Studies of cyclic and linear poly(dimethylsiloxanes): 21. High temperature thermal behaviour

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(Received 15 August 1985)

The high temperature thermal behaviour of cyclic and linear poly(dimethylsiloxanes) (PDMS) have been investigated using differential scanning calorimetry and thermogravimetry. The cyclic and linear polymers were found to have similar thermal stabilities. They depolymerized at temperatures above 623 K, apparently by a common mechanism. The cyclic PDMS were sealed under vacuum in borosilicate glass or quartz ampoules and heated at temperatures greater than 623 K. Detailed chromatographic analyses of the products formed showed that these were consistent with ring opening polymerizations of the cyclic siloxanes (catalysed ionically by the surfaces of the vessels) and not with bond interchange reactions, as had previously been suggested.

(Keywords: cyclic; linear; poly(dimethylsiloxane); differential scanning calorimetry; thermogravimetry)

INTRODUCTION

A variety of applications of the silicones result from their stabilities at elevated temperatures[1]. Detailed information on the thermal degradation of linear poly(dimethylsiloxane) (PDMS) has been obtained during the past thirty years by studies of the depolymerization products under a variety of degradation conditions. In addition, thermogravimetry (t.g.) has been applied to investigate the weight loss of the material either at a fixed temperature or upon increasing the temperature.

It has been shown that the thermal degradation of linear PDMS under vacuum results in depolymerization to produce cyclic oligomers[2-10]. The trimer $((CH_3)_2SiO)_3$ is reported to be the most abundant product, with decreasing amounts of tetramer, pentamer, hexamer and higher oligomers[2,6]. It has also been demonstrated that hydroxyl terminated PDMS is less thermally stable than polymer end-blocked with $(CH_3)_3Si$-groups[4,5,7,10] and it is believed to depolymerize by a mechanism proceeding via the terminal hydroxyl groups[10].

Thomas and Kendrick[6] investigated the depolymerization products of trimethylsilyl end-blocked linear PDMS under non-equilibrium conditions in a catalyst free environment. They accounted for the low activation energy of depolymerization as measured by t.g. (180 kJ mol^{-1}), compared with the energy of the siloxane bond (452 kJ mol^{-1}) by proposing a randomly initiated, cyclic four-centred transition state accompanied by siloxane band rearrangement. Substituent effects on other siloxane polymers have provided further evidence to support this hypothesis[11]. In a preliminary study of the thermal degradation of cyclic as well as linear PDMS, the results were interpreted in terms of the siloxane bond interchange process[12]. In this paper, we report more detailed investigations of the high temperature thermal behaviour of these materials. Differential scanning calorimetry and thermogravimetry were applied and the polymerization of cyclic and linear PDMS fractions at elevated temperatures was examined after sealing under vacuum in both borosilicate glass and quartz tubes.

EXPERIMENTAL

Materials

Fractions of cyclic $[(CH_3)_2SiO]_x$ and linear $(CH_3)_3SiO[(CH_3)_2SiO]_ySi(CH_3)_3$ compounds were prepared by methods described previously[13-15]. All the fractions had heterogeneity indices $M_w/M_n < 1.1$.

Differential scanning calorimetry (d.s.c.)

The instrument used for this investigation was a Mettler DSC 30 interfaced to a Mettler TC 10 TA microprocessor. Typically, 15–20 mg of polymer sample was placed in a platinum crucible, which was handled with tweezers. An empty platinum crucible was used as a reference.

For the studies under non-oxidative conditions, the samples were heated to 373 K and maintained at this temperature to remove oxygen. An atmosphere of white-spot grade nitrogen was used for the experiments, flowing through the d.s.c. cell containing the sample and reference at a rate of 70 cm^3 min^{-1}. The materials were then heated from 373 K to 873 K at a rate of 10 K min^{-1} by microprocessor control.

For the studies under oxidative conditions, an atmosphere of oxygen was used, flowing over the samples at a rate of 70 cm^3 min^{-1}. In this case, the samples were heated directly from 298 K to 873 K at a rate of 10 K min^{-1}. The endothermal and exothermal events in each experiment were recorded by the microprocessor and the resulting thermograms were transferred to a plotter.

Thermogravimetry (t.g.)

