD_3 \text{ and } - Si(CD_3)_4)^+$
622	$Si_8O_8C_{15}D_{45}$	$(octamer - CD_3)^+$
702	$Si_9O_9C_{17}D_{51}$	$(nonamer - CD_3)^+$

Clearly all the EI sepctra show no evidence for the presence of protonated PDMS despite the normal exposure of the deuterated dimethylsiloxanes to typical laboratory methodology - glassware, solvents etc.. The presence of the peak m/z 82 is in good agreement with a time-of-flight secondary ionisation mass spectrometry (TOFSIMS) study of fully deuterated PDMS carried out by Zhang and co-workers [71], as well as results obtained previously for the corresponding small hydrogenated PDMS cyclics [40] [41], and is thought to be due to a number of different rearrangements including a rearrangement of the skeletal -$[(CD_3)_2SiO]$- backbone of the hydroxyl- terminated deuterated siloxane $HO[(CD_3)_2SiO]_nH$, with a subsequent methyl shift to give -$Si(CD_3)_3$.

To try and confirm the presence of any linear hydroxyl- terminated deuterated siloxanes, which are not easily resolved from the cyclic siloxanes by GLC, the technique of GC/CI-MS was applied to the sample. This technique has been reported to clearly show the presence of hydroxyl end-groups in the analogous hydrogenated PDMS [70].

Gas Chromatography/Ammonia Chemical Ionisation Mass Spectroscopic Analysis Of The Small Per-Deuterated Dimethylsiloxane Cyclics. The CI spectra were also recorded of the small perdeuterated dimethylsiloxane cyclics using the same instrument as previously with ammonia. Three competing processes are known to occur with ammonia in the case of PDMS [70]. Quasimolecular ions are formed either by hydrogen or ammonium ion addition as well as subsequent trideuteriomethyl loss. Ions can be observed at M +18, M + 2(18 - 19), M + 1, and M - 18. Each of these processes are observed for the cyclics upto the decamer and spectra were obtained for the pentamer up to the decamer inclusive (Figures 33 and 34 show those of the hexamer and the nonamer respectively).

It has been reported that silanol terminated linear PDMS produces the (M + $NH_4)^+$ ion in ammonia CI [70]. Whilst the EI spectra of an hydroxyl terminated per-deuterated linear PDMS would appear indistinguishable from that of the cyclic per-deuterated PDMS of the same chain length, the facile trideutriomethyl loss followed by water ejection from the linear diol would result in the same (M + $NH_4)^+$ ion as the trideuteriomethyl loss from the cyclic. This would result in a series of quasimolecular peaks at 18 m/z higher for the linear than the corresponding cyclic. No such peaks were observed in this study and hence the amount of hydroxyl terminated per-deuterated linear PDMS produced may be taken as negligible. A table of the common quasimolecular peaks observed for the per-deuterated cyclic dimethylsiloxanes in the CI-MS spectra is given in Table III.

Preparation of Larger Per-Deuterated Siloxanes.

