Cyclic polysiloxanes: 5. Preparation and characterization of poly(hydrogenmethylsiloxane)

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The preparation and characterization of sharp fractions of cyclic and linear oligomeric and polymeric hydrogenmethylsiloxane are described and the refractive indices, densities and bulk viscosities of the fractions are reported. The preparation and physical properties of the cyclic materials are compared with those of other cyclic siloxanes.

(Keywords: poly(hydrogenmethylsiloxane); polysiloxanes; cyclic)

INTRODUCTION

Poly(hydrogenmethylsiloxane) (PHMS) is of particular interest both commercially and scientifically because of the reactive Si–H sites on the polymer backbone. These permit the incorporation of alkenyl moieties (CH2=CHR) into the polymer as pendant side chains via a hydrosilylation reaction. Similarly, the polymer can be reacted with alkene-containing surfaces or fibres to provide waterproof coatings for papers and textiles. When used in copolymers (often with dimethylsiloxane), the Si–H sites will interact with divinyl crosslinking agents to cause the low temperature vulcanization of synthetic rubbers. PHMS has also been used in the preparation of liquid crystalline polymers since mesogenic side chains are easily appended to the polymer.

The preparation of a number of cyclic siloxanes of the type [R(CH3)SiO]n, where R is methyl, ethyl, propyl, 3,3,3-trifluoropropyl, phenyl or vinyl, has been reported previously. Cyclic siloxanes are normally prepared via a base-catalysed ring-chain equilibration reaction; however, in the case of PHMS it is not possible to employ the usual alkali metal hydroxide catalysts owing to the high activity of the Si–H bond towards such species. PHMS has also been used in the preparation of liquid crystalline polymers since mesogenic side chains are easily appended to the polymer.

The preparation of cyclic siloxanes by the dilute solution hydrolysis of methyldichlorosilane has also been reported. Hydrolysis may be carried out at the interface of an aqueous and an organic phase. In this way the acid formed remains in the aqueous layer whilst the polymer is kept away from the acid in the organic layer. This separation limits the contact between acid and siloxane, thus reducing the risks of backbone and Si–H hydrolysis. High dilution of the organic phase ensures that intramolecular cyclization of the silanols formed predominates over intermolecular chain extension. In view of the fact that the hydrolysis is exothermic, crushed ice is usually added to the water–solvent mixture. In this way, the cyclic tetramer (H4) and pentamer (H5) and hexamer (H6) were prepared as long ago as 1946. Since then, the presence of smaller amounts of larger rings has been demonstrated by gas-liquid chromatography (g.l.c.). It is possible to isolate these rings by molecular distillation.

The cationic polymerization of cyclic siloxanes has been shown to proceed in conjunction with the formation of cyclic and macrocyclic species in addition to long linear chains. Equilibrium cyclic populations may be obtained which are similar to those found for anionic ring-chain equilibrations. However, by stopping the reaction prior to attainment of equilibrium conditions (usually 45% monomer conversion) it is possible to attain a considerable kinetic enhancement of the equilibrium cyclic populations. The cyclic nature of this material, in both the dimethyl and hydrogenmethyl cases, has been verified.

The thermal depolymerization of poly(dimethylsiloxane) (PDMS) has been extensively studied. It is generally agreed that the main degradation products are cyclic oligomers, although there is some dispute over the product distribution. Reports range from 99% cyclic trimer (D3) through 63% D3 to 44% D4, with the balance consisting of larger ring sizes. In the latter case there are reported to be 24% D4, 10% D5, 11% D6, 7.2% D7 and 5% D8. The most likely reason for the disagreement is that the thermal depolymerization reaction is highly sensitive to the reaction conditions.
Cyclic polysiloxanes. 5: R. D. C. Richards et al.

Thermal stability being reduced by the presence of active chain ends or trace amounts of ionic impurities. The presence of oxygen also accelerates the reaction. This sensitivity is borne out by the temperature-dependent nature of the product distribution from the depolymerization of PHMS.

In this paper we report a route to the preparation of a range of PHMS cyclics via the thermal depolymerization of a high-molar-mass PHMS resin. The preparation of linear PHMS is also described. The products were fractionated and the refractive indices, densities and bulk viscosities of the characterized sharp fractions were recorded for the first time. These results are compared with those reported for other siloxane systems.

