ELSEVIER

PII: S0032-3861(97)00503-X

Polymer Vol. 39 No. 12, pp. 2621–2627, 1998

0032-3861/98/$19.00+0.00

Studies of cyclic and linear poly(dimethylsiloxanes): 33. Preparation and characterization of per-deuterated linears and cyclics

A. C. Dagger and J. A. Semlyen*
Department of Chemistry, University of York, Heslington, York Y01 5DD, UK
(Received 24 April 1997; revised 19 June 1997)

A series of small cyclic per-deuterated dimethylsiloxanes have been prepared in good yield *via* a new convenient synthetic route. The cyclic per-deuterated dimethylsiloxanes produced have been characterized by gas liquid chromatography (GLC), gel permeation chromatography (g.p.c.), infra-red absorption spectroscopy (i.r.) ^{1}H, ^{13}C, and ^{29}Si nuclear magnetic resonance spectroscopy (n.m.r.), gas chromatography/electron ionization mass spectrometry (GC/EI-MS) and also by gas chromatography/ammonia chemical ionization mass spectroscopy (GC/CI-MS). The results of the various techniques showed the main products to be the per-deuterated cyclic tetramer, pentamer and hexamer—with small amounts of higher cyclics also present. GC/EI-MS and GC/CI-MS spectra were obtained for all of the cyclic species from the tetramer to the nonamer inclusive. No evidence was found for the production of linear per-deuterated PDMS *via* this route. A sample of the per-deuterated cyclic oligomers was polymerized to a high molecular weight per-deuterated linear polymer and analysed by g.p.c. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: per-deuterated dimethylsiloxanes; neutron scattering)

INTRODUCTION

The technique of neutron scattering relies on the selective deuterium labelling of parts of the system of interest. As part of a long-term programme investigating the statistical conformations and equilibrium/dynamic properties of poly(dimethylsiloxane) (PDMS), this paper describes a convenient preparation of per-deuterated poly(dimethylsiloxane) for future use in neutron scattering studies.

Beltzung *et al.*[1] previously reported a preparation of the per-deuterated cyclic trimer and tetramer from per-deuterated methanol. Their preparation began by synthesizing per-deuterated methyl iodide (CD_3I) *via* a classical method. The CD_3I was then reacted with magnesium to produce a Grignard reagent which was subsequently reacted with a dichlorodiphenylsilane to produce bis(trideuteriomethyl)diphenylsilane ($(CD_3)_2SiPh_2$). Freidel–Crafts 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 ($(CD_3)_2SiCl_2$). 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).

Extensive investigations into the preparation of per-deuterated poly(dimethlysiloxane) for use in neutron scattering studies revealed the Beltzung preparation to be a difficult one to achieve in high yields without intense purification of the reagents (especially for the Friedel–Crafts reaction) and the glassware, so an alternative route was sought.

The method described here details a route to the per-deuterated small cyclic dimethylsiloxanes from CD_3I. The preparation of the intermediate bis(trideuteriomethyl)-diphenylsilane ($(CD_3)_2SiPh_2$) is described to display details of the preparation, including analysis of the Grignard reagent, omitted by Beltzung. The synthesis reported here is more convenient to carry out, requires less purification of reagents and produces per-deuterated dimethylsiloxanes in an improved yield (83% cyclic oligomers obtained compared to 63% obtained by Beltzung from CD_3I).

EXPERIMENTAL

A range of per-deuterated cyclics have been achieved in improved yield *via* the route shown in *Scheme 1* from per-deuterated methyl iodide.

The per-deuterated cyclic dimethylsiloxanes produced in these reactions can be further polymerized in various ways to yield mixtures of larger cyclic and linear polymers which can be separated and fractionated using preparative gel permeation chromatography (g.p.c.)[2] in a recognized fashion[3].

$$\mathbf{CD_3I + Mg \rightarrow CD_3MgI}$$

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

$$\mathbf{\mathit{n}(CD_3)_2SiPh_2 + 2\mathit{n}\,CF_3SO_3H + \mathit{n}H_2O \rightarrow \underset{\text{cyclic dimethyl siloxanes}}{(\text{-}Si(CD_3)_2O\text{-})_{\mathit{n}}}}$$

Scheme 1 Convenient synthesis of per-deuterated dimethylsiloxanes

---

* To whom correspondence should be addressed

REAGENTS

The starting material for the synthesis (CD_3I (98%D)) was distilled before use. The magnesium turnings, purchased from Fisons, were washed with diethyl ether and dried at 200°C for 24 h before use. Diphenyldichlorosilane (purchased from Fluorochem Ltd) was distilled under reduced pressure before use. Trifluoromethanesulfonic (Triflic) acid was used as purchased from Aldrich.