The successful preparation of the small per-deuterated cyclic dimethylsiloxanes now meant that larger cyclics and linears could in theory be prepared in a recognised fashion from the small rings via either the Brown and Sluzarczuk [4] or the Chojnowski [30] [31] [32] [33] methods. The investigations in to the triflic acid reaction with dimethyldiphenylsilane, however, showed the possibility that the reaction might be catalytic and so this was attempted with deuterated materials and is described below.
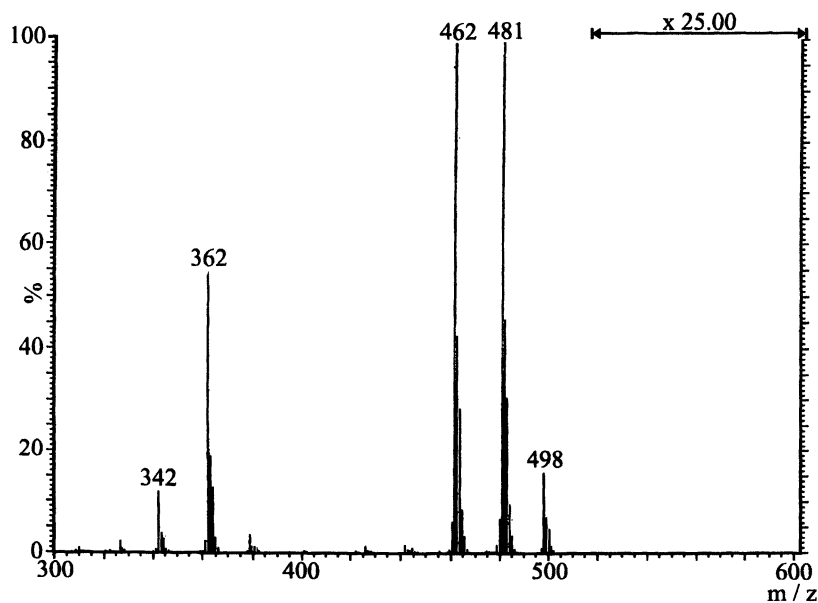
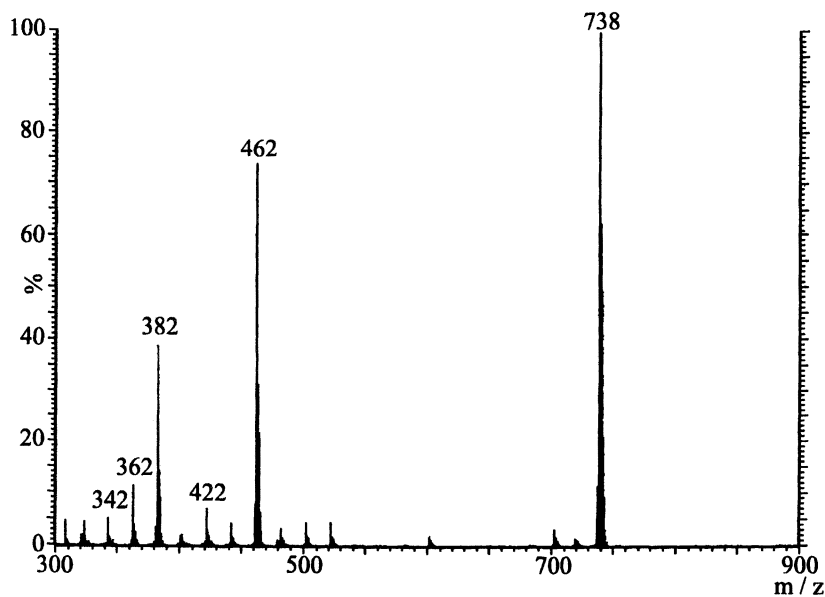**Figure 33:** GC/CI-MS of the per-deuterated cyclic dimethylsiloxane hexamer.

Figure 34: GC/CI-MS of the per-deuterated cyclic dimethylsiloxane nonamer.

Table III: Peak assignments for the GC/CI-MS spectra of the small per-deuterated cyclic dimethylsiloxanes.

m/z	Composition	Species
382	$Si_5O_5C_9D_{27}$	$(\text{pentamer - CD}_3)^+$
401	$Si_5O_5C_{10}D_{30}H$	$(\text{pentamer + H})^+$
418	$Si_5O_5NC_{10}D_{30}H_4$	$(\text{pentamer + NH}_4)^+$
462	$Si_6O_6C_{11}D_{33}$	$(\text{hexamer - CD}_3)^+$
481	$Si_6O_6C_{12}D_{36}H$	$(\text{hexamer + H})^+$
498	$Si_6O_6NC_{12}D_{36}H_4$	$(\text{hexamer + NH}_4)^+$
542	$Si_7O_7C_{13}D_{39}$	$(\text{septamer - CD}_3)^+$
561	$Si_7O_7C_{14}D_{42}H$	$(\text{septamer + H})^+$
578	$Si_7O_7NC_{14}D_{42}H_4$	$(\text{septamer + NH}_4)^+$
622	$Si_8O_8C_{15}D_{45}$	$(\text{octamer - CD}_3)^+$
641	$Si_8O_8C_{16}D_{48}H$	$(\text{octamer + H})^+$
658	$Si_8O_8NC_{16}D_{48}H_4$	$(\text{octamer + NH}_4)^+$
702	$Si_9O_9C_{17}D_{51}$	$(\text{nonamer - CD}_3)^+$
721	$Si_9O_9C_{18}D_{54}H$	$(\text{nonamer + H})^+$
738	$Si_9O_9NC_{18}D_{54}H_4$	$(\text{nonamer + NH}_4)^+$

Catalytic Preparation Of Both Linear And Cyclic Per-Deuterated PDMS. As proposed, the probability that the triflic acid reaction with the bis(trideuteriomethyl)diphenylsilane was catalytic was extremely high and has been confirmed in the first catalytic preparation of both linear and cyclic per-deuterated dimethlysiloxanes from the same reaction [13] [14].

