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[1]. These permit the incorporation of alkenyl moieties ($CH_2{=}CHR$) into the polymer as pendant side chains via a hydrosilylation reaction[2]. Similarly, the polymer can be reacted[1] 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[3] 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 $[R(CH_3)SiO]_x$, where R is methyl, ethyl, propyl, 3,3,3-trifluoropropyl, phenyl or vinyl, has been reported[4] previously. Cyclic siloxanes are normally prepared via a base-catalysed ring–chain equilibration reaction[5]; 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[6]. Although the use of butyllithium as an anionic catalyst at 273 K does, in part, overcome this problem[5], there still remains a significant degree of degradation of the Si–H bonds in the equilibrate with the result that the cyclic product cannot be isolated. In the case of PHMS equilibrates there also appears to be an overlap[7] between the cyclic and linear populations and, once again, the cyclic material cannot be isolated. The overlap is to be expected since Wright and Semlyen estimate[5] the number average degree of polymerization (x_n) for the linear material to be as low as about 100.

The preparation of cyclic PHMS by the dilute solution hydrolysis of methyldichlorosilane has also been reported[8]. 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 (H_4), pentamer (H_5) and hexamer (H_6) were prepared[8] 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.)[9]. It is possible to isolate these rings by molecular distillation[10].

The cationic polymerization of cyclic siloxanes has been shown[11,12] 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[7,10].

The thermal depolymerization of poly(dimethylsiloxane) (PDMS) has been extensively studied[13]. 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 (D_3)[13], through 63% D_3 to 44% D_3[14,15], with the balance consisting of larger ring sizes. In the latter case there are reported to be 24% D_4, 10% D_5, 11% D_6, 7.2% D_7 and 5% D_{8-12}. The most likely reason for the disagreement[13] is that the thermal depolymerization reaction is highly sensitive to the reaction conditions,

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thermal stability being reduced by the presence of active chain ends or trace amounts of ionic impurities[15]. 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[7] 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 methyldichlorosilane (CH_3SiHCl_2). This was achieved by the dropwise addition of the dichlorosilane (100 cm^3) to a stirred mixture of iced water (500 cm^3) and diethyl ether (500 cm^3) 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 intermolecular 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[10] by dilute solution hydrolysis or isolated[10] 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 ^1H 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 trifluoromethanesulfonic 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 ^1H 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 ^1H n.m.r.

Physical measurements

Polymer densities were measured at 25°C to within $\pm 3.5 \times 10^{-6}\ g\,cm^{-3}$ using a DMA02C precision densitometer.

Viscosities were measured to within ±1% on a Wells Brookfield cone and plate microviscometer with a sample volume of 0.5 cm^3. 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*

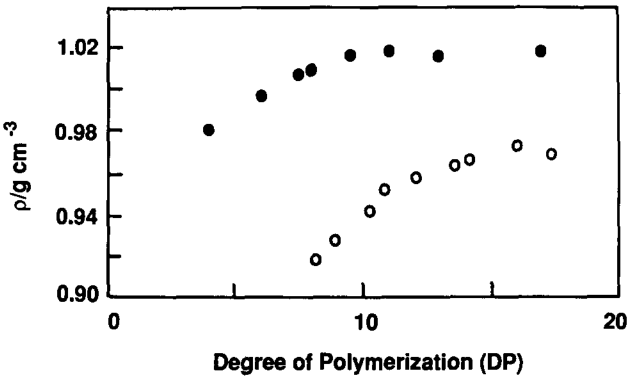

Figure 1 Density (ρ) *versus DP* plot for cyclic (●) and linear (○) PHMS fractions

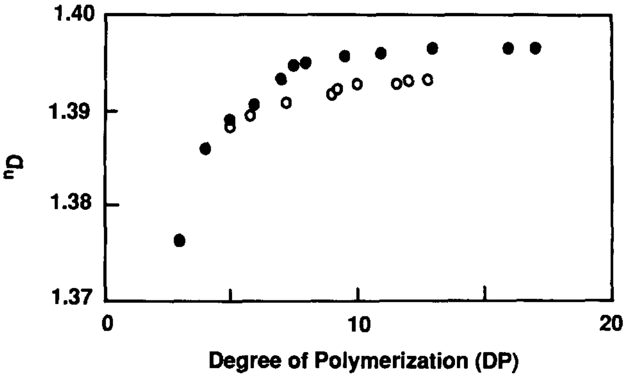

Figure 2 Refractive index (n_D) *versus DP* plot for cyclic (●) and linear (○) PHMS fractions

