Studies of cyclic and linear poly(dimethyl siloxanes): 5. Diffusion behaviour in dilute solution

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The diffusion coefficients of cyclic and linear oligomeric and polymeric dimethyl siloxanes, containing number-average numbers of skeletal bonds in the range $6 < \bar{n}_n < 650$, have been measured in toluene solution at 298K. Impermeable diffusion behaviour was observed for all the siloxanes studied, in agreement with previous findings for ethylene oxide and hexamethylene oxide oligomers and polymers. The ratio of the friction coefficients f_r/f_l for the ring (r) and linear (l) dimethyl siloxanes was found to be $8/3\pi$ (within the limits of experimental error) over the whole range of molecular weights studied. Values of the expansion factor α_f for the linear poly(dimethyl siloxanes) (obtained from the diffusion measurements) were found to be approximately equal to the corresponding values for α_η (found previously by viscometric studies) for small values of the excluded volume parameter z; and α_f was larger than α_η for large z, as predicted by first-order perturbation theory. Mean-square radii of gyration $\langle s_G^2 \rangle$ were calculated from the diffusion data for both cyclic and linear poly(dimethyl siloxanes) assuming Gaussian statistics, and found to be in good agreement with the corresponding values obtained by neutron scattering. However, the values of $\langle s_{G,l}^2 \rangle$ for the short chain poly(dimethyl siloxanes) did not agree with the corresponding values of $\langle s_{0,l}^2 \rangle$, calculated using the rotational isomeric state model of Flory, Crescenzi and Mark. This discrepancy is thought to arise from deviations from Gaussian behaviour, and considerably better agreement between experiment and theory was achieved by using appropriate values of a function $\psi_l(x)$, which relates radii of gyration and impermeable hydrodynamic diffusion radii.

INTRODUCTION

The isolation and characterization of cyclic poly(dimethyl siloxanes) have been described in previous papers[1-3]. Many sharp fractions have been obtained, each on a scale of several grammes, using preparative gel permeation chromatography (g.p.c.)[2]. The fractions consist of ring molecules $((CH_3)_2SiO)_x$, with number-average numbers of skeletal bonds, $\bar{n}_n$, up to ~700. Already several studies of cyclic poly(dimethyl siloxanes) have been made, comparing their properties with those of the corresponding linear polymers. For example, g.p.c. retention volumes[2,4], dilute solution viscosities[1], neutron scattering behaviour and radii of gyration in dilute solution[3], and bulk viscosities[5] have all been investigated experimentally.

Although cyclic poly(dimethyl siloxane) is the only synthetic cyclic polymer to have been fully characterized up to the present time, circular deoxyribonucleic acid (DNA) molecules have been known since 1962[6,7]. These cyclic macromolecules can be isolated from many organisms, including viruses, bacteria and mitochondria. Their circularity has been demonstrated by electron microscopy (see, for example, refs 8,9), as well as by a wide range of physical techniques[7]. The circular molecules occur in a wide variety of modifications including double-stranded nicked circles, where one strand forms a ring by covalent bonding and the other forms a ring by base-pairing to the first.

The ratio of sedimentation coefficients, s_l/s_r, for linear and nicked circular DNA has been measured for polyoma virus[10] and λ DNA[11] and found to be 0.91 and 0.88, respectively. Values of 0.90 and 0.89 were calculated for these molecules by Gray, Bloomfield and Hearst[12], who had to take account of 'chain stiffness' as well as excluded volume effects in order to obtain agreement with experiment.

Here we report the results of an experimental investigation into the diffusion behaviour of cyclic and linear poly(dimethyl siloxanes) in dilute solution. Toluene was chosen as the solvent since it is a 'good' solvent for the polymer and has been used in several related studies of poly(dimethyl siloxanes)[1,4,13-15].

Translational friction coefficients, f, diffusion coefficients, D, and sedimentation coefficients, s, can be related using the following expression:

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Table 1 Molecular weights ($\bar{M}_n$), number-average numbers of bonds ($\bar{n}_n$), heterogeneity indices ($\bar{M}_w/\bar{M}_n$), diffusion coefficients (D) and the mean concentrations ($\bar{c}$) for the linear (L1–L9) and cyclic (R1–R9) poly(dimethyl siloxane) samples in toluene at 298K