**EXPERIMENTAL**

**Preparation of high-molar-mass resins**

PHMS resins of high molar mass were prepared by the careful hydrolysis of methylidichlorosilane (CH₃SiHCl₂). This was achieved by the dropwise addition of the dichlorosilane (100 cm³) to a stirred mixture of iced water (500 cm³) and diethyl ether (500 cm³) cooled in a salt-ice bath to approximately 270 K. After the addition of the dichlorosilane was complete the reaction mixture was permitted to come to room temperature and was stirred for a further 12 h. The aqueous layer was then removed and the organic phase stirred over an excess of sodium bicarbonate to remove any traces of acid. This procedure is also thought to promote the intramolecular condensation of low-molar-mass silanols to form longer PHMS chains. The liquor was then filtered and the ether removed at the rotary evaporator to yield a clear, colourless oil. After several days the low-molar-mass cyclic material was removed by vacuum distillation. Over a period of several days the residue formed a gel.

**Thermal depolymerization**

Thermal depolymerization was achieved by heating an evacuated flask containing the PHMS gel in a methane flame to ca. 850 K. The cyclic depolymerization products readily condensed on an angled cold probe (ca. 280 K) positioned just above the resin. The condensate ran along the probe and was collected in a receiver tube well away from the heat. After complete reaction, a brittle glassy material (ca. 30% by mass), assumed to be silicon carbide, remained in the flask. The condensate was fractionated by slow molecular distillation under high vacuum. In this way, sharp fractions of cyclic PHMS with $M_n > 1400$ were obtained. The fractions were characterized by gas-liquid chromatography (g.l.c.) and gel permeation chromatography (g.p.c.); the retention times and retention volumes were compared with those of cyclic materials prepared by dilute solution hydrolysis or isolated from cationic equilibrates. Comparisons were also drawn between the retention times of cyclic and linear PHMS. The absence of end-groups in the cyclic fractions was demonstrated by $^{29}$Si and $^1$H n.m.r.

**Preparation of linear PHMS**

Trimethylsilyl end-blocked PHMS oligomers were prepared by the equilibration of a trimethylsilyl end-blocked polymer (supplied by Dow Corning) with hexamethyldisiloxane in the presence of trifluoro-methanesulfonic acid to yield a broad product with a number average degree of polymerization $DP = 10$.

Low-molar-mass cyclic by-products (about 10% by mass) were removed by stirring the product under a low vacuum (10 mbar) at 320 K. Narrow molar mass distribution fractions were prepared by molecular distillation. These were characterized by g.l.c., g.p.c. and $^1$H n.m.r. Owing to the susceptibility of PHMS to thermal rearrangement it was not possible to distil fractions with $M_n > 950$. Higher molar masses were attained by preparative g.p.c. fractionation of the original polymer sample. These fractions were characterized by g.p.c. and $^1$H n.m.r.

**Physical measurements**

Polymer densities were measured at 25°C to within $\pm 3.5 \times 10^{-6} \text{g cm}^{-3}$ using a DMA02C precision densitometer. Viscosities were measured to within $\pm 1\%$ on a Wells-Brookfield cone and plate microviscometer with a sample volume of 0.5 cm³. The measurements were made at 25°C unless otherwise stated.

A Bellingham Abbé refractometer was used to measure refractive indices to within $\pm 10^{-3}$ at 25°C.

**RESULTS AND DISCUSSION**

As has been previously stated, the product distribution from the thermolysis is temperature dependent: reactions at temperatures of approximately 850 K gave rise to cyclics with up to 70 skeletal bonds, whereas at lower temperatures (525–600 K) only small cyclics (fewer than 16 skeletal bonds) were formed. Rings prepared at 850 K were fractionated and characterized by density, refractive index and bulk viscosity measurements. These results, along with those for the linear oligomers and polymers, are shown in Figures 1, 2 and 3, respectively. Figure 4

![Figure 1](image1.png) Density ($\rho$) versus $DP$ plot for cyclic (●) and linear (○) PHMS fractions

![Figure 2](image2.png) Refractive index ($n_d$) versus $DP$ plot for cyclic (●) and linear (○) PHMS fractions

4966 POLYMER, 1993, Volume 34, Number 23
systems at low molar masses) and theoretically on the basis that small and medium-sized rings have fewer available conformations than chains and are thus less able to deform under the conditions of viscous flow.

The molar mass dependences of the viscosities of both the rings and the chains fit the Fox and Loshak equation for polymer viscosity

\[ \eta = K M_w^a \]

where \( \eta \) is the polymer bulk viscosity, \( K \) is a constant of proportionality, \( M_w \) is the weight average molar mass of the polymer and \( a \) is 1 for polymers below the critical mass for entanglement and 3.4 for those above.

