Studies of cyclic and linear poly(dimethylsiloxanes): 11. Shapes of ring and chain molecules

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The equilibrium shapes of cyclic and linear poly(dimethyl siloxane) (PDMS) molecules have been investigated using Flory, Crescenzi and Mark's rotational isomeric state model, together with a Monte Carlo method described previously. The principal axes of the equivalent ellipsoids have been computed and the major change on ring formation was found to be a reduction in the longest axis of the ellipsoid. This result is in agreement with previous studies of other ring molecules. The shapes of the cyclics $[(CH_3)_2SiO]_{w/2}$ in the region $w=20$ are disc-like and this observation is related to the different bond angles at silicon and oxygen atoms. Bulk densities and refractive indices of PDMS rings are discussed in relation to the calculated molecular shapes. Histograms are used to illustrate the proportional frequency functions of the radii of gyration and their components s_x, s_y and s_z.

Keywords Cyclic poly(dimethyl siloxane); linear poly(dimethyl siloxane); Monte Carlo calculations; molecular shapes; inertia tensor; radial frequency functions

INTRODUCTION

In the preceding paper of this series[1], calculations of the radii of gyration of cyclic (r) and linear (l) poly(dimethyl siloxanes) (PDMS) were described. The ratio of the mean-square radii of gyration $\langle s_l^2\rangle/\langle s_r^2\rangle$ was calculated to be 2.0 ± 0.1 for siloxane molecules with more than thirty skeletal atoms, in agreement with theoretical predictions[2-4] and experimental results[5] for the cyclic and linear polymers.

This paper reports calculations of the relative shapes of cyclic and linear PDMS molecules, thus providing a more detailed understanding of the relative properties of cyclic and linear PDMS. In general, the shape of a polymer molecule can be characterized in terms of the three principal axes of an equivalent ellipsoid. The ellipsoid describes the average shape of the molecule in a molecular reference frame, whereas the mean-square radius of gyration uses an external frame of reference and, as a result, contains no information about the shape of the molecule. However, the lengths of the principal axes of the ellipsoid are related to the components of s along those axes[6-8]. It has been recognized for some time that the three principal axes of the ellipsoid of a linear polymer molecule are unequal and that the relative length of the longest axis increases with the 'stiffness' of the molecule. Previous calculations by Šolc[9] and Mattice[10] have indicated that cyclic molecules are less asymmetric than the corresponding linear molecules. Here, the results of Monte Carlo calculations of the shapes of cyclic and linear PDMS molecules with up to 100 skeletal bonds are compared. Histograms are used to illustrate the changes in the distributions of s, and of its components s_x, s_y and s_z. Finally, the particular shapes of rings in the region of 22 skeletal atoms are shown to reflect changes in some bulk properties of cyclic PDMS at the same chain lengths.

THEORY

Characterizing the shape of a polymer molecule

For a polymer molecule comprising w identical segments (of unit mass), the inertia tensor may be written[8,11]:

$$\boldsymbol{T}' = \begin{bmatrix} T'_{xx} & T'_{xy} & T'_{xz} \\ T'_{yx} & T'_{yy} & T'_{yz} \\ T'_{zx} & T'_{zy} & T'_{zz} \end{bmatrix} \tag{1}$$

where the diagonal elements are given by:

$$T'_{xx}=\Sigma(y'_i+z'_i) \tag{2}$$

$$T'_{yy}=\Sigma(z'_i+x'_i) \tag{3}$$

$$T'_{zz}=\Sigma(x^i+y'_i) \tag{4}$$

x'_i, y'_i and z'_i are the coordinates of the ith segment in a centre-of-mass Cartesian reference frame, and the sums are from $i=1$ to $i=w$. The off-diagonal elements are:

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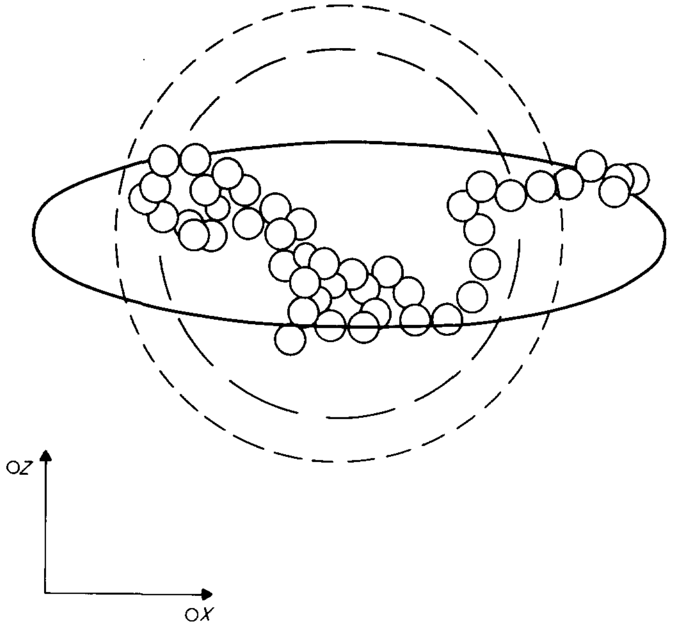


Figure 1 **View along OY principal axis of a PDMS chain of 100 skeletal atoms with sections of the average equivalent ellipsoid of constant segment density and spheres corresponding to the spherically-averaged radii. (———) Ellipse of semi-axes $\langle a^2\rangle^{1/2}$ and $\langle c^2\rangle^{1/2}$ along OX and OZ respectively. (— — —) Circle of radius $\langle r_s^2\rangle^{1/2}$ corresponding to sphere of constant segment density, and (—— ——) circle of radius $\langle s^2\rangle^{1/2}$**

$$T'_{xy}=T'_{yz}=-\Sigma x'_i.y'_i \qquad (5)$$

$$T'_{yz}=T'_{zy}=-\Sigma y'_i.z'_i \qquad (6)$$

$$T'_{xz}=T'_{zx}=-\Sigma x'_i.z'_i \qquad (7)$$

Diagonalization of the matrix $\boldsymbol{T}'$ yields $\boldsymbol{T}$, the inertia tensor in the principal axes reference frame. Here:

$$\boldsymbol{T}=\begin{bmatrix}\Sigma(y_i^2+z_i^2) & & \\ & \Sigma(z_i^2+x_i^2) & \\ & & \Sigma(x_i^2+y_i^2)\end{bmatrix} \qquad (8)$$

and

$$\Sigma(y_i^2+z_i^2)=w.k_x^2 \qquad (9)$$

$$\Sigma(z_i^2+x_i^2)=w.k_y^2 \qquad (10)$$

$$\Sigma(x_i^2+y_i^2)=w.k_z^2 \qquad (11)$$

where k_x^2, k_y^2 and k_z^2 are the squares of the radii of gyration about the principal axes OX, OY, and OZ, with the radii ordered so that $k_x \leqslant k_y \leqslant k_z$.

The square of the spherically averaged radius of gyration, s^2, is given by the equation:

$$s^2=\Sigma(x_i^2+y_i^2+z_i^2)/w \qquad (12)$$

and can be evaluated from $\boldsymbol{T}$ as:

$$s^2=\mathrm{trace}(\boldsymbol{T})/2w \qquad (13)$$

Similarly, the components of s along OX, OY and OZ are given by:

$$s_x^2=\Sigma x_i^2/w=(k_y^2+k_z^2-k_x^2)/2 \qquad (14)$$

$$s_y^2=\Sigma y_i^2/w=(k_z^2+k_x^2-k_y^2)/2 \qquad (15)$$

$$s_z^2=\Sigma z_i^2/w=(k_x^2+k_y^2-k_z^2)/2 \qquad (16)$$

Hence, using $\boldsymbol{T}$, a single conformation of a polymer molecule can be described in terms of an equivalent ellipsoid of uniform density with the same principal moments of inertia as the molecule. If the semi-axes of the ellipsoid are denoted by a, b and c, with $a \geqslant b \geqslant c$, then:

$$\frac{x^2}{a^2}+\frac{y^2}{b^2}+\frac{z^2}{c^2}=1 \qquad (17)$$

with

$$k_x^2=\tfrac{1}{5}(b^2+c^2) \qquad (18)$$

$$k_y^2=\tfrac{1}{5}(c^2+a^2) \qquad (19)$$

$$k_z^2=\tfrac{1}{5}(a^2+b^2) \qquad (20)$$

Thus, using equations (13)–(16)