Fractions	$\bar{M}_n$	$\bar{n}_n$	$\bar{M}_w/\bar{M}_n$	$D/\mu m^2 s^{-1}$	$\bar{c}$ (% w/w)
L1	312.2	6	1.0	1240.0	1.405
L2	386.3	8	1.0	1071.0	1.375
L3	608.6	14	1.03	800.0	1.388
L4	1053	26	1.02	589.2	1.333
L5	1442	36.5	1.02	494.2	1.371
L6	3573	94	1.04	335.2	1.243
L7	6018	160	1.05	266.5	1.337
L8	14460	388	1.07	150.3	1.249
L9	23570	631	1.08	108.8	1.750
R1	222.3	6	1.0	1452.0	1.483
R2	296.4	8	1.0	1233.0	1.294
R3	741.0	20	1.07	780.0	1.180
R4	1189	30.2	1.08	647.3	1.512
R5	1534	41.4	1.05	571.3	1.180
R6	3171	85.6	1.06	409.5	1.504
R7	4172	112.6	1.04	370.7	1.351
R8	9077	245	1.06	242.2	1.237
R9	17673	477	1.07	162.6	1.432

$$f = \frac{kT}{D} = \frac{(1 - \bar{\nu}\rho_0)}{s} \qquad (1)$$

where $\bar{\nu}$ is the partial molar volume of the polymer, ρ_0 is the density of the solvent, k is the Boltzmann constant and T is the absolute temperature. Thus, experimental values of the ratio f_r/f_l to be reported here can be compared directly with theoretical predictions[16–18] and with the experimental and calculated values of s_l/s_r for DNA molecules. In addition, a preliminary interpretation of the absolute values of f_l and f_r in terms of the mean-square radii of gyration $\langle s^2 \rangle$ is given, and comparison is made with previous data obtained by small-angle neutron scattering[3]. Furthermore, the chain-length dependence of D, for linear poly(dimethyl siloxane) in toluene, is compared with that found for other polymer–solvent systems[19–21].

The diffusion measurements were carried out using a diffusiometer employing the classical boundary-spreading technique[19], which allows diffusion measurements to be made over a wide range of molecular weights.

EXPERIMENTAL

Preparation of samples

The cyclic and linear poly(dimethyl siloxane) samples were obtained by a range of methods. Samples R1, R2, L1 and L2 (see *Table 1*) were purchased pure. The remaining cyclic fractions were recovered from a poly(dimethyl siloxane) cyclic–linear equilibration reaction in toluene solution[1,14,22]. Fraction R3 was separated by fractional distillation and characterized using gas–liquid chromatography (g.l.c.). Fractions R4–R9 were separated and characterized using preparative and analytical g.p.c.[2]. The linear poly(dimethyl siloxane) fractions were recovered from Dow Corning DC 200 series Dimethicones, using fractional distillation (fractions L3–L5) and preparative g.p.c. (fractions L6–L9). Fractions L3–L5 and L6–L9 were characterized using g.l.c. and g.p.c., respectively. The heterogeneity indices of all the fractionated samples were in the range $1.02 < \bar{M}_w/\bar{M}_n < 1.08$.

Diffusion measurements

The diffusiometer was a modified Perkin–Elmer electrophoresis apparatus, employing free diffusion from an initially sharp boundary between solution and solvent. The spreading of the boundary with time was followed with the aid of Rayleigh interference fringes. A modified, greaseless Tiselius cell was used[23] and the boundary between solvent and solution was formed by layering and then sharpening, using the capillary-siphoning procedure described by Kahn and Polson[24]. Such a procedure enables diffusion in a wide range of solvents to be studied as the cell has no moving parts and, in contrast to a conventional Tiselius cell, grease is not required to lubricate surfaces during boundary formation. Fringes were photographed at various times during an experiment and the plates were measured using Longsworth's procedure[25]. The diffusion cell was thermostatically controlled to within ±0.01K in a small insulated jacket connected to a water bath and circulating pump. The solvent used was fresh Analar-grade toluene. The precision of the method is sensitive to the difference in refractive index between solution and solvent. In order to obtain a precision of about 0.1%, the concentrations used were in the range 2.5–3.0% (w/w).

RESULTS AND DISCUSSION

Concentration dependence of the diffusion coefficient

The concentration dependences of samples L3 and R2 and a chain fraction with $\bar{n}_n = 49$ (used only for this part of the work) have been determined and are shown graphically in *Figure 1*.