A Mettler TG 50 thermogravimetric balance interfaced to a Mettler TC 10 TA microprocessor was used for this study. The temperature scale of the balance was calibrated

0032-3861/86/010091-05$03.00
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prior to use with inorganic thermal standards as described in the instrumental handbook[16]. An atmosphere of white-spot grade nitrogen was maintained by flowing the gas at a rate of 70 cm^3 min^{-1} through the balance. The samples were placed in platinum crucibles and they were weighed directly on the thermogravimetric balance to within ± 0.0001 g. The quantity of sample used was typically 15–20 mg. The samples were maintained at 323 K for 20 min before being heated at a rate of 10 K min^{-1} over the temperature range 323–873 K. The microprocessor was used to control the heat flow to the balance and to record the weight loss. The thermograms were transferred to a plotter at the end of each experiment.

Heating of samples under vacuum

Following extensive degassing involving usually ten or more freeze–thaw cycles under vacuum, the siloxane samples (each on a scale of 0.10–10 g) were sealed in Pyrex (borosilicate glass) or quartz ampoules. The ampoules, with pressures lower than 0.1 N m^{-1}, were heated in a furnace for various time intervals at a temperature in the range $623 < T < 693$ K. After cooling, the samples tubes were opened and the products analysed using gas-liquid chromatography (g.l.c.) and gel permeation chromatography (g.p.c.).

RESULTS AND DISCUSSION

Differential scanning calorimetry

Typical d.s.c. thermograms from heating cyclic and linear PDMS fractions in an inert atmosphere (nitrogen) are shown in *Figure 1*. For all the fractions studied, no evidence was detected for thermal depolymerization at temperatures below 623 K. Above 623 K, a process which is initially endothermic was detected for all the cyclic and linear PDMS samples. This corresponds to the weight loss (depolymerization) process reported previously for end-blocked linear PDMS using t.g.[6].

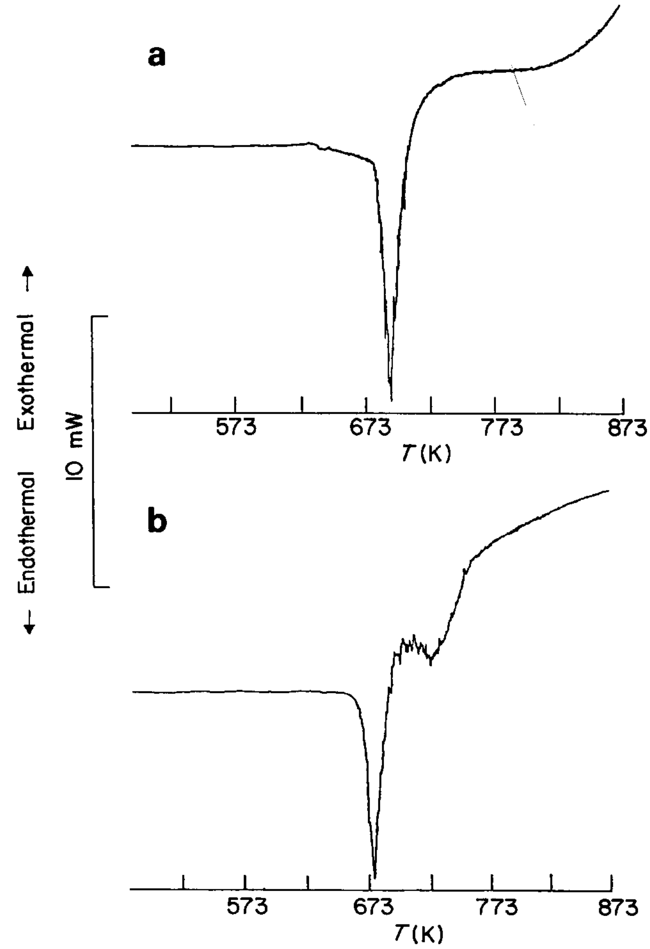

Figure 1 D.s.c. thermograms of (a) 109 bond cyclic PDMS and (b) 166 bond linear PDMS, heated under nitrogen

