Studies of cyclic and linear poly(dimethyl siloxanes): 3. Neutron scattering measurements of the dimensions of ring and chain polymers

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The dimensions of both cyclic and linear poly(dimethyl siloxanes) in dilute solution in benzene-d_6 have been measured by small-angle neutron scattering. The mean-square radii of gyration of the linear polymers are consistent with values predicted from published data, including experimental molar cyclization equilibrium constants. The average dimensions of the cyclic poly(dimethyl siloxanes) in fractions containing z-average numbers of bonds $\bar{n}_z$ in the range $130 < \bar{n}_z < 550$, were found to be considerably smaller than those of the corresponding linear polymers. The neutron scattering results give a value for the ratio of the z-average radii of gyration for linear and ring poly(dimethyl siloxanes) (containing the same number of monomer units) $\langle s^2\rangle_{z,l}/\langle s^2\rangle_{z,r} = 1.9 \pm 0.2$. This ratio may be compared with the value of 2.0 predicted theoretically for 'flexible' high molecular weight linear and cyclic polymers, unperturbed by excluded volume effects.

INTRODUCTION

Recently, we have initiated a general investigation of the preparation and properties of synthetic cyclic polymers. In Parts 1 and 2 of this series, fractions of cyclic (and also linear) poly(dimethyl siloxanes) were prepared and characterized, and their hydrodynamic properties studied[1,2]. In this paper, we report the first measurements of the average dimensions of random-coil cyclic polymers in solution. Small-angle neutron scattering was used for these measurements. Although this technique has only recently been applied to polymer systems, it has proved a valuable addition to the older X-ray and light scattering methods because of the different 'contrast factors' and range of scattering vectors available[3–5]. In particular, the large differences between the neutron scattering properties of hydrogen and deuterium atoms have made possible observation of single chains in bulk and in solution environments[6–8]. For the studies reported here, the large 'contrast' has made measurements on the relatively low molecular weight samples feasible[9].

The cyclic poly(dimethyl siloxanes) $[(CH_3)_2SiO]_x$ studied were fractions with weight-average values of x in the range $65 < \bar{x}_w < 275$. The linear poly(dimethyl siloxanes) $(CH_3)_3SiO[(CH_3)_2SiO]_ySi(CH_3)_3$ studied for purposes of comparison were fractions with weight-average values of y in the range $65 < \bar{y}_w < 280$. The heterogeneity indices of all the cyclic and linear fractions were in the range $1.04 < \bar{M}_w/\bar{M}_n < 1.06$. All the cyclic fractions are believed to contain less than 5% (w/w) linear polymer, and for the purposes of this study they were considered to be chain-free (see later).

EXPERIMENTAL

Preparation of the samples

The cyclic and linear poly(dimethyl siloxane) fractions studied were prepared and characterized using preparative and analytical gel permeation chromatography (g.p.c.) as described in Part 2 of this series[2]. The cyclic poly(dimethyl siloxanes) were recovered from a poly(dimethyl siloxane) cyclic–linear equilibration reaction in toluene solution at 383 K. The equilibrate used contained a total of 1029.3 g of dimethyl siloxanes at a concentration of 223.2 g dm^{-3}. The extent of reaction of functional groups p in the high molecular weight linear siloxane part of the equilibrate (present at a concentration of 20.35 g dm^{-3}) was determined viscometrically and found to be 0.9996. This p value was used to calculate an upper limit for the linear siloxane concentration in each of the cyclic fractions. For details of this procedure see ref 2.

The linear poly(dimethyl siloxane) fractions were obtained by preparative g.p.c. fractionation of Dow Corning DC 200 series Dimethicones.

The molecular weight averages and heterogeneity indices of the cyclic fractions R1–R4 and the linear fractions L1–L4 are given in *Table 1*. The calculated upper limits of linear siloxane concentrations in the cyclic fractions are also given in *Table 1*.

Benzene-d_6 solvent (C_6D_6, 99.5% D) was used without further purification. All the sample solutions were made up by weighing the solute and the solvent individually.

