Studies of cyclic and linear poly(dimethyl siloxanes):7. Diffusion behaviour in a poor solvent

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The diffusion coefficients (D) of cyclic and linear poly(dimethylsiloxanes) (PDMS) have been measured in bromocyclohexane at 288 K and 301 K. Bromocyclohexane has previously been reported to be a θ-solvent for high molar mass linear PDMS at 301 K, but the hydrodynamic radii reported here apparently show the effects of molecular expansion at both temperatures. In addition, the hydrodynamic radii of both linear and cyclic PDMS are found to be insensitive to whether the solvent is toluene or bromocyclohexane. The ratio of friction coefficients f_r/f_l for the ring (r) and linear (l) molecules of the same number of segments (x) is in good agreement with the theoretical value of $8/3\pi$ in the impermeable limit and with the experimental value found previously in toluene solution. As x decreases the ratio f_r/f_l tends to unity, illustrating the increasing importance of free-draining at low molar mass.

Keywords Cyclic poly(dimethyl siloxane); linear poly(dimethyl siloxane); diffusion; bromocyclohexane

INTRODUCTION

The preparation and characterization of cyclic poly(dimethyl siloxanes) (PDMS) using preparative and analytical gel permeation chromatography (g.p.c.) have been described previously[1-6]. Many sharp fractions of these cyclic polymers have been obtained, each on a scale of several grams. The fractions contain ring molecules with number-average numbers of skeletal bonds up to 700. Some of the properties of these polymers have been investigated already and compared with the properties of the corresponding linear PDMS, including intrinsic viscosities[1], radii of gyration from neutron scattering measurements[3], bulk viscosities[4], diffusion coefficients[5], densities[6] and refractive indices[6].

In part 5 of this series of papers, the diffusion behaviours of cyclic and linear PDMS were compared using measurements in toluene at 298 K, which is a good solvent for the polymers[5]. Here we compare the diffusion behaviours of cyclic and linear PDMS in dilute solution in bromocyclohexane at 288 K and 301 K. The data for linear PDMS in bromocyclohexane at 288 K have been published previously[7]. Like toluene, bromocyclohexane has a refractive index which allows optical measurements of the concentration gradients in the boundary-spreading diffusiometer[8].

Previous light scattering measurements by Schulz and Haug[9], have shown that bromocyclohexane is a θ-solvent for high molar mass linear PDMS. In support of these findings, we have found[10] negligible second virial coefficients (A_2) (measured by light scattering) for the linear polymer in bromocyclohexane above molar masses of $\sim$4000 g mol^{-1}. This is also in agreement with Adank and Elias, who, in addition, found appreciable second virial coefficients for low molar mass linear PDMS under these solvent conditions[11]. Intrinsic viscosity measurements reported by Haug and Meyerhoff[12] indicate that high molar mass linear PDMS is unperturbed by excluded volume effects in bromocyclohexane at 301 K. It has a characteristic ratio $\langle r_0^2\rangle/nl^2$ (where n is the number of bonds each of length l) $= 6.3$, which is very close to that found in other θ-solvents. (2-butanone at 293 K and bromobenzene at 351.5 K[13].) However, specific solvent effects have been found[13] for a mixed Freon θ-solvent, with $\langle r_0^2\rangle/nl^2 = 7.7$.

In the previous diffusion studies[5], measurements were made in toluene at 298 K, using the boundary-spreading technique[14], and the ratio of friction coefficients for the linear and cyclic species, f_r/f_l ($= D_l/D_r$) was found to be 0.84 ± 0.01. This ratio is in excellent agreement with theoretical predictions[15-17] in the impermeable limit and is unaffected by molecular expansion over the range studied. The insensitivity of this ratio to excluded volume has also been predicted theoretically.

Our previous suggestion[5] that PDMS was diffusing impermeably down to low molar mass appears to have been an oversimplification. We have since shown[7] that

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Table 1 Number-average molar masses (M_n) number-average number of friction centres (x_n), heterogeneity indices (M_w/M_n), diffusion coefficients (D) and mean concentrations ($\bar{c}$) of diffusion measurements, for linear (L1–L8) and cyclic (R1–R8) poly(dimethylsiloxane) fractions in bromocyclohexane at 288K

Fraction	M_n (g mol^{-1})	x_n	M_w/M_n	D (μm^2 s^{-1})	$\bar{c}$ (%w/w)
L1	312	4	1.0	282*	0.69
L2	386	5	1.0	235*	0.77
L3	700	9.3	1.01	174*	0.80
L4	1130	15	1.04	133*	0.76
L5	2130	28.5	1.11	96.9*	0.72
L6	5280	71	1.03	59.6*	0.98
L7	10240	138	1.20	43.2*	0.71
L8	14980	202	1.14	32.7*	0.80
R1	222	3	1.0	337	0.74
R2	296	4	1.0	274	0.78
R3	520	7	1.02	217	0.76
R4	1070	14.5	1.04	150	0.79
R5	2080	28	1.01	109	0.76
R6	3710	50	1.04	83.0	0.73
R7	8480	114.5	1.14	55.6	0.73
R8	17380	234.5	1.08	35.3	0.73

