Studies of cyclic and linear poly(dimethyl siloxanes). 4. Bulk viscosities

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(Received 29 October 1979)

The bulk viscosities η of over fifty sharp fractions of cyclic and linear poly(dimethyl siloxanes) in the weight-average molecular weight range $500 < \bar{M}_w < 25\,000$ have been measured at 298 K using a cone-and-plate microviscometer. In the low molecular weight region ($\bar{M}_w < 1000$) the η values for the cyclics were found to be at least three times as large as the values for the corresponding chain molecules. By contrast, in the highest molecular weight region ($\bar{M}_w > 16\,000$), the η values for the cyclics were approximately one-half those for the corresponding linears. Cyclics and linears containing about one hundred skeletal bonds were found to have similar bulk viscosities. The temperature dependence of the bulk viscosities of eighteen of the cyclic and linear fractions were investigated, and the relationship $\eta = A \exp(E_{visc}/RT)$ was used to deduce values for the energies of activation for viscous flow E_{visc} and the constants A.

INTRODUCTION

Following experimental and theoretical studies of cyclic concentrations in ring-chain equilibration reactions at the University of York[1-4], the first synthetic cyclic polymers have been prepared[5-7]. These polymers are cyclic poly(dimethyl siloxanes) $[(CH_3)_2SiO]_x$, and many fractions with heterogeneity indices $\bar{M}_w/\bar{M}_n = 1.05 \pm 0.02$ (containing ring molecules with number average numbers of skeletal bonds $\bar{n}_n$ in the range $100 < \bar{n}_n < 600$) have been obtained on a 2–10 g scale using preparative gel permeation chromatography (g.p.c.)[6]. Each fraction consists almost entirely of simple cyclic molecules, with negligible quantities of other topologically different species, such as catenated rings and linear chains. They are the first examples of synthetic cyclic polymers to be fully characterized.

Recently, some of the properties of these cyclic polymers have been investigated and compared with those of the corresponding linear poly(dimethyl siloxanes) $(CH_3)_3SiO$ $[(CH_3)_2SiO]_y Si(CH_3)_3$. For example, the ratio of the limiting viscosity numbers of the ring and linear polymers $[\eta]_r/[\eta]_l$ has been determined in a θ-solvent[5], and found to be in agreement with the theoretically predicted value of 0.66[8-10]. Furthermore, the ratio of the squares of the z-average radii of gyration of linear and cyclic poly(dimethyl siloxanes) $\langle s^2 \rangle_l/\langle s^2 \rangle_r$ has been measured in benzene-d_6 by small-angle neutron scattering, and found to be 1.9 ± 0.2[7]. This value may be compared with the theoretical value of 2.0 predicted for 'flexible' high molecular weight linear and cyclic polymers under θ-point conditions[11-14]

It is the purpose of this paper to report the bulk viscosities of cyclic poly(dimethyl siloxane) fractions with weight average numbers of bonds $\bar{n}_w$ in the range $8 < \bar{n}_w < 640$, and to compare the results with those obtained for the corresponding open chain molecules.

EXPERIMENTAL

Preparation of the samples

The cyclic poly(dimethyl siloxanes) were obtained from poly(dimethyl siloxane) ring-chain equilibration reactions carried out in toluene solution at 383K[2-5]. Dow Corning DC 200 Dimethicones with the formulae $(CH_3)_3SiO[(CH_3)_2SiO]_y Si(CH_3)_3$ were the source of the linear poly(dimethyl siloxanes).

Both the cyclic and the linear poly(dimethyl siloxane) fractions studied were prepared using vacuum fractional distillation techniques and preparative g.p.c. They were all characterized by analytical g.p.c. as described in ref. 6. The molecular weights and heterogeneity indices of all the fractions used are shown in *Table 1*.

Viscometric measurements

The bulk viscosities η of the cyclic and linear poly(dimethyl siloxane) fractions were measured using a Wells–Brookfield cone-and-plate microviscometer[15]. The viscometer was fitted with a rhodium plated stainless steel cone, with a radius $r = 2.4$ cm and an angle $\theta = 1.565°$. The base of a jacketed sample cup formed the plate.

The clearance between the cone and plate was set below 2.54×10^{-4} cm, by following the calibration procedure recommended by the manufacturer. The instrument was capable of operation at eight different pre-calibrated shear rates, which were selected by changing the speed of rotation of the cone. This feature of the instrument enabled the measurement of η values in eight ranges from 0–10 centipoise to 0–2000 centipoise.

