Cyclic polysiloxanes: 2. Neutron scattering from poly(phenylmethylsiloxane)

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The z-average radii of gyration $\langle s^2\rangle_z$ of both cyclic (r) and linear (l) poly(phenylmethylsiloxanes) (PPMS) in dilute solution in benzene-d_6 were measured by small-angle neutron scattering. The PPMS samples studied consisted of fractions with heterogeneity indices in the range $1.04 < M_w/M_n < 1.15$ and z-average molar masses in the range $3500 < M_z < 21\,200$ g mol^{-1}. The neutron scattering results were found to be in agreement with the theoretically predicted ratio $\langle s^2\rangle_l/\langle s^2\rangle_r = 2$ for 'flexible' linear and cyclic polymers unperturbed by excluded volume effects. The neutron scattering functions of cyclic and linear PDMS with scattering vectors Q in the region $Q\langle s^2\rangle^{1/2} > 1$ were also examined.

(Keywords: cyclic poly(phenylmethylsiloxane); linear poly(phenylmethylsiloxane); small-angle neutron scattering)

INTRODUCTION

Small-angle neutron scattering (SANS) has previously been used to measure the z-average mean square radii of gyration $\langle s^2\rangle_z$ of cyclic and linear poly(dimethylsiloxanes) (PDMS). The polymers were narrow fractions with molar masses in the range $4900 < M_z < 21\,000$ g mol^{-1}. They were measured in dilute solutions of benzene-d_6[1]. The experimental ratio $\langle s^2\rangle_{z,l}/\langle s^2\rangle_{z,r} = 1.9 \pm 0.2$ agreed with the theoretical ratio of 2.0, predicted for 'flexible' high molar mass linear (l) and ring (r) polymers unperturbed by excluded volume effects[2-8]. The corresponding experimental ratio of 1.82 ± 0.15 has recently been reported for cyclic and linear polystyrenes in the molar mass range $12\,000 < M_z < 22\,000$ g mol^{-1}, for polymers in dilute solution in toluene-d_8[9]. Neutron scattering from cyclic polymers has been reviewed by Dodgson and Higgins[10], including considerations of particle scattering functions[11].

This paper reports the first neutron scattering investigations of cyclic PPMS, together with the corresponding linear polymers. One purpose of this study was to characterize the recently prepared cyclic PPMS as a ring polymer, another was to compare the scattering properties of cyclic PPMS with those of the commercially-important linear PPMS.

EXPERIMENTAL

Neutron scattering measurements

The cyclic and linear PPMS fractions were prepared and characterized by methods described previously[12-14]. The neutron scattering measurements were carried out at A.E.R.E., Harwell, using the small-angle scattering apparatus. PPMS in solution in benzene-d_6 (C_6D_6, 99+atom% D, supplied by Aldrich Chemicals) at concentrations of *ca.* 5% w/w were contained in 2 mm quartz cells (Hellman Ltd., UK). The measurements were carried out at 293 K.

The incident neutron beam was monochromated to a wavelength $\lambda = 6$ Å and values of the wave vector

$$Q = \frac{4\pi}{\lambda}\sin\frac{\theta}{2} \qquad (1)$$

(where θ represents the scattering angle) were in the range $0.024 < Q < 0.18$ Å^{-1} for samples R1–R3 and L1–L3. The values were in the range $0.024 < Q < 0.30$ Å^{-1} for samples R3 and L3.

Determination of radii of gyration

The normalized scattering intensities $I(Q)$ were determined as described previously[1]. In the Guinier region ($Q\langle s^2\rangle^{1/2} \leqslant 1$), the following relation applies for a polydisperse polymer sample in a thermodynamically ideal environment[15-18]

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Table 1 z-Average number of skeletal bonds n_z, z-average molar masses M_z, hetereogeneity indices M_w/M_n and M_z/M_w and radii of gyration $\langle s^2\rangle_z^{1/2}$ of the cyclic (R1–R3) and linear (L1–L3) poly(phenylmethylsiloxane) fractions

Fractions	n_z	M_z (g mol^{-1})	M_w/M_n	M_z/M_w	$\langle s^2\rangle_z^{1/2}$ [a] (Å)
R1	53	3590	1.04	1.04	8.1
R2	118	8010	1.05	1.05	13.7
R3	291	19870	1.04	1.04	19.0
L1	55	3890	1.04	1.04	11.9
L2	123	8500	1.14	1.14	18.6
L3	307	21130	1.15	1.13	26.7

