Studies of cyclic and linear poly(dimethyl siloxanes):
14. Particle scattering functions

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Particle scattering functions $P(Q)$ (where Q represents the wave vector), have been calculated using a Monte Carlo method for cyclic and linear poly(dimethyl siloxanes) (PDMS) containing up to 100 skeletal bonds. A maximum is found in the Kratky plot at u $(=Q\langle s^2 \rangle^{1/2}) \approx 2.0$ for cyclic PDMS (with root-mean-square radii of gyration $\langle s^2 \rangle^{1/2}$) and this is in satisfactory agreement with the analytical calculations of Casassa and of Burchard and Schmidt. In addition, other clearly-defined maxima are found at $u \approx 5.0$ for PDMS ring molecules with less than ≈ 40 skeletal atoms. These maxima are believed to be characteristic of small cyclic molecules as they are also predicted for small polymethylene rings. Comparisons are made with experimental small-angle neutron scattering (SANS) data for cyclic and linear PDMS. A single maximum in the experimental Kratky plot at $u \approx 2.0$ is found for PDMS ring molecules with an average of 550 skeletal atoms. The experimental data for cyclic PDMS are in better agreement with the Monte Carlo calculations of $P(u)$ than with analytical predictions up to $u \approx 2.0$.

Keywords Cyclic poly(dimethyl siloxane); linear poly(dimethyl siloxane); cyclic polymethylene; Monte Carlo calculations; particle scattering functions; neutron scattering

INTRODUCTION

Calculations of the radii of gyration[1] and shapes[2] of cyclic and linear poly(dimethyl siloxanes) (PDMS) have been described in recent publications in this series. In this paper, calculations are presented of the particle scattering function $P(Q)$ for cyclic PDMS. A comparison is made with Monte Carlo calculations[3] of $P(Q)$ for linear PDMS and with experimental particle scattering functions for cyclic and linear PDMS obtained using small-angle neutron scattering (SANS). In addition, $P(Q)$ has been calculated for short cyclic polymethylene (PM) chains and the general form of this function for small ring molecules is discussed.

The wave vector Q is given by[4-6]:

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

where λ represents wavelength and θ the scattering angle. The particle scattering function, $P(Q)$, is related to the intensity of scattered radiation in the following way[4-6]:

$$P(Q) = I(Q)/I(0) \tag{2}$$

where $I(Q)$ is the scattered intensity at scattering vector Q and $I(0)$ is the corresponding intensity when $Q = 0$.

$P(Q)$ contains detailed information about the segment distribution of a molecule on a wide range of distance scales. For example, at low Q (in the so-called Guinier

regime as $Q\langle s^2 \rangle^{1/2} \rightarrow 0$) $P(Q)$ is given by[4-6]:

$$P(Q) = 1 - \frac{Q^2 \langle s^2 \rangle_z}{3} \qquad (3)$$

The average of $\langle s^2 \rangle$ in equation (3) for polydisperse systems is only strictly the z-average if $\langle s^2 \rangle \propto M^a$ with $a = 1$.

Hence, measurements of $I(Q)$ as a function of Q allow the 'z-average' mean-square radius of gyration, $\langle s^2 \rangle_z$, to be determined when $a \approx 1$. In this connection, SANS has been used to measure[7] the radii of gyration of some cyclic and linear PDMS molecules in benzene-d_6. The ratio $\langle s_l^2 \rangle / \langle s_r^2 \rangle = 1.9 \pm 0.2$ (where l and r denote linear and cyclic, respectively) and this result is in good agreement with theoretical predictions[8] that $\langle s_l^2 \rangle / \langle s_r^2 \rangle = 2.0$ for 'flexible' polymers at the θ-point; despite the fact that benzene is a good solvent for PDMS. The relative insensitivity of the ratio $\langle s_l^2 \rangle / \langle s_r^2 \rangle$ to chain expansion has been discussed previously[9].

