polymer papers

Studies of cyclic and linear poly(dimethyl siloxanes):
12. Observation of diffusion behaviour by quasielastic neutron scattering

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High resolution neutron scattering experiments have been used to observe the diffusive motion of low molecular weight linear and cyclic poly(dimethyl siloxane) molecules in dilute solution in deuterated benzene. Diffusion coefficients (D) and hydrodynamic radii (R_H) have been compared with values obtained by light scattering for higher molecular weight samples and with radii of gyration (R_g) obtained by small-angle neutron scattering. While the ratio D_{ring}/D_{chain} is close to the predicted value of 0.85, the ratio R_g/R_H falls below the theoretical value for both ring and chain molecules. The scattering curves show effects arising from both centre of mass diffusion and internal molecular motion, and the observed inverse correlation times are compared with calculated behaviour as a function of scattering vector, Q.

Keywords Cyclic; linear; poly(dimethyl siloxane); quasielastic neutron scattering

INTRODUCTION

The isolation and characterization of cyclic molecules of poly(dimethyl siloxane), with number average monomer units per molecule $\bar{n} \leqslant 500$ have been described in a series of papers[1-3]. Studies comparing linear and cyclic species in terms of such properties as gel permeation chromatographic retention volumes[2,4], dilute solution[1] and bulk viscosities[5] and radii of gyration in dilute solution[3], show differences which can largely be ascribed to their differing dimensions.

Macroscopic diffusion behaviour has been studied in dilute solution by boundary spreading techniques[6]. The molecular diffusion coefficients of some of the larger molecules have been measured directly by light scattering[7] but the signal is too weak below molecular weights around 10000 ($\bar{n} \simeq 140$). The use of a deuterated solvent provides sufficient contrast for a neutron scattering experiment to detect motion of even the smallest molecules ($\bar{n} \simeq 30$), while the experimentally explored distances are larger than the molecular dimensions and allow centre of mass motion to be followed. We are thus able to compare macroscopic and molecular diffusion coefficients for cyclic and linear molecules over a wide molecular weight range.

DYNAMIC SCATTERING FROM POLYMER MOLECULES

The type of motion observed in a scattering experiment from polymer molecules in dilute solution depends on the frequency and distance scales explored. The frequency scale is limited by the experimental energy resolution, while the distance scale is defined by Q^{-1} where Q, the scattering vector, is inversely proportional to the wavelength of the probing radiation. For reasonably large molecules, centre of mass diffusion has been observed by light scattering[8] (e.g. photon correlation spectroscopy) in the range $QR_g < 1$ where R_g is the radius of gyration of the polymer molecule. Neutron scattering[9] explores rather short distances and is sensitive to local conformational changes ($Q^{-1} < 30$ Å). Motion of such short chain segments is governed by bond lengths and potentials and is therefore sensitive to chemical structure while the long range diffusive motion depends on the molecular dimensions. Between these two extremes the connectivity of the chain leads to a universal behaviour independent of both molecular structure and dimensions where the characteristic frequency is proportional to $(k_BT/\eta_s)Q^3$ where η_s is the solvent viscosity. The range of this universal behaviour is limited at low Q by $QR_g \gg 1$ and at high Q by

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Table 1 Molecular weights of PDMS samples

Linear samples		Cyclic samples	
$\bar{M}_n$	$\bar{n}$	$\bar{M}_n$	$\bar{n}$
1100	24	800	20
2100	54	2000	54
2700	74	2700	73
6400	172	6300	170
15100	408	15400	415

$Q\sigma \ll 1$, where σ is an imprecisely defined length below which chemical structure becomes important. It is conventionally taken to be the statistical segment length. The scattering behaviour in this Q^3 range has been dealt with in some detail by both Pecora[10] and de Gennes[11,12] using concepts introduced by Rouse[13] for a bead-spring model (where σ then becomes the spring length). Zimm[14] subsequently modified the calculation to incorporate the solvent hydrodynamic effects. The Q^3 behaviour of the characteristic frequency is, however, a general result and arises directly from the connectivity of the molecular structure. The range $QR_g > 1$ has been explored in light scattering experiments for very large molecules[15,16] ($M_w > 10^6$, $R > 1000$ Å) while the highest resolution neutron experiments[17] can now achieve $Q\sigma \leqslant 1$. Both light and neutron data are well fitted by calculations of Akcasu *et al.*[18] which extend the calculations of Dubois–Violette and de Gennes beyond the two inequalities $R_g^{-1} < Q < \sigma^{-1}$. For most polymers studied[17] values of σ are apparently of order 20 or larger so that most neutron data lie in the range $Q \geqslant \sigma^{-1}$ where deviation away from Q^3 towards Q^2 behaviour may be observed. For poly(dimethyl siloxane) (PDMS), however, σ is quite short ($\simeq 15$ Å) and a reasonable range of Q^3 behaviour is observed at low Q. However, if R_g is made very small the lower limit appears within the neutron scattering Q range and for small PDMS molecules, therefore, a region of Q^2 behaviour associated with centre of mass diffusion should appear at low Q below the Q^3 behaviour. The results reported here for low molecular weight PDMS molecules were designed to explore this possibility and to look for differences in behaviour of linear and cyclic molecules.

