Cyclic polysiloxanes: 1. Preparation and characterization of poly(phenylmethylsiloxane)

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A ring–chain equilibration reaction of poly(phenylmethylsiloxane) (PPMS) was carried out on a kilogram scale in toluene at 383 K. The cyclic oligomeric and polymeric phenylmethylsiloxanes formed were isolated and then fractionated using preparative gel permeation chromatography (g.p.c.). Fifteen sharp fractions were obtained, containing cyclics $[C_6H_5(CH_3)SiO]_x$ with (an average) from nine to over three hundred skeletal bonds. Linear PPMS was also prepared and fractionated using preparative g.p.c. The cyclic and linear oligomers and polymers were characterized using gas–liquid chromatography (g.l.c.), high performance liquid chromatography (h.p.l.c.) and low-angle laser light scattering (LALS).

(Keywords: poly(phenylmethylsiloxane); cyclic; linear; ring–chain equilibration)

INTRODUCTION

The linear polysiloxanes or 'silicones', which may be represented as $[RR'SiO]_y$ (where the substituent groups R and R′ may be the same or different) are commercially important polymers, with a wide variety of applications[1]. For example, linear poly(phenylmethylsiloxanes) (PPMS), where $R = C_6H_5$ and $R' = CH_3$, are used as lubricating fluids, gas–liquid chromatographic stationary phases and in crosslinked elastomers[2].

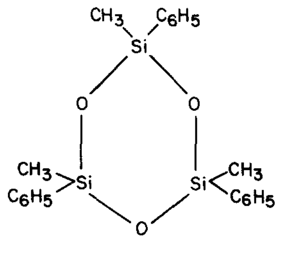
In previous publications[3], we have reported investigations of the properties of cyclic and linear poly(dimethylsiloxanes) (PDMS). It is the purpose of this paper and the next in the series to describe the preparation and characterization of the first narrow fractions of cyclic PPMS.

Cyclic siloxanes $[RR'SiO]_x$, with different substituent groups R and R′, consist of mixtures of configurational isomers. Lewis[4] was the first to obtain crystals of the two cyclic trimer stereoisomers of phenylmethylsiloxane and one of the isomers of the tetramer was subsequently prepared by Young[5]. The synthesis and full characterization of all four configurational isomers of the tetramer was achieved by Hickton[6], Harris[7] and Pierron[8] and their coworkers using gas–liquid chromatography (g.l.c.), nuclear magnetic resonance (n.m.r.) spectroscopy and X-ray crystallography. The concentrations of cyclic oligomeric and polymeric phenylmethysiloxanes in ring–chain equilibrium reactions of PPMS were investigated previously[9,10]. The concentrations of the individual configurational isomers of the cyclic trimers, tetramers and pentamers, as measured by g.l.c., were found to be those expected from the cyclization of an atactic polymer.

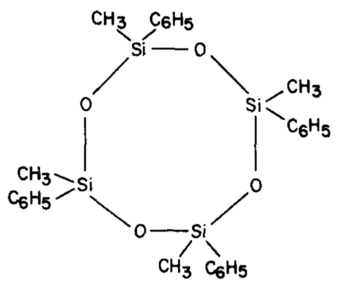
In this paper, a ring–chain equilibration reaction of PPMS is described. It was carried out on a larger scale than previously[9,10] and was used to prepare the first narrow fractions of cyclic PPMS, with number average numbers of skeletal bonds n_n up to 350. A series of sharp fractions of linear PPMS was also prepared. The cyclic and linear polymers were characterized by analytical g.p.c., g.l.c., high performance liquid chromatography (h.p.l.c.) and low-angle laser light scattering.