Neutron scattering measurements

The neutron scattering measurements were carried out

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Table 1 Molecular weights and radii of gyration $\langle s^2\rangle_{z,c=0}^{1/2}$ of the cyclic (RI–R4) and linear (L1–L4) poly(dimethyl siloxane) fractions

Fractions	$\bar{M}_z$*	$\bar{M}_w/\bar{M}_n$*	$\bar{M}_z/\bar{M}_w$*	$\langle s^2\rangle_{z,c=0}^{1/2}$ (Å) at 292 K
R1†	4950	1.05	1.05	13.7
R2	7540	1.05	1.05	18.5
R3	11 640	1.06	1.06	23.7
R4	20 210	1.04	1.04	34.1
L1	4990	1.05	1.05	18.6
L2	8670	1.05	1.06	25.2
L3	12 890	1.05	1.05	33.8
L4	20 880	1.05	1.05	49.4

* $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_z$ denote number-average, weight-average and z-average molecular weights, respectively

† Concentrations of linear siloxanes in the cyclic fractions were calculated as described previously[2]. They are 0.13% for R1, 0.43% for R2, 1.39% for R3 and 4.61% for R4

using the small-angle scattering apparatus D11 at the Institute Laüe–Langevin, Grenoble, France[10]. Solutions of the cyclic and linear poly(dimethyl siloxane) fractions R1, R2, L1 and L2 in dilute solution in benzene-d_6 at 292K were placed in 2 mm quartz cells at a distance of 2.503 m from the detector, in order to observe the range of solid angles θ from $1.83° < \theta < 8.42°$. The incident neutron beam was monochromated to a wavelength $\lambda = 9.96$ Å (resolution $\Delta\lambda/\lambda = 8\%$). Hence, the wave vector Q[5] :

$$Q = \frac{4\pi}{\lambda}\sin\frac{\theta}{2} \tag{1}$$

was in the range $0.02 < Q < 0.093$ Å^{-1}. For solutions of the fractions R3, R4, L3 and L4 in benzene -d_6 at 292K, the distance from the sample to the detector was 10.503 m and the incident neutron beam was monochromated to a wavelength $\lambda = 6.01$ Å. In this case, the solid angles observed were in the range $0.44° < \theta < 2.01°$. This gives the scattering vector Q in the range $0.008 < Q < 0.037$ Å^{-1}.

Determination of the radii of gyration of the cyclic and linear poly(dimethyl siloxanes)

The scattering observed on the detector was found to be isotropic in all experiments. Therefore, the measured neutron counts were integrated over equal radial distances from the centre of the detector to give a radial distribution of scattering intensities. The distribution of scattering intensities resulting from the dissolved polymer in each of the solutions studied was obtained by subtracting the background distribution of scattering intensities produced by pure benzene-d_6. The distributions of polymer scattering intensities obtained in this way were each normalized using the incoherent scattering produced by a sample of pure water (for details of this procedure see Jacrot[11]). The normalized scattering intensities $I(Q)$ for a monodisperse polymer sample are given by an equation in the form due to Zimm[3–5,12]:

$$\frac{Kc}{I(Q)} = \frac{1}{M}\left\{1 + \frac{Q^2\langle s^2\rangle}{3}\right\} + 2A_2c \tag{2}$$

where M is the molecular weight of the polymer, c is the concentration, $\langle s^2\rangle$ is the mean-square radius of gyration and A_2 is the second virial coefficient. The constant K contains instrumental parameters and a contrast factor for neutrons. Equation (2) is applicable in the Guinier region, where $Q\langle s^2\rangle^{1/2} \leqslant 1$. For a polydisperse polymer system, the values of M and $\langle s^2\rangle$ appearing in equation (2) are replaced by the weight-average molecular weight $\bar{M}_w$ and the z-average mean-square radius of gyration $\langle s^2\rangle_z$.