EXPERIMENTAL

Samples

Samples of linear and cyclic poly(dimethyl siloxane) were prepared and characterized using preparative and analytical gel permeation chromatography[6]. Linear samples were obtained by g.p.c. fractionation of the Dow Corning DC200 series Dimethicones, and cyclic fractions recovered from a PDMS cyclic-linear equilibration reaction in toluene solution at 383 K. Benzene-d$_6$ solvent (C_6D_6, 99+ atom % D) as supplied by Aldrich Chemicals was used without further purification.

Table 1 lists the molecular weights ($\bar{M}_n$) and corresponding number average numbers of backbone bonds ($\bar{n}$) for the samples used. In all cases the polydispersity ($\bar{M}_w/\bar{M}_n$) was <1.2.

For the study of the molecular weight dependence of the chain dynamics of the systems, solutions of the order of 2.5–3% (w/v) in C_6D_6 were prepared. Investigation of the concentration dependence of the diffusion coefficient was made over a range of concentrations 2–5% for the ring and chain pair of molecular weight ~ 2000, again using deuterated benzene as the solvent.

All solutions were held in sealed quartz cells of optical thickness 7 mm, thermostatically controlled at the required temperaure.

Apparatus

Experiments were performed at the high flux reactor at the Institut Laue-Langevin, Grenoble, France, using the IN11 spin-echo spectrometer[19]. This instrument allows measurement of very small changes in energy of a beam of polarized neutrons scattered by a sample by monitoring the neutron beam polarization non-parallel to the magnetic guide field. The resultant polarization, when normalized against a purely elastic scatterer, is directly proportional to the cosine Fourier transform of the coherent scattering law[8,20], $S_{\mathrm{coh}}(Q,\omega)$, i.e. $S_{\mathrm{coh}}(Q,t)$ is measured directly. The scattering vector, $Q = \left(\frac{4\pi}{\lambda}\right)\sin\left(\frac{\theta}{2}\right)$ (where θ is the scattering angle) for these neutron experiments, where $\Delta E/E$ is small. Using the spin-echo apparatus at ILL, Grenoble, energy changes down to 3 neV may be measured. The incident wavelength in the experiments described here was 8.3 Å, with a spread $\Delta\lambda/\lambda$ of 10%. The Q values covered the range 0.026 to 0.106 Å^{-1}.

Data analysis

Methods of data analysis used in the investigation of the behaviour of the dynamics of dilute solutions have been given in some detail elsewhere[17,19,21], and this section is intended only as a summary.

The intermediate scattering law $S_{\mathrm{coh}}(Q,t)$ has been calculated by Dubois–Violette and de Gennes[12] for bead-spring models in the so-called Zimm limit in the intermediate Q region $R_g^{-1} < Q < \sigma^{-1}$. In addition, Akcasu *et al.*[18] have further developed the calculations to predict $S_{\mathrm{coh}}(Q, t)$ throughout the entire Q regime. The intermediate scattering law is expressed in terms of an inverse correlation time, Ω, which characterizes the frequency of the motion being observed, and is defined as the first cumulant of the intermediate coherent scattering law, i.e.

$$\Omega = -\lim_{t\to 0} \frac{\mathrm{d}\ \ln(S_{\mathrm{coh}}(Q,t))}{\mathrm{d}t} \qquad (1)$$

In the intermediate Q region, for θ solvent conditions

$$\Omega = \frac{1}{6\pi}\frac{kT}{\eta_s}Q^3 \qquad (\mathrm{s}^{-1}) \qquad (2)$$

The factor $\frac{1}{6\pi}$ becomes 0.0625 if the Oseen tensor is not preaveraged. $S_{\mathrm{coh}}(Q,t)$ has not been calculated for good solvent conditions, but Ω shows the same Q^3 dependence, with the numerical prefactor increasing from 0.053, i.e. $(1/6\pi)$ to 0.071[18] (or 0.079 for non preaveraging).

At low Q ($QR_g \ll 1$) and low frequencies ($\omega \leqslant 1/\tau_1$, where τ_1 is the correlation time of the first Rouse mode), Brownian diffusion of the whole molecule dominates and $S_{\mathrm{coh}}(Q,t)$ is a simple exponential of the form $e^{-\Omega t}$. Ω, which is now proportional to Q^2 gives the temperature dependent diffusion coefficient, $D(T) = \Omega/Q^2$ in this $Q \to 0$ limit[8,16].