EXPERIMENTAL

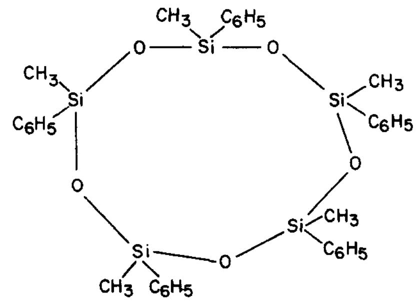
A PPMS ring–chain equilibration reaction was carried out in toluene at 383 K. The reaction mixture contained 869.1 g of a mixture of the cyclic trimer, tetramer and pentamer (supplied by Dow Corning), toluene (432.8 g) and diglyme(2-methoxyethylether (10 cm^3) added as a promoter. The structures of the cyclic phenylmethylsiloxanes are as follows:



Cyclic trimer



Cyclic tetramer



Cyclic pentamer

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The toluene and diglyme were dried over sodium wire and calcium hydride, respectively, and distilled before use. The equilibrate mixture was dried by azeotropically distilling out a small quantity of toluene from the reaction flask prior to initiation of the reaction.

The reaction was initiated using *ca.* $\frac{1}{8}$ pellet of potassium hydroxide. This was crushed in a pestle and mortar under a small quantity of the reaction mixture and the resulting mull was pipetted into the reaction vessel. The reaction was carried out under an atmosphere of dry nitrogen and the condenser was fitted with a silica drying tube.

The progress of the reaction to equilibrium was monitored over a period of several days using analytical g.p.c. On attaining equilibrium conditions (*Figure 1*) the reaction was terminated by the addition of 10 cm^3 glacial acetic acid. The reaction mixture was then dissolved in an excess of toluene and was washed several times with distilled water to remove residual ions. The toluene layer was then dried over anhydrous magnesium sulphate and the solvent subsequently removed by rotary evaporation.

The equilibrate was then divided into several portions, which were each washed a number of times with methanol in order to remove the low molar mass cyclic phenylmethylsiloxanes. After combining the methanol washings, the solvent was removed to yield 296.1 g of cyclic oligomers $[C_6H_5(CH_3)SiO]_x$, where $x = 4, 5, 6$. The linear PPMS was then removed from the remainder of the equilibrate by fractional precipitation, using toluene as the solvent and methanol as the non-solvent. This was achieved by dissolving the equilibrate in toluene to give a 10% w/v solution. Methanol was then added via a burette until a slight but permanent turbidity was seen. The mixture was then refluxed and allowed to settle overnight. The solution was siphoned away from the precipitated linear polymer. This procedure was repeated, adding a small quantity of methanol each time, until there was no trace of the linear polymer, as indicated by analytical g.p.c. This method gave 285.6 g linear PPMS. The methanol and toluene were then removed from the macrocyclic phenylmethylsiloxanes by rotary evaporation.

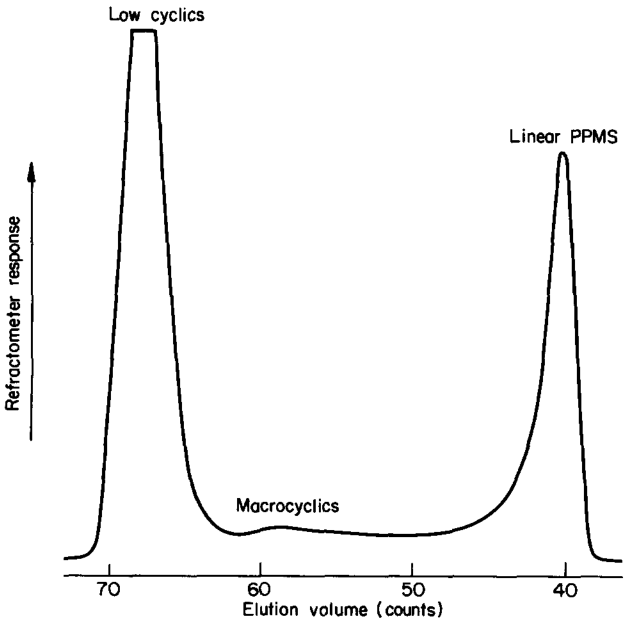

Figure 1 Analytical g.p.c. of ring-chain equilibration reaction of PPMS in toluene at 383 K