The diffusion coefficients refer to the mean concentrations, $\bar{c} = c/2$, where c is the concentration of the solution in g of solute/100 g of solution. The straight lines in *Figure 1* are taken to be typical of the concentration dependences expected for the complete range of fractions used in the present work. It can be seen that there is no marked difference between the concentration dependences of rings and chains. Furthermore, extrapolation of the data to infinite dilution from the values of $\bar{c}$ used (see *Table 1*), would typically increase the absolute values of the diffusion coefficient, D, by about 2%. For these reasons, and because

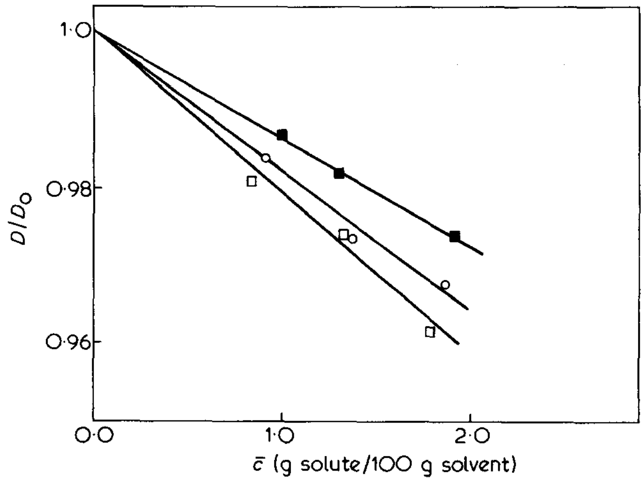

Figure 1 Concentration dependences of samples L3 (○), R2 (■) and a chain fraction with $\bar{n}_n = 49$ (□) in toluene at 298K. D/D_0 = value of D at $\bar{c}$ relative to extrapolated value at infinite dilution (D_0)

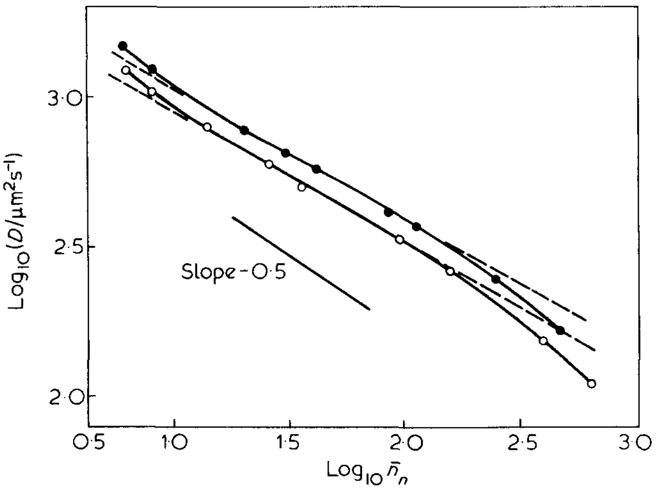

Figure 2 $\log_{10}D$ for linear (○) and cyclic (●) poly(dimethyl siloxanes) in toluene at 298K plotted against $\log_{10}\bar{n}_n$. The straight lines were constructed using a linear least-squares procedure over the range $15 < \bar{n}_n < 100$

of the length of classical diffusion experiments, extrapolation to infinite dilution has not been attempted and all diffusion coefficients refer to the mean concentrations given in *Table 1*. More importantly, because of the similarities between the concentration dependences found, relative values of D have maximum uncertainties of only ±0.5% as compared with relative values at infinite dilution. This uncertainty is negligible for considerations of the variation of D with chain length.

Diffusion coefficients of linear and cyclic polymers and the ratio f_r/f_l

The diffusion data for the linear and cyclic poly(dimethyl siloxane) samples studied are summarized in *Table 1*.

In *Figure 2*, $\log_{10}D$ is plotted against $\log_{10}\bar{n}_n$ for the linear and cyclic poly(dimethyl siloxane) samples. At intermediate molecular weights the data can best be represented by straight lines, and the gradients of the straight-line portions of the plots for the linear and cyclic polymers in *Figure 2* are essentially identical at -0.436 ± 0.002 and -0.434 ± 0.002, respectively.

The ratio f_r/f_l ($= D_l/D_r$) has been predicted to be 0.85 for cyclic and linear molecules of the same molecular weight in the absence of free-draining and excluded volume effects[17]. The least-squares lines from *Figure 2* give a value of 0.84 ± 0.01 for this ratio in the range $15 < \bar{n}_n < 100$.

For free-draining flow, the chain segments behave as independent, hydrodynamic entities and f is determined solely by the number of segments and their friction coefficient (ζ). Hence, $f = n\zeta$, and assuming ζ is the same for segments in linear and cyclic molecules, $f_r = f_l$. In this work the ratio f_r/f_l shows no tendency to unity with decreasing $\bar{n}_n$, clearly indicating that the free-draining contribution to the total diffusion radius is negligible[21]. This conclusion is supported by the fact that the slopes of the straight lines in *Figure 2* are close to the value of −0.5 expected for completely impermeable behaviour[19–21].