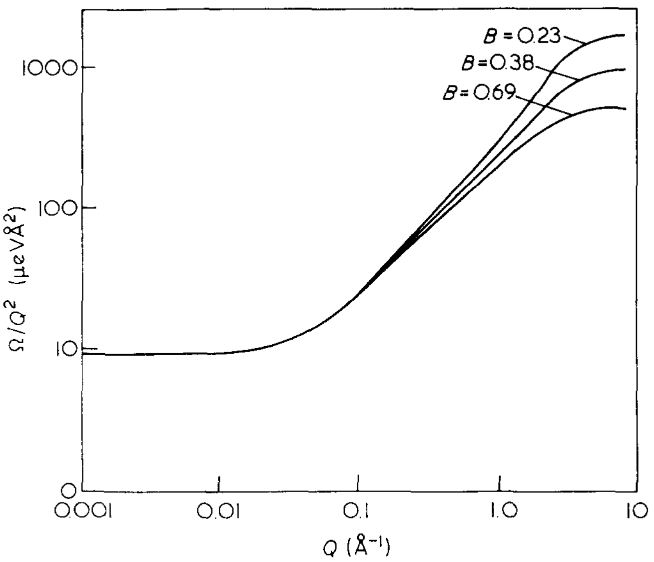

Figure 1 Variation of Ω/Q^2 with Q, calculated for C_6D_6 at 30°C, for three different values of B (after ref. 18)

Interpretation of neutron scattering data involves extracting Ω from the measured scattering functions. As discussed in ref. 17, the approach taken in the intermediate Q region is to fit the appropriate de Gennes correlation function[12] to the data and obtain the corresponding inverse correlation time Γ. It can be shown[17,18] that Γ is then simply related to Ω, the initial slope of $S_{\mathrm{coh}}(Q,t)$ *via* the expression $\Omega = \sqrt{2}\,\Gamma$. For the low Q regime, where simple diffusion is observed, and the scattering law is a single exponential, Ω may be obtained directly from the slope of a logarithmic plot of $S_{\mathrm{coh}}(Q,t)$ against time. It will become clear in the next section that for most of the samples investigated, the molecular weights and Q range are such that crossover from simple diffusion to internal segmental motion is being observed. Under these circumstances, the form of $S(Q,t)$ must be studied closely[16-18] and the appropriate method of obtaining Ω decided upon at each Q value. Having obtained Ω as a function of Q, it is possible to compare the experimental variation of Ω/Q^2 *versus* Q with that predicted theoretically.

Akcasu[18] calculates the normalized expression $(\Omega\sigma\eta_s)/(k_BT(6\pi^3)^{\frac{1}{2}}B)$ as a function of Q, where T is the absolute temperature, η_s the solvent viscosity and B is a draining parameter, defined by $[1/(6\pi^3)^{\frac{1}{2}}]\xi_0/\eta_s\sigma$. ξ_0 is the friction coefficient of a setment of length σ.† B is identical except for a factor of $2^{\frac{1}{2}}$ to the reduced 'draining parameter' $h^* = h/N^{\frac{1}{2}}$ where N is the number of segments in the chain. B (or h) was introduced by Kirkwood and Riseman[22] as a measure of the strength of hydrodynamic interaction. As an example, *Figure 1* shows Akcasu's[18] calculated curve for $N = 10^4$, $\sigma = 1$ and different values of B. Appropriate values of η_s and T have been used in the above expression for deuterated benzene at 30°C.

At the low Q range of interest in this discussion, it may be seen that the rate of motion is determined solely by the overall molecular dimensions (i.e. value of N), and in this case, the values of σ and B chosen for use in the calculation of the expression $(\Omega\sigma\eta_s)/(k_BT(6\pi^3)^{\frac{1}{2}}B)$ are of no significance, since, as can be seen in *Figure 1*, curves for different values of B coincide for any given N, provided N is large enough. The asymptotic value reached in the low Q limit corresponds directly to the temperature dependent diffusion coefficient, $D(T)$. The experimental data may be simply fitted to the theoretical master curve by arbitrarily setting values of σ and B, and sliding the theoretical curve diagonally along the data points until an acceptable fit is obtained, thus defining the best value of N, in a similar way to that described in ref. 17, for the high $Q\sigma$ regime, when the parameter of interest to be fitted was σ. In principle, an iterative process should then be used to establish the final values of N and σ, although in general, the quality of the data is not good enough to warrant this.

Having established N and σ, the radius of gyration for a randomly coiled Gaussian chain may be calculated directly, since $R_g^2 = N\sigma^2/6$. These theoretical predictions are all made in the limiting case of infinite dilution, and the question of interpretation of measurements made at finite concentrations now arises.