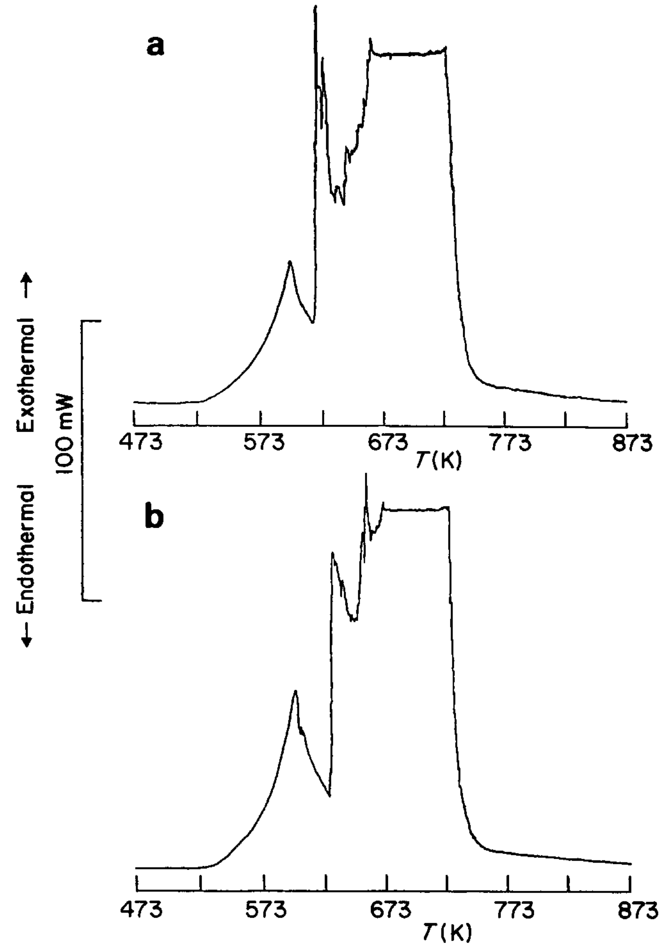

Figure 2 D.s.c. thermograms of (a) 109 bond cyclic PDMS and (b) 166 bond linear PDMS, heated under oxygen

The effect of oxygen on the high temperature thermal stability of the cyclic and linear PDMS fractions is shown in *Figure 2*. The resulting thermograms show the onset of an exothermic process at *ca.* 523 K, which attains a maximum rate at *ca.* 598 K. This is believed to be associated with the oxidative crosslinking via the methyl groups that has been reported previously for high molar mass linear PDMS[17,18].

The weights of residues were found by accurately weighing the platinum crucibles before and after the heating process. For the samples shown in *Figures 1* and *2* a residue corresponding to 0.3% of both the cyclic and linear material remained after heating under nitrogen and 62% of the linear and 63% of the cyclic remained as thermally inert white powders after heating under oxidative conditions.

Thermogravimetry

The t.g. thermograms showing the weight loss profiles of a number of cyclic and linear PDMS fractions over the temperature range 323 K–873 K are presented in *Figure 3*. The onset of weight loss for all the fractions occurred at *ca.*

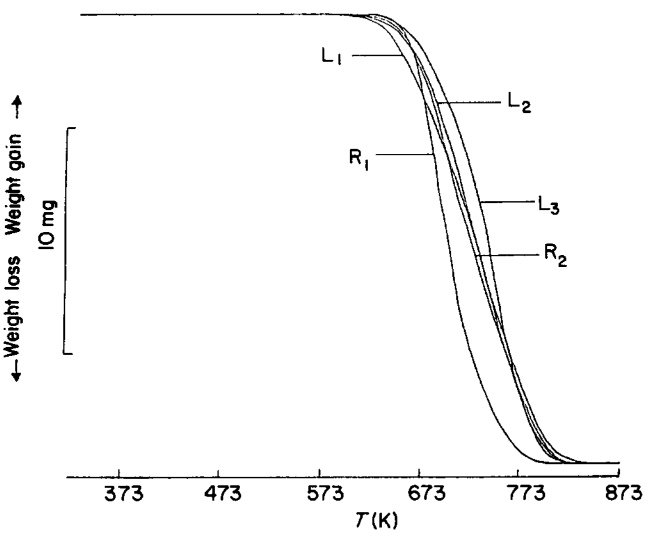

Figure 3 T.g. traces of cyclic PDMS fractions R1 ($n_n = 109$) and R2 ($n_n = 372$) and linear PDMS fractions L1 ($n_n = 166$), L2 ($n_n = 204$) and L3 ($n_n = 393$) heated under nitrogen

623 K and essentially 100% weight loss was obtained by *ca.* 850 K.

The similar depolymerization profiles for the cyclic and linear PDMS samples in platinum under an inert atmosphere (nitrogen) indicates a common depolymerization mechanism for the cyclic and linear polymers under these conditions. Furthermore, the results obtained are in agreement with earlier t.g.[6] and thermal volatilization analysis (t.v.a.)[7] studies of linear PDMS, where the interchange of siloxane bonds has been successfully used to account for the depolymerization reactions.