The macrocyclic portion of the equilibrate (96.7 g) was divided into a number of sharp fractions using preparative g.p.c., as described previously[11]. Traces of benzaldehyde and benzoic acid, which were formed as oxidative by-products of toluene in the preparative instrument, were removed from the samples. This was achieved by precipitating the siloxanes from solution in toluene using methanol as the non-solvent. Any residual traces of methanol and toluene in the fractions were removed by rotary evaporation and then by placing the samples in a vacuum oven at 333 K for 72 h.

Preparation of linear oligomeric phenylmethylsiloxanes

Several synthetic routes for preparing linear oligomeric phenylmethylsiloxanes $(CH_3)_3SiO[C_6H_5(CH_3)SiO]_y Si(CH_3)_3$ have been reported[1,4,12]. The method employed here was as follows: 50 cm^3 phenylmethyldichlorosilane was mixed with 150 cm^3 chlorotrimethylsilane in a separating funnel. The mixture was then added dropwise to 200 cm^3 of an ice/water mixture, which was stirred magnetically. After the hydrolysis was complete ($\sim$1 h), 100 cm^3 diethylether were added to the mixture. The ether layer was then separated and washed several times with distilled water, before being dried over anhydrous magnesium sulphate. The ether was removed by rotary evaporation.

The siloxanes were then dissolved in toluene (50 cm^3) and hexamethyldisilazane (10 cm^3) was added in order to trimethyl end-block any remaining hydroxyl terminated siloxane. This mixture was refluxed for 24 h under a dry nitrogen atmosphere. The toluene solution was then washed with distilled water and dried over anhydrous magnesium sulphate. The toluene was removed by rotary evaporation. The resulting product consisted of an homologous series of linear phenylmethylsiloxane oligomers, which were identified using g.l.c./mass spectrometry. The individual oligomers were subsequently obtained by vacuum distillation.

Preparation of linear polymeric phenylmethylsiloxanes

The linear PPMS were prepared by a ring-opening polymerization of a mixture of cyclic trimer, tetramer and pentamer in toluene at 383 K. Potassium hydroxide was used to catalyse the reaction and it was crushed under a small portion of the reaction mixture before being transferred to the reaction vessel as a mull. Hexamethyldisiloxane (Hopkins and Williams) was added to limit the chain growth of the polymerization by trimethylsilyl end-terminating the polymer chains. The reaction was carried out under an atmosphere of dry nitrogen.

Upon completion of the reaction, the mixture was dissolved in an excess of toluene and was washed several times with distilled water to remove the residual ionic species. The toluene layer was then dried over anhydrous magnesium sulphate. Hexamethyldisilazane (10 cm^3) was then added to the solution and the mixture refluxed under an atmosphere of dry nitrogen for 24 h. The toluene solution was washed with distilled water, dried and the solvent was then removed from the polymer by rotary evaporation.

The resulting linear PPMS had a weight-average molar mass (M_w) or 19 820 and a heterogeneity index M_w/M_n of 1.9. The low cyclic oligomers were then removed by washing the polymer with methanol and the PPMS was fractionated using the preparative g.p.c.[11].

High performance liquid chromatography

The cyclic and linear phenylmethylsiloxanes have low vapour pressures, so that the hexamers ($n_n = 12$) were the highest species to be observed by g.l.c. In addition, h.p.l.c. was applied to analyse rings and chains with $2 \leqslant n_n \leqslant 50$.