The upward curvature at low molecular weights appears to be due to the assumption that $\bar{n}_n$ is proportional to a diffusion radius, and the deviations from linearity at high molecular weights are believed to be due to the onset of excluded volume effects. The latter cause a relative increase in the effective hydrodynamic radius of the molecule and a corresponding decrease in the diffusion coefficient. The effect of excluded volume appears to be approximately the same for rings and chains and commences at $\bar{n}_n \cong 100$, as observed previously for poly(dimethyl siloxanes) in toluene and cyclohexane[1,14,15].

Excluded volume effects

The effect of excluded volume on the ratio f_r/f_l appears to be negligible. For $\bar{n}_n \cong 500$, the ratio f_r/f_l, estimated from *Figure 2*, is 0.83 ± 0.01. This is in satisfactory agreement with the predictions of Fukatsu and Kurata[17], whose first-order perturbation calculations indicate that in a θ-solvent, $f_r/f_l = 8/3\pi = 0.85$, and that this ratio is approximately independent of excluded volume effects. The expression for f_r/f_l, derived by Fukatsu and Kurata, is:

$$f_r/f_l = \frac{8}{3\pi}(1 + 0.021z - \ldots) \tag{2}$$

where z is the normal excluded volume parameter[26]. Thus, f_r/f_l would be expected to increase slightly with molecular expansion. In addition, Bloomfield and Zimm[16] and later Kumbar[18], using the Rouse–Bueche–Zimm model of a chain, predict a greater sensitivity of f_r/f_l to excluded volume. For flexible chains, such as in synthetic polymers with simple skeletal structures, f_r/f_l increases from 0.85 to 0.87 as ϵ in the expression $\langle r^2\rangle \propto N^{1+\epsilon}$ changes from 0 to 0.2. The apparent slight decrease in f_r/f_l with increase in molecular expansion, found experimentally in the present work, is within the limits of experimental error and is not considered to be significant.

The experimental value of $f_r/f_l = 0.84 \pm 0.01$ for the poly(dimethyl siloxanes) may also be compared with the experimental values of 0.91 for polyoma virus DNA[10] and 0.88 for λ DNA[11]. The values of f_r/f_l are markedly greater for the circular DNA molecules than for the poly(dimethyl siloxanes). In this context, it may be noted that Gray, Bloomfield and Hearst[12] have been able to calculate the value 0.90 for polyoma virus DNA and 0.89 for λ DNA only by assuming that the DNA molecule behaves as a stiff, wormlike coil.

Values of the expansion factor α_f, resulting from excluded volume effects, can be estimated for fractions L8, L9, R8 and R9 (see *Figure 2*), using the relation:

$$\alpha_f = \frac{f}{f_\theta} \tag{3}$$

where f_θ is the friction coefficient of the unperturbed chain, calculated by extrapolation of the least-squares lines in *Figure 2*. The values of α_f obtained in this way are compared in *Table 2* with those of α_η calculated from previously published viscosity data[1].

Table 2 Values of the expansion factors α_f and α_η for linear and cyclic poly(dimethyl siloxanes)

Fraction	$\bar{n}_n$	α_f	α_η^*
L8	388	1.18	1.19
L9	631	1.34	1.24
R8	245	1.07	1.06
R9	477	1.21	1.12

* Interpolated from published data[1]

