Studies of cyclic and linear poly(dimethyl siloxanes): 9. Quasi-elastic light scattering and concentration dependences of diffusion coefficients

C. J. C. Edwards
Department of Chemistry, University of York, York YO1 5DD, UK and Department of Polymer and Fibre Science, The University of Manchester Institute of Science and Technology (UMIST), Manchester, M60 1QD, UK

and S. Bantle and W. Burchard
Institute of Macromolecular Chemistry, University of Freiburg, D-7800, Freiburg, W. Germany

and R. F. T. Stepto
Department of Polymer and Fibre Science, UMIST, Manchester M60 1QD, UK

and J. A. Semlyen
Department of Chemistry, University of York, York YO1 5DD, UK
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The concentration dependences of the diffusion coefficients (*D*) of linear and cyclic poly(dimethyl siloxanes) (PDMS) in toluene at 298K are reported. Three cyclic/linear pairs of fractions with molar masses in the range 300 to 23 500 g mol^{-1} were used. The values of *D* obtained by quasi-elastic scattering were in good agreement with those measured by the classical boundary-spreading technique. Analysis of the concentration dependences in terms of the theory of Pyun and Fixman indicates that the solute molecules show a minimum of interpenetration in toluene at 298K.

Keywords Cyclic poly(dimethyl siloxane); linear poly(dimethyl siloxane); quasi-elastic light scattering; diffusion coefficients

INTRODUCTION

In recent years, quasi-elastic light scattering (QELS) has become a powerful and frequently-applied technique for the measurement of translational diffusion coefficients[1]. Results can be obtained more quickly by this method than by the classical boundary-spreading method and QELS is an ideal technique for the measurement of the concentration dependence of diffusion coefficients. The physical principles underlying the two techniques are essentially different. With the boundary-spreading technique, a macroscopic transport process is followed; whilst in QELS, microscopic concentration fluctuations of a system at thermodynamic equilibrium are measured. Since Einstein's relationship[2] for the Brownian motion of particles applies to each, the diffusion coefficients determined by the two methods should be the same.

This paper has two primary aims. The first is to compare the diffusion coefficients of samples which have been measured by the two techniques, and to demonstrate that the two methods complement one another. The classical boundary-spreading technique is particularly suitable for precise measurements of the diffusion coefficients of species of low molar mass; whereas QELS is more suitable at high molar mass. Thus, the present work should help to establish the low molar mass limit for QELS. The second aim is to compare the concentration dependences of the friction coefficients of cyclic and linear poly(dimethyl siloxanes) (PDMS) in a good solvent and to analyse the results in terms of current theory. In this connection, it is noted that the molar mass dependences of the diffusion coefficients of cyclic and linear PDMS in a 'good' solvent[3] and in a 'poor' solvent[4] have been investigated previously using the boundary-spreading technique.

EXPERIMENTAL

Well-fractionated samples of cyclic and linear PDMS were prepared as described previously[5,6]. In all cases the heterogeneity indices (M_w/M_n) were less than 1.20. Translational diffusion coefficients were measured using QELS for two linear and two cyclic PDMS fractions at three or four concentrations in toluene at 298 K. The samples were chosen so that the members of the cyclic-linear pairs had almost the same molar mass, namely $M_w \simeq 23\,200$ g mol^{-1} or $M_w \simeq 12\,000$ g mol^{-1}. We also consider some previously published[3] measurements of the concentration dependences of the diffusion coefficients of a cyclic-linear pair of very low molar mass ($M_w < 630$ g mol^{-1}), which were obtained using the boundary-

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spreading technique. Measurements on the same sample by both QELS and the classical technique have not been possible due to the small amounts of each fraction available. However, the results from QELS measurements can be compared with diffusion coefficients interpolated from previously published data from the boundary-spreading technique in toluene solution[3].