The instrument used was a Du Pont 830 Liquid Chromatograph and was equipped with a u.v./visible detector used at a wavelength of 254 nm. The column used was a Whatman Partisil PXS 10/25 ODS-2 and the stationary phase consisted of octadecyl (C_{18}) chains chemically attached to 10 μm silica particles. The solvents employed were methanol and a variety of methanol/tetrahydrofuran mixtures. A chromatogram showing the resolution of the cyclic phenylmethylsiloxane oligomers with $8 < n_n < 20$ using methanol is shown in *Figure 2*. The internal standard employed throughout was toluene and the solvent flow rate was typically *ca.* 1 cm^3 min^{-1}.

Analytical g.p.c.

Two instruments were used. One was equipped with columns packed with Styragel (Waters Associates Ltd.) with nominal porosities 25, 100, 300, 300 and 300 nm, respectively. The other was fitted with columns packed with PL-gel (supplied by Polymer Laboratories Ltd.). The calibration of the g.p.c. columns was carried out by using cyclic and linear fractions, which had previously been characterized using g.l.c., h.p.l.c., ^{29}Si n.m.r. spectroscopy and low-angle laser light scattering (see the discussion to follow). All the chromatograms were corrected for axial broadening by the methods of Pierce and Armonas[13,14].

RESULTS AND DISCUSSION

The yields, number average molar masses M_n and heterogeneity indices M_w/M_n of the PPMS fractions are listed in *Tables 1* and *2*. The yields of the cyclic fractions were found to show a minimum in the region $x \simeq 12$, as has been observed for a variety of siloxane ring–chain equilibration reactions[9,15–19].

The linear PPMS recovered from the equilibrate was characterized by dilute solution viscometry in toluene at 298 K using the relationship[20]

$$[\eta] = 3.9 \times 10^{-5} M_w^{0.78}$$

where $[\eta]$ is in units of dl g^{-1}. A value for M_w of 186 300 g mol^{-1} was obtained, corresponding to an extent of reaction p of 0.9985. Thus, for a most probable distribution of chain lengths[21], the cyclic fractions are calculated to contain negligible amounts of linear species, as was demonstrated previously for cyclic poly(dimethylsiloxanes) (PDMS)[11,22].

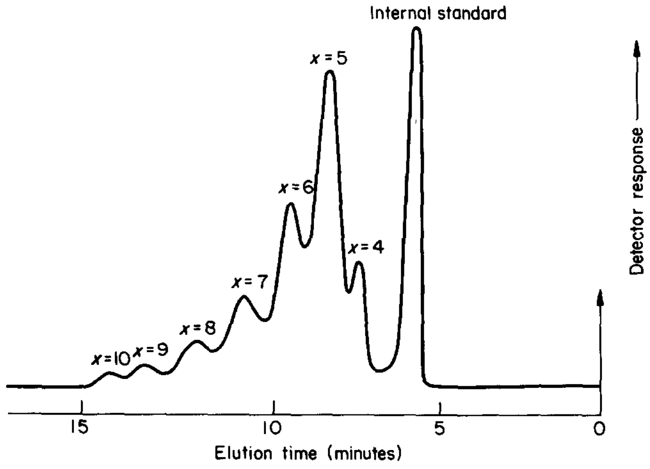

Figure 2 H.p.l.c. of oligomeric phenylmethylsiloxane cyclics $[C_6H_5(CH_3)SiO]_x$

Table 1 Number-average number of skeletal bonds n_n, number average molar masses M_n, heterogeneity indices M_w/M_n and yields of the cyclic PPMS fractions obtained by preparative g.p.c. from the macrocyclic portion of the ring-chain equilibrium reaction

Preparative g.p.c. elution volume (count numbers)	n_n	M_n (g mol^{-1})	M_w/M_n	Weight of fraction (g)
29	326	22190	1.02	0.16
30	268	18320	1.04	0.35
31	231	15700	1.04	0.68
32	177	12020	1.03	0.85
33	135	9190	1.06	1.13
34	107	7280	1.05	1.39
35	85	5790	1.04	1.67
36	66	4520	1.04	1.97
37	49	3340	1.04	1.59
38	48	3250	1.05	1.18
39	31	2120	1.06	0.54
40	20	1390	1.16	0.19
41	11	730	1.04	5.37
42	9	620	1.01	14.34
43	9	590	1.01	13.55