The z-average radii of gyration $\langle s^2\rangle_z^{1/2}$ for molecules in each of the cyclic and linear poly(dimethyl siloxane) fractions were obtained by plotting $c/I(Q)$ against Q^2 (see *Figure 1*), and using a relationship obtained from equation (2):

$$\langle s^2\rangle_z^{1/2} = \left\{\frac{3 \times \text{Gradient}}{\text{Intercept}}\right\}^{1/2} \tag{3}$$

Benzene-d_6 is expected to be a 'good' solvent for the poly(dimethyl siloxanes) at 292K since benzene is a 'good' solvent for linear poly(dimethyl siloxane) at this temperature[13]. Hence, the experimental $\langle s^2\rangle_z$ values were expected to be concentration-dependent, as a result of excluded volume effects. Therefore, measurements of $\langle s^2\rangle_z$ values were made at four different concentrations for each cyclic and each linear poly(dimethyl siloxane) fraction studied. These concentrations were typically in the range $0.6 < 10^2c < 4.3$ g cm^{-3}. Plots of $1/\langle s^2\rangle_z$ against concentration c were used to obtain values for the mean-square z-average

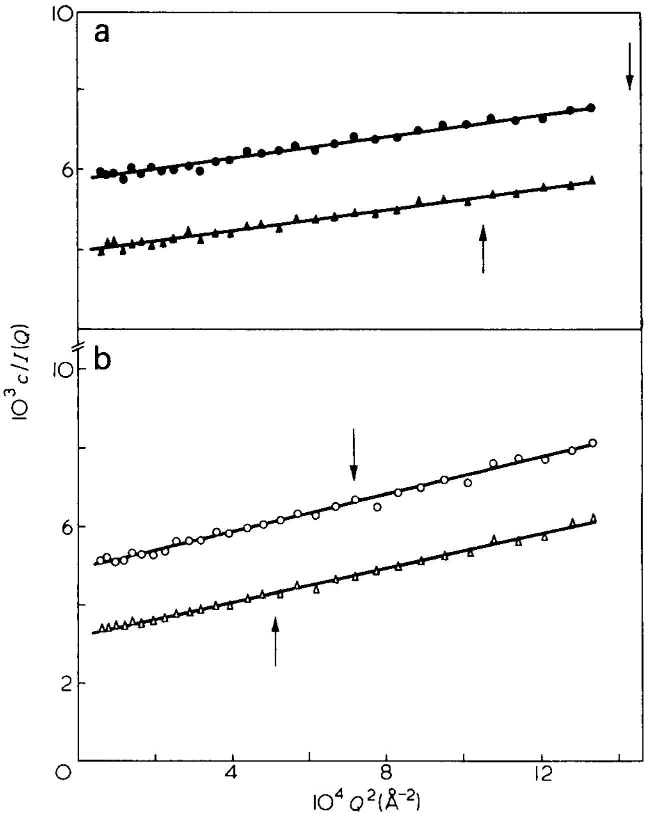

Figure 1 Examples of the effect of concentration on the plots of the inverse neutron scattering intensities $c/I(Q)$ against the scattering vectors Q^2 (with Q^2 in the range $0.06 < 10^3Q^2 < 1.4$) for: (a) a cyclic poly(dimethyl siloxane) fraction R4 at concentrations $c = 0.0349$ and $c = 0.0087$ g cm^{-3} in benzene-d_6 at 292K (denoted by ● and ▲, respectively), and (b) a linear poly(dimethyl siloxane) fraction L4 at concentrations $c = 0.0362$ and $c = 0.0084$ g cm^{-3} in benzene-d_6 at 292K (denoted by ○ and △, respectively). The arrows indicate the upper limits of the Guinier ranges where $Q\langle s^2\rangle_z^{1/2} = 1$