$$s^2=(a^2+b^2+c^2)/5 \qquad (21)$$

and

$$s_x^2/a^2=s_y^2/b^2=s_z^2/c^2=\tfrac{1}{5} \qquad (22)$$

The averages over all conformations of the semi-axes of the equivalent ellipsoid and the components of s can be written as $\langle a^2\rangle$, $\langle b^2\rangle$ and $\langle c^2\rangle$ and $\langle s_x^2\rangle$, $\langle s_y^2\rangle$ and $\langle s_z^2\rangle$ respectively. *Figure 1* shows that in a typical conformation of a linear molecule, the segments lie within a section through the ellipsoid averaged over all conformations, but that several segments lie outside the radius of gyration. This illustrates the general point that the usual mean-square radius of gyration is an underestimate of the effective spherically averaged size of a molecule.

A more appropriate measure can be defined in terms of the dimensions of the semi-axes of the equivalent ellipsoid.

$$\langle r_s^2\rangle=(1/3)(\langle a^2\rangle+\langle b^2\rangle+\langle c^2\rangle)=(5/3)\langle s^2\rangle \qquad (23)$$

where $\langle r_s^2\rangle$ denotes the mean-square radius of the equivalent sphere of constant segment density. The volume of the sphere (V_{sph}) is

$$V_{\mathrm{sph}}=\frac{4\pi}{3}\langle r_s^2\rangle^{3/2}=\frac{4\pi}{3}\left(\frac{\langle a^2\rangle+\langle b^2\rangle+\langle c^2\rangle}{3}\right)^{3/2} \qquad (24)$$

and from equation (23) the volume based on $\langle s^2\rangle$ is V_s, where

$$V_s=\frac{4\pi}{3}\langle s^2\rangle^{3/2}=0.465\,V_{\mathrm{sph}} \qquad (25)$$

RESULTS AND DISCUSSION

The shapes of PDMS molecules

The computational methods described in the preceding paper[1] have been used to calculate the conformational averages of the principal axes of the equivalent ellipsoids, $\langle a^2\rangle$, $\langle b^2\rangle$ and $\langle c^2\rangle$, of linear and cyclic PDMS molecules containing numbers of skeletal atoms (w) between 12 and 100 and unperturbed by excluded volume

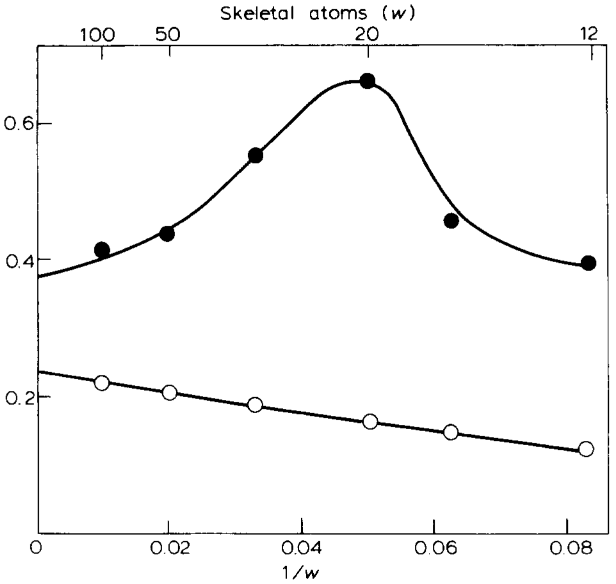


Figure 2 **Ratio of second largest to largest mean-square (m.s.) semi-axes of average equivalent ellipsoid ($\langle b^2\rangle/\langle a^2\rangle$) against reciprocal number of skeletal atoms (1/*w*). ● Cyclic PDMS; ○ linear PDMS**