Table 2 Number-average number of skeletal bonds n_n, number average molar masses M_n, heterogeneity indices M_w/M_n and yields of the linear PPMS fractions obtained by preparative g.p.c. from a broad distribution linear polymer

Preparative g.p.c. elution volume (count numbers)	n_n	M_n (g mol^{-1})	M_w/M_n	Weight of fraction (g)
24	882	60260	1.14	0.8
25	786	53700	1.14	1.0
26	692	47320	1.16	1.9
27	596	40740	1.15	2.3
28	489	33500	1.10	3.5
29	396	27100	1.09	4.0
30	332	22760	1.10	5.5
31	284	19510	1.12	5.8
32	235	16190	1.13	5.6
33	186	12860	1.15	5.2
34	153	10560	1.16	3.7
35	122	8490	1.17	2.9
36	94	6540	1.14	1.8
37	79	5560	1.14	0.8

G.p.c. retention behaviour of cyclic and linear PPMS

The calibration plots for the cyclic and linear PPMS samples (shown in *Figure 3*) were found to be parallel, as had previously been reported for cyclic and linear PDMS[22,23]. For the higher molar mass samples, laser light scattering was used for the calibration in tetrahydrofuran at 298 K. The M_w values of one ring fraction ($M_w = 8500$) and four linear fractions ($M_w = 7100$, 10 500, 20 000 and 182 000) were measured in this way. Error limits of ±10% were estimated for the values obtained.

The ratio of the M_n values for ring (r) and chain (l) PPMS with the same g.p.c. distribution coefficients was found to be 1.25 ± 0.05. This is in agreement with the theoretically predicted ratio of 1.26[24,25].

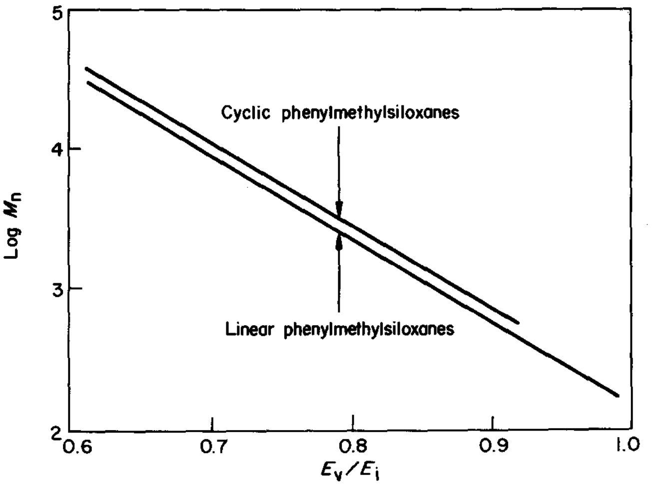

Figure 3 Analytical g.p.c. calibration plot for cyclic and linear PPMS showing log M_n plotted against sample elution volume E_v (E_i is the internal standard elution volume)

The g.p.c. elution behaviour of the siloxanes was also compared, using the relationships proposed by Casassa[24,25] and the methods described in previous work[23]. Hence, a characteristic ratio of 8.8 was deduced for linear PPMS, based on the value $\langle r^2 \rangle_0/nl^2 = 6.3$ for linear PDMS in a θ-solvent (methylethylketone at 293 K)[26]. This value is in agreement with the literature value of 8.8 for PPMS in a θ-solvent (di-isobutylamine at 303.4 K)[20].

A ratio $\langle r^2 \rangle/100l^2$ of 10.7 at 383 K has also been reported for phenylmethylsiloxane chains with 100 skeletal bonds[9].

The cyclic and linear PPMS fractions have been investigated in some detail and the results of these studies will be the subject of further communications.

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