The viscosity η of each cyclic and linear poly(dimethyl siloxane) fraction was measured at $298 \pm 0.01K$. A minimum of 1.0 cm^3 of sample was introduced into the sample cup to

Table 1 Molecular weights and bulk viscosities η of the cyclic (R1-R24) and linear (L1-L32) poly(dimethyl siloxane) fractions at 298K

Fraction	Weight average number of skeletal bonds $\bar{n}_w$	Weight average molecular weight $\bar{M}_w$	Hetero-geneity index $\bar{M}_w/\bar{M}_n$	η (10^{-3} kg m^{-1}s^{-1}) (centipoise)
R1	14.1	523	1.01	10.12
R2	16.1	598	1.05	12.36
R3	22.2	823	1.05	17.32
R4	22.3	828	1.13	17.98
R5	26.8	993	1.05	21.70
R6	29.2	1084	1.03	21.95
R7	29.9	1109	1.04	24.30
R8	31.1	1154	1.05	23.25
R9	31.3	1162	1.02	24.75
R10	34.2	1268	1.01	25.10
R11	35.6	1321	1.01	25.20
R12	40.6	1507	1.09	25.60
R13	40.9	1519	1.04	25.00
R14	51.8	1921	1.05	24.95
R15	67.6	2507	1.07	26.80
R16	88.8	3293	1.07	27.40
R17	119.6	4434	1.08	36.55
R18	147.6	5472	1.06	38.65
R19	195.6	7254	1.05	45.45
R20	242.9	9008	1.06	54.20
R21	322.2	11 947	1.07	72.00
R22	355.5	13 182	1.04	72.40
R23	504.8	18 718	1.08	118.0
R24	639.4	23 710	1.06	171.8
L1	14.7	707	1.03	3.24
L2	16.9	788	1.01	3.91
L3	18.4	843	1.01	4.52
L4	19.9	900	1.01	5.03
L5	21.2	949	1.01	5.57
L6	22.9	1010	1.01	6.21
L7	23.8	1040	1.01	6.64
L8	24.6	1070	1.01	6.98
L9	25.7	1110	1.01	7.27
L10	27.6	1190	1.01	7.89
L11	28.5	1220	1.01	8.15
L12	29.8	1270	1.01	8.90
L13	30.7	1300	1.01	9.02
L14	31.8	1340	1.01	9.48
L15	34.0	1420	1.01	10.58
L16	35.3	1470	1.01	10.98
L17	36.2	1500	1.01	11.52
L18	37.4	1550	1.01	11.88
L19	40.8	1670	1.01	13.08
L20	44.1	1800	1.01	14.30
L21	46.0	1870	1.01	15.50
L22	50.0	2010	1.01	17.04
L23	61.3	2430	1.11	18.50
L24	85.3	3320	1.14	27.95
L25	130.9	5020	1.23	39.50
L26	207.8	7870	1.20	66.40
L27	246.9	9320	1.24	87.20
L28	330.2	12 400	1.20	124.3
L29	404.7	15 170	1.17	175.2
L30	459.2	17 190	1.14	222.8
L31	559.2	20 900	1.10	327.3
L32	624.4	23 310	1.09	352.2

ensure that the space between the cone and plate was completely filled. For a given sample, the shear rate of the viscometer was selected so that the instrument stabilized with the maximum on-scale reading to ensure optimum precision. Measurements of the deflection d (the percentage of the full scale torque on the viscometer scale) were found to be reproducible to ±0.2 divisions. The mean of at least four separate determinations of d (in 10^{-5} kg m^2 s^{-1}) was used

to calculate the value of η (in 10^{-3} kg m^{-1} s^{-1} (centipoise)) by using the expression[15]:

$$\eta = \frac{\text{shear stress} \times 100}{\text{shear rate}} \qquad (1)$$

where the shear stress (in 10^{-5} kg m^{-1} s^{-2}) and shear rate (in s^{-1}) were calculated using the following equations[15]:

$$\text{shear stress} = \frac{d}{(2/3)\pi r^3} \qquad (2)$$

$$\text{shear rate} = \frac{\omega}{\tan\theta} \qquad (3)$$

where ω is the cone speed (in radian s^{-1}).

The η values of some of the cyclic and linear poly(dimethyl siloxane) fractions were measured over the temperature range 298—358K in order to obtain values for the activation energies of viscous flow E_{visc}. In these experiments, measurements were made using the same volume of sample at each temperature in order to minimize uncertainties in the experimental E_{visc} values due to thermal expansion effects.