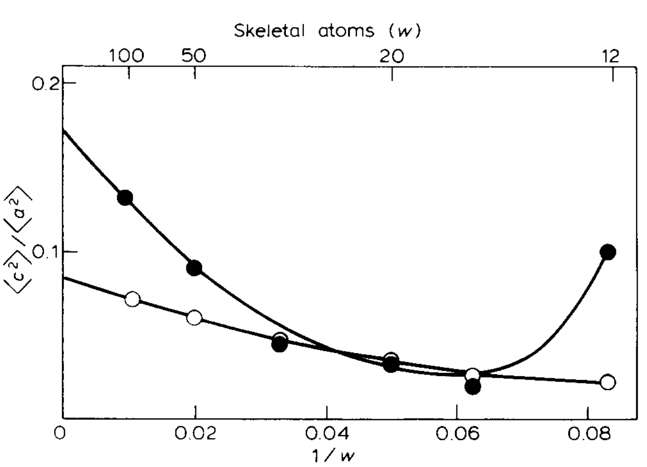


Figure 3 **Ratio of smallest to largest m.s. semi-axes of average equivalent ellipsoids ($\langle c^2\rangle/\langle a^2\rangle$) against reciprocal number of skeletal atoms (1/*w*). ● Cyclic PDMS; ○ linear PDMS**

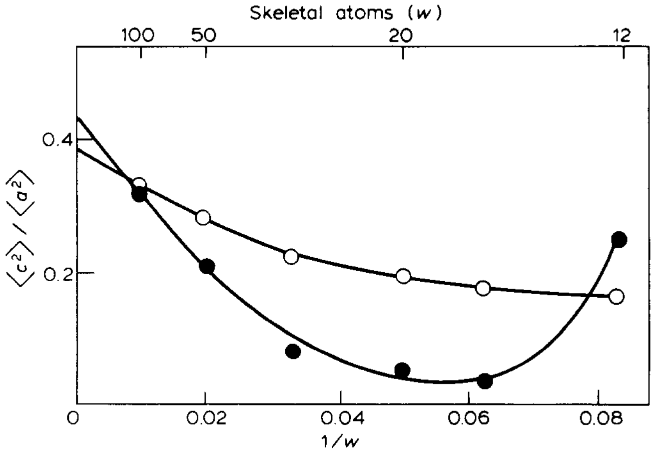


Figure 4 **Ratio of smallest to second largest m.s. semi-axes of average equivalent ellipsoid ($\langle c^2\rangle/\langle b^2\rangle$) against reciprocal number of skeletal atoms (1/*w*). ● Cyclic PDMS; ○ linear PDMS**

effects. The inertia tensor was evaluated and diagonalized for each accepted conformation, before averaging into the sample taken.

Figures 2, 3 and *4* show the variation of the ratios $\langle b^2\rangle/\langle a^2\rangle$, $\langle c^2\rangle/\langle a^2\rangle$ and $\langle c^2\rangle/\langle b^2\rangle$ with $1/w$ for cyclic and linear PDMS. For linear PDMS, these quantities increase monotonically with decrease in $1/w$ and the limiting values of the ratios $\langle a^2\rangle$:$\langle b^2\rangle$:$\langle c^2\rangle$ at infinite chain length are 11.9:2.56:1, in excellent agreement with the results obtained previously[8-10] (as shown in *Table 1*).

For cyclic PDMS, quite different results are obtained. The ratios $\langle b^2\rangle/\langle a^2\rangle$, $\langle c^2\rangle/\langle a^2\rangle$ and $\langle c^2\rangle/\langle b^2\rangle$ show a well-defined maximum or minimum centred around $w \cong 22$. Such behaviour is not unexpected, as the all-*trans* low-energy conformation of the PDMS chain with 22 skeletal atoms corresponds to a closed loop, which is a consequence of the unequal skeletal bond angles at the oxygen and silicon atoms[12]. Obviously, the shape of this all-*trans* conformation is that of a flat disc. Independent preliminary calculations for cyclic and linear PDMS molecules with $w \cong 24$ corroborate this behaviour, as do the experimental densities (ρ) and refractive indices (n_D). These quantities for cyclic PDMS with $w = 12$–100 are shown in *Figure 5*[13,14]. Well defined maxima in both properties are found in the region $w \cong 22$. These may reflect the changes in molecular 'packing' which would be expected to occur given the special disc-like shapes of the rings in that region. This change in 'packing' would produce an increase in density, due to the efficient way in which flat discs 'pack' in comparison to ellipsoids.

The limiting values of the ratios $\langle a^2\rangle$:$\langle b^2\rangle$:$\langle c^2\rangle$ at infinite chain length are 5.9:2.6:1 which are in good agreement with the values obtained for other large rings by Šolc[9] and Mattice[10] (see *Table 1*).