For values of $Q \gg 1/\langle s^2 \rangle^{1/2}$, $P(Q)$ depends on correlations between segments in the molecule which are separated by distances much shorter than $\langle s^2 \rangle^{1/2}$. The exact isotropic expression for $P(Q)$ is[10]:

$$P(Q) = \frac{\Sigma\Sigma g_i g_j \left\langle \dfrac{\sin(Q \cdot r_{ij})}{Q \cdot r_{ij}} \right\rangle}{\Sigma\Sigma g_i g_j} \qquad (4)$$

where r_{ij} represents the separation of segments i and j, and g_i and g_j are their respective contrast factors. The appropriate value of g for neutron scattering is given by:

$$g = (\rho - \rho_m)^2 \qquad (5)$$

where $\rho \ (= \Sigma b/v)$ and ρ_m are the scattering length densities of a segment and of the background medium, respectively. Σb is the total scattering length of a segment and v is its volume. The latter may be obtained from experimental densities or van der Waals radii. Values of b for commonly occurring nuclei are given elsewhere[6].

Previous approaches to the calculation of $P(Q)$ for ring molecules have used analytical methods. Casassa[11] and Burchard and Schmidt[12] assumed that for sufficiently large rings, the segmental pair distribution function differs from that of a Gaussian chain only in that the first and last segments are joined together. Hence, the pair distribution function can be represented by the convolution of two Gaussian distributions for the subchains connecting any pair of segments. This method gives rise to the following expression[11,12]:

$$P(u) = (2^{1/2}/u)\mathscr{D}(u/2^{1/2}). \qquad (6)$$

where $u = Q\langle s^2 \rangle^{1/2}$ and $\mathscr{D}(x)$ denotes the Dawson integral, which is tabulated in ref. 13. The corresponding expression for a Gaussian chain was first derived by Debye[14]:

$$P(u) = \frac{2}{u^4}(u^2 - 1 + e^{-u^2}) \qquad (7)$$

Equation (6) predicts a maximum in the Kratky plot $(u^2 . P(u)$ versus $u)$ at $u = 2.15$, as shown in *Figure 1*. As $u \rightarrow \infty$, the normalized Kratky plots for cyclic and linear species according to equations (6) and (7) tend to asymptotic limits of 1.0 and 2.0, in accord with $\langle s_l^2 \rangle / \langle s_r^2 \rangle = 2.0$.
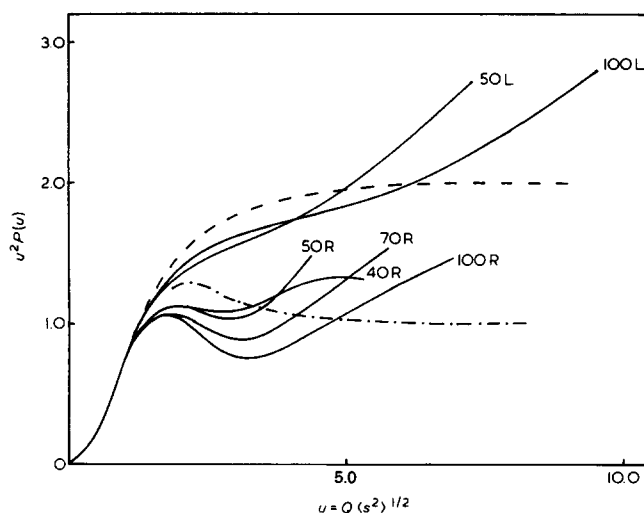

Figure 1 Normalized Kratky plots of $u^2.P(u)$ *versus* u, where $u = Q\langle s^2 \rangle^{1/2}$ (see text), calculated for PDMS molecules at 298 K with the numbers of skeletal atoms indicated. Ratio of contrast factors $g_i/g_j = 0.135$. Cyclic PDMS is denoted R, linear PDMS is denoted L. — · — · —, the Gaussian approximation to $P(u)$ for cyclic PDMS using equation (6); — — —, the Gaussian approximation to $P(u)$ for linear PDMS using equation (7)

This paper reports the results of calculations of $P(Q)$ for cyclic PDMS molecules containing up to 100 skeletal bonds. The calculations used equation (4) and a Monte Carlo method, which employs Metropolis sampling[15,16] as described in ref. 1.