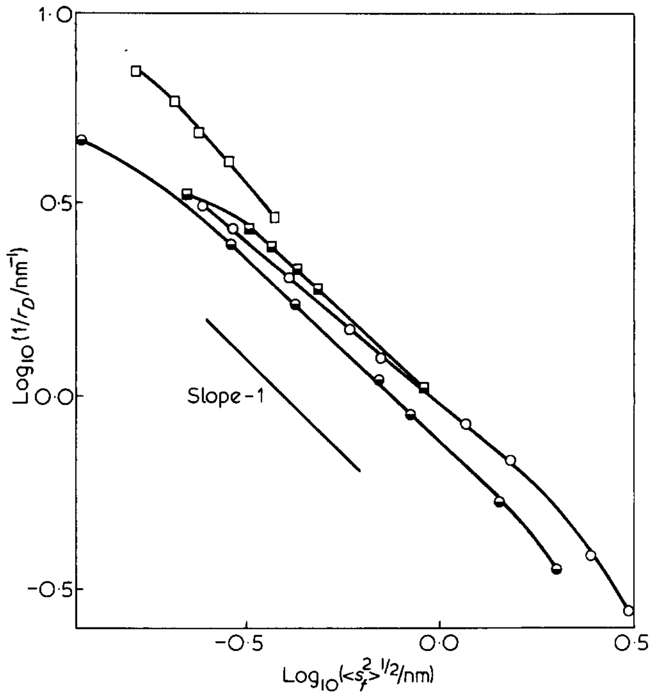

Figure 3 Log$_{10}$(l/r_D) plotted against log$_{10}\langle s_f^2\rangle^{1/2}$ for linear polymers at 298K. Poly(dimethyl siloxane)/toluene (○); polymethylene/benzene[20] (□); poly(ethylene oxide)/water[19,27] (◒) and poly(hexamethylene oxide)/quinoline[21] (⬓)

Following Yamakawa[26], the first-order perturbation expressions for α_f and α_η for linear molecules are as follows:

$$\alpha_f = 1 + 0.609\,z - \ldots \qquad (4)$$

$$\alpha_\eta = 1 + 0.517\,z - \ldots \qquad (5)$$

It can be seen from *Table 2* that for small excluded volume effects (fractions L8 and R8) α_f is sensibly equal to α_η. For the linear fraction L9 with a larger excluded volume effect, $\alpha_f > \alpha_\eta$, in qualitative accord with equations (4) and (5).

Comparison with previous diffusion studies

In *Figure 3*, the diffusion data obtained for the linear poly(dimethyl siloxane) samples are compared with data previously obtained for the systems poly(ethylene oxide)–water[19,27], polymethylene–benzene[20], and poly(hexamethylene oxide)–quinoline[21]. The results[27] for the two samples of longest chain length for the system poly(ethylene oxide)–water have not been published previously. The logarithmic plots show reciprocal Stokes–Einstein diffusion radii ($1/r_D$) as a function of root mean-square free-rotation radii of gyration ($\langle s_f^2\rangle^{1/2}$). The ordinate is derived from the familiar equation:

$$D = kT/6\pi\eta_0 r_D \qquad (6)$$

and has been chosen[21] to remove the gross effects of solvent viscosity on the diffusion coefficient. The abcissa is taken as representing the 'core' dimension of an impermeable chain[21]. The data for cyclic poly(dimethyl siloxanes) are not included, as computational methods for calculating the radii of gyration of ring molecules are still being developed in our laboratories.

It is interesting to note that the use of $\langle s_f^2\rangle^{1/2}$ rather than $\bar{n}_n$ removes the pronounced upward curvature at low molecular weight seen in *Figure 2*. The linear poly(dimethyl siloxanes) in toluene show similar diffusion behaviour to the systems poly(ethylene oxide)–water and poly(hexamethylene oxide)–quinoline. The slopes of these plots are all approximately equal to or just less than −1, indicating impermeable behaviour at all chain lengths[21], and supporting the previous conclusion that the poly(dimethyl siloxanes) are showing impermeable diffusion behaviour in toluene (see *Figure 2*).

By contrast, the system polymethylene–benzene has a slope considerably greater than −1 and can be taken as approximately representative of Kirkwood–Riseman behaviour[21], with the free-draining contribution increasing in importance with decreasing chain length.

In *Figure 3*, the curvature characteristic of the onset of excluded volume effects is occurring at $\bar{n}_n \cong 100$ for the poly(dimethyl siloxanes), as has been previously observed in cyclization studies[14,15]. However, for poly(ethylene oxide) at 298K excluded volume effects do not apparently become important until $\bar{n}_n \cong 250$. This is a reflection of the relatively smaller effects of excluded volume for poly(ethylene oxide) at 298K.

Dimensions of linear and cyclic poly(dimethyl siloxanes) in solution

Assuming impermeable behaviour, the diffusion data for linear poly(dimethyl siloxanes) can be used to calculate mean-square radii of gyration $\langle s_{G,l}^2\rangle$ using a relation[21] derived from Kirkwood–Riseman theory[28]:

$$\langle s_l^2\rangle^{1/2} = \psi_l(x) r_{D,l} \qquad (7)$$

where $r_{D,l}$ is the diffusion radius for a chain of x segments. In the Gaussian limit[21] ($x \to \infty$), $\psi_l(x) = 8/3\pi^{1/2}$ and hence apparent values of $\langle s_{G,l}^2\rangle$ can be calculated for the linear poly(dimethyl siloxanes).