The change in the shape of linear PDMS molecules on

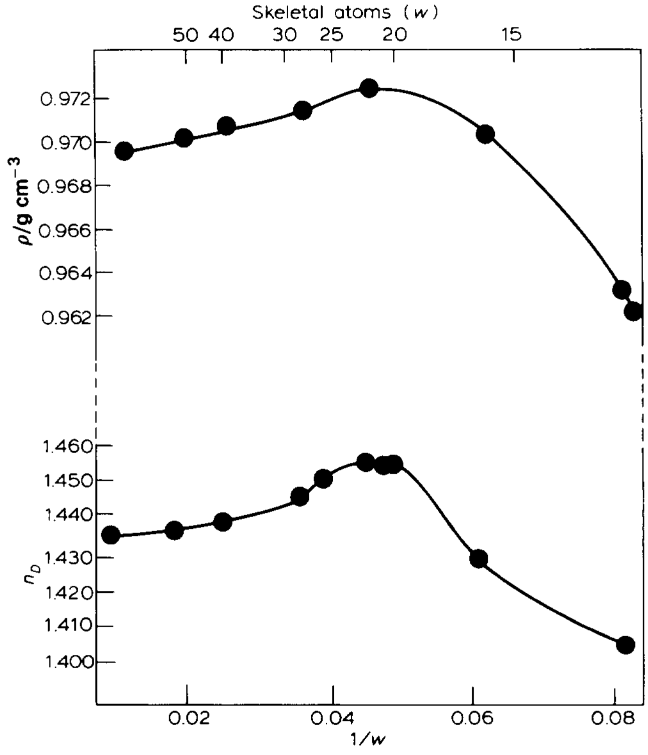
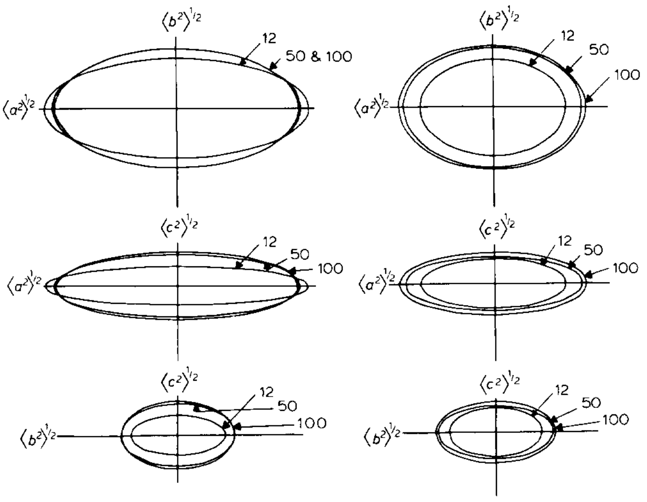


Figure 5 **Densities ρ and refractive indices (n_D) at 298 K plotted against reciprocal number of skeletal atoms (1/*w*) for cyclic PDMS ● (data from references 13 and 14)**

Table 1 Ratios of shape parameters for some cyclic and linear polymers

	$\langle a^2\rangle$	:	$\langle b^2\rangle$	:	$\langle c^2\rangle$
Linear molecule: cubic lattice[9]	11.8	:	2.7	:	1
Linear molecule: freely-jointed chain[10]	12.2	:	2.7	:	1
Linear molecule: polymethylene[8]	12.9	:	3.6	:	1
Linear molecule: PDMS (this work)	11.9	:	2.6	:	1
Cyclic molecule: cubic lattice[9]	6.5	:	2.4	:	1
Cyclic molecule: freely-jointed chain[10]	6.5	:	2.7	:	1
Cyclic molecule: PDMS (this work)	5.9	:	2.6	:	1