The solvents involved—diethyl ether and dichloromethane—were both distilled before use, the diethyl ether was stored over molecular sieves (4 Å).

PREPARATION OF BIS(TRIDEUTERIOMETHYL)-DIPHENYLSILANE

$(CD_3)_2SiPh_2$ was prepared (as in the Beltzung synthesis) by a Grignard reaction[4]. A solution of 7.43×10^{-1} mol (107.5 g) of CD_3I in 100 ml of diethyl ether was introduced slowly into a three-necked round-bottomed flask containing 7.79×10^{-1} mol (18.69 g) of magnesium turnings and 100 ml of diethyl ether. The reaction was stirred magnetically under gentle reflux under an argon atmosphere.

The resulting grey/brown Grignard solution was filtered under argon and a small amount was titrated to determine the solution's concentration. The Grignard solution was titrated under nitrogen against a 0.05 M solution of *N*-phenylnaphthylamine (freshly re-crystallised from ethanol) and 0.25 M 2-butanol (as purchased from Aldrich) in *m*-xylene (as purchased from Aldrich) according to the method of Bergbreiter and Pendergrass[5].

The remaining Grignard solution was added slowly in a 2% excess to a stoichiometric quantity of diphenyldichlorosilane (Ph_2SiCl_2) (2.77×10^{-1} mol (69.99 g)) in 100 ml diethyl ether under an argon atmosphere. Once complete, the reaction was cooled to < 5°C and de-ionized water was slowly added. The excess Grignard was necessary to prevent the polymerization by condensation of any of the chlorosilane on hydrolysis.

Two layers were obtained. The ether solution was separated off, washed with an approximately 1 M aqueous solution of sodium thiosulfate (to remove any iodine created from the hydrolysis of the excess Grignard) and twice with de-ionized water before being evaporated under reduced pressure. A pale yellow oil was obtained and this was distilled under reduced pressure to yield the $(CD_3)_2SiPh_2$—a clear, colourless oil (b.p. = 114°C @ 1.5 mmHg in good agreement with the value of 108°C @ 1.9 mmHg reported by Beltzung[1]) in a yield of 96.1% (2.66×10^{-1} mol (57.95 g)).

ANALYSIS OF BIS(TRIDEUTERIOMETHYL)-DIPHENYLSILANE.[6-8]

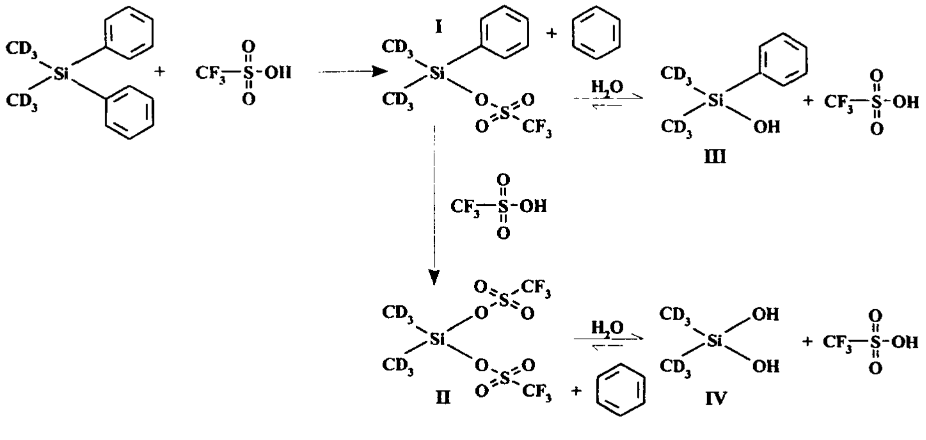
The structure and purity of the product was confirmed by infra-red (i.r.) ν(C–D): 2214 cm^{-1}, ν(Si–Ph): 1425 and 1108 cm^{-1}, $\nu(Si–CD_3)$: 997 cm^{-1}. ^1H nuclear magnetic resonance (n.m.r.) ($CDCl_3$; δ, ppm): 7.3–7.7 (Ph). ^{13}C n.m.r. ($CDCl_3$; δ, ppm): 127.8, 129.1, 134.1 and 138.2 (PhSi). Electron ionization mass spectroscopy (EI-MS) (*m*/*z*): 218 (M^+, 24), 200 $(Ph_2Si(CD_3))^+$, 100), 141 ($((CD_3)_2SiPh^+$, 8).