For small Q values, at a given T, where $\Omega/Q^2 \rightarrow D(c)$ where $D(c)$ is the diffusion coefficient at concentration c, the problem may be approached by considering $D(c)$ in terms of $D(0)$, the diffusion coefficient at infinite dilution, and $\phi(N)$, which is a proportionality factor dependent on both molecular weight, and the quality of the solvent[23]. (Consideration as to actual values of $\phi(N)$ will be given in the next section).

The relevant expression is then

$$D(c) = D(0)[1 + \phi(N)c] \qquad \text{for } c < c^* \tag{3}$$

where c^* is the concentration at which molecules begin to overlap.

This implies that the effect of concentration in the low Q range is simply to shift the asymptotic value of $D(0)$ to $D(c)$. For $Q \sim 1/R_g$, i.e. in the crossover from simple diffusion to segmental motion, the behaviour of Ω/Q^2 as a function of concentration is not established, and the usual approach is to assume that within this Q range the effect will again be simply a constant shift[16].

For the study of the concentration dependence of the diffusion coefficient, a low molecular weight sample ($\bar{M}_n \sim 2000$) was deliberately chosen so that the intermediate coherent scattering law would be of the form $e^{-\Omega t}$ up to high values of $Q (> 0.106\ \text{Å}^{-1})$, and Ω simply obtained from the slope of a logarithmic plot of $S_{\mathrm{coh}}(Q,t)$ against time. Since, in this Q^2 region, $D(c) = \Omega Q^2$, measurement of Ω at only a single value of Q of 0.04 Å^{-1} was considered sufficient to define D for a number of concentrations.

RESULTS AND INTERPRETATION OF RESULTS

Experimentally determined behaviour of $S_{coh}(Q,t)$ *and* Ω

Figure 2 shows the normalized correlation functions obtained at 30°C for a dilute solution of linear PDMS, of molecular weight 6400. At lower Q values ($Q \leqslant 0.053\ ^{-1}$), the intermediate scattering law, $S_{\mathrm{coh}}(Q,t)$ shows no deviation from a single exponential, indicating overall molecular diffusion. At higher Q values, the more complex intermediate scattering function associated with internal segmental motion gives rise to small deviations from an exponential. Values of Γ obtained by fitting the de Gennes correlation functions[12] to the experimental data are indicated on the Figure for higher Q values.

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† In the original paper (ref. 18), Akcasu denotes the segment length by a, instead of σ. σ is used here for consistency throughout this paper.

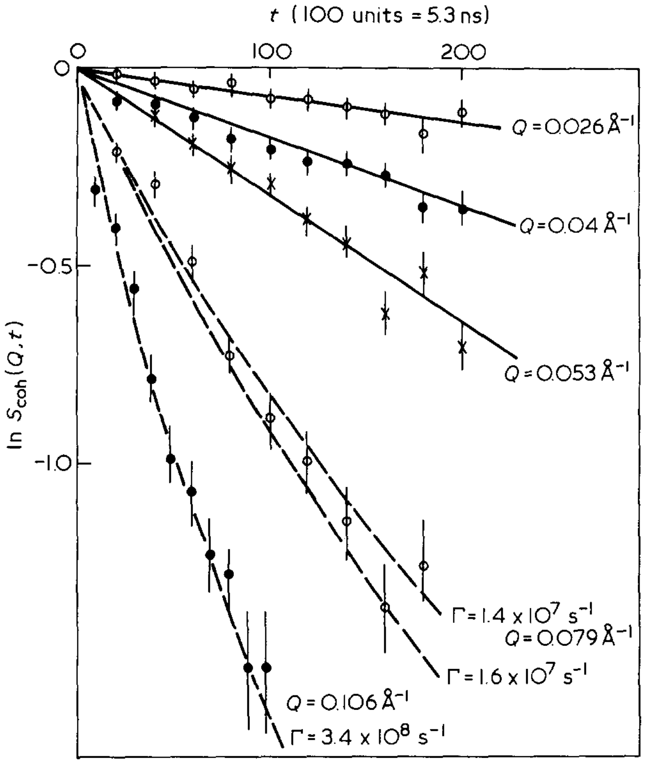

Figure 2 Intermediate scattering functions, ln $S(Q, t)$ for 3.5% PDMS chain in C_6D_6 ($\bar{M}_n$=6400)