The $(CD_3)_2SiPh_2$ was prepared from trideuteriomethyliodide (CD_3I) as detailed elsewhere [12]. 145.0 g (0.665 mol) of the silane was dissolved in 220 ml of CH_2Cl_2 under a nitrogen atmosphere. 20.0 g (0.133 mol) of triflic acid was slowly added over ½hr and the solution gently stirred at room temperature. The concentrations were chosen such that complete conversion of the silane to siloxanes would result in an overall siloxane concentration of ~230 g l^{-1} shown by Brown and Slusarczuk [4] (in the case of PDMS in toluene) and by Lebrun and coworkers [34] (in the case of PDMS in dichloromethane) to yield good amounts of cyclic PDMS in dilute solution conditions. The amount of triflic acid added was one tenth of the stoichiometric amount required to replace the phenyl groups with triflate groups as carried out in earlier investigations in to this reaction [12]. Once the triflic acid was completely added, one drop of de-ionised water was added and the reaction continued to be gently stirred at room temperature under nitrogen.

The reaction was monitored using GLC, and as observed previously, was seen to produce a series of phenyl terminated linear siloxane oligomers over time. Once the distribution of these oligomers was seen not to change with time a further drop of de-ionised water was added to the reaction. Eventually, the smaller siloxanes were produced, and the distribution of phenyl terminated linear oligomers was seen to reduce. Further evidence enabling a mechanism to be proposed came from the observation of turbidity in the reaction mixture after the addition of the water which was seen to clear after some time. This turbidity has been reported previously by Lebrun and co-workers [34] as a result of the water released on condensation of silanol groups produced in a ring/chain equilibration of hexamethylcyclotrisiloxane (D_3) with triflic acid in dichloromethane (such silanol groups would result here from the rapid hydrolysis of the highly reactive silyl triflates produced).

The cycle of dropwise addition of water and monitoring of the reaction by GLC until no further change in the distribution of products occurred, was continued for 10 days. (Once all of the phenyl groups have been removed from the reaction this becomes essentially a ring-chain equilibration as identified by Chojnowski and co-workers [30] [31] [32] [33]).

Once equilibrated, a copious amount of sodium hydrogen carbonate $(NaHCO_3)$ was added to neutralise the triflic acid. The dichloromethane solution was then washed several times with de-ionised water before being evaporated down under reduced pressure.

This resulted in 45.9 g of a clear colourless viscous oil containing a mixture of cyclic and linear polymers. The small cyclic per-deuterated dimethylsiloxanes were carefully distilled off this residue. The cyclics and high molar mass linear polymer in the residue were separated in a recognised fashion by precipitating the linear polymer from a hot solution of the equilibrate in acetone (10% w/v), allowing the solution to cool to room temperature and stand for 24hrs. The supernatant solution containing the cyclics was decanted from the viscous linear polymer and the acetone removed by evaporation under reduced pressure yielding 6.5g of polydisperse cyclic polymer.

Table IV: Data from the fractionation of the deuterated cyclic PDMS.

Fraction	Yield g	Weight average molar mass (M_w) g mol^{-1}	Number average molar mass (M_n) g mol^{-1}	Dispersity (M_w/M_n)	Number average number of bonds (N_n)
1	0.03	25500	24200	1.05	605
2	0.19	21200	20100	1.05	503
3	0.42	18400	17400	1.06	435
4	0.53	15100	14000	1.08	350
5	0.63	12400	11400	1.09	285
6	0.64	10300	9300	1.11	233
7	0.60	8000	6900	1.16	173
8	0.55	6200	5400	1.15	135
9	0.52	4400	3900	1.13	98
10	0.48	3300	2900	1.14	73
11	0.39	2600	2200	1.18	55
12	0.22	2000	1800	1.11	45