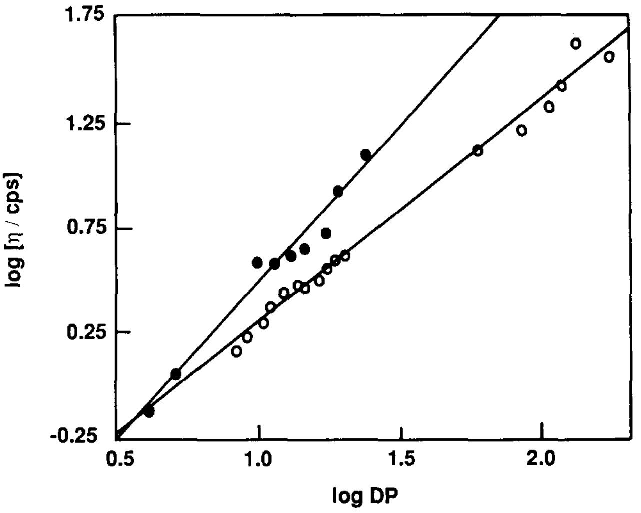

Figure 3 Bulk viscosity (η) *versus DP* double logarithmic plot for cyclic (●) and linear (○) PHMS fractions

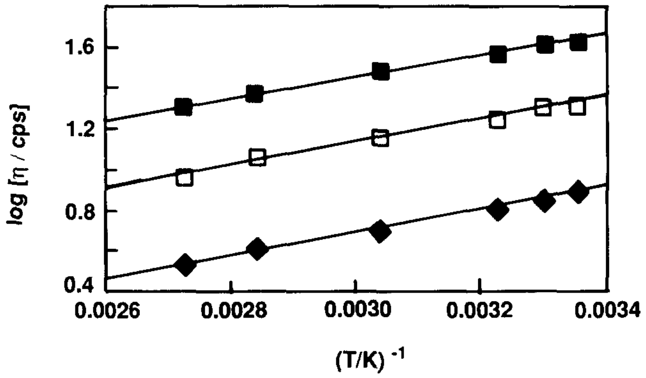

Figure 4 Arrhenius-type plots for viscous flow of three linear PHMS fractions with 254 (■), 208 (□) and 83 (◆) skeletal bonds

shows the temperature dependence of the bulk viscosity of three linear fractions.

The refractive indices and densities of the smaller cyclics are in accord with those measured by Dow Corning ($3 \leqslant DP \leqslant 6$) and with values obtained by the authors from samples prepared by dilute solution hydrolysis ($4 \leqslant DP \leqslant 7$) and kinetically controlled cationic polymerization ($12 \leqslant DP$)[10].

It is interesting to note that the well-defined maxima in the mass-dependence plots of both the refractive indices and the densities observed for cyclic poly(dimethylsiloxane) (PDMS)[16] and poly(vinylmethylsiloxane) (PVMS)[17] are not observed for PHMS rings (*Figures 1* and *2*). The density maximum (which results in the refractive index maximum) and the minimum in the plot of the molar cyclization equilibrium constant K_{DP} against $\log_{10} DP$ arise from the fact that siloxane rings of $DP = 11$ can adopt a planar all-*trans* low energy conformation[18]. The absence of such a low energy state for PHMS rings is to be expected theoretically[18] and is a reflection of the great flexibility of PHMS arising from the low energy barrier for bond rotation resulting from the low steric bulk of the PHMS side chains.

As can be seen from *Figure 3*, low-molar-mass cyclic PHMS fractions are more viscous than their linear analogues. This is to be expected both experimentally (from observations made of dimethyl[16] and vinylmethyl[17] systems at low molar masses) and theoretically on the basis that small and medium-sized rings have fewer available conformations than chains[19] 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 Loshaek equation[20] for polymer viscosity

$$\eta = KM_w^a$$

where η 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[20]. 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[21]. 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[20]. 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[16,17]. 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[22]. Such a dependence does exist in the case of PHMS, but is minimal in the range $8 < n_n < 25$ (ca. 5%, where n_n 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[23]

$$\eta = \exp(\Delta S^\dagger/R)\exp(\Delta H^\dagger/RT)$$

where R is the molar gas constant, T is the absolute temperature, $\Delta S^\dagger$ is the entropy of activation for viscous flow and $\Delta H^\dagger$ 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_n (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 $\Delta G^\dagger$ since

$$\Delta G^\dagger = \Delta H^\dagger - T\Delta S^\dagger$$

Table 1 Arrhenius parameters of some linear PDMS and PVMS fractions compared with analogous PHMS fractions

Polymer	n_n	E_a (kJ mol^{-1})	Pre-exponential factor (kg^{-1} m^{-1} s)
PHMS	208	10.66	28.6
PHMS	83	10.62	10.4
PHMS	254	9.73	82.7
PDMS	131	14.9	9.75
PDMS	50.0	14.3	5.22
PDMS	247	14.7	22.6
PVMS	207	16.7	20.5
PVMS	83	15.5	9.79
PVMS	275	17.0	26.2

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[10]. 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[7]. The thermal products did, however, eventually disproportionate[10] 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[9].

The samples reported in this paper have been used in the preparation of cyclic and linear polymer liquid crystals[7,10,24]. Further work in this field is in progress.

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