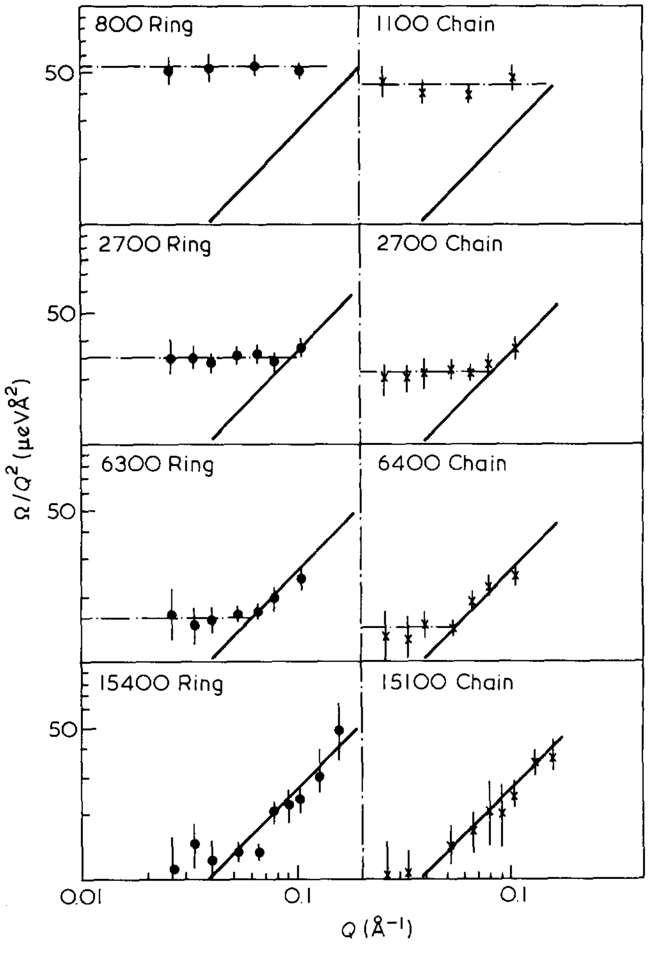

Figure 3 Experimentally determined behaviour of Ω/Q^2 for various samples of linear and cyclic PDMS. The broken line indicates the experimental value of $D(c)$. whilst the solid line shows the theoretical Q^3 line as given by equation (2)

Figure 3 shows the crossover from Q^2 to Q^3 behaviour for the different linear and cyclic polymers. In this Figure, the solid line indicates the Q^3 behaviour predicted by de Gennes[12] (equation (2)), whilst the broken line shows the Q^2 behaviour in the limit $Q \leqslant \sim R_g^{-1}$. It can be seen that the critical value of Q, Q^*, defining the crossover point $Q^*R_g \sim 1$ is in general rather lower for the linear samples, and this is due to the fact that for equivalent samples (i.e. a linear–cyclic pair with the same number of bonds) R_g(chain) > R_g(ring).

Comparison of Ω variation observed experimentally with calculation

Figure 3, showing the variation of Ω/Q^2 with Q, allows direct comparison of the experimental data with the theoretical predictions of Akcasu *et al.*[18]. Before making such a comparison, however, the problems of concentration dependence must be considered. *Figure 4* shows the concentration dependence of the diffusion coefficient for the 2000 molecular weight ring and chain pair (obtained using spin-echo neutron scattering) at 25°C in C_6D_6, at $Q = 0.04$ Å^{-1}. The absolute value for the width of the resolution function obtained using this instrument is limited to, or greater than, 3 neV (which is of the order of 10% for the values of D shown in the Figure) as indicated by the size of the error bars. Within these error bars no effect of concentration can be observed and we can therefore put a limit of $\pm 0.12 \times 10^{-6}$ cm^5 s^{-1} g^{-1} on the concentration dependence ($dD(c)/dc$). This is in agreement with results obtained by other workers[6] who observed that for a ring and chain pair of similar molecular weight over the concentration range 2–4% in toluene, which is also a good solvent for PDMS, $dD(c)/dc$ is of the order -0.16×10^{-6} cm^5 s^{-1} g^{-1}.

Although the concentration dependence appears effectively negligible for the low molecular weight samples, for high molecular weights the problem is a little more complicated.

Recent quasielastic light scattering measurements[7] on linear and cyclic PDMS of molecular weight 10 000 and 20 000 in toluene over a concentration range 1–2.5% (w/v) suggest that the concentration dependence of the diffusion coefficient is by no means negligible. This indicates that for the highest molecular weight samples studied in this series of experiments, ($\bar{M}_n \sim 15\,000$), some consideration should be given to the question of concentration dependence in interpreting the data. The expected $D(c)$ variation with concentration is given by equation (3). The problem arises in estimating a value of

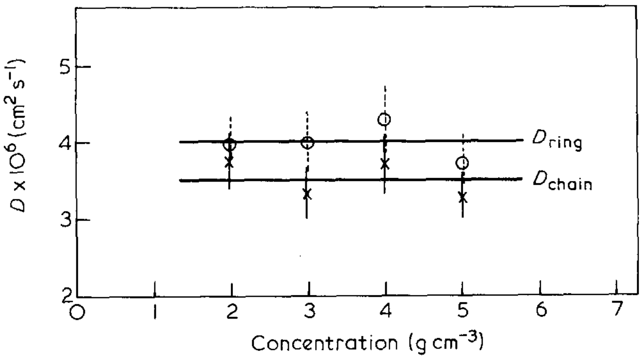

Figure 4 Concentration dependence of the diffusion coefficients of linear PDMS ($\bar{n}$=54) and cylic PDMS ($\bar{n}$=54) at 25°C in C_6D_6