PREPARATION OF SMALL CYCLIC PER-DEUTERATED DIMETHYLSILOXANES

Trifluoromethanesulfonic (Triflic) acid has previously been reported to selectively remove phenyl groups from methylphenylsilanes under mild conditions[9,10], produce siloxanes in the presence of water [11], as well as catalyse the polymerization of cyclic PDMS[12,13]. It was for these reasons that triflic acid was chosen here to remove the phenyl groups from the bis(trideuteriomethyl)diphenylsilane and polymerize the hydrolysis products in situ.

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. 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 (*Scheme 2*). The silyl triflates have been previously identified as valuable reagents in organosilicon chemistry[14] and can be hydrolysed to silanol functionalities which will 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 for the polymerization of D_4 with triflic acid[12].

The silyl triflates have been isolated and characterized previously [10,11] and are reported to be extremely reactive, so 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 2 h. The reaction was then cooled to



Scheme 2 Production of silyl triflates and silanol intermediates

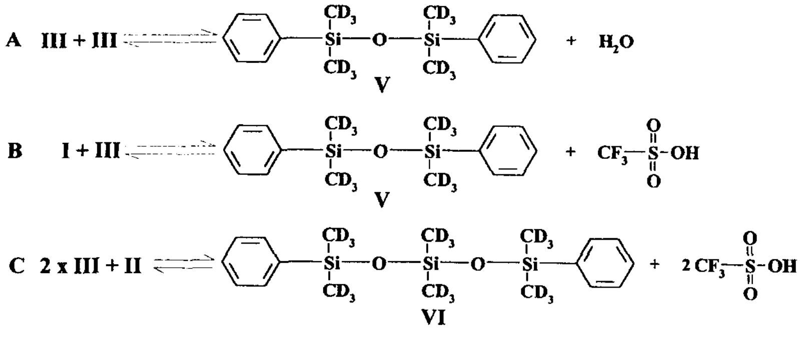
$< 5°C$ before 200 ml of an approximately 1 M aqueous sodium carbonate solution was added to neutralize the acid. The mixture was allowed to come to room temperature and once clear and colourless the two layers obtained were separated, the dichloromethane layer was washed with deionized water and evaporated down under reduced pressure before being analysed by gas liquid chromatography (GLC).

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 GLC, i.r., ^{1}H, ^{13}C and ^{29}Si n.m.r., gas chromatography/electron ionization mass spectrometry (GC/EI-MS) and gas chromatography/ammonia chemical ionization mass spectrometry (GC/CI-MS).

reagent and therefore it is expected that catalytic amounts of the acid may achieve the same reaction over a longer time scale.

In an attempt to confirm the production of the phenyl terminated dimethylsiloxane oligomers a sample of chlorodimethylphenylsilane was hydrolysed in the presence of a small amount of dichlorodimethylsilane to produce a series of such oligomers and this was then analysed by GLC. The retention times of these oligomers matched those observed from the triflic acid reaction.

The structures of the per-deuterated dimethylsiloxanes were confirmed by i.r., ν(C–D): 2217 cm^{-1}, ν(Si–O–Si): 1076 cm^{-1} (broad), ν(Si–CD$_3$): 1013 cm^{-1}. ^{1}H n.m.r., (CDCl$_3$; δ, ppm): no signals. ^{13}C n.m.r., (CDCl$_3$; δ, ppm): no signals.