(i) Linear (ii) Cyclic

Figure 6 **Sections of average equivalent ellipsoids for cyclic and linear PDMS normalized to unit $\langle s_l^2\rangle^{1/2}$ for 12, 50 and 100 skeletal atoms**

ring formation is illustrated in *Figures 6(i)*, *6(ii)* and *7*, where ellipses are used to represent three mutually perpendicular sections through the equivalent ellipsoids for PDMS molecules containing 12, 50 and 100 skeletal atoms. All the ellipses have been scaled to unit root-mean-square radius of gyration of the linear chains. For linear PDMS, *Figure 6(i)* shows that there is a trend towards the limiting shape with increasing chain length and that short chains ($w=12$) are more asymmetric than longer ones ($w=50$ and $w=100$). For cyclic PDMS, *Figure 6(ii)* shows that the cyclic molecules are less asymmetric than the corresponding linear molecules and that the change in shape with increasing ring size is more gradual than in the linear case. In *Figure 7*, the change in shape with ring formation of a linear PDMS molecule with $w=100$ is illustrated. This figure emphasises the results in *Table 1*, showing that the largest change is in the longest axis *a*, and that the two smaller axes *b* and *c* are less affected.

Distributions of s, s_x, s_y *and* s_z

Histograms illustrating the proportional frequency functions of the sperically-averaged radii of gyration, *s*, and their components s_x, s_y and s_z have been constructed for cyclic and linear PDMS molecules with $w=12$–100 skeletal atoms. The main features shown by these histograms do not vary markedly with *w* except in the region of $w=20$. *Figures 8* and *9* are used to illustrate the frequency functions that have been obtained for molecules with $w=20$ and $w=50$.

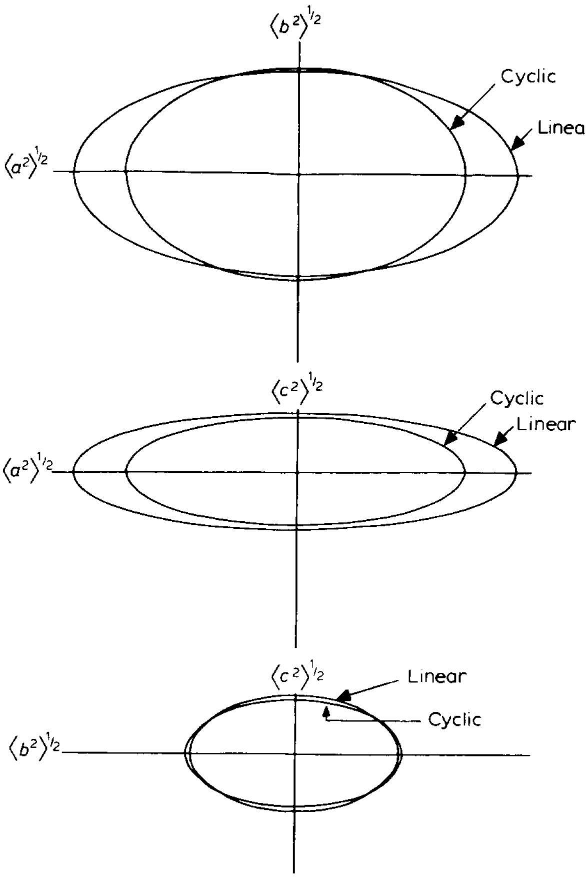


Figure 7 **Sections of average equivalent ellipsoids for linear and cyclic PDMS of 100 skeletal bonds normalised to unit $\langle s_l^2\rangle^{1/2}$**

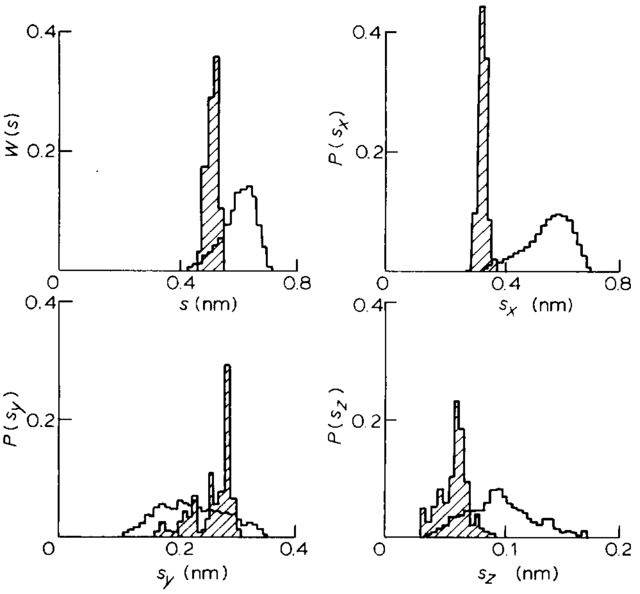


Figure 8 **Histograms of proportional frequency functions for cyclic and linear PDMS of 20 skeletal atoms. $W(s)$ – radial frequency function. $P(s_x)$, $P(s_y)$, $P(s_z)$ – frequency functions along the principal axes, OX, OY and OZ, respectively. The histograms for the cyclic molecules are shaded**