RESULTS AND DISCUSSION

Experimental bulk viscosities

The bulk viscosities η at 298K of the cyclic and linear poly(dimethyl siloxane) fractions used in this study are listed in *Table 1*. All the η values were measured with a precision of better than ±3%. A plot of log η against log $\bar{M}_w$ is shown in *Figure 1*, where $\bar{n}_w$ values are also given*.

* As in previous studies[5-7] the number of skeletal bonds for the linear molecule (CH$_3$)$_3$SiO [(CH$_3$)$_2$SiO] $_y$ Si(CH$_3$)$_3$ is taken to be $2y$, the (CH$_3$)$_3$SiO— and (CH$_3$)$_3$Si— residues are considered as end-groups. In this connection, it is noted that the name poly(dimethyl siloxane) strictly applies only to the cyclic, and not to the linear polymer

Table 2 Values of E_{visc} and A for some cyclic and linear poly(dimethyl siloxanes)

Fraction	E^*_{visc} (in kJ)	$10^5 A$
R4	17.7	1.42
R8	17.5	2.00
R13	16.8	2.83
R14	16.3	3.72
R15	16.0	4.23
R17	15.5	6.88
R19	15.4	9.06
R21	15.6	13.2
R23	15.4	23.8
L3	13.0†	2.37
L9	13.3	2.44
L18	14.0	4.14
L22	14.3	5.22
L24	14.6	7.75
L25	14.9	9.75
L27	14.7	22.6
L29	14.8	45.1
L30	14.9	53.4

* These values are subject to an estimated experimental uncertainty of ±5%
† The value of 13.0 kJ for fraction L3 with a number average molecular weight $\bar{M}_n$ = 834 may be compared with the value of 13.7 kJ for a linear dimethyl siloxane (CH$_3$)$_3$SiO[(CH$_3$)$_2$SiO] $_9$ Si(CH$_3$)$_3$ with a molecular weight of 830 (see ref. 19).
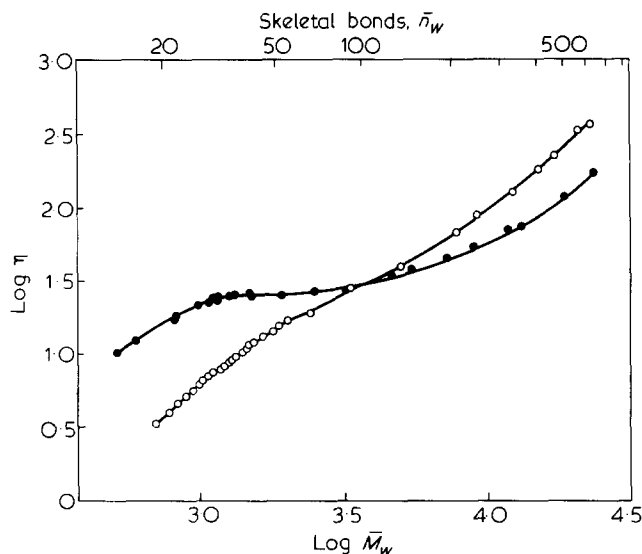
Figure 1 Plots of the logarithms of the bulk viscosities η of the cyclic (●) and linear (○) poly(dimethyl siloxanes) at 298K against the logarithms of their weight average molecular weights $\bar{M}_w$

No attempt will be made to compare the experimental bulk viscosities of the linear poly(dimethyl siloxanes) and the small cyclic dimethyl siloxanes with values obtained over thirty years ago by Barry[16], Hunter and his coworkers[17,18] and Wilcock[19], because of uncertainties in the characterization procedures used in these early studies. However, all the bulk viscosities were found to be independent of shear rate, as expected for Newtonian fluids. Incidentally, previous workers had established Newtonian behaviour for linear poly(dimethyl siloxane) fractions of considerably higher molecular weight[20].

The bulk viscosity-molecular weight relationship for the cyclic poly(dimethyl siloxanes) shown in *Figure 1* is quite different from that of the corresponding linear poly(dimethyl siloxanes). In the molecular weight range $\bar{M}_w < 1000$, the η values for the cyclics are larger by factors of at least three than those of the corresponding linears. By contrast, in the molecular weight range $18\,000 < \bar{M}_w < 24\,000$, the η values for the cyclics are only about one-half those of chains containing the same number of skeletal bonds. The log η versus log $\bar{M}_w$ plots for the cyclic and linear polymers cross-over at $\bar{n}_w = \sim100$, so that cyclic and linear poly(dimethyl siloxanes) containing 89 and 85 skeletal bonds respectively have nearly identical bulk viscosities (27.40 centipoise for fraction R16, and 27.95 centipoise for fraction L24).