A similar expression is proposed for ring molecules, namely:

$$\langle s_{G,r}^2\rangle^{1/2} = \psi_r(x) r_{D,r} \qquad (8)$$

with

$$r_{D,r} = f_r/6\pi\eta_0 \qquad (9)$$

Taking $f_r/f_l = 8/3\pi$ and $\langle s_r^2\rangle/\langle s_l^2\rangle = 0.5$[29], then equations (7)

Table 3 Diffusion radii, r_D, calculated unperturbed mean-square radii of gyration, $\langle s_{0,l}^2\rangle$, and mean-square radii of gyration derived from diffusion data: (i) in the Gaussian limit, $\langle s_{G,l}^2\rangle$; and (ii) using the values of $\psi_l(x)$ for polymethylene chains, $\langle s_l^2\rangle$

$\bar{n}_n$	r_D (nm)	$\langle s_{0,l}^2\rangle$ (nm^2)	$\langle s_{G,l}^2\rangle$ (nm^2)	$\langle s_l^2\rangle$ (nm^2)	$\psi_l(x)$[21]
6	0.319	0.0739	0.230	0.0598	0.767
8	0.369	0.112	0.308	0.105	0.877
14	0.494	0.247	0.552	0.278	1.067
26	0.671	0.549	1.018	0.684	1.233
36.5	0.800	0.811	1.447	1.08	1.299
94	1.180	2.35	3.15	2.83	1.426
160	1.484	4.12	4.98	4.84	1.482
388	2.631	10.21	15.65	15.68	1.505
631	3.634	16.69	29.86	29.91	1.505

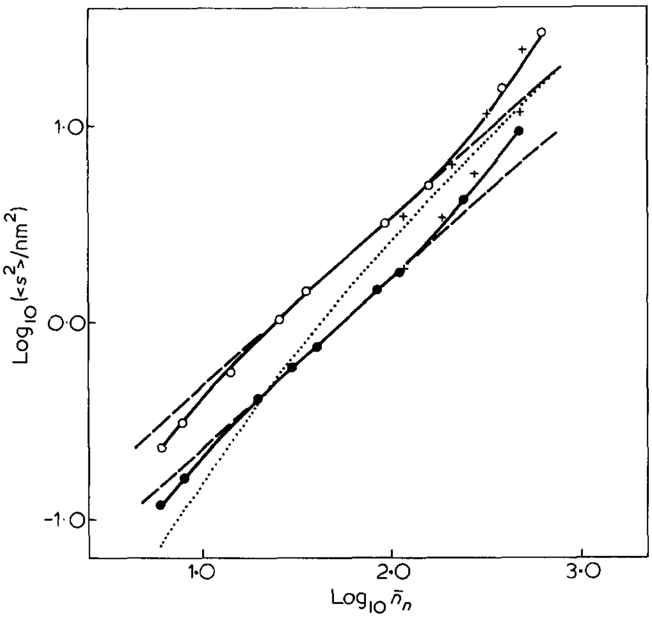

Figure 4 $\log_{10}\langle s^2\rangle$ plotted against $\log_{10}\bar{n}_n$ for linear and cyclic poly(dimethyl siloxanes); apparent values of $\langle s^2_{G,l}\rangle$ and $\langle s^2_{G,r}\rangle$ obtained from diffusion data in the Gaussian limit (see text), linear (○) and cyclic (●); $\langle s^2\rangle_z$ from neutron scattering measurements (+)[3]. Linear extrapolations of central portions of the experimental curves (— — — —). $\langle s^2_{0,l}\rangle$ values, calculated using Flory, Crescenzi and Mark's rotational-isomeric-state model[30] (. . . . .)

and (8) give $(2/\pi)^{1/2}$ as the limiting value of $\psi_r(x)$*. Thus, equation (8) may be used to calculate $\langle s^2_r\rangle$ from the experimental values of $r_{D,r}$.

Such a use of equation (8) is justified, at least for $\bar{n}_n > 100$, as (i) $f_r/f_l = 0.84 \pm 0.01$ in the range of $\bar{n}_n$ studied (see *Figure 2*), as compared with the value of 0.85 assumed above, and (ii) $\langle s^2_r\rangle_z/\langle s^2_l\rangle_z \cong 0.5$ in the range $100 < \bar{n}_n < 500$ as found by neutron scattering[3].

The apparent mean-square radii of gyration obtained from equations (7) and (8) and denoted $\langle s^2_{G,l}\rangle$ and $\langle s^2_{G,r}\rangle$ are shown in *Figure 4* with $\log_{10}\langle s^2\rangle$ plotted against $\log_{10}$ $\bar{n}_n$ for the linear and cyclic poly(dimethyl siloxanes). Mean-square radii of gyration obtained previously by small-angle neutron scattering[3] are also shown in *Figure 4*. The agreement between the data is good, supporting the various assumptions made in the present calculations.