Effect of heat on cyclic dimethylsiloxanes

Cyclic PDMS. Cyclic PDMS with an average number of skeletal bonds $n_n = 85$ was heated under vacuum at 693 K in both Pyrex and quartz ampoules (as described above). The products formed were colourless fluids, which were completely soluble in toluene. The products were analysed by g.p.c. in more detail than in a previous study in our laboratory[12].

In addition to lower cyclics (whose identity was established by gas-liquid chromatography) and high molar mass (probably linear) PDMS, there is an indication that small amounts of macrocyclics are formed (see *Figure 4*). Their presence suggests that there are ionic ring-opening polymerization reactions in the ampoules with the subsequent formation of a distribution of cyclic species. This is consistent with Nielsen's[8] proposal that cationic reactions on the surface of borosilicate glass may contribute to the depolymerization mechanisms of linear PDMS. It is also in agreement with the suggestion of Zeldin and coworkers[9] that ionic impurities leached from the walls of Pyrex glass vessels may catalyse the depolymerization of linear PDMS.

Octamethylcyclotetrasiloxane. Figure 5 shows a g.p.c. of the products obtained by heating octamethylcyclotetrasiloxane at 693 K sealed under vacuum in Pyrex. The chromatogram is consistent with a ring-opening polymerization catalysed by ions on the surface of the glass vessel, followed by the formation of cyclic species from the resulting high molar mass linear PDMS. The main oligomeric product was found to be the cyclic tetramer by g.l.c. (see *Figure 5*) and this is consistent with an ionic mechanism, because the siloxane bond interchange reaction would be expected to give the cyclic trimer as the primary oligomeric product.

Cyclic PDMS with hexamethyldisiloxane. Hexamethyldisiloxane is used as a chain terminating agent in a variety of ionic siloxane polymerization reactions[1]. It would not be expected to participate in four-centred siloxane bond interchange reactions and would be expected simply to act as a solvent for such reactions.

Figure 6 shows g.p.c.'s of a cyclic PDMS fraction with $n_n = 135$ before and after heating in Pyrex at 693 K. Again