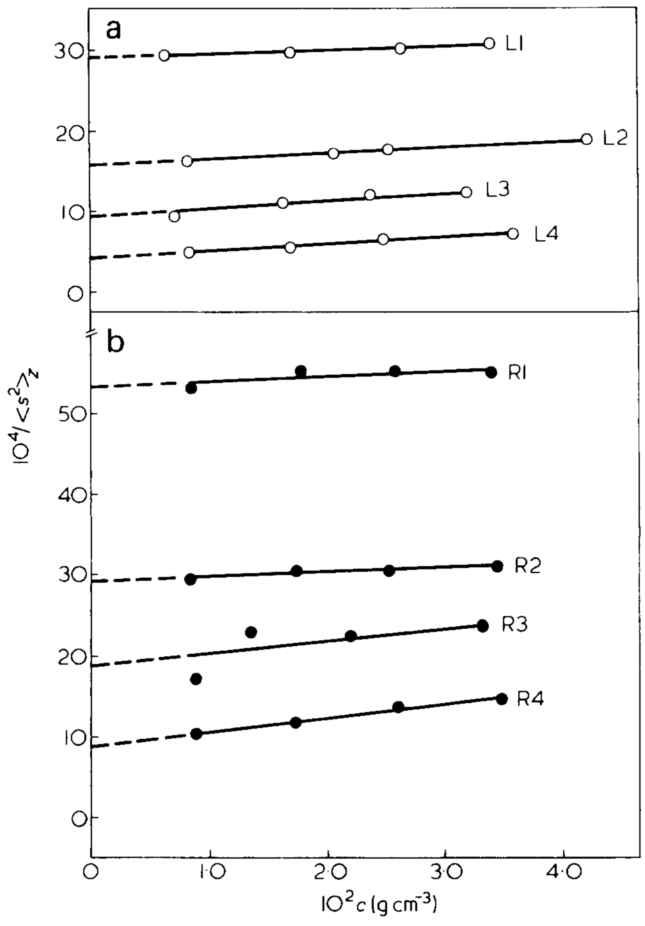

Figure 2 Extrapolation of the reciprocals of the *z*-average mean square radii of gyration $\langle s^2\rangle_z^{-1}$ to zero concentration (according to equation (4), see text): (a) for linear poly(dimethyl siloxane) fractions L1–L4, and (b) for cyclic poly(dimethyl siloxane) fractions R1–R4. All the measurements were made in benzene-d_6 solution at 292K

radii of gyration at infinite dilution $\langle s^2\rangle_{z,c=0}$ (from the intercepts), by making use of the relationship[14] (see *Figure 2*).

$$\frac{1}{\langle s^2\rangle_z} = \frac{1}{\langle s^2\rangle_{z,c=0}}\left\{1 + 2A_2\bar{M}_w Kc\right\} \qquad (4)$$

RESULTS AND DISCUSSION

Small-angle neutron scattering relationships

In *Figure 1*, $c/I(Q)$ values are plotted against Q^2 values for the cyclic and linear fractions R4 and L4. The plots relate to the solutions with the highest and the lowest concentrations that were studied, and they may be represented by straight lines as shown in *Figure 1*. Similar behaviour was observed for all the other fractions over the range of wave-vectors chosen.

The values of the *z*-average radii of gyration $\langle s^2\rangle_z^{1/2}$ for each of the cyclic fractions (R1 – R4) and linear fractions (L1–L4), and at each of the four concentrations studied, were calculated from the gradients and intercepts of the plots of $c/I(Q)$ against Q^2 using equation (3). The $1/\langle s^2\rangle_z$ values were plotted against concentration for each of the cyclic and linear fractions and then extrapolated to zero concentration as shown in *Figure 2*. The values of the *z*-average radii of gyration at infinite dilution $\langle s^2\rangle_{z,c=0}^{1/2}$ for all the fractions were obtained from the intercepts of the plots. They are listed in *Table 1*.

The experimental $c/I(Q)$ values for each of the fractions were also treated by Zimm's method[12]. An example of a Zimm plot for data obtained using the cyclic fraction R4 is shown in *Figure 3*. The scatter in the experimental $c/I(Q)$ values appears to be greater when the data are presented in this form. However, extrapolation of the data to zero concentration yields $\langle s^2\rangle_{z,c=0}^{1/2}$ values which were found to differ by less than 2% from those obtained as described above by applying equation (4).