* Data from Ref. 7

Table 2 Number average molar masses (M_n), number-average number of friction centres (x_n), heterogeneity indices (M_w/M_n), diffusion coefficients (D) and mean concentrations ($\bar{c}$) of diffusion measurements, for linear (L9–L11) and cyclic (R9–R11) poly(dimethylsiloxane) fractions in bromocyclohexane at 301 K

Fraction	M_n (g mol^{-1})	x_n	M_w/M_n	D (μm^2 s^{-1})	$\bar{c}$ (%w/w)
L9	4030	54	1.08	96.1	0.68
L10	10240	138	1.20	57.5	0.71
L11	14980	202	1.12	44.7	0.63
R9	3710	50	1.04	115	0.77
R10	8480	115	1.06	76.7	0.72
R11	17380	235	1.08	48.1	0.73

free-draining is important for low molar mass linear PDMS and that the friction centres must be taken as $\text{-}(CH_3)_2SiO\text{-}$ segments, rather than separate $\text{-}(CH_3)_2Si\text{-}$ and –O– segments. This was only revealed by a detailed theoretical study of the diffusion behaviour of short chain molecules[7,18].

EXPERIMENTAL

Preparation of samples

The cyclic PDMS fractions (with the exception of fractions R1 and R2, which were purchased pure) were recovered from ring-chain equilibrates as described previously[1,2,19,20]. The linear samples L1 and L2 were obtained as pure components and all other linear fractions were obtained from Dimethicones (Dow Corning DC200 series) using preparative g.p.c. The molar masses (M_n), number-average numbers of bonds (n_n) and heterogeneity indices (M_w/M_n) are given in *Tables 1* and *2*. The bromocyclohexane (from B.D.H.) was purchased 95% pure and redistilled before use.

Diffusion measurements

The diffusion measurements were carried out using the classical boundary-spreading technique. The diffusiometer, which has been described in more detail elsewhere[5,8] consists of a modified Perkin-Elmer electrophoresis apparatus, employing Rayleigh–Svensson optics and a greaseless diffusion cell. The diffusion cell was thermostatically controlled to ±0.01 K using a water bath and circulating pump.

RESULTS AND DISCUSSION

Concentration dependence of the diffusion coefficient

The diffusion data for the linear and cyclic fractions in bromocyclohexane at 288 K and 301 K are listed in *Tables 1* and *2* respectively, together with the mean concentrations ($\bar{c}$) at which the measurements were made. The boundary-spreading technique is not well-suited to the measurement of the concentration dependences necessary to allow extrapolation of the data to infinite dilution. However, quasi-elastic scattering has been used to investigate the concentration dependence of the diffusion coefficient in toluene at 298 K[21]. These measurements support our previous assumption that extrapolation of measured diffusion coefficients to infinite dilution would alter the absolute values by less than 3% in a good solvent. It is expected that the concentration dependences would be even less in a poor solvent.

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

The diffusion data for the linear and cyclic fractions in bromocyclohexane at 288 K and 301 K are shown graphically in *Figure 1*. The data are plotted as $\log_{10}D$ *versus* $\log_{10}x$, where x is the number-average number of $\text{-}(CH_3)_2SiO\text{-}$ units or friction centres in themolecule. The data at 288 K cover the range $3<x<235$, whereas the data at 301 K cover the range $50<x<235$.

It can be seen from *Figure 1* that in bromocyclohexane at 288 K, the ratio of friction coefficients, f_r/f_l ($=D_l/D_r$) tends to unity as x decreases. The same behaviour is shown by cyclic and linear PDMS in toluene at 298 K if the data[5] are plotted in this way, indicating that free-draining cannot be neglected at short chain lengths. For free-draining flow, the chain segments behave as separate friction centres and the total molecular friction coefficient,

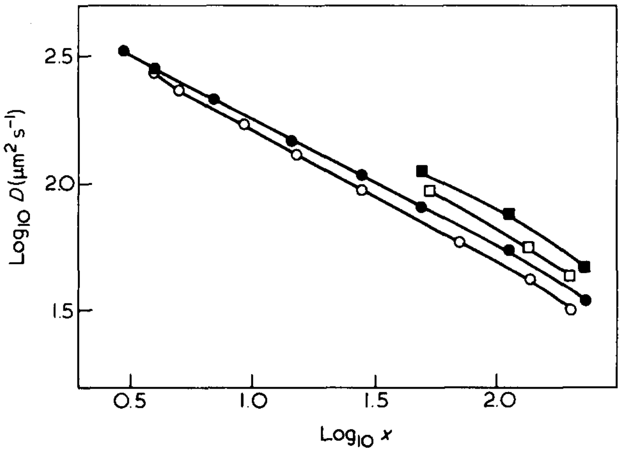

Figure 1 $\log_{10}D$ plotted against $\log_{10}x$ (where x is the number-average number of $\text{-}(CH_3)_2SiO\text{-}$ friction centres per molecule) for linear and cyclic PDMS in bromocyclohexane at 288 K (linear (○) and cyclic (●)) and at 301 K (linear (□) and cyclic (■))