Scheme 3 Proposed production of phenyl terminated oligomers

ANALYSIS OF THE SMALL PER-DEUTERATED DIMETHYLSILOXANES[6–8,15]

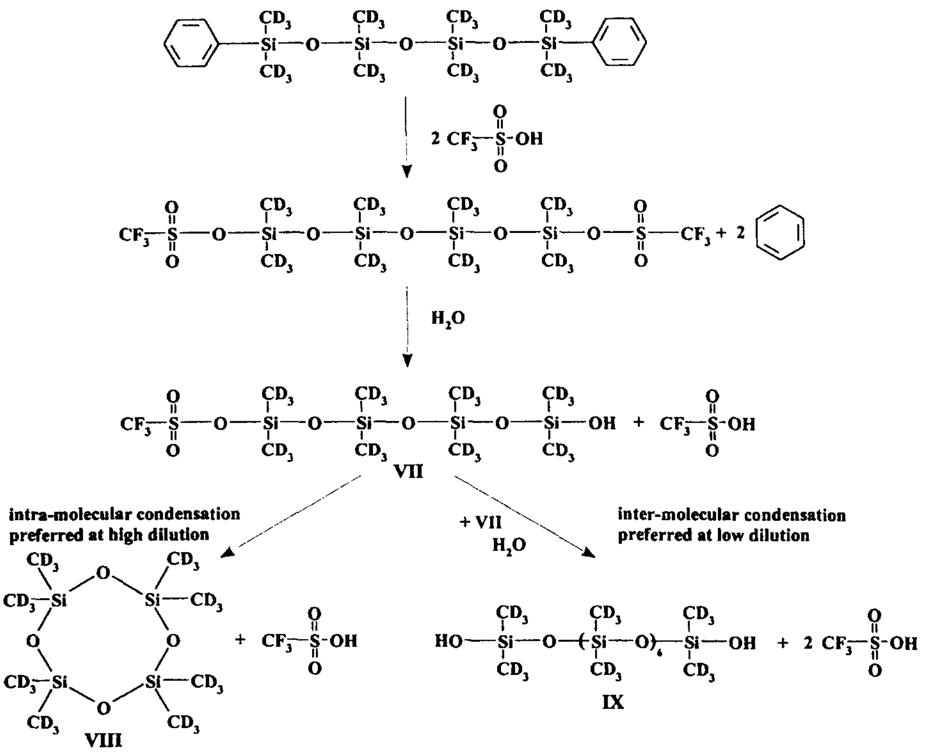
The products from the triflic acid reaction were monitored using GLC. This technique is a rapid method of studying the volatile silanes and siloxanes being produced[15]. A Pye series 104 instrument was used for the analysis. The katharometer detector response was monitored with a Chessel chart recorder. Samples of between 0.3 and 0.5 μl were injected undiluted. The glass column contained Gas Chrome Q 100–200 silica mesh coated with a phenylmethylsiloxane (OV 17 at 4% by weight of silica) and the carrier gas was nitrogen. The column was held at about 350 K for three minutes after injection before the temperature was raised at 12°C per minute to about 600 K.

The traces obtained clearly showed the production of what were suspected as being 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. The production of phenyl terminated dimethylsiloxane oligomers can be accounted for *via* the reactions shown in *Scheme 3*. 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 *Scheme 4*. Again it is noted that the reactions regenerate the triflic acid

^{29}Si n.m.r. has been identified as another convenient technique for characterizing small cyclic poly(dimethylsiloxanes)[16]. The technique allows individual ring species to be identified up to 15 repeat units in size, i.e. D_{15}. This arises due to the fact that the silicon nuclei in a given ring lie in the same environment, however the environments in different sized rings are sufficiently different for the silicon nuclei to give different chemical shifts in a spectrum recorded at high resolution. A sample of the per-deuterated dimethylsiloxane was analysed undiluted using a Bruker 500 MHz instrument and the spectrum is shown (*Figure 1*). 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[16], 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 and it is hoped that soon a silicon/deuterium de-coupled spectrum will be obtained at high resolution to confirm the presence of the higher cyclics.