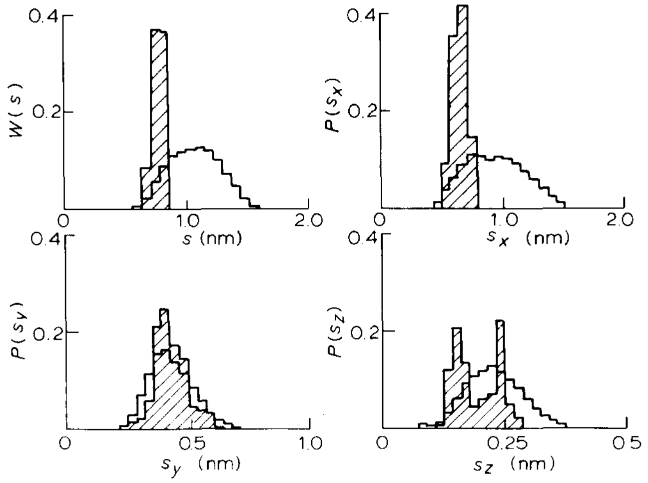


Figure 9 **Histograms of proportional frequency functions for cyclic and linear PDMS of 50 skeletal atoms. $W(s)$ – radial frequency function. $P(s_x)$, $P(s_y)$, $P(s_z)$ – frequency functions along the principal axes OX, OY and OZ, respectively. The histograms for the cyclic molecules are shaded**

The spherically-averaged radii of gyration of both the 20 and the 50 atom molecules show a considerable narrowing of their frequency functions ($W(s)$) on ring formation and the change in the mean values is approximately in the ratio $1{:}2^{\frac{1}{2}}$ as expected. Some unexpected features are revealed by the histograms for s_x, s_y and s_z for the cyclic molecules. The histograms for s_x are much narrower than those for s_y and s_z, and, for $w=50$, the latter are only slightly narrower than the corresponding linear histograms. In addition there is an increase in the y component of s on ring formation which is particularly marked for the 20 atom ring, and corresponds to a maximum in the ratio $\langle b^2\rangle/\langle a^2\rangle$ $(=\langle s_y^2\rangle/\langle s_x^2\rangle)$ concurrent with minima in the ratios $\langle c^2\rangle/\langle a^2\rangle$ and $\langle c^2\rangle/\langle b^2\rangle$. These conditions are believed to be associated with a dominant disc-like all-*trans* cyclic conformation in the region $w=22$. The bimodal nature of s_z at 50 atoms may be significant, but has not been investigated in detail.

CONCLUSIONS

Equivalent ellipsoids of constant segment density have been shown to provide useful descriptions of the shapes of cyclic and linear PDMS and, in the limit of infinite chain length, the shapes deduced are in agreement with those calculated previously for other models of ring and chain polymers[9–11]. There are secondary dependences of the ratios $\langle a^2\rangle{:}\langle b^2\rangle{:}\langle c^2\rangle$ on chain structure, but the main variation is the reduction in the major axis, $\langle a^2\rangle$, on ring formation.

Use of the equivalent ellipsoid or equivalent sphere of constant segment density is to be preferred to that of the more usual spherically-averaged radius of gyration ($\langle s^2\rangle$) if an effective size of a molecule is required.

Histograms illustrating the proportional frequency functions of the radii of gyration, s, and their components s_x, s_y and s_z confirm that the main change in shape that occurs on ring formation is that the frequency function for the component along the major principal axis of the ellipsoid is markedly reduced, both in mean value and in the breadth of the distribution.

A conformational transition region for cyclic PDMS around $w=22$ is predicted by the calculations and correlates with observed changes in density and refractive index. Its origin lies in the markedly unequal skeletal bond angles of the PDMS molecule.

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