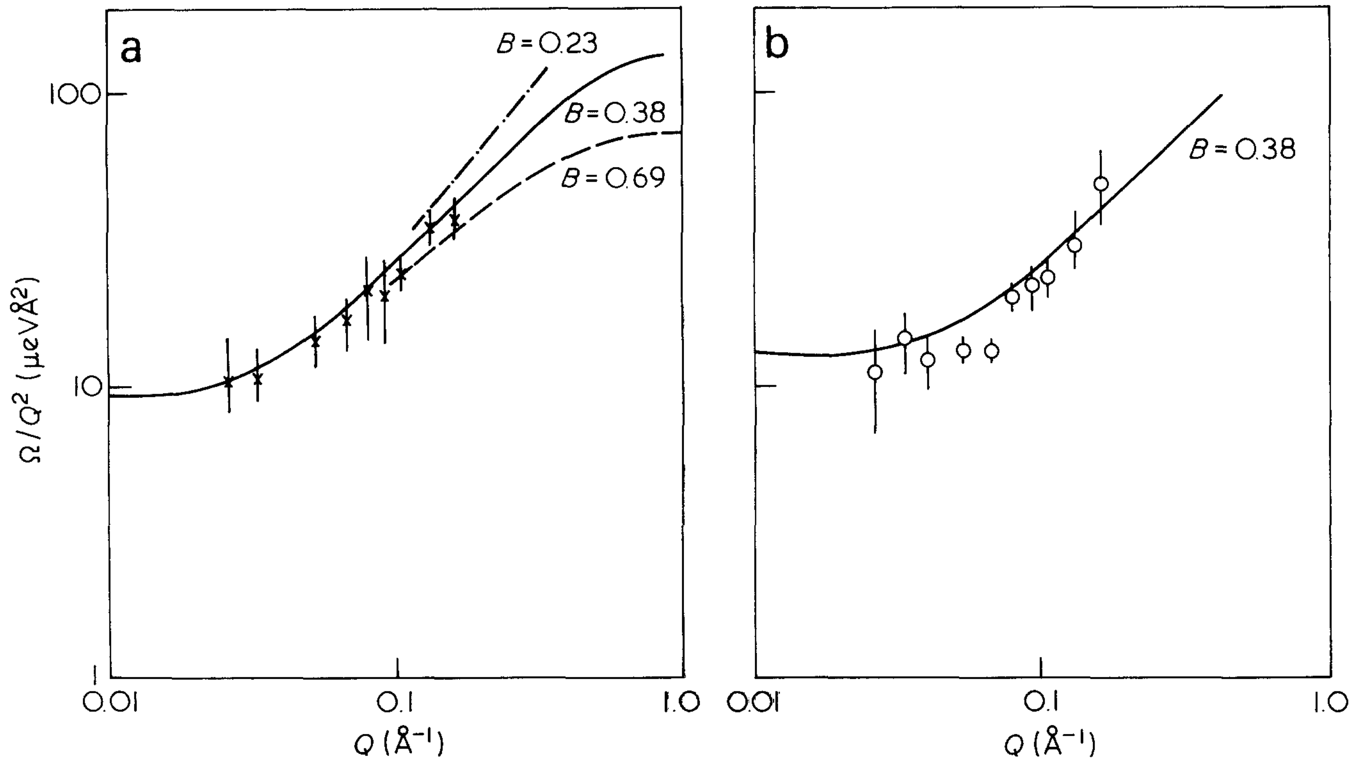

Figure 5 Comparison of experimental data obtained for (b) 15000 molecular weight ring (0) and (a) chain (×) pair with theoretical calculations (after ref. 18). Values of R_g used in the calculation were 30 Å for the ring and 40 Å for the chain