QELS measurements

The QELS measurements were performed with a Malvern 4300 Photon Correlation Spectrometer which had been modified for precision alignment of the optical system[7]. Great care was taken to align the axis of the cylindrical cell with the axis of rotation of the supporting arm carrying the detector and to align the laser beam (Coherent argon laser CR13) with the centre of the diffusion cell. The scattered intensity was measured by a low dark-current and low after-pulsing photomultiplier (PM) tube (ITTFW130) in the range 20° to 140°. Optical clarification was achieved by a two-step procedure. First the solutions were centrifuged for about $2\frac{1}{2}$ hours at 40 000 r.p.m. in an ultracentrifuge (Spinco model L50) using a fixed angle rotor. Then about 2 cm^3 of the top half of each solution were sealed into a cylindrical glass cell. Immediately prior to a measurement, these sealed cells were centrifuged at 17 000 r.p.m. for about 2 h in a swinging bucket rotor applying the flotation technique[8]. No sedimentation was observed under these conditions in an analytical centrifuge using schlieren optics.

The measured values of $\langle i(0).i(t)\rangle$, the intensity autocorrelation function, were converted to the far point (A) normalized correlation function $G_1(t)$

$$G_1(t) \simeq B^{\frac{1}{2}} g_1(t) = ((\langle i(0).i(t)\rangle/A) - 1)^{\frac{1}{2}} \qquad (1)$$

where A denotes the baseline, B is a constant depending on the quantum efficiency of the PM tube and the quality of the correlation volume, and where $g_1(t)$ is the normalized electric field correlation function

$$g_1(t) = |\langle E(0)^*.E(t)\rangle| / |\langle E(0)^* E(0)\rangle| \qquad (2)$$

Here, $E(t)$ and $E(0)$ are the electric fields at times t and zero, and $i(t)$ and $i(0)$ the corresponding scattered intensities. A 96-channel autocorrelator (Malvern Instruments) was used and the far-point was calculated from the monitor channels of the autocorrelator. The log plot of $G_1(t)$ was found to be linear for about the first 20 channels. Deviations from linearity at higher channel numbers were probably due to traces of dust remaining in the sample after centrifugation. The best fit of log $G_1(t)$ was obtained using a quadratic fit and by taking the first 25 channels only, which corresponded to about two coherence times[9]. The slope of the linear portion of log $G_1(t)$ gives the first cumulant (Γ) which for small molecules is related to the translational diffusion coefficient (D) as:

$$\Gamma = q^2 D \qquad (3)$$

where $q = (4\pi/\lambda)\sin(\theta/2)$, with θ being the scattering angle and $\lambda = 488$ nm the wavelength of light *in vacuo*. The ratio Γ/q^2 was found to be independent of the scattering angle for angles greater than 50°. At lower angles a down-turn is observed which results from traces of dust.

Boundary-spreading measurements

The boundary-spreading diffusiometer has been described previously[3,4,10]. Individual diffusion coefficients refer to the mean concentration at which the experiment was performed, namely, $\bar{c} = c/2$, where c is the concentration of the solution. Since different values of c were used for different experiments, the interpolated values to be reported are taken as referring to the average of all the various values of $\bar{c}$ used (equal to 15 ± 2 g l^{-1}).

RESULTS AND DISCUSSION

Comparison of QELS and the classical technique

Figure 1 shows the translational diffusion coefficient, D, as a function of concentration for three cyclic and three linear PDMS fractions. The data for the cyclic-linear pair of lowest molar mass were obtained using the classical boundary-spreading technique and have been published previously[3]. The data for the higher molar mass samples were obtained using QELS. Also shown (+) are the diffusion coefficients obtained by interpolation, with respect to molar mass, of the previous data[3] measured using the classical technique. The points are plotted at