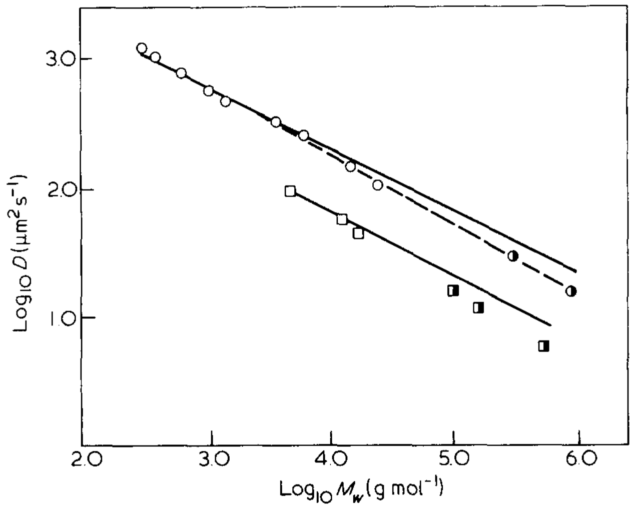

Figure 2 $\log_{10} D$ plotted against $\log_{10} M_w$ for linear PDMS in toluene at 298 K (○) and in bromocyclohexane at 301 K (□). Also included are the data of Haug and Meyerhoff[12] in toluene at 298 K (◑) and in bromocyclohexane at 301 K (◨). (———) $\log_{10} D$ calculated from unperturbed dimensions as described in text. (— — — —) curve through experimental points

f, where $f = kT/D$, (where k is the Boltzmann constant and T is the absolute temperature) depends only on the number of these friction centres and the friction coefficient per segment[18]. Hence, for complete free-draining flow the ratio of friction coefficients, f_r/f_l, becomes equal to unity.

In the impermeable limit ($x > 50$), the ratio $f_r/f_l = 0.83$ in bromocyclohexane at both 288 K and 301 K. This ratio is in excellent agreement with the theoretically predicted value of $8/3\pi = 0.85$[15-17] and with the value of 0.84 ± 0.01 found previously[5].

Comparison with the data of Haug and Meyerhoff

The diffusion data for linear PDMS can be compared with data obtained previously by Haug and Meyerhoff[12] for high molar mass linear PDMS in toluene at 298 K and bromocyclohexane at 301 K. *Figure 2* shows a comparison of the data for linear PDMS plotted as $\log_{10} D$ *versus* $\log_{10} M_w$. The unbroken lines in *Figure 2* show the unperturbed diffusion coefficients calculated using the familiar Kirkwood equation[22,23]:

$$D = \frac{kT}{x\zeta} + \frac{kT}{6\pi\eta_0}\frac{x^2}{[R^{-1}]} \qquad (1)$$

where $\zeta = 6\pi\eta_0 a$, η_0 is the solvent viscosity, a is the radius of a $\{(CH_3)_2SiO\}$ segment (taken[7] as 0.25 nm), and $[R^{-1}] = \sum_{\substack{i \neq j \\ i,j}} \langle r_{ij}^{-1} \rangle$, where $\langle r_{ij}^{-1} \rangle$ is the mean reciprocal separation of segments i and j. For $x > 75$, $x^2/[R^{-1}]$ was calculated from the unperturbed mean-square radius of gyration $\langle s_0^2 \rangle$ using the relationship[18]

$$\langle s_0^2 \rangle^{1/2} = \frac{8}{3\pi^{1/2}}\frac{x^2}{[R^{-1}]} \qquad (2)$$

It can be seen from *Figure 2* that the data of Haug and Meyerhoff[12] are in good agreement with our results. Furthermore, for $M_w < 10^4$ there is excellent agreement with the calculated diffusion coefficients for unperturbed chains. The data in toluene show that the effects of excluded volume are negligible for $x < 50$ and the slope of the dashed line is -0.54 ± 0.02 which is close to the value expected for a linear polymer in a good solvent. However the data in bromocyclohexane at 301 K also appear to show the effects of molecular expansion, although bromocyclohexane at this temperature is a well-established θ-solvent.