Using the measured values of $\langle s^2\rangle_z^{1/2}$, the parameter $Q\langle s^2\rangle_z^{1/2}$ was found to fall in the range $0.2 < Q\langle s^2\rangle_z^{1/2} < 1.2$ for the most dilute solution of the cyclic fraction R4. The corresponding range of $Q\langle s^2\rangle_z^{1/2}$ for the most dilute solution of the linear fraction L4 was found to be $0.3 < Q\langle s^2\rangle_z^{1/2} < 1.7$. Although the experimental range of $Q\langle s^2\rangle_z^{1/2}$ exceeds the Guinier limit of $Q\langle s^2\rangle^{1/2} \leqslant 1$ in some cases, the linearity of the relationships shown in *Figure 1* indicates that equation (2) can be considered to apply over the range of scattering vectors used.

Experiments with fractions R4 and L4 were also carried out using a wider range of Q^2 values. The corresponding plots of $c/I(Q)$ against Q^2 are shown in *Figure 4*. In this Figure, the parameter $Q\langle s^2\rangle_z^{1/2}$ is in the range $0.7 < Q\langle s^2\rangle_z^{1/2} < 3.2$ for fraction R4, and $1.0 < Q\langle s^2\rangle_z^{1/2} < 4.6$ for fraction L4. Over a wide range of Q^2 values, the plot of $c/I(Q)$ against Q^2 for a monodisperse solution of a linear polymer chain obeying Gaussan statistics would be expected to show upward curvature as the scattering vector Q is increased from within the Guinier Q range described in equation (2) (i.e. $Q\langle s^2\rangle^{1/2} < 1$) to the high Q range where the following proportionality applies[5]:

$$\frac{1}{I(Q)} \propto \frac{\langle s^2\rangle Q^2}{2} \qquad (5)$$

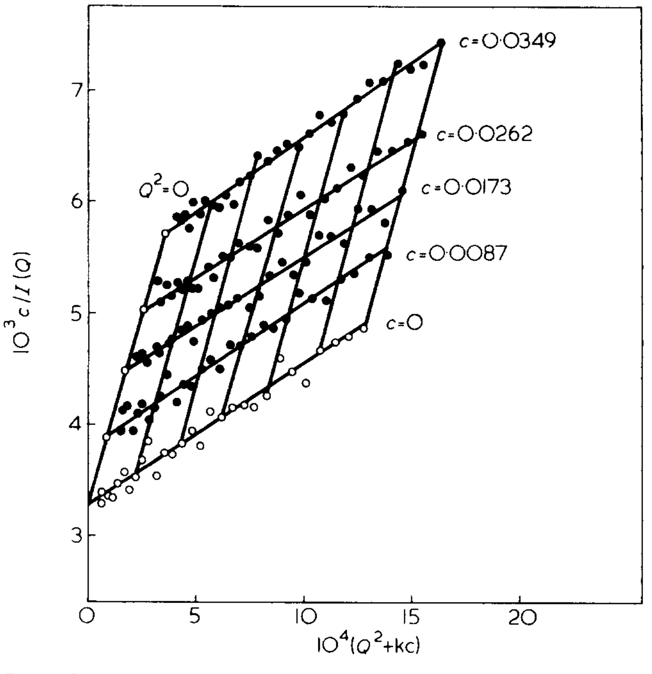

Figure 3 Zimm plot of the neutron scattering data of solutions of the cyclic poly(dimethyl siloxane) fraction R4 at four concentrations in benzene-d_6 at 292K. The closed circles represent the experimental data and the open circles represent the data obtained by extrapolation to zero concentration and zero Q^2. The concentrations are expressed in units of g cm^{-3}