The ring molecules generated are not perfect rings in that they comprise that fraction of chain conformations* with end separations which are less than 2 Å[1,2]. This imperfection has been discussed previously, and can be assumed to be unimportant in the following calculations. However, it is noted that it may be important in the calculation of properties which depend on sums of bond vectors (for example, dipole moments). For PDMS, the calculations used the rotational isomeric state model (RISM) developed by Flory, Crescenzi and Mark[17] to describe the statistical conformations of the chain. Similarly, for PM the RISM used was that developed by Abe, Jernigan and Flory[18]. Scattering centres were taken as being situated on atoms in the molecular backbone and appropriate values of the contrast factors g_i and g_j were used. The effective centre of the $-Si(CH_3)_2-$ scattering unit in PDMS molecules is slightly offset from the skeletal atom, but it has been shown[3] that this produces a relatively small effect at high values of Q and it is not taken into account here.

COMPUTATIONAL RESULTS AND DISCUSSION

Normalized Kratky plots $(u^2 . P(u)$ *versus* $u)$ for cyclic PDMS molecules at 298 K containing 40–100 skeletal bonds are shown in *Figure 1*, together with the plots predicted by equations (6) and (7). The latter are independent of chain length. The ratio of the contrast factors used corresponds to PDMS in benzene-d_6, the solvent employed in ref. 7.

There is an essentially common maximum in the calculated Kratky plots for cyclic PDMS at $u \approx 2.0$. This is in reasonable agreement with Cassasa[11] and Burchard

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* The term 'conformation' is used to specify the shape of a molecule, in keeping with the earlier papers of this series

and Schmidt's[12] prediction of a maximum at $u = 2.15$ for Gaussian rings. However, the maximum is less pronounced than that predicted by the analytical method and the plots do not attain the limiting value of 1.0, as $u \to \infty$. In addition, the plots for linear PDMS do not attain the expected asymptotic limit of 2.0. This reflects deviations from the Gaussian statistics assumed in the derivation of equations (6) and (7). Although the pair distribution function $W(r_{ij})$ may be Gaussian for large separations $|i-j|$ for both linear and cyclic molecules (i.e. at low Q), this approximation fails for small values of $|i-j|$, resulting in the observed discrepancies at high Q in *Figure 1*.

In addition, as shown in *Figure 1*, cyclic PDMS with 40 skeletal atoms displays a second maximum in the Kratky plot in the region $u = 5.0$. This is not shown by the rings with 50 or more skeletal atoms. Calculations of $P(Q)$ were extended to higher values of Q for PDMS rings with 12–26 skeletal atoms. The results of these calculations are shown in *Figure 2* and demonstrate that second maxima again occur with these smaller rings in the region $u \approx 5.0$. Furthermore, the maximum is most pronounced for the PDMS ring with 22 skeletal atoms, suggesting that this is another illustration of the special character of this particular PDMS ring molecule. Previously[2], it has been noted that the all-*trans* low-energy conformation of the PDMS chain with 22 skeletal atoms corresponds to a planar loop, which is a consequence of the unequal skeletal bond angles of the oxygen and silicon atoms. This results in special disc-like shapes which dominate the conformational statistics of PDMS rings in the region $n \approx 22$.

To explore this feature further, calculations of $P(Q)$ were carried out for short polymethylene (PM) rings. The results shown in *Figure 3* demonstrate that maxima corresponding to those observed for cyclic PDMS occur for cyclic PM at the same values of u. However, the second maxima for cyclic PM are less pronounced and show no enhancement at $n \approx 22$ as expected because the low-energy all-*trans* conformation for PM is linear.