$\phi(N)$ for samples of this particular molecular weight and in this particular solvent. Interpolation of Edwards' data[7] gives a value of $\phi(N)$ of the order of $5.8\,g^{-1}\,cm^3$ for a 15000 molecular weight chain, and a value close to zero for the corresponding ring. If it is assumed that C_6D_6 and toluene are solvents of similar quality for PDMS, this would suggest that $D(0)$ is of the order of 15% lower than any value of D obtained from the neutron scattering data using a 2.5% solution for the linear sample, and that $D(0)$ is approximately the same as $D(2.5)$ for the ring. In view of the fact that the actual values of $\phi(N)$ are not known, and could be quite different to those estimated above, and also that the precision in any value of $D(c)$ obtained is probably no better than 10%, it is not considered justifiable to correct the data for concentration dependence. Consequently, for this high molecular weight pair, $D(0)$ is assumed to be approximately identical to $D(c)$, as for the lower molecular weight samples. *Figure 5* shows the 15000 molecular weight data fitted to the theoretical curve[18] for both the ring and the chain. In principle, by suitable scaling, it should be possible to extract both R_g and $D(c)$. In practice, due to the uncertainty in the experimental data, it is easier to obtain a value of R_g from other sources (R_g may be obtained directly from small-angle neutron scattering experiments[3]) and compare the theoretical curve calculated for this value of R_g to the data, as shown in *Figure 5*. It is important to note that although deuterated benzene is expected to be a good solvent for PDMS, it is found that a much better fit to the data is obtained using the curve for theta conditions, although even this does not match the data well in the transition region. This effect has also been observed in most high Q data from solutions of higher molecular weight polymers than reported here[17]. In this case, however, the question arises as to the validity of the theoretical prediction when applied to small rings and chains. For small molecules, the two characteristic distances R_g and σ approach each other, so that the Q^3 region of the curve becomes very small, and for low molecular weight samples disappears altogether. This can be seen for the 15000 chain in *Figure 5*, where the lower part of the curve has been fitted for the appropriate radius of gyration, and the upper part for the appropriate value of σ for PDMS (taken as 15 Å, the value calculated by Yamakawa[24] using the Kratky–Porod wormlike chain approach, which is in good agreement with the value of 15 Å determined experimentally using quasielastic neutron scattering by Nicholson *et al.*[17]). It is evident that whilst, in general, for high molecular weight samples (i.e. large N), the curve in the region $Q \lesssim R_g^{-1}$ is insensitive to the value of B, for small N this is no longer true, and a reliable fit to the data cannot be made without some alternative method of determining B. For the samples of lower molecular weight, the Q^3 region is even less well defined, and the problem of fitting the data satisfactorily without knowing B is even more difficult. Another factor of importance associated with molecular weight is the breakdown of the relationship between R_g and R_H, the hydrodynamic radius, which in Akcasu)s analysis[16] is taken in the randomly coiled Gaussian chain limit[25], and is given by $R_g = 1.5R_H$. Experimental results presented later in this paper show that this relationship is clearly not obeyed by the PDMS rings and chains studied here, and consequently Akcasu's calculated curve is not expected to be strictly applicable. Another point to be considered is the possibility of increase in chain stiffness with decrease in molecular weight. It is quite possible that the lower molecular weight samples studied, particularly the rings, could be considerably stiffer than their high molecular weight counterparts. Benmouna and Akcasu[26] have considered the effect of chain stiffness on the behaviour of Ω, and have shown large effects at low Q. This suggests that any change in chain stiffness with decreasing molecular weight could lead to some discrepancy between the experimental data and Akcasu's theoretical curve.

Diffusion coefficients and hydrodynamic radii

For the lower molecular weight samples, where the Q^2 region is well defined experimentally, the diffusion coefficient may be obtained directly. For the 15 000 molecular weight pair, $D(c)$ may be obtained from the limiting value of Ω/Q^2 found by fitting Akcasu's curve to the data. (Due to difficulties in making a good fit, for reasons mentioned above, these values are inherently less accurate than those obtained directly).

Figure 6 combines the values of the diffusion coefficients obtained using quasielastic neutron scattering with those obtained using boundary spreading[6] and photon correlation spectroscopy techniques[7], as a function of the average number of backbone bonds, for a wide range of linear and cyclic PDMS samples. The values of $D(c)$ shown in the Figure were obtained using solutions of concentration between 2 and 3% and the data have been normalized (according to $D = D_{\text{measured}}(\eta_s/T)(298\text{ K}/\eta_{\text{toluene}})$) to account for measurements made in different solvents at different temperatures to allow direct comparison of data sets. The absolute precision of the neutron scattering data is no better than 3 neV, which typically corresponds to an error of $\pm 10\%$ on a value of $D(c)$ of the order of $3 \times 10^{-6}\text{ cm}^2\text{ s}^{-1}$, whilst data obtained using light scattering give values of D with an experimental error of order of $\pm 5\%$ and the precision of the boundary spreading data is estimated to be even better[6]. The ratio $D_{\text{chain}}/D_{\text{ring}}$ is found to be 0.84 ± 0.016, which compares favourably with the predicted value of $8/3\pi = 0.85$ for cyclic and linear samples of the same molecular weight in the absence of free draining and excluded volume effects[25,27]. Knowing the diffusion coefficients for all the samples, it is possible to calculate the hydrodynamic radius and compare this with data obtained from other sources.