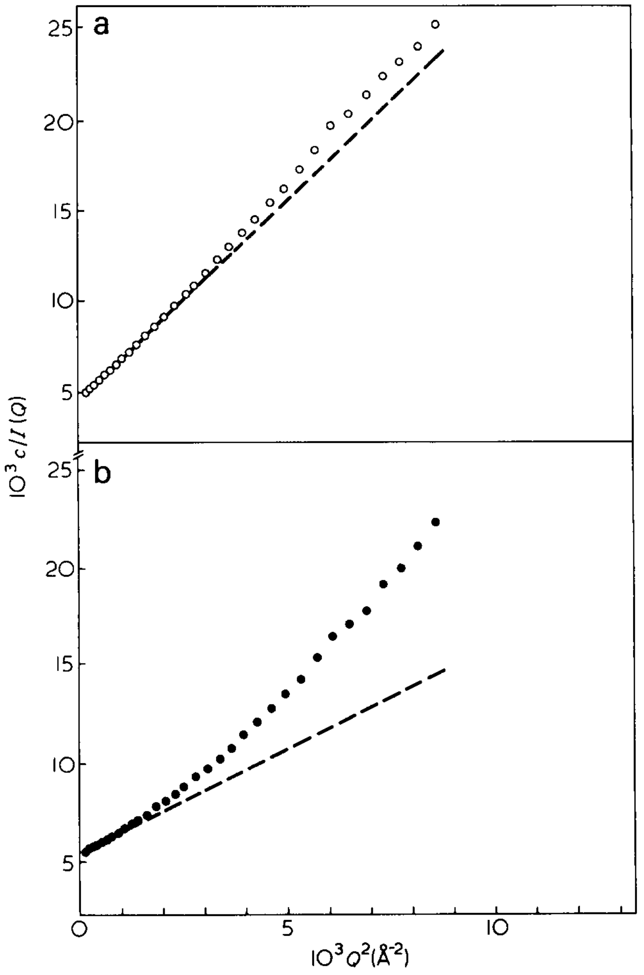

Figure 4 Plots of the inverse neutron scattering intensities $c/I(Q)$ against the scattering vectors Q^2 (with Q^2 in the range $0.4 < 10^3 Q^2 < 8.6$, see text) for: (a) a linear poly(dimethyl siloxane) fraction L4 with z-average molecular weight $\bar{M}_z = 20\,880$ and concentration $c = 0.0362$ g cm^{-3} in benzene-d_6 at 292K, and (b) a cyclic poly(dimethyl siloxane) fraction R4 with $\bar{M}_z = 20\,210$ and $c = 0.0349$ g cm^{-3} in benzene-d_6 at 292K. The broken lines were obtained by extrapolation, using the points in the linear region of the plots

The high Q range is described by the condition $\langle s^2\rangle^{-1/2} < Q < a^{-1}$ where a is a parameter of the polymer chain ('persistence length'). The slope of the plot of $c/I(Q)$ against Q^2 in the high Q range is proportional to $\langle s^2\rangle/2$, which is higher by a factor of 1.5 than the slope in the Guinier Q range where the slope is proportional to $\langle s^2\rangle/3$. Slight upward curvature is observed in the plot of $c/I(Q)$ against Q^2 for the linear poly(dimethyl siloxane) fraction L4 (see *Figure 4a*). The limiting gradient of this plot in the range where $Q^2 > 6 \times 10^{-3}$ Å^{-2} is higher than the limiting gradient in the Guinier Q range by a factor of approximately 1.2.

Casassa[15] has predicted that using low Q values in the Guinier Q range should give plots of $c/I(Q)$ against Q^2 for cyclic polymers that have gradients proportional to $\langle s^2\rangle/6$, which is exactly one half of that for the corresponding linear molecules, whereas in the high Q region the gradients for both cyclic and linear polymers should be the same and proportional to $\langle s^2\rangle/2$. Hence, the limiting gradient of the plot of $c/I(Q)$ against Q^2 for a cyclic polymer in the high Q region should be higher than the limiting gradient in the low Q region by a factor of 3. The plot of $c/I(Q)$ against Q^2 for the cyclic poly(dimethyl siloxane) fraction R4 (see *Figure 4b*) shows pronounced upward curvature in agreement with Casassa's prediction. Furthermore, the limiting gradient of this plot in the range where $Q^2 > 6 \times 10^{-3}$ Å^{-2} is higher than the limiting gradient in the Guinier Q range by a factor close to 3 (i.e. 2.6).

The measured differences between the limiting gradients in the high and low Q ranges of the $c/I(Q)$ against Q^2 plots for fractions R4 and L4 are both somewhat lower than theoretical predictions. This may be because the plots have not been extended to high enough values of Q^2, so that the true limiting gradients have not been attained. In future, it is hoped to examine this feature of the scattering curves more closely.