The double logarithmic plots yield values of the exponent \( a \) of 1.05 and 1.43 for linear and cyclic PHMS, respectively. These values compare favourably with the theoretical value of unity for polymers below the critical mass for entanglement. This confirms that the polymer samples measured are below the critical mass, and it is likely that the quality of the agreement reflects the flexibility of the polymer backbone, and thus the similarity of PHMS to the theoretical freely jointed chain. Indeed, it is worth noting that PHMS is structurally very similar to poly(dihydrogensiloxane), which has been found not only to be remarkably flexible but also to have virtually no restrictions to rotation about its skeletal bonds.

The observation that the rings deviate from the theory more than the chains highlights the restricted conformation of cyclic species and the concomitant reduction in flexibility. This is further borne out by comparison with the linear dimethylsiloxane and vinylmethylsiloxane, which have values of \( a \) of 1.25 and 1.29, respectively. Clearly, as the side-chain bulk decreases, the segmental flexibility is increased, and hence the value of \( a \) is reduced. A similar comparison for rings cannot be readily drawn because of anomalies in the dimethyl and vinylmethyl data at 22 bonds. It has been stated that the principal reason for deviation from this theory is the dependence of polymer density upon molar mass. Such a dependence does exist in the case of PHMS, but is minimal in the range 8 < \( n_s \) < 25 (ca. 5%, where \( n_s \) is the number average number of bonds), and the chains show a slightly greater dependence than the rings (see Figure 3). It is thus improbable that polymer density plays a significant role in the viscosity of these materials.

**Temperature dependence**

The temperature dependence plots shown in Figure 4 demonstrate excellent agreement with the predicted Arrhenius-type behaviour

\[ \eta = \exp(\Delta S^f/R) \exp(\Delta H^+/RT) \]

where \( R \) is the molar gas constant, \( T \) is the absolute temperature, \( \Delta S^f \) is the entropy of activation for viscous flow and \( \Delta H^+ \) is the enthalpy of activation for viscous flow.

Comparisons can be drawn with both the dimethyl and vinylmethyl systems. On comparing polymers with similar values of \( n_s \) (see Table 1) it is apparent that PHMS has a lower enthalpy of activation and a higher entropy parameter than other siloxane polymers. Both these factors result in an overall reduction in the free energy of activation for viscous flow \( \Delta G^f \) since

\[ \Delta G^f = \Delta H^+ - T \Delta S^f \]
Table 1 Arrhenius parameters of some linear PDMS and PVMS fractions compared with analogous PHMS fractions

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$n_a$</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>Pre-exponential factor (kg$^{-1}$ m$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHMS 208</td>
<td>208</td>
<td>10.66</td>
<td>28.6</td>
</tr>
<tr>
<td>PHMS 83</td>
<td>83</td>
<td>10.62</td>
<td>10.4</td>
</tr>
<tr>
<td>PHMS 254</td>
<td>254</td>
<td>9.73</td>
<td>82.7</td>
</tr>
<tr>
<td>PDMS 131</td>
<td>131</td>
<td>14.9</td>
<td>9.75</td>
</tr>
<tr>
<td>PDMS 50.0</td>
<td>50.0</td>
<td>14.3</td>
<td>5.22</td>
</tr>
<tr>
<td>PDMS 247</td>
<td>247</td>
<td>14.7</td>
<td>22.6</td>
</tr>
<tr>
<td>PVMS 207</td>
<td>207</td>
<td>16.7</td>
<td>20.5</td>
</tr>
<tr>
<td>PVMS 83</td>
<td>83</td>
<td>15.5</td>
<td>9.79</td>
</tr>
<tr>
<td>PVMS 275</td>
<td>275</td>
<td>17.0</td>
<td>26.2</td>
</tr>
</tbody>
</table>

This is in keeping with the comparative flexibility of PHMS chain segments, resulting in less resistance to shear forces under flow conditions.

The stability (with respect to spontaneous polymerization) of the rings prepared by the thermal depolymerization route was found to be far greater than that of those prepared by hydrolysis. This may be attributed to the difficulty in removing reactive silanols from the hydrolysis products. These silanols tend to initiate ring-opening polymerization which results in high-molar-mass gels. Similar problems were encountered with active chain ends in the cationic polymerization reactions, causing crosslinking before the cyclic products could be distilled. The thermal products did, however, eventually disproportionate over a period of several months to give a mixture of smaller rings, higher cyclic polymers and silanols which eventually gelled. The rearrangement appeared to proceed fastest in samples of PHMS containing the 22 bond ring. This behaviour is analogous to, but less rapid than, the tendency of PHMS rings to rearrange spontaneously.

The samples reported in this paper have been used in the preparation of cyclic and linear polymer liquid crystals. Further work in this field is in progress.

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REFERENCES

5. Wright, P. V. and Semljen, J. A. Polymer 1970, 11, 462