Figures 3 and *4* show the diffusion data for cyclic and linear PDMS respectively in toluene at 298 K and bromocyclohexane at 288 K and 301 K, plotted as $\log_{10} (1/r_D)$ *versus* $\log_{10} M_w$. Plotting the data as $\log_{10} (1/r_D)$ rather than $\log_{10} D$ removes the effect of solvent viscosity and *Figures* 3 and 4 show that the diffusion radii of both cyclic and linear PDMS are insensitive to change of solvent over the complete molar-mass range studied.

CONCLUSIONS

The data presented here and in Part 5 of this series[5] have demonstrated that the ratio of friction coefficients in the impermeable limit for linear and cyclic species of the same molar mass is in excellent agreement with the theoretical prediction of $8/3\pi$. The ratio is also insensitive to changes in solvent and to the effects of chain expansion.

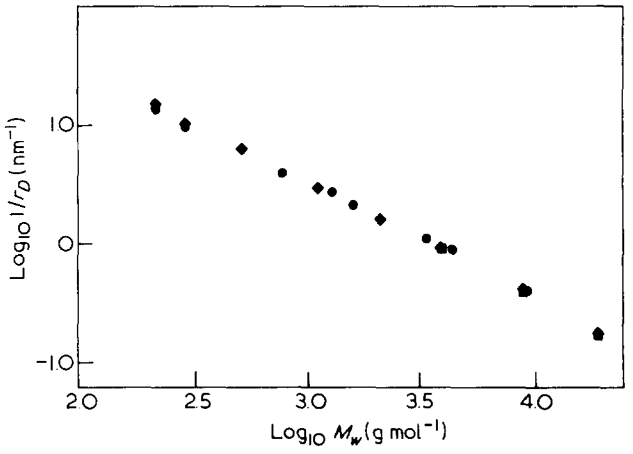

Figure 3 $\log_{10} (1/r_D)$ plotted against $\log_{10} M_w$ for cyclic PDMS in toluene at 298 K (●), in bromocyclohexane at 301 K (■) and in bromocyclohexane at 288 K (◆)

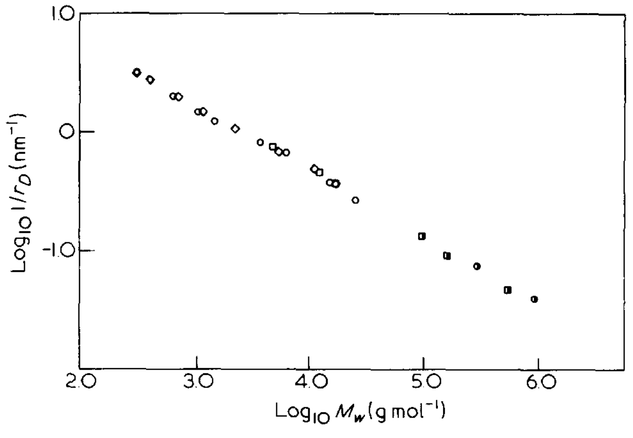

Figure 4 $\log_{10} (1/r_D)$ plotted against $\log_{10} M_w$ for linear PDMS in toluene at 293 K[5] (○), in bromocyclohexane at 301 K (□), in bromocyclohexane at 288 K (◇), in toluene at 298 K[12] (◑) and in bromocyclohexane at 301 K[12] (◨)

We have shown previously[7] that free-draining cannot be neglected for low molar-mass linear PDMS in toluene and bromocyclohexane and that the friction centres must be taken as $\left(CH_3\right)_2SiO$ segments. The data presented here for linear and cyclic PDMS in bromocyclohexane confirm these observations and that the ratio f_r/f_l tends to unity as x decreases, illustrating the increasing importance of free-draining at short chain lengths.

The authors' data for linear PDMS in toluene at 298 K and in bromocyclohexane at 301 K are in good agreement with the high molar-mass data of Haug and Meyerhoff[12]. However, the data obtained in bromocyclohexane at 301 K, which is apparently a well established θ-solvent, unexpectedly show the effects of chain expansion. This expansion was not evident from Haug and Meyerhoff's intrinsic viscosity measurements[12], which were restricted to a limited range of chain lengths. It may be a specific polymer–solvent effect, but data on the comparative behaviour of intrinsic viscosities and diffusion coefficients of PDMS as a function of molar mass, in other θ-solvents may help to resolve the anomaly.

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NOTE ADDED IN PROOF

The apparent expansion of the hydrodynamic radius of PDMS in bromocyclohexane at 301 K found in the present work has also recently been reported by J. P. Munch, J. Herz, S. Boileau and S. Candau (*Macromolecules*, 1981, **14**, 1370). These authors used quasi-elastic light scattering to measure the diffusion coefficient of a single fraction of high molar mass linear PDMS ($M_w = 148\,000$ g mol^{-1}) as a function of temperature in several solvents.

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