Thus, the results show that small cyclic molecules have a special annular character whether they be PDMS or PM rings. This character becomes less pronounced with increasing ring size. In the limit of infinite chain length, the only distinctions between a cyclic molecule and the
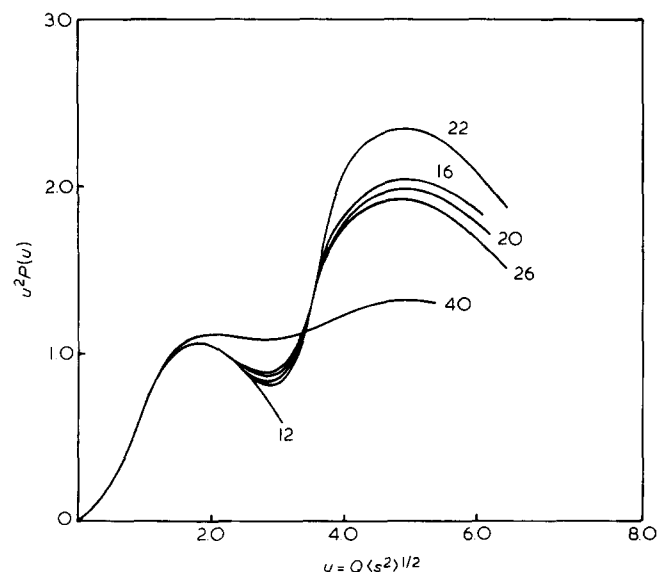

Figure 3 Normalized Kratky plot of $u^2 . P(u)$ *versus* u calculated for small PM rings at 298 K with the numbers of skeletal atoms indicated

equivalent linear molecule are the markedly increased segment density and the slightly more spherically symmetrical segment distribution of the cyclic species[2].

COMPARISON WITH EXPERIMENTAL DATA

Neutron scattering measurements were carried out at AERE, Harwell, UK using the small-angle diffractometer. Values of the wave vector Q were in the range $0.024 < Q < 0.20$ Å^{-1}. PDMS solutions in benzene-d_6 at concentrations of $\approx 5\%$ wt/wt were contained in 2 mm quartz cells. The ambient temperature was approximately 296 K. Scattered intensities were corrected for incoherent background scattering by subtracting the scattered intensity of mixtures of benzene and benzene-d_6 with the same total scattering length density as the solutions. The intensities were then normalized to the incoherent scattering from pure water.

Cyclic and linear PDMS fractions with number-average molar masses of 2.14×10^4 g mol^{-1} and 2.13×10^4 g mol^{-1}, respectively (corresponding to ≈ 550 skeletal bonds) and with heterogeneity indices (M_w/M_n) of 1.09 were prepared and characterized as described in previous papers of this series (see for example, ref. 19).

In *Figure 4*, the experimental normalized Kratky plots of $u^2 . I(u)$ *versus* u at 296 K are shown for the cyclic and linear PDMS together with plots calculated using equations (6) and (7). Also shown in *Figure 4* is the curve for cyclic PDMS with 100 skeletal bonds, calculated using equation (4) and the Monte Carlo method. The calculated curves were evaluated in terms of $u^2 P(u)$ and converted to values of $u^2 I(u)$ by multiplying by a constant factor of 2.6 which is equal to the ratio of the experimental value of $u^2 I(u)$ at high u for linear PDMS to the Gaussian asymptotic value of 2.0. In addition, values of the 'z-average' radii of gyration $\langle s^2 \rangle_z^{1/2}$ have been chosen to yield the best agreement between the experimental data and the calculated plots at low u. The values of $\langle s_r^2 \rangle_z^{1/2}$ and $\langle s_l^2 \rangle_z^{1/2}$ obtained in this way are 25 ± 4 Å and 36 ± 4 Å for the cyclics and linears, respectively, giving a ratio $\langle s_l^2 \rangle_z / \langle s_r^2 \rangle_z = 2.1 \pm 0.3$. These values can be compared with those interpolated from previous experimental measurements[7] at low Q, viz $\langle s_r^2 \rangle_z^{1/2} = 29$ Å and $\langle s_l^2 \rangle_z^{1/2} = 40$ Å.