GAS CHROMATOGRAPHY/ELECTRON IONISATION MASS SPECTROSCOPIC ANALYSIS OF THE SMALL PER-DEUTERATED DIMETHYLSILOXANE CYCLICS

A sample of the perdeuterated PDMS oil was analysed using



Scheme 4 Example of rearrangement to per-deuterated dimethylsiloxane oligomers

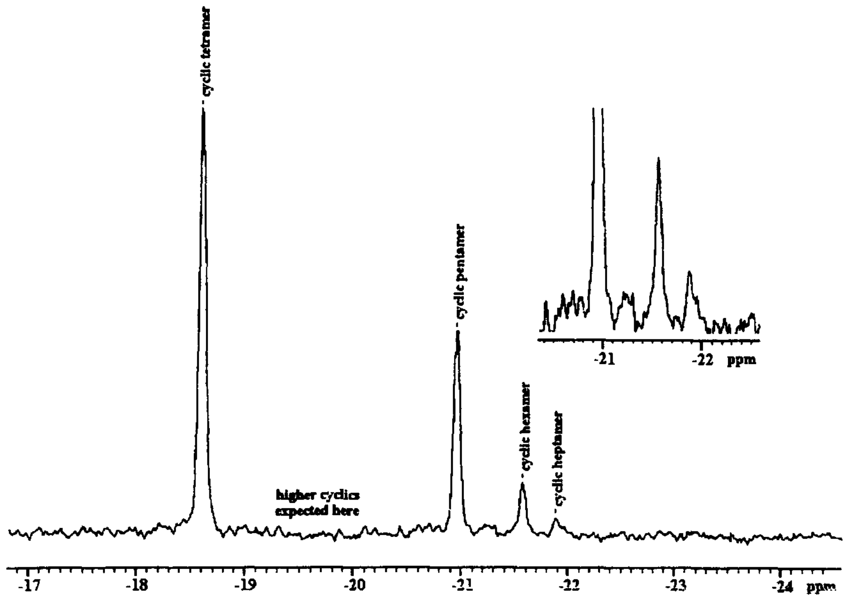


Figure 1 Spectrum of the small D-PDMS cyclics

GC/EI-MS. This technique separates the volatile siloxane oligomers present and produces a mass spectrum of each component[8]. 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 2*) 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 (*Figure 3* shows that of the nonamer). 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[17,18]. A table of the common peaks observed in the EI-MS spectra is given in *Table 1*.

Clearly all the EI spectra 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 TOFSIMS (time of flight secondary ionization mass spectrometry) study of fully deuterated PDMS carried out by Zhang and coworkers[19], as well as results obtained