The differences between the bulk viscosities of these ring (r) and linear (l) poly(dimethyl siloxanes) are markedly different from the differences between their limiting viscosity numbers. In *Figure 2*, the ratio η_r/η_l at 298K is plotted as a function of molecular weight, and compared with the ratio $[\eta]_r/[\eta]_l$ determined in a θ-solvent, butanone at 293K[5]. Although no attempt will be made here to interpret the experimental results on the bulk viscosities of cyclic polymers in any detail, it is of interest to note that Bueche[21] has predicted that in the absence of 'entanglements', the ratio of the bulk viscosity of a branched polymer η_b to that of a linear polymer of the same molecular weight η_l is given by:

$$\eta_b/\eta_l = g \tag{4}$$

where g represents the ratio of the mean-square radii of gyration of the branched and linear species. Extending

Bueche's arguments to ring and linear polymers, where both theory and experiment have established that[7,22-24]:

$$\langle s^2\rangle_r/\langle s^2\rangle_l \cong 0.5 \tag{5}$$

It follows that:

$$\eta_r/\eta_l \cong 0.5 \tag{6}$$

and this is the value found in the highest molecular weight range studied (for example, $\eta_r/\eta_l = 0.51 \pm 0.02$ at $\bar{M}_w = 16\,000$ and $\eta_r/\eta_l = 0.45 \pm 0.02$ at $\bar{M}_w = 24\,000$ (see *Figure 2*)).

In the low molecular weight region, where $\bar{M}_w < 1000$, equation (6) obviously no longer applies, and the ratio of the bulk viscosities $\eta_r/\eta_l > 3$. In this region, the possibilities for motion of the chains (or chain segments) should be far greater than those for the corresponding rings, and it is not surprising that the linears are much less viscous than the cyclics.

Temperature dependences of bulk viscosities

The effect of temperature on the bulk viscosities η of eighteen of the cyclic and linear poly(dimethyl siloxane) fractions listed in *Table 1* was investigated over the range 298–358K. For all the fractions studied, a linear relationship was found between ln η and $1/T$. Hence, it was assumed that for these siloxanes, the temperature dependence of the bulk viscosity η could be described using the familiar relationship[25-27]:

$$\eta = A \exp(E_{\text{visc}}/RT) \tag{7}$$

where E_{visc} is termed the activation energy for viscous flow, A is a constant, R is the gas constant and T is the temperature. Values of E_{visc} and A were obtained from plots of ln η against $1/T$ using a least squares procedure (see *Figure 3* for some examples).

The values of E_{visc} for all the fractions investigated are shown plotted against log $\bar{M}_w$ in *Figure 4*. The E_{visc} values
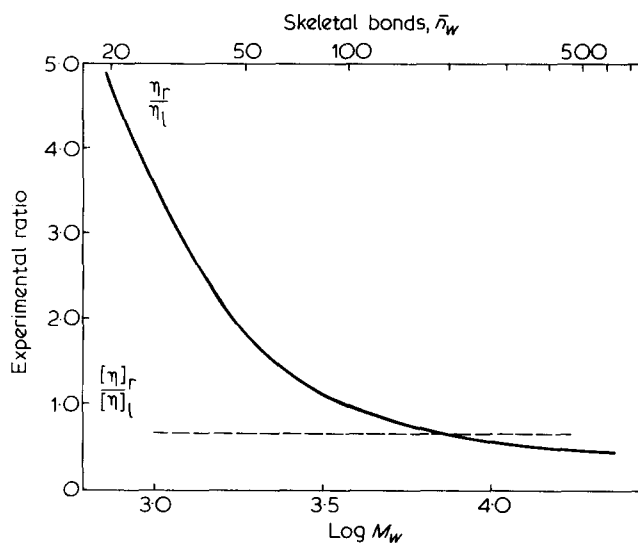