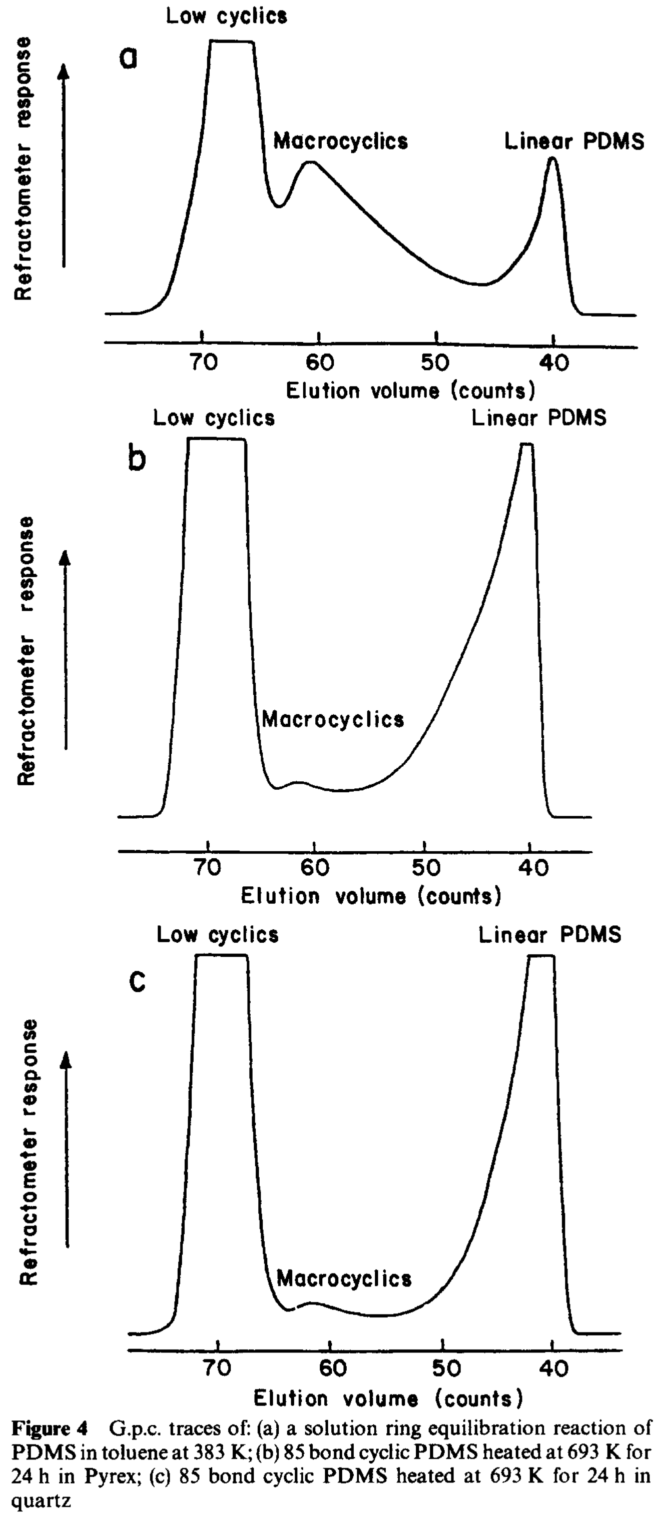

Figure 4 G.p.c. traces of: (a) a solution ring equilibration reaction of PDMS in toluene at 383 K; (b) 85 bond cyclic PDMS heated at 693 K for 24 h in Pyrex; (c) 85 bond cyclic PDMS heated at 693 K for 24 h in quartz

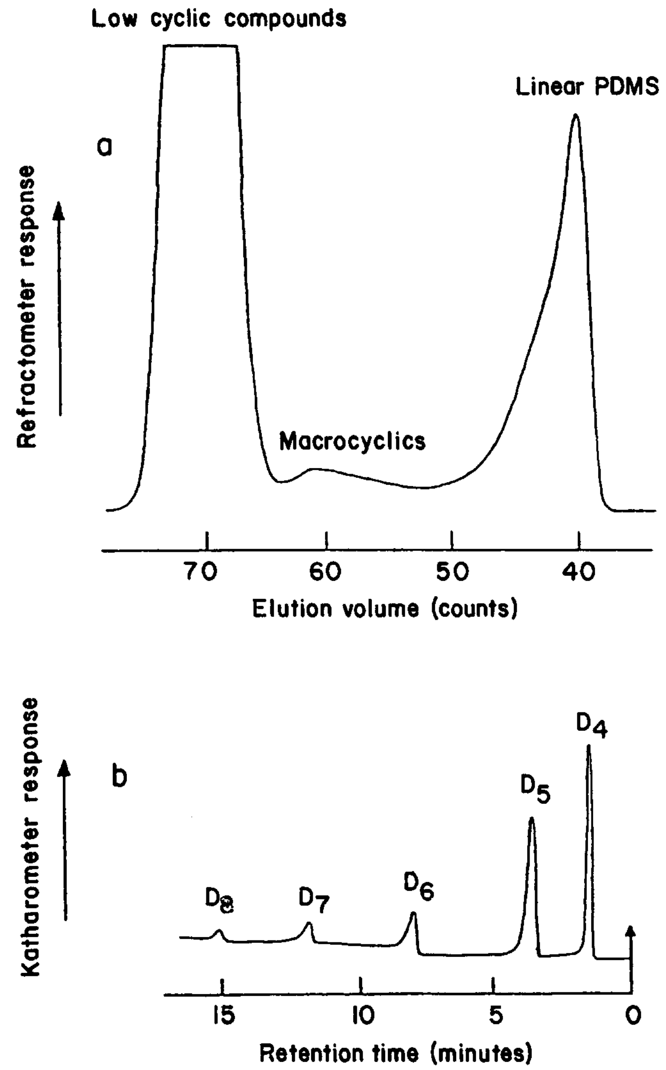

Figure 5 G.p.c. trace of octamethylcyclotetrasiloxane heated at 693 K for 24 h in Pyrex (a) and a g.l.c. trace of the cyclic oligomers formed (b)

the products were found to be in agreement with the ionic ring-opening polymerization of the cyclic PDMS. The g.p.c. trace of the ring fraction's products after heating in Pyrex at 693 K together with hexamethyldisiloxane showed that the high molar mass polymer was not formed and the products are assigned as shown in *Figure 6*.