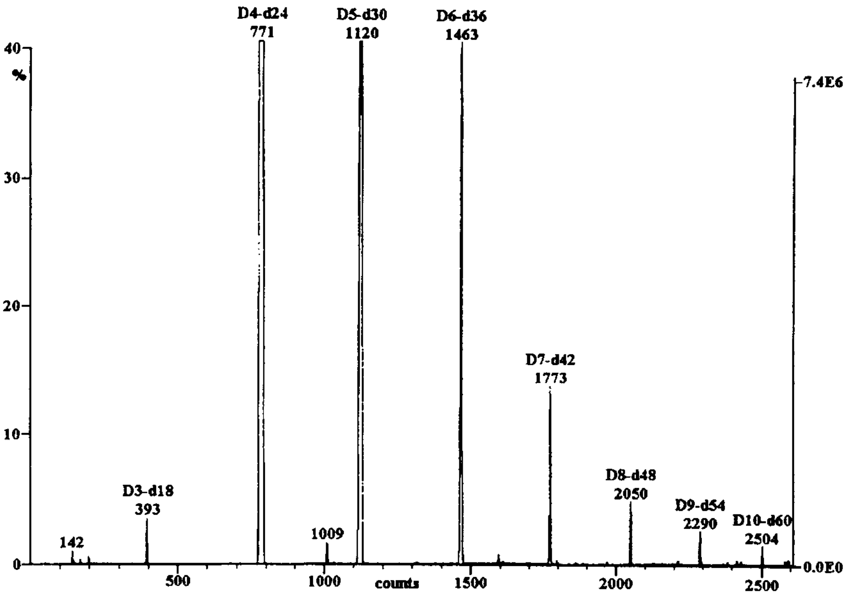


Figure 2 GC of the small per-deuterated dimethylsiloxane cyclics prior to EI-MS

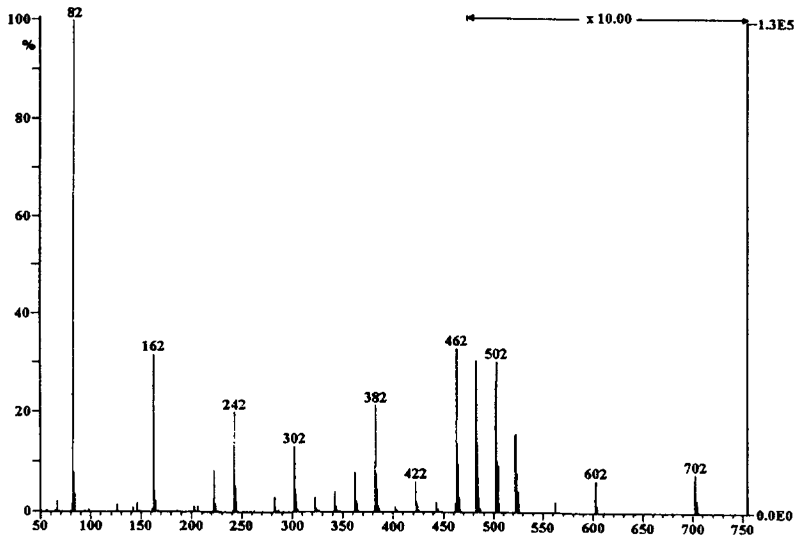


Figure 3 GC/EI-MS of the per-deuterated cyclic dimethylsiloxane nonamer

Table 1 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	$Si_2O_2C_3D_9$	$(\text{dimer} - CD_3)^+$
162	$Si_2OC_5D_{15}$	$(Si(CD_3)_2OSi(CD_3)_3)^+$
202	$Si_3O_4C_3D_9$	$(\text{tetramer} - CD_3 \text{ and } - SiCD_3)_4)^+$
222	$Si_3O_3C_5D_{15}$	$(\text{trimer} - CD_3)^+$
242	$Si_3O_2C_7D_{21}$	$(Si(CD_3)_2OSi(CD_3)_2OSi(CD_3)_3)^+$
282	$Si_4O_5C_5D_{15}$	$(\text{pentamer} - CD_3 \text{ and } - Si(CD_3)_4)^+$
302	$Si_4O_4C_7D_{21}$	$(\text{tetramer} - CD_3)^+$
322	$Si_4O_3C_9D_{27}$	$(Si(CD_3)_2O[Si(CD_3)_2O]_2Si(CD_3)_3)^+$
362	$Si_5O_6C_7D_{21}$	$(\text{hexamer} - CD_3 \text{ and } - Si(CD_3)_4)^+$
382	$Si_5O_5C_9D_{27}$	$(\text{pentamer} - CD_3)^+$
402	$Si_5O_4C_{11}D_{33}$	$(Si(CD_3)_2O[Si(CD_3)_2O]_3Si(CD_3)_3)^+$
422	$Si_6O_8C_7D_{21}$	$(\text{octamer} - CD_3 - Si(CD_3)_4 \text{ and } - Si(CD_3)_4)^+$
442	$Si_6O_7C_9D_{27}$	$(\text{septamer} - CD_3 \text{ and } - Si(CD_3)_4)^+$
462	$Si_6O_6C_{11}D_{33}$	$(\text{hexamer} - CD_3)^+$
482	$Si_6O_5C_{13}D_{39}$	$(Si(CD_3)_2O[Si(CD_3)_2O]_4Si(CD_3)_3)^+$
502	$Si_7O_9C_9D_{27}$	$(\text{nonamer} - CD_3, - Si(CD_3)_4 \text{ and } - Si(CD_3)_4)^+$
522	$Si_7O_8C_{11}D_{33}$	$(\text{octamer} - CD_3 \text{ and } - Si(CD_3)_4)^+$
542	$Si_7O_7C_{13}D_{39}$	$(\text{septamer} - CD_3)^+$
602	$Si_8O_9C_{13}D_{39}$	$(\text{nonamer} - CD_3 \text{ and } - Si(CD_3)_4)^+$
622	$Si_8O_8C_{15}D_{45}$	$(\text{octamer} - CD_3)^+$
702	$Si_9O_9C_{17}D_{51}$	$(\text{nonamer} - CD_3)^+$

previously for the corresponding small hydrogenated PDMS cyclics[17,18], 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 readily 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[8].