Figure 2 The experimentally-determined ratios of bulk viscosities η_r/η_l and limiting viscosity numbers $[\eta]_r/[\eta]_l$ for ring (r) and linear (l) poly(dimethyl siloxanes) plotted against the logarithms of the weight average molecular weights (see text)
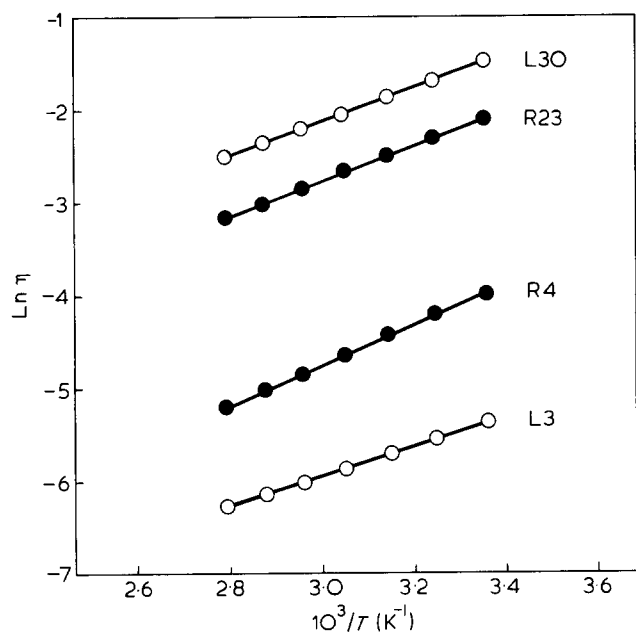
Figure 3 Plots of the natural logarithms of the bulk viscosities η against the reciprocal of the temperatures T for cyclic (●) and linear (○) poly(dimethyl siloxane) fractions. The lines were constructed using a least squares procedure
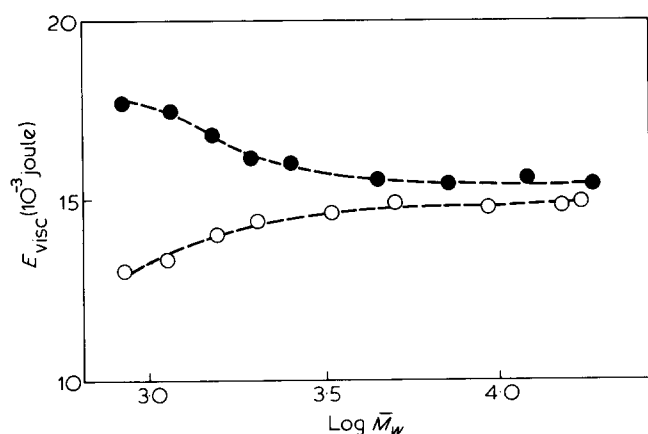

Figure 4 Experimentally-deduced values of the activation energy for viscous flow E_{visc} for cyclic (●) and linear (○) poly(dimethyl siloxanes) plotted against the logarithms of their weight average molecular weights $\bar{M}_w$

for the linear polymers increase with molecular weight to a constant value of ~ 14.8 kJ, whereas the E_{visc} values for the cyclic polymers decrease to a somewhat higher value of ~ 15.5 kJ. The corresponding plots of log A against log $\bar{M}_w$ are shown in *Figure 5*.

It should be possible to provide an explanation for the experimental observations reported in this paper, using the realistic rotational isomeric state model for poly(dimethyl siloxane) set up by Flory, Crescenzi and Mark[28]. Further experimental and theoretical studies of the properties of cyclic and linear poly(dimethyl siloxanes) are in progress.
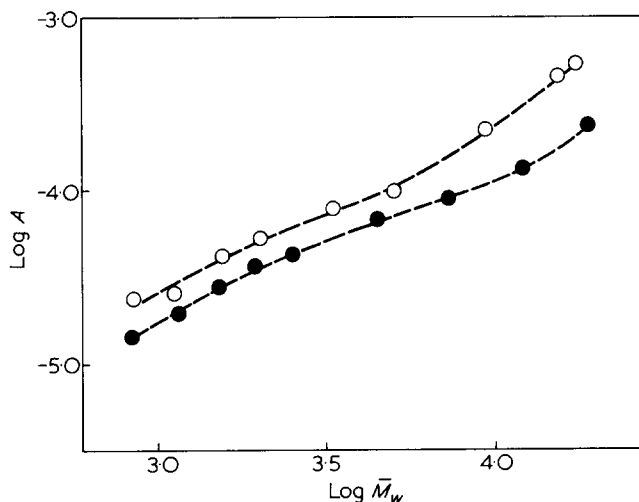
ACKNOWLEDGEMENTS

Figure 5 Experimentally-deduced values of the constant A for cyclic (●) and linear (○) poly(dimethyl siloxanes) plotted against the logarithms of their weight average molecular weights

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