[a] In benzene-d_6 at 293 K

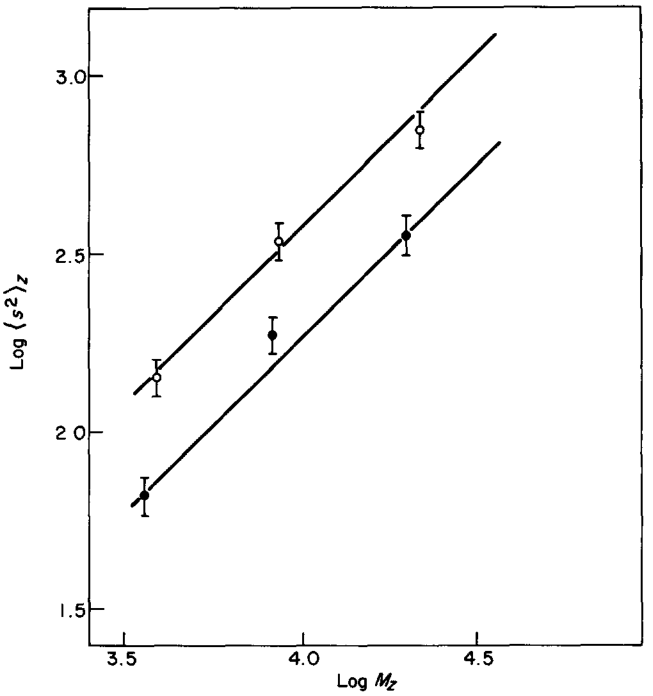

Figure 1 Plots of the logarithms of the z-average mean-square radii of gyration $\langle s^2\rangle_z$ of the linear (○) and cyclic (●) poly(phenylmethylsiloxane) fractions against the logarithms of their z-average molar masses M_z in benzene-d_6 at 293 K

$$\frac{Kc}{I(Q)}=\frac{1}{M_w}\left[\frac{1+Q^2\langle s^2\rangle_z}{3}\right] \tag{2}$$

where M_w is the weight average molar mass of the polymer, c is the solution concentration, $\langle s^2\rangle_z$ is the z-average mean-square radius of gyration and K is an instrumental constant. The radii of gyration for the ring and chain polymers were obtained from plots of $I(Q)^{-1}$ against Q^2 using the relationship

$$\langle s^2\rangle_z^{1/2}=\left[\frac{3\times\text{gradient}}{\text{intercept}}\right]^{1/2} \tag{3}$$

RESULTS AND DISCUSSION

Experimental radii of gyration

The $\langle s^2\rangle_z^{1/2}$ values for cyclic and linear PPMS fractions are presented in *Table 1*. In *Figure 1*, a log–log plot of $\langle s^2\rangle_z$ against M_z is shown. A straight line with unit gradient was constructed through the linear points and a parallel line was then constructed for cyclic PPMS in accordance with the relationship $\langle s^2\rangle_{z,l}/\langle s^2\rangle_{z,r}=2.0$. The experimental points for the cyclics were found to be in good accord with the predicted line (see *Figure 1*), which relates to ring molecules unperturbed by excluded volume effects.

Neutron scattering in the region $Q\langle s^2\rangle^{1/2}>1$

Maconnachie and Richards[17] have described four distinct regions of scattering behaviour, which depend upon Q and the molecular parameters of the polymer chain involved. For the high Q region where $\langle s^2\rangle^{-1/2}\leqslant Q\leqslant a^{-1}$ (a is the persistence length of the polymer chain[19]), the scattering intensity $I(Q)$ is expressed by the relationship

$$\frac{Kc}{I(Q)}=\frac{Q^2\langle s^2\rangle_z}{2M_w}$$

This expression refers to a polydisperse polymer unperturbed by excluded volume effects. Thus, for a dilute solution of a linear polymer obeying Gaussian statistics, plots of $c/I(Q)$ in the Guinier region and the high Q range are expected to have slopes that are proportional to $\langle s^2\rangle/3$ and $\langle s^2\rangle/2$ respectively, in accordance with equation (2) and equation (4). Casassa[4] has also predicted that the corresponding slopes for a dilute solution of a cyclic polymer obeying Gaussian statistics in the Guinier region and the high Q range would be proportional to $\langle s^2\rangle/6$ and $\langle s^2\rangle/2$, respectively.

Plots of $I(Q)^{-1}$ against Q^2 for a cyclic and linear PPMS fraction are shown in *Figures 2* and *3* respectively for Q values extended beyond the Guinier regions. These are delineated using the experimental radii of gyration. Although the plot for the linear PPMS fraction is a straight line, the corresponding plot for the cyclic PPMS fraction shows well marked upward curvature, as predicted theoretically[4] and found experimentally for cyclic poly(dimethylsiloxane)[1].