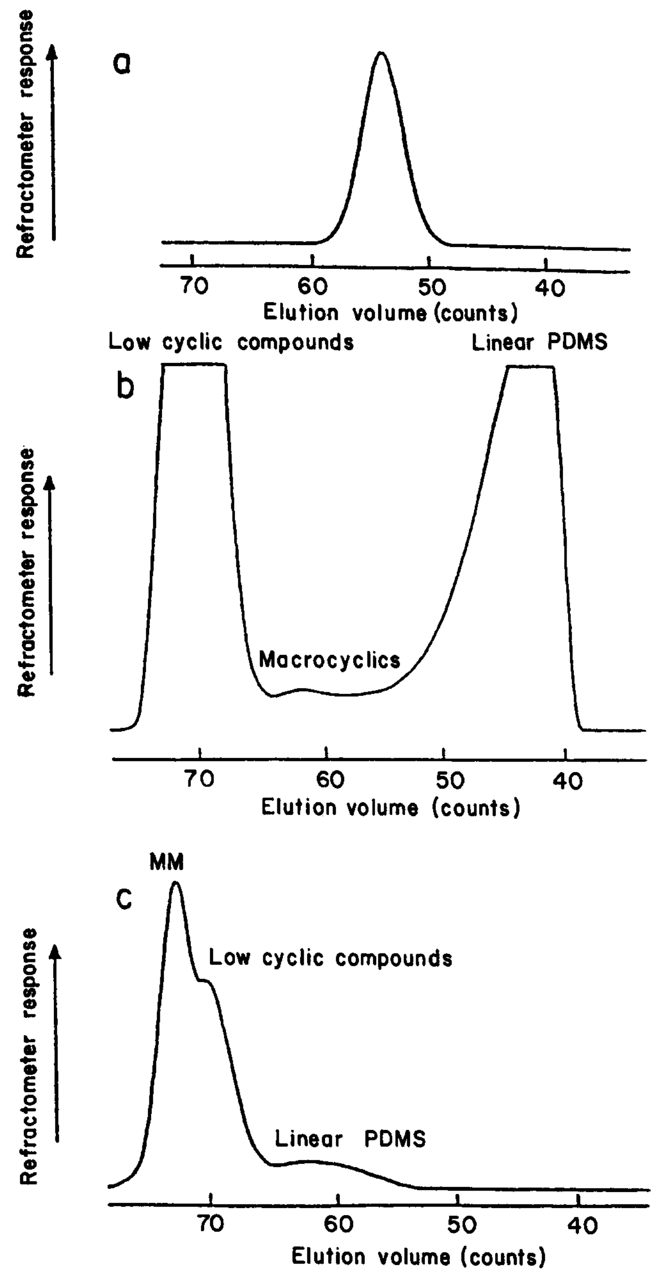

Figure 6 G.p.c. traces of: (a) 135 bond PDMS before heating; (b) 135 bond cyclic PDMS heated at 693 K for 24 h in Pyrex; (c) 135 bond cyclic PDMS heated at 693 K for 24 h in Pyrex in the presence of hexamethyldisiloxane (MM)

CONCLUSIONS

The degradation behaviour of cyclic and linear PDMS investigated here using d.s.c. and t.g.a. with platinum surfaces and in the absence of oxygen was found to be consistent with previous studies of linear PDMS, where an interchange of siloxane bonds has successfully accounted for the depolymerization. The possibility of synthetically utilising the bond interchange reaction to produce cyclic polymeric siloxanes does not seem feasible in Pyrex or quartz due to the catalytic activity of the vessels at the required temperatures (i.e. greater than 623 K). It may be possible to reduce the catalytic activity of the glass by reacting the surface hydroxyl groups with hexamethyldisilazane[21]. However, Stober has reported that only *ca.* one-third of surface groups were found to react[22,23] and the possibility of ions leaching from the vessels[9] would not be solved by this method. The use of platinum boats inside glass vessels would still allow the volatile cyclic oligomers produced to come into contact with the glass surface. The production of platinum metal vessels which could be sealed under high vacuum, however, may allow the rearrangement of siloxane bonds at elevated temperatures to be further explored.

ACKNOWLEDGEMENTS

We are indebted to the Science and Engineering Research Council for a Fellowship (to S.J.C.). We would like to thank Dr K. Dodgson, Sheffield City Polytechnic, for making available thermal analysis facilities and Mr T. M. Elsworth, University of York, for help in the preparation and characterization of PDMS fractions. Our thanks are also extended to Miss L. Andreassen, Miss P. Cooper and

Mr D. Henderson for carrying out some preliminary studies in this area.

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