The dotted line in *Figure 4* represents values of $\langle s^2_{0,l}\rangle$ calculated for the linear poly(dimethyl siloxanes) using Flory, Crescenzi and Mark's rotational isomeric state model[30]. At high chain lengths, there is good agreement between the calculated values of $\langle s^2_{0,l}\rangle$ and the extrapolated unperturbed mean-square radii of gyration (represented by the upper dashed line in *Figure 4*). However, with decreasing chain length there is an increasing discrepancy between the calculated values of $\langle s^2_{0,l}\rangle$ and the experimental values of $\langle s^2_{G,l}\rangle$. The disagreement is thought to arise from the deviations from Gaussian statistics shown by short chains.

In an earlier paper[21], Kirkwood–Riseman diffusion radii $(x^2/[R^{-1}])$ have been calculated for short polymethylene chains at 298K and $\psi_l(x)$ in the expression:

$$\langle s^2_l\rangle^{1/2} = \psi_l(x)(x^2/[R^{-1}]) = \psi_l(x)r_{D,l} \tag{10}$$

(see previous footnote) could be evaluated down to short chain lengths. Using the same values of $\psi_l(x)$, the mean-square radii of gyration, $\langle s^2_l\rangle$, have been recalculated using equation (7), for the linear poly(dimethyl siloxanes). The values of $\langle s^2_l\rangle$ calculated in this way are given in *Table 3*, together with the apparent values of $\langle s^2_{G,l}\rangle$ calculated previously.

In *Figure 5*, values of $\log_{10}\langle s^2_l\rangle$ are plotted against $\log_{10}$ $\bar{n}_n$. The agreement between the values of $\langle s^2_l\rangle$ from diffusion data and those from neutron scattering is improved in the region $\bar{n}_n > 100$. Also there is far better agreement between the values of $\langle s^2_l\rangle$ and $\langle s^2_{0,l}\rangle$ than that found previously (see *Figure 4*).

Thus, the use of values of $\psi_l(x)$ appropriate for polymethylene chains with the linear poly(dimethyl siloxanes) appears to be justified. While $\psi_l(x)$ will depend on chain structure, such dependence appears to be of secondary importance. In addition, the improved agreement with the neutron scattering data at longer chain lengths indicates that deviations from equation (7) (due to excluded volume and chain structure variations) are less important than deviations resulting from the use of the limiting value of $\psi_l(x)(=8/3\pi^{1/2})$.

CONCLUSIONS

The ratio of friction coefficients for linear and cyclic poly(dimethyl siloxane)(f_r/f_l) is found to be relatively insensitive to chain length, indicating impermeable diffusion behaviour (see *Figure 2*), even for chains with as few as ten skeletal bonds. Such behaviour is confirmed by a comparison of the present results for linear poly(dimethyl siloxane) with those for other polymer–solvent systems (see *Figure 3*). In

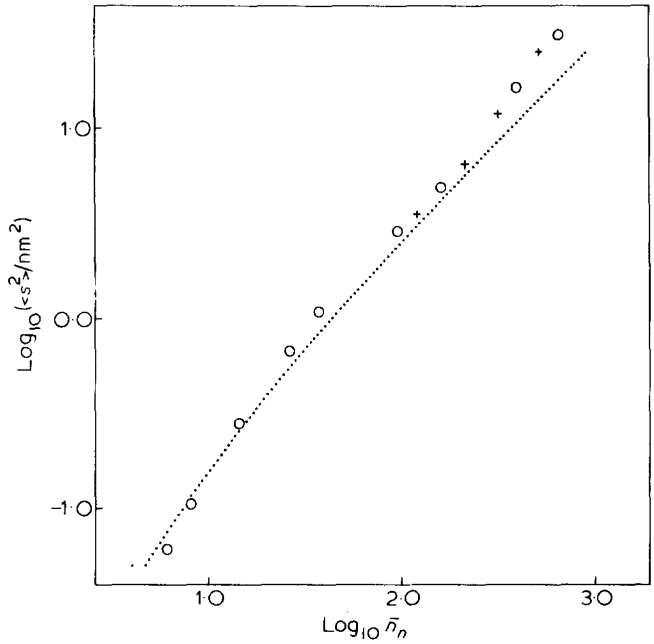

Figure 5 $\log_{10}\langle s^2\rangle$ plotted against $\log_{10}\bar{n}_n$ for linear poly(dimethyl siloxanes); $\langle s^2_l\rangle$ derived from diffusion data using the $\psi_l(x)$ values listed in *Table 3* (○); $\langle s^2\rangle_z$ from neutron scattering measurements[3] (+); $\langle s^2_{0,l}\rangle$ values, calculated using Flory, Crescenzi and Mark's rotational-isomeric-state model[30] (. . . . .)