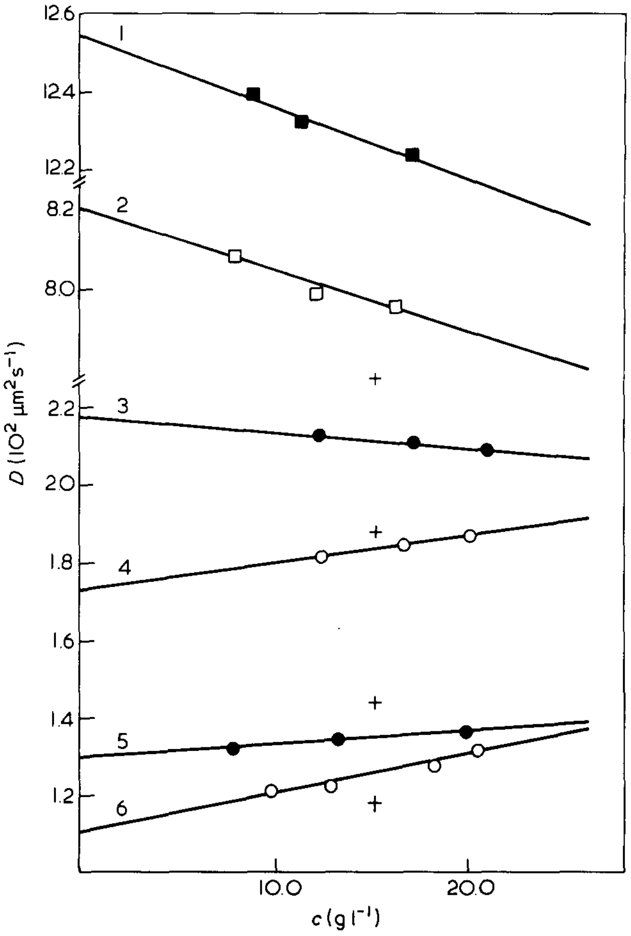

Figure 1 D in toluene at 298 K from boundary-spreading (■, □, +) and QELS (●, ○) measurements plotted against c and $\bar{c}$, respectively. 1: (■) cyclic PDMS[3], M_w = 296 g mol^{-1}. 2: (□) linear PDMS[3], M_w = 627 g mol^{-1}. 3: (●) cyclic PDMS, M_w = 11 500 g mol^{-1}. 4: (○) linear PDMS, M_w = 12 400 g mol^{-1}. 5: (●) cyclic PDMS, M_w = 23 200 g mol^{-1}. 6: (○) linear PDMS, M_w = 23 300 g mol^{-1}. (+) Points interpolated with respect to M from boundary-spreading data[3] and plotted at $\bar{c}$ = 15 g l^{-1}. The interpolated values of D correspond to those for the values of M for the present systems 3–6

Table 1 Diffusion coefficients D_0 for three pairs of linear and cyclic PDMS molecules in toluene at 298 K. The second virial coefficients A_2 and the coefficients in the concentration dependence of $D(c)$ and $f(c)$ respectively. k_{f0} was calculated from Equation 6

M_w (g mol^{-1})	D_0 (μ m^2 s^{-1})	A_2 (10^{-4} cm^3 g^{-2} mol)	k_D (cm^3 g^{-1})	k_f (cm^3 g^{-1})	k_{f0}
Linear 23300	111.5	8.74	8.18	31.55	6.54
Cyclic 23200	130.5	6.55	2.33	27.12	8.96
Linear 12400	173.5	9.69	3.36	19.66	8.17
Cyclic 11500	217.5	7.89	−2.00	19.21	14.64
Linear 627	820.5	15.76	−2.08	2.509	7.93
Cyclic 296	1254	17.80	−1.503	1.505	6.65

$c=15$ g l^{-1} for the reasons previously discussed. Agreement between the QELS data and the interpolated classical data is within $\pm 5\%$. This is larger than the relative error in both techniques, but is still satisfactory in view of the nature of the interpolation procedure. The good agreement between the two techniques suggests that a combination of the classical boundary-spreading method and QELS can be used to obtain translational diffusion coefficients in dilute solution over the complete range of molar masses, with QELS being most useful for molar masses in excess of 10^4 g mol^{-1}.

Concentration dependences of the diffusion coefficients

The concentration dependences of the cyclic and linear polymers are well represented by the linear relationship:

$$D(c)=D_0(1+k_D c) \tag{4}$$

The diffusion coefficients at zero concentration (D_0) obtained by extrapolation of $D(c)$ to zero concentration are listed in *Table 1* together with the coefficients k_D. The values of k_D are positive for the cyclic-linear pair of highest molar mass and become increasingly negative with decreasing molar mass, in agreement with previous measurements in a 'good' solvent[8]. The change in sign of k_D occurs at a higher molar mass for the cyclic molecule.