Ring and chain dimensions in solution

In *Figure 5*, log $\langle s^2\rangle_{z,c=0}$ values are plotted against log $\bar{M}_z$ values for all the cyclic and linear fractions studied. In *Table 2*, $\langle s^2\rangle_{z,c=0}^{1/2}$ values of the linear poly(dimethyl siloxane) fractions in benzene-d_6, which were measured by small-angle neutron scattering, are compared with calculated values deduced from data obtained by other experimental approaches.

The calculated $\langle s^2\rangle_z^{1/2}$ values in *Table 2* were obtained for each poly(dimethyl siloxane) fraction using the equation[16]:

$$\langle s^2\rangle_z = (\bar{M}_w)^{-1}\, \Sigma_i M_i \langle s_i^2\rangle w_i \qquad (6)$$

where w_i is the weight fraction of a poly(dimethyl siloxane) chain with molecular weight M_i and mean-square radius of gyration $\langle s_i^2\rangle$. Values of w_i and M_i were obtained from gel permeation chromatographic tracings, and values of $\langle s_i^2\rangle$ were deduced from the corresponding mean-square end-to-end distances $\langle r_i^2\rangle$ by assuming the relationship[17]:

$$\langle s_i^2\rangle = \langle r_i^2\rangle/6 \qquad (7)$$

This equation, which is known to be valid for very long chain molecules unperturbed by excluded volume effects, should be obeyed to a good approximation by the linear poly(dimethyl siloxanes) considered here.

In column (I) of *Table 2*, $\langle s^2\rangle_z^{1/2}$ values were deduced from end-to-end distances $\langle r_i^2\rangle_0$ which were obtained by the mathematical methods of Flory and Jernigan[18] using the rotational isomeric state model of poly(dimethyl siloxane). This model was set up by Flory, Crescenzi and Mark[19] following viscometric measurements of the dimensions of linear poly(dimethyl siloxanes) under theta-point conditions[20,21].

Table 2 Radii of gyration $\langle s^2\rangle_z^{1/2}$ of the linear (L1–L4) poly(dimethyl siloxane) fractions as measured by neutron scattering compared with values computed using data in the literature

Fractions	z-average number of bonds $\bar{n}_z$	$\langle s^2\rangle_{z,c=0}^{1/2}$ in Å at 292K by neutron scattering	$\langle s^2\rangle_z^{1/2}$ (Å) (I)*	(II)†	(III)†	(IV)†
L1	130.3	18.6	18.9	20.2	21.0	22.2
L2	229.4	25.2	25.5	26.7	28.0	30.8
L3	343.2	33.8	31.4	32.6	34.2	38.6
L4	558.7	49.4	40.4	41.2	43.4	50.7

* (I) $\langle s_0^2\rangle_z^{1/2}$ values at 383K calculated using the Flory, Crescenzi and Mark rotational isomeric state model of poly(dimethyl siloxane) (see text)

† $\langle s^2\rangle_z^{1/2}$ values computed from experimental molar cyclization equilibrium constants measured in the undiluted polymer at 383K (II), in diglyme at 333K (III) and in toluene at 383K (IV) (see text)