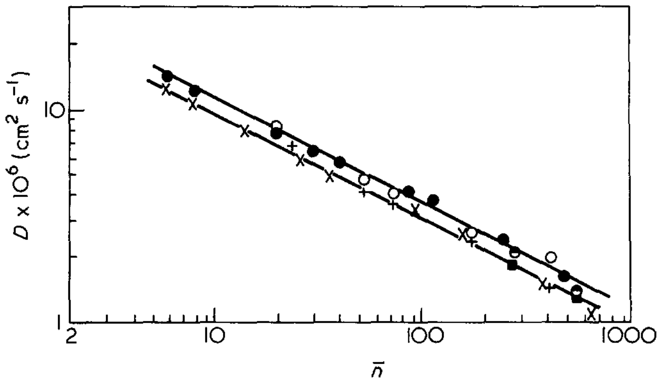

Figure 6 Comparison of values of the diffusion coefficient obtained using quasielastic neutron scattering with those obtained by other methods. All data are normalized to solvent viscosity and temperature (toluene at 25°C): (× chain, ● ring) Data obtained using boundary spreading (after ref. 6) $c \sim 3\%$; (+ chain, o ring) Data obtained from QENS, $c \sim 2.5$–3%; (■ chain, ◑ ring) Data obtained from QELS (after ref. 7), $c \sim 2\%$

(a) The hydrodynamic radius, R_H, may be calculated directly from D *via* the Stokes–Einstein equation[6,27]

$$D = \frac{kT}{6\pi\eta_s R_H} \tag{4}$$

where all symbols carry their usual meaning.

(b) For both cyclic and linear polymers, R^*, which defines overall molecular dimensions, and is thus comparable with R_g, is defined by Q^*, the crossover from Q^2 to Q^3 behaviour. For θ solvent conditions, Akcasu's curve shows this crossover to be defined by $Q^*R^* \sim 1$. Thus a crude experimental value of R^* may be obtained directly from the data plotted in *Figure 3* by taking $R^* = 1/Q^*$. These values are quoted in *Table 2*, and are of the same order of magnitude as the actually measured molecular dimensions.

As mentioned earlier, R_g may be measured directly using small-angle neutron scattering. *Table 2* compares values calculated according to (a) and (b) with those measured using small-angle neutron scattering, and where appropriate, with values obtained using other techniques such as boundary spreading or quasielastic light scattering.

The ratio R_g/R_H has been calculated to allow some comparison with theory. For the linear samples, it may be shown that in the Gaussian limit[25] the radius of gyration is expected to be related to the hydrodynamic radius *via*

Table 2 Dimensions of PDMS rings and chains (all dimensions are in Å)
(a) Linear samples (T = 20°C)

M_n	R_g (SAS)	R^* (=1/Q^*)	R_H (QENS)	R_g/R_H	R_H (boundary spreading or QELS)
1100	7	6	6.4	1.1	6.7
2100	10.2	–	7.6	1.34	–
2700	12.4	12	12.1	1.02	–
6400	21.2	18	19.6	1.1	–
15100	40	–	26.4	1.5	26.4

(b) Cyclic samples (T = 20°C)

M_n	R_g (SAS)	R^* (=1/Q^*)	R_H (QENS)	R_g/R_H	R_H (boundary spreading or QELS)
800	–	5	5.1	–	–
2000	7.8	–	6.8	1.15	–
2700	9.5	11	10.7	0.89	9.9
6300	14.3	16	14.7	0.97	–
15400	29	22	18.9	1.5	–

$$R_g = \frac{8}{3\pi^{\frac{1}{2}}} R_H = 1.505\, R_H \tag{5}$$

However, recent experimental determinations of the relationship[28] R_g/R_H suggest a somewhat lower value than this of 1.27 ± 0.06. Certainly, the experimental values presented here are closer to this value with an average of 1.21. For the cyclic samples the theoretical ratio of R_g/R_H, again in the Gaussian limit, is predicted[6,29] to be $\left(\frac{2}{\pi}\right)^{-\frac{1}{2}} = 1.2533$.

The values presented in section (b) of *Table 2* suggest that again the experimentally determined value appears to be somewhat lower than that predicted, with an average of 1.15.

CONCLUSIONS

(i) Low molecular weight samples of cyclic and linear PDMS show a variation of Ω/Q^2 with Q which is in general agreement with that predicted[8]. Detailed comparison of experimental data with the calculated curves shows discrepancies probably due to the breakdown of theory for small molecules.

(ii) Diffusion coefficients obtained from quasielastic neutron scattering agree well with those obtained using other techniques.

(iii) The ratio of R_g/R_H determined experimentally is found to be 1.21 for linear samples and 1.15 for cyclic PDMS, and lower in each case than the theoretical predictions.

(iv) The ratio $R_{H\,\mathrm{ring}}/R_{H\,\mathrm{chain}}$ is found to be 0.84 in good agreement with predictions.

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