The various regimes of scattering behaviour of polymers in dilute solution may be distinguished from

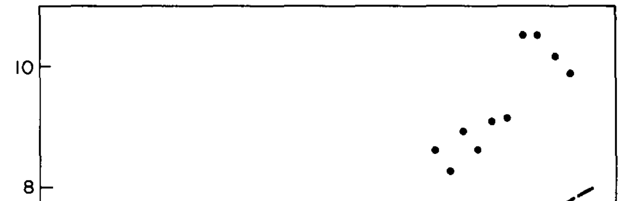

Figure 2 Plot of the inverse scattering intensities $I(Q)^{-1}$ against the scattering vectors Q^2 for cyclic PPMS fraction R2 ($n_z=118$) in benzene-d_6 at 293 K. The broken line was obtained using points in the Guinier region, the upper limit of this range being indicated by the arrow

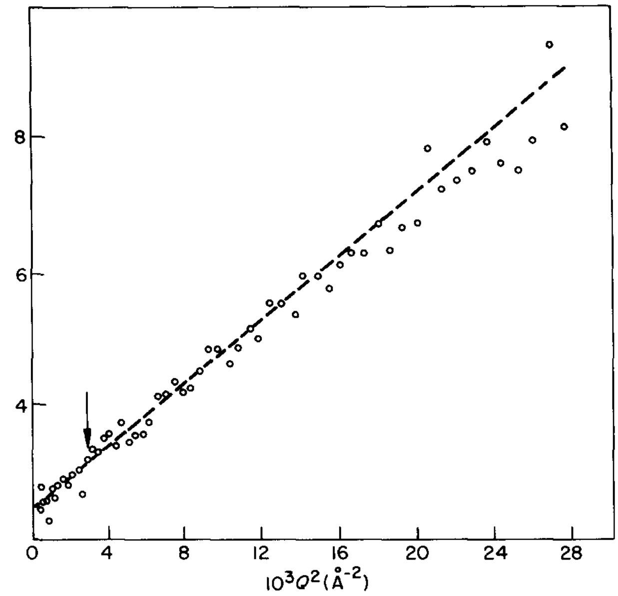

Figure 3 Plot of the inverse neutron scattering intensities $I(Q)^{-1}$ against the scattering vectors Q^2 for linear PPMS fraction L2 ($n_z = 123$) in benzene-d_6 at 293 K. The broken line was obtained using points in the Guinier region, the upper limit of this range being indicated by the arrow

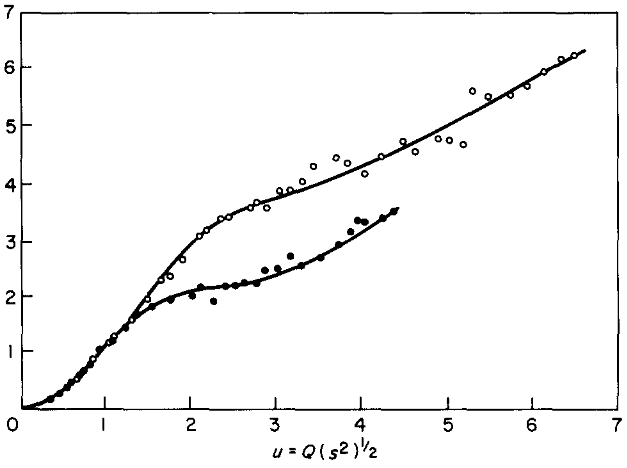

Figure 4 Kratky plots of $u^2I(Q)$ *versus* u for cyclic PPMS fraction R3 (●) and linear PPMS fraction L3 (○) in benzene-d_6 at 293 K

each other by plotting $Q^2I(Q)$ against Q[17,20]. Experimentally the following relationship applies

$$\frac{I(Q)}{I(0)} = P(Q).S(Q) \qquad (5)$$

where $I(Q)$ and $I(0)$ represent the scattering intensity at $Q = Q$ and $Q = 0$ respectively. $P(Q)$ is the particle scattering function that characterizes scattering from individual molecules and $S(Q)$ is a structure factor associated with intermolecular correlations. For a polymer molecule in dilute solution, $S(Q) \simeq 1$ and therefore $I(Q)/I(0) \simeq P(Q)$. Debye[21] has predicted that the particle scattering function $P(u)$ for linear polymers obeying Gaussian statistics is given by the following expression

$$P(u) = \frac{2}{u^4}(u^2 - 1 + e^{-u^2}) \qquad (6)$$

where $u = Q\langle s^2\rangle^{1/2}$. Casassa[4] and Burchard and Schmidt[22] have applied analytical methods to derive the following relationships for cyclic polymers obeying Gaussian statistics

$$P(u) = (2^{1/2}/u)D(u/2^{1/2}) \qquad (7)$$

where D denotes the Dawson integral. Equation (6) and equation (7) predict that as $u \to \infty$ the normalized Kratky plots ($u^2P(u)$ *versus* u) for cyclic and linear polymers approach their asymptotic limits of 2.0 and 1.0 respectively, in accordance with $\langle s^2\rangle_l/\langle s^2\rangle_r = 2.0$. Furthermore, equation (7) predicts a maximum in the Kratky plot of a cyclic polymer at $u = 2.15$.[22]