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[8].

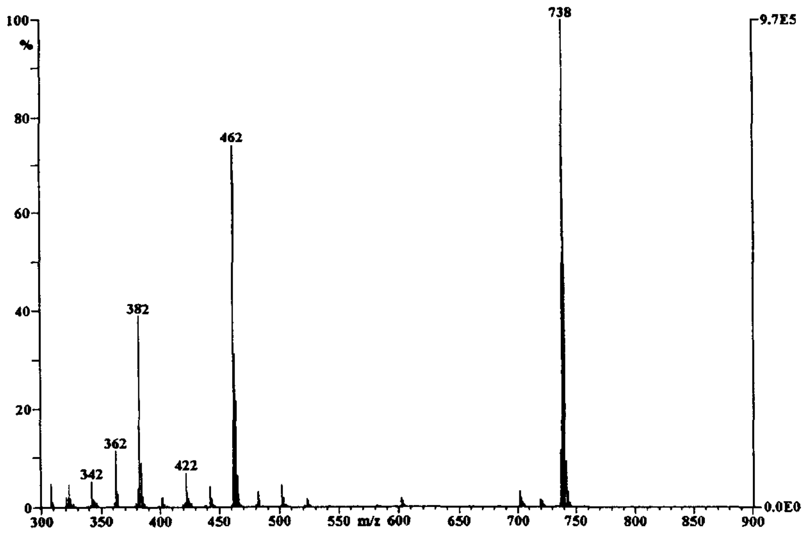


Figure 4 GC/CI-MS of the per-deuterated cyclic dimethylsiloxane nonamer

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 (*Figure 4* shows that of the nonamer).

It has been reported that silanol terminated linear PDMS produces the $(M + NH_4)^+$ ion in ammonia CI[8]. 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 2*.

PREPARATION OF LINEAR PER-DEUTERATED PDMS

In order to show that the per-deuterated dimethylsiloxane cyclics produced could be polymerized in a recognised fashion[3] without disrupting the trideuteriomethyl groups, 13.69 g of the oil obtained from the triflic acid reaction was heated under an argon atmosphere to 140°C. Potassium hydroxide (0.36 g, ~2% w/w) was added and the mixture stirred for 1 h before being allowed to cool to room temperature. Glacial acetic acid was added to neutralize the base and the viscous product was taken up in dichloromethane, washed with water and rotary evaporated down.

Table 2 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	$Si_9O_9NC_{18}D_{54}H_4$	$(\text{nonamer} + NH_4)^+$

A g.p.c. trace of the small D-PDMS cyclics prior to polymerisation was recorded with an instrument fitted with four PLgel 3μ E-type columns. The g.p.c. trace of the viscous product showed a small amount of residual small cyclics which were removed by a reflux in acetone (10% w/v). The per-deuterated linear PDMS (10.78 g) precipitated out of solution on cooling and a further g.p.c. was recorded. Analysis of the trace showed the polymer to have a weight average molecular weight $M_w = 100\,300$ and a polydispersity $M_w/M_n = 1.3$ (against linear hydrogenated PDMS standards).

The purity of the linear per-deuterated PDMS was confirmed as before using n.m.r. and i.r.

CONCLUSIONS

Pure per-deuterated cyclic dimethylsiloxanes have been prepared in good yield via a three step synthesis from CD_3I. The main products of the reaction were the tetrameric, pentameric and hexameric per-deuterated cylic oligomers. A comprehensive series of analytical techniques have displayed the purity of the products and demonstrated the apparent lack of linear products most probably due to the high dilution conditions employed for the reaction.