Figure 2 Normalized Kratky plot of $u^2 . P(u)$ *versus* u calculated for small PDMS rings at 298 K with the numbers of skeletal atoms indicated. $g_i/g_j = 0.135$
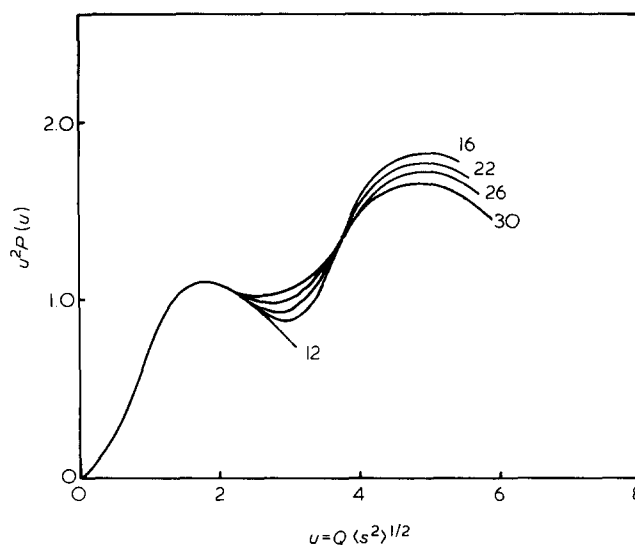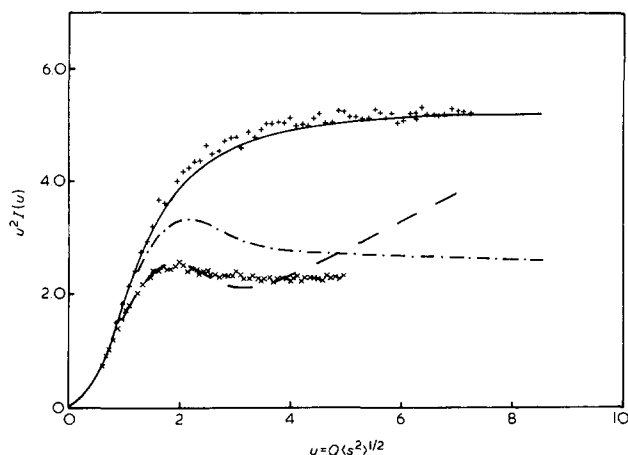
Figure 4 Normalized Kratky plots of $u^2.I(u)$ *versus u* for linear and cyclic PDMS. The experimental data for the linear ($M_n = 2.13 \times 10^4$ g mol^{-1}) and cyclic ($M_n = 2.14 \times 10^4$ g mol^{-1}) fractions are denoted + and ×, respectively. ——, calculated for linear PDMS using equation (7) and normalized to the same asymptotic limit as the experimental data (see text); —·—·—, calculated for cyclic PDMS using equation (6) and assuming that $\langle s_l^2 \rangle / \langle s_r^2 \rangle = 2.0$; ———, calculated using equation (4) and the Monte Carlo method for a 100-bond PDMS ring and reproduced from *Figure 1*

There is good agreement between the experimental data for linear PDMS and the plot obtained using equation (7), over the complete range of u. The agreement between the experimental data and the curve given by equation (6) which is based on Gaussian statistics is not so good. However, the experimental data for cyclic PDMS agree well with the curve calculated for a 100 bond ring using the Monte Carlo method up to $u \approx 2$. The calculated curve then exhibits a shallow minimum which is not shown by the experimental data. This may be due to the polydispersity of the sample, for the Monte Carlo calculations show that $P(u)$ is sensitive to ring size in this region of u.

Further experimental SANS studies of cyclic and linear PDMS are in progress. It is hoped that the theoretical treatment developed here will prove useful in the interpretation of the data obtained.

ACKNOWLEDGEMENTS

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