In light of the findings of our work so far, it is suggested that the acid removes the phenyl group from the silane producing the silyl triflate ester (I) and di-ester (II) as intermediates (Figure 36). The silyl triflates have been previously identified as valuable reagents in organosilicon chemistry [72] and are readily hydrolysed to silanol functionalities in the presence of water which is an excellent nucleophile under the reaction conditions. The silanols will readily self condense or condense with the silanoate ester groups to yield siloxane linkages and regenerate the triflic acid in an analogous process to that proposed by Chojnowski and co-workers for the polymerisation of D_4 with triflic acid.
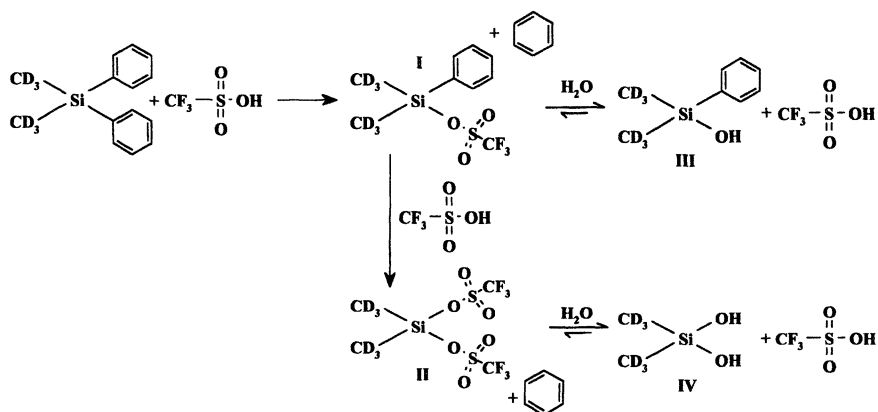

Figure 36: Production of silyl triflates and silanol intermediates.

The production of phenyl terminated dimethylsiloxane oligomers can be accounted for via the reactions shown in Figure 37. Reactions A and B show how silanol self condensation and silanol/silanoate ester condensation respectively yield the diphenyltetra(trideuteriomethyl)disiloxane oligomer (V). Reaction C shows an example of how condensation of larger silanols and silanoate esters may lead to the higher oligomers. An example of the rearrangement to cyclic (VIII) or linear hydroxyl-terminated (IX) dimethylsiloxanes (depending on reaction conditions) is given in Figure 38. Again it is noted that the reactions regenerate the triflic acid reagent and therefore account for the fact that catalytic amounts of the acid are able to achieve the same reaction over a longer time scale.

Summary.

Narrow fractions of hydrogenated cyclic poly(dimethylsiloxanes) have been prepared in good yield. A comprehensive series of analytical techniques have displayed the purity of the products and demonstrated the isolation of cyclic polymers.
The further work carried out investigating the effects of dilution and triflic acid concentration on the reaction with bis(trideuteriomethyl)diphenylsilane has optimised a catalytic route to both linear and cyclic per-deuterated PDMS of high purity in good yields enabling the first narrow fractions of deuterated cyclic polymers to be prepared.
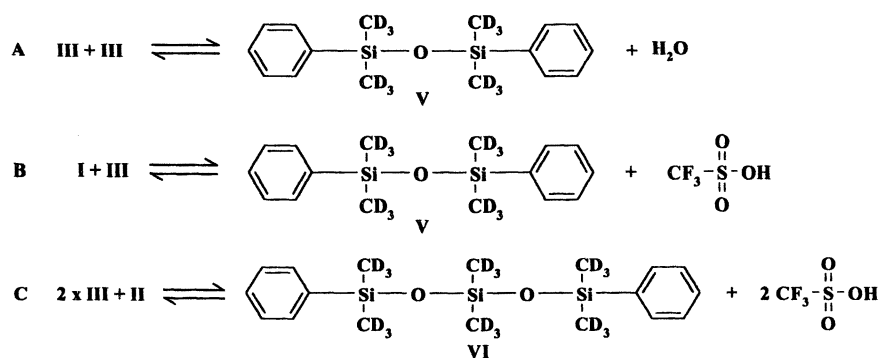
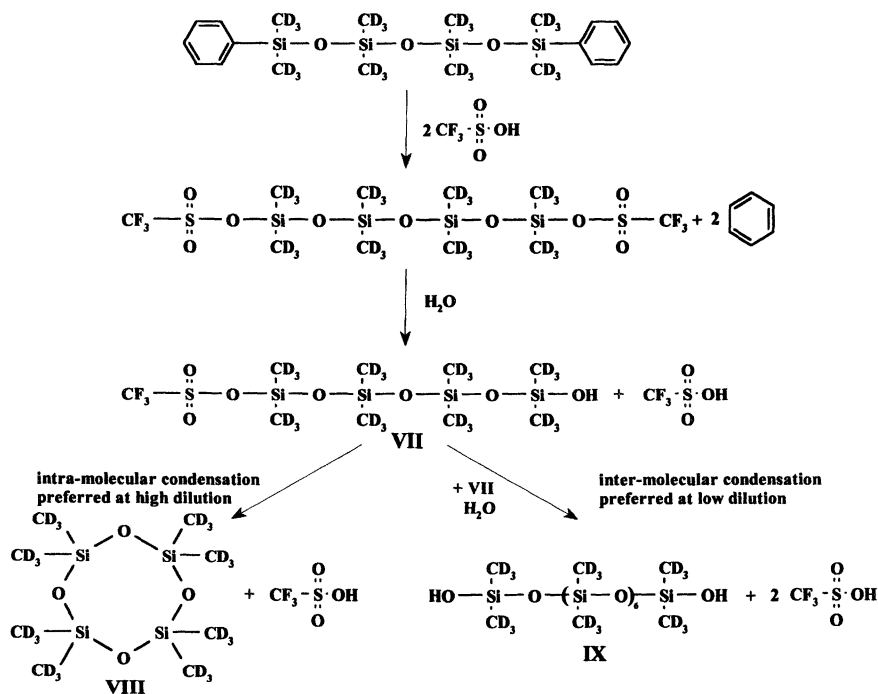**Figure 37:** Condensations leading to phenyl-terminated linear oligomers.