A mechanism for the reaction has been proposed and this accounts for the production of phenyl terminated linear oligomers which were observed *via* GLC analysis of the reaction mixture.

Mass spectral data correspond well with previous studies of per-deuterated PDMS and hydrogenated PDMS macrocyclics and the spectra presented provide useful analytical references for the per-deuterated dimethylsiloxane cyclics up to the decamer.

Further work being carried out is investigating the effects of dilution and triflic acid concentration on the reaction with an aim to optimising a catalytic route to both linear and cyclic per-deuterated PDMS of high purity in good yields. The reaction is also expected to provide a convenient route to well defined hydogenated/deuterated PDMS copolymers for neutron scattering studies.

ACKNOWLEDGEMENTS

The authors would like to thank Dow Corning (Barry, South Wales) for the financial funding of this project and useful discussions. They would also like to thank Dr Martyn Shenton and Mr Ian Weatherhead for preliminary investigations into the Beltzung synthesis of per-deuterated PDMS.

REFERENCES

1. Beltzung, M., Picot, C., Rempp, P. and Herz, J., *Macromolecules*, 1982, **15**, 1594–1600.
2. Dodgson, K., Sympson, D. and Semlyen, J. A., *Polymer*, 1978, **19**, 1285–1289.
3. Wright, P. V. and Beevers, M. S., in *Cyclic Polymers*, ed. J. A. Semlyen. Elsevier Applied Science, London, 1986, chap. 3.
4. *Organic Synthesis*, Vol. 2. Wiley, New York, 1950, Vol. 2, p. 26.
5. Bergbreiter, D. E. and Pendergrass, E., *J. Org. Chem.*, 1981, **46**, 219–220.
6. Lipp, E. D. and Smith, A. L., in *The Analytical Chemistry of Silicones*, ed. A. L. Smith, Chemical Analysis Vol. 112. John Wiley, New York, 1991, chap. 11.
7. Taylor, R. B., Parbhoo, B. and Fillmore, D. M., in *The Analytical Chemistry of Silicones*, ed. A. L. Smith, Chemical Analysis Vol. 112. John Wiley, New York, 1991, chap. 12.
8. Moore, J. A., in *The Analytical Chemistry of Silicones*, ed. A. L. Smith, Chemical Analysis Vol. 112. John Wiley, New York, 1991, chap. 13.
9. Howells, R. D. and Mc Cown, J. D., *Chemical Reviews*, 1977, **77**(1), 69–92.
10. Matyjaszewski, K. and Chen, Y. L., *Journal of Organometallic Chemistry*, 1988, **340**, 7–12.
11. Uhlig, W., *Organometallics*, 1994, **13**, 2843–2848.
12. Chojnowski, J. and Wilczek, L., *Makromol. Chem.*, 1979, **180**, 117–130.
13. Lebrun, J. -J., Sauvet, G. and Sigwalt, P., *Makromol. Chem. Rapid Commun.*, 1982, **3**, 757–763.
14. Emde, H., Domsch, D., Feger, H., Frick, U., Götz, A., Hergott, H., Hoffmann, K., Kober, W., Krägeloh, K., Oesterle, T., Steppan, W., West, W. and Simchen, G., *Synthesis*, 1982, **1**, 1–26.
15. Steinmeyer, R. D. and Becker, M. A., in *The Analytical Chemistry of Silicones*, ed. A. L. Smith, Chemical Analysis, Vol. 112. John Wiley, New York, 1991, chap. 10.
16. Burton, B. J., Harris, R. K., Dodgson, K., Pellow, C. J. and Semlyen, J. A., *Polym. Commun.*, 1983, **24**, 278–281.
17. VandenHeuvel, W. J. A., Smith, J. L., Firestone, R. A. and Beck, J. L., *Analytical Letters*, 1972, **5**, 285–292.
18. Pickering, G. R., Olliff, C. J. and Rutt, K. J., *Organic Mass Spectrometry*, 1975, **10**, 1035–1045.
19. Zhang, X. K., Stuart, J. O., Clarson, S. J., Sabata, A. and Beaucage, G., *Macromolecules*, 1994, **27**, 5229–5231.