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* These assumptions define the function $\psi_r(x)$ in the Gaussian limit. In general[21], $\psi(x) = \langle s^2\rangle^{1/2}/r_D = \langle s^2\rangle^{1/2}/(x^2/[R^{-1}])$, where

$$[R^{-1}] = \sum_{i\neq j} r_{ij}^{-1}$$

and r_{ij} is the instantaneous separation of segments i and j. Thus $\psi(x)$ may be considered to be the ratio of the effective equilibrium radius and the effective impermeable diffusion radius of a molecule.

Table 4 Properties of cyclic and linear poly(dimethyl siloxanes) unperturbed by excluded volume effects

Ratio of the property for ring (*r*) and linear (*l*) polymers*	Experimental value for temperatures in the range 292–298K	Theoretical prediction
Number-average molecular weights of rings and chains with the same g.p.c. distribution coefficients M_r/M_l	1.24[4,31] (±0.04)	1.26[32–33]
Limiting viscosity numbers $[\eta]_r/[\eta]_l$	0.67[1] (±0.01)	0.66[16,17,35]
Mean-square radii of gyration $\langle s_r^2\rangle_z/\langle s_l^2\rangle_z$	0.53[3] (±0.05)	0.50[29,36,37]
Bulk viscosities η_r/η_l	0.51–0.45[5]† (±0.02)	0.50[38]‡
Translational friction coefficients f_r/f_l	0.84 § (±0.01)	0.85[16–18]

* Except for M_r/M_l all the ratios refer to cyclic and linear polymers containing the same number of skeletal bonds

† For poly(dimethyl siloxanes) with $16000 < \bar{M}_w < 24000$

‡ In the absence of entanglements

§ This study

Figure 2, the ratio f_r/f_l is shown to be relatively insensitive to excluded volume effects. The value obtained for this ratio is in overall agreement with the theoretical predictions for molecules unperturbed by excluded volume effects.

In translational diffusion, excluded volume effects are shown to become significant for values of $\bar{n}_n$ greater than ~100, for both cyclic and linear poly(dimethyl siloxanes) in toluene at 298K. Values of the expansion factor for linear and cyclic poly(dimethyl siloxanes), α_f, are generally larger than those deduced from measurements of limiting viscosity numbers, α_η. First-order perturbation theory is in qualitative agreement with this result for the linear molecules. However, a more detailed analysis of α_f awaits further experimental data, as well as more accurate theoretical treatments.

Absolute values of the mean-square radii of gyration for linear and cyclic poly(dimethyl siloxanes) ($\langle s_l^2\rangle$ and $\langle s_r^2\rangle$) have been calculated from the diffusion data, using an approximate analysis based on impermeable Kirkwood–Riseman behaviour. For linear molecules, the analysis assumes that the relationship between equilibrium and diffusion radii is independent of chain structure, and for cyclic molecules uses the experimental relationships $f_r/f_l = 8/3\pi$ and $\langle s_r^2\rangle/\langle s_l^2\rangle \cong 0.5$. In the highest molecular weight range, agreement between $\langle s_l^2\rangle$ and $\langle s_r^2\rangle$ and the corresponding $\langle s^2\rangle_z$ values obtained by neutron scattering is excellent. At lower molecular weights, good agreement is achieved between $\langle s_l^2\rangle$ values and those calculated using Flory, Crescenzi and Mark's rotational-isomeric-state model. A more detailed analysis of the experimental data awaits calculations of the relationships between equilibrium and hydrodynamic diffusion radii for linear and cyclic poly(dimethyl siloxanes), as well as calculations of $\langle s_{0r}^2\rangle$ for the cyclic polymers.

In *Table 4,* experimental and theoretical values for the ratios of some other properties of cyclic and linear poly(dimethyl siloxanes) are listed together with results from the present study. All the data refer to polymers unperturbed by excluded volume effects. The experimental results shown are all in excellent agreement with the theoretical predictions of Kramers, Zimm, Stockmayer, Bueche, Casassa and others[16–17,32–38] and further investigations of cyclic polymers are in progress.

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