The Kratky plots for cyclic and linear PPMS fractions R3($n_z = 291$) and L3($n_z = 307$) in benzene-d_6 at 293 K are shown in *Figure 4*, where they may be compared with the theoretical predictions described above. Neither the cyclic nor the linear polymer plots asymptote as predicted by equations (6) and (7). Furthermore, the Kratky plot for the cyclic PPMS does not show a well-defined maximum at $u = 2.15$. However, the upward curvature observed for both the cyclic and linear PPMS at u values greater than *ca.* 3 has been predicted theoretically by Edwards, Richards and Stepto[23] for cyclic and linear PDMS with $n_n < 150$ using a rotational isomeric state model (RISM). They showed that deviations from the Gaussian statistics assumed in equations (6) and (7) would explain some of the discrepancies between the experiments and the theories. Edwards and coworkers[23] have carried out similar calculations on linear polyethene and linear poly(ethylene oxide). They found that the form of the particle scattering functions over the intermediate and high Q ranges to be sensitive to the effects of chain length, chain structure and chain flexibility.

Attempts to interpret the data from the small-angle neutron scattering experiments (as well as other conformationally dependent properties of cyclic and linear PPMS) using the RISM of the linear polymer[24,25] are in progress. Further investigations of the synthesis, characterization and properties of cyclic and linear polysiloxanes are being carried out.

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REFERENCES

1 Higgins, J. S., Dodgson, K. and Semlyen, J. A. *Polymer* 1979, **20**, 553
2 Kramers, H. A. *J. Chem. Phys.* 1946, **14**, 415
3 Zimm, B. H. and Stockmayer, W. H. *J. Chem. Phys.* 1949, **17**, 1301
4 Casassa, E. F. *J. Polym. Sci.* (*A*) 1965, **3**, 605
5 Yamakawa, H., 'Modern Theory of Polymer Solutions', Harper and Row, New York, 1971
6 Naghizadeh, J. and Sotobayashi, H. *J. Chem. Phys.* 1974, **60**, 3104

7 Boots, H. and Deutch, J. M. *Macromolecules* 1977, **10**, 1163

8 Prentis, J. J. *J. Chem. Phys.* 1982, **76**, 1574

9 Ragnetti, M., Geiser, D., Hocker, H. and Oberthur, R. C. *Makromol. Chem.* 1985, **186**, 1701

10 Dodgson, K. and Higgins, J. S. in 'Cyclic Polymers', (Ed. J. A. Semlyen), Applied Science, London, 1986

11 Edwards C. J. C., Richards, R. W., Stepto, R. F. T., Dodgson, K., Higgins, J. S. and Semlyen, J. A. *Polymer* 1984, **25**, 365

12 Clarson, S. J. and Semlyen, J. A. *Polymer* 1986, **27**, 1633

13 Clarson, S. J. *D.Phil. Thesis*, University of York, 1985

14 Clarson, S. J., Dodgson, K. and Semlyen, J. A. *Polymer*, in press

15 Zimm, B. H. *J. Chem. Phys.* 1948, **16**, 1093

16 Zimm, B. H. *J. Chem. Phys.* 1948, **16**, 1099

17 Maconnachie, A. and Richards, R. W. *Polymer* 1978, **19**, 739

18 Richards, R. W. in 'Developments in Polymer Characterization', (Ed. J. V. Dawkins), Applied Science, London, 1978

19 de Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, 1979

20 Kirste, R. L. and Oberthur, R. L. in 'Small-Angle X-ray Scattering', (Eds. O. Glatter and O. Kratky), Academic Press, London, 1982

21 Debye, P. *J. Phys. Chem.* 1947, **51**, 18

22 Burchard, W. and Schmidt, M. *Polymer* 1980, **21**, 745

23 Edwards, C. J. C., Richards, R. W. and Stepto, R. F. T. *Macromolecules* 1984, **17**, 2147

24 Mark, J. E. and Ko, J. H. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 2221

25 Freire, J. J. and Rubio, A. M. *J. Chem. Phys.* 1984, **81**, 2112