Figure 38: Further reaction of phenyl-terminated oligomers leading to cyclic or linear siloxane production depending on reaction conditions.

The reaction is also expected to provide a convenient route to well controlled random hydogenated/deuterated PDMS copolymers with specific amounts of labelling for neutron scattering studies. This may be achieved by blending the required amounts of $(CH_3)_2SiPh_2$ and $(CD_3)_2SiPh_2$ prior to reacting with a catalytic amount of triflic acid.

The identification of a viable route which yields sufficient quantities of per-deuterated cyclic polymers to allow fractionation in to very sharp fractions, now enables us for the first time to carry out neutron scattering experiments investigating the conformations and properties of cyclic and linear polymers in chemically identical blends.

The conformational and dynamic properties of cyclic polymers have been the subject of considerable interest over a number of years [73] [74]. The new synthetic procedure developed for the preparation of per-deuterated cyclic and linear poly(dimethylsiloxane) (PDMS) polymers [12] [13] [14] now offers unique possibilities for neutron scattering studies. For the first time, it has allowed sufficient deuterated materials to be available for fractionation using our preparative GPC instrument. The resulting narrow fractions are ideally suited for both static and dynamic studies of cyclic and linear polymers. This range incorporates the critical molar mass for entanglement in PDMS.

Despite the extensive literature which is available on the behaviour of cyclic polymers in solution, the static properties and indeed the dynamic properties of ring polymers in the melt remain largely unexplored. As recently pointed out by Müller, Wittmer and Cates [75] "no experimental study of the radius of gyration of rings in the melt appears to have been made. A good understanding of the static properties of the system is of course an indispensable starting point for a reasonable description of the dynamics, so this is unfortunate."

Small angle neutron scattering (SANS) techniques are extremely powerful methods for studying the conformations of polymers. SANS is the only probe of the polymer conformation in the bulk state, relying on the large difference between the scattering lengths of hydrogen and deuterium.

Only two limited SANS studies of linear PDMS have been reported in the literature. Lapp et al. [76] carried out SANS experiments on an asymmetric mixture of h-PDMS (M_w=14600) and d-PDMS (M_w =267000) at low concentration of deuterated chains (0.9 and 6%) whereas Beaucage et al. [77] have recently extended these experiments to symmetric 50/50 h-PDMS/d-PDMS blends with M_w ranging from 15000 to 300000 g/mol.

In collaboration with Heriot-Watt University (Edinburgh), the University of Surrey and Imperial College, we have carried out a series of SANS experiments which have begun to investigate a wide range of linear and cyclic PDMS polymers in chemically identical blends using the materials described in this chapter. The preliminary results obtained are extremely interesting. They will be compared with current theories, computer simulations and the results of previous studies in dilute solution and are to be reported in the near future [78].

Acknowledgments.

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