The diffusion coefficient at finite concentration is determined by both thermodynamic and hydrodynamic interactions. Consequently, k_D is related to the second virial coefficient (A_2) and the concentration coefficient (k_f) in the concentration-dependence of the friction coefficient by the relationship[11]:

$$k_D+k_f=2A_2M_w-\bar{v}, \tag{5}$$

with

$$f(c)=f_0(1+k_f c) \tag{6}$$

$\bar{v}$ is the partial specific volume of the polymer, obtained from density measurements on the pure polymer[12], assuming no volume change on mixing. f_0 is related to D_0 via the Einstein relationship $D_0=kT/f_0$, where k is the Boltzmann constant and T the absolute temperature.

Second virial coefficients of cyclic and linear PDMS in toluene at 298 K have been reported in the preceding paper[13]. Values of A_2 interpolated from these data and the data of Huglin and Sokro[14] for very low molar mass linear PDMS are given in *Table 1*. They can be used to calculate values of k_f using Equation 5. It can be seen from *Table 1* that the values of k_f calculated in this way are similar for each cyclic-linear pair and decrease with decreasing molar mass as expected.

Various theories of the concentration coefficient[15–17], k_f, indicate that:

$$k_f=k_{f0}(N_A V_h/M_w) \tag{7}$$

where N_A is the Avogadro constant and V_h is the hydrodynamic volume of a molecule of molar mass M_w. The expression in brackets represents the effective hydrodynamic volume of a molecule per unit mass, and k_{f0} is a constant which characterizes the extent of coil interpenetration.

Pyun and Fixman[16] have used an equivalent-sphere, uniform segment density model to derive values of $k_{f0}=2.27$ for maximum interpenetration of solute molecules (the θ-state for high molar mass polymer) and $k_{f0}=7.18$ for hard spheres (the 'good' solvent condition for high molar mass polymer). Previous experimental measurements on poly(methyl methacrylate)[8] have found $k_{f0}=2.78$ in a theta solvent and $k_{f0}=9.0$ in a good solvent, in good agreement with Pyun and Fixman's predictions. The values of k_{f0} in *Table 1* have been calculated by approximating the hydrodynamic volume by:

$$V_h=(4\pi/3)(kT/6\pi\eta_0 D)^3=(4\pi/3)r_D^3, \tag{8}$$

where r_D is the Stokes-Einstein radius and with $\eta_0=0.522$ cP for toluene at 298 K.

The values of k_{f0} for the linear PDMS samples (7.93, 8.17 and 6.54) are in good agreement with the value of 7.18 predicted by Pyun and Fixman for hard spheres or a 'good' solvent. The constancy in k_{f0} is particularly gratifying in view of the different techniques used (QELS gives 8.17 and 6.54 and boundary-spreading gives 7.93).

The values of k_{f0} for the cyclic samples show greater variation. Those of 8.96 and 5.65 for the cyclic samples of highest and lowest molar mass are apparently in satisfactory agreement with Pyun and Fixman's[16] value of 7.18. However, a value of 14.64 is obtained for

$M_w = 11\,500$ g mol^{-1}. At present there is no obvious explanation for this large value of k_{f0}.

In the preceding discussion, the values of k_{f0} have been compared with those predicted by the Pyun–Fixman theory in the non-interpenetrating limit. The hydrodynamic model used by Pyun and Fixman is, in that limit, independent of the molecular structure of the diffusing sphere and should, therefore, apply to both cyclic and linear polymers of low as well as high molar mass. Differences in the values of k_{f0} for cyclic and linear molecules may be expected in a theta solvent, when according to the Pyun and Fixman model k_{f0} is sensitive to the distribution of segments about the centre of mass. It should be noted that, non-draining with respect to solvent was also assumed by Pyun and Fixman, and this may mean that the agreement between theory and experiment for the cyclic-linear pair of lowest molar mass is fortuitous. Previous work has shown significant free-draining contributions to the friction coefficients of low molar mass PDMS molecules[18].

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