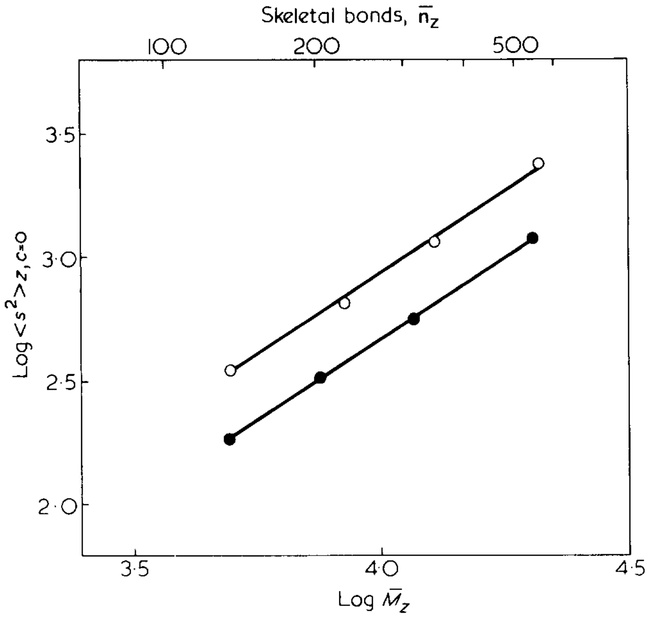

Figure 5 Plots of the logarithms of the z-average mean square radii of gyration $\langle s^2\rangle_{z,c=0}$ at zero concentration of the linear (○) and cyclic (●) poly(dimethyl siloxane) fractions against the logarithms of their z-average molecular weights $\bar{M}_z$ in benzene-d_6 at 292K. The lines shown were constructed using a least squares procedure applied to both sets of data

In columns (II), (III), (IV) values of $\langle s^2\rangle_z^{1/2}$ for chains in the undiluted polymer, in diglyme and in toluene, respectively, were deduced from Wright's [2] experimental molar cyclization equilibrium constants K_x using equation (7) and the Jacobson–Stockmayer[23] expression:

$$K_x = (3/2\pi\langle r_x^2\rangle)^{3/2}(1/2N_A x) \tag{8}$$

where N_A is the Avogadro constant.

As shown in *Table 2,* the experimental neutron scattering $\langle s^2\rangle_{z,c=0}^{1/2}$ values for each linear poly(dimethyl siloxane) fraction are in good agreement with the values calculated from dilute solution and cyclization data, particularly when account is taken of chain expansion by excluded volume effects in the 'good' solvents (benzene-d_6 and toluene). Excluded volume effects have been shown to be present for linear poly(dimethyl siloxanes) with $\bar{n}_z > \sim 100$ in toluene[22], and they would also be expected to be appreciable in benzene-d_6. The $\langle s^2\rangle_{z,c=0}^{1/2}$ values determined by neutron scattering are believed to be accurate to within ±10%, and the $\langle s^2\rangle_z^{1/2}$ values deduced from the cyclization data should be at least as precise, although some uncertainty is associated with them, resulting from the use of equation (7). The effect of temperature on the $\langle s^2\rangle_z^{1/2}$ values is expected to be small because the corresponding $\langle r^2\rangle_0$ values have been found to change by only ~2% over the temperature range 298–383K[19,22].

The ratio $\langle s^2\rangle_l/\langle s^2\rangle_r$ (where l and r refer to linear and ring molecules respectively) is predicted theoretically to be 2.0 for discrete chain and ring molecules containing the same number of bonds and unperturbed by excluded volume effects[15,23]. The least-squares lines for the log $\langle s^2\rangle_{z,c=0}^{1/2}$ against log $\bar{M}_z$ plots shown in *Figure 5* give a value for the ratio:

$$\frac{\langle s^2\rangle_{z,l}}{\langle s^2\rangle_{z,r}} = 1.9 \tag{9}$$

in the region $\bar{n}_z = 500$. For present purposes we shall adopt the approximation recommended by Berry and Casassa[16] for moderately inhomogeneous polymers, that:

$$\frac{\langle s^2\rangle_z}{\bar{M}_z} = \frac{\langle s^2\rangle}{M} \tag{10}$$

where the ratio $\langle s^2\rangle/M$ applies to a homogeneous polymer with M equal to $\bar{M}_z$. Hence, the theoretical ratio for $\langle s^2\rangle_l/\langle s^2\rangle_r$ of 2.0 can be compared directly with the experimental ratio for $\langle s^2\rangle_{z,l}/\langle s^2\rangle_{z,r}$ of 1.9 ± 0.2 (both at infinite dilution).

The results presented in this paper provide support for the validity of the general theoretical approach to the problem of the conformational statistics of 'flexible' cyclic polymers[15,23–25]. However, they do not allow a definite conclusion to be reached as to whether the $\langle s^2\rangle_{z,l}/\langle s^2\rangle_{z,r}$ ratio at infinite dilution is greater or less than 2.0 in 'good' solvent media, such as the benzene-d_6 used here (see ref 15, 26–32 for conflicting predictions). We intend to investigate this question and related matters in future studies.

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