Statistical conformations of cyclic dimethylsiloxanes

S. J. Mumby* and M. S. Beevers†

Speciality Polymer Group, Chemical Engineering and Applied Chemistry, The University of Aston, Aston Triangle, Birmingham B4 7ET, UK

(Received 14 May 1987; accepted 2 July 1987)

Rotational-isomeric-state models have been used to describe the statistical conformations of cyclic oligomers of dimethylsiloxane possessing 8–20 skeletal bonds. The results are compared with similar calculations made on linear-chain molecules of dimethylsiloxane. Cyclic dimethylsiloxanes, $[(CH_3)_2SiO]_x$, with $x=4$–10, appear to be relatively rigid, compared with their linear-chain counterparts, and their average shape is disc-like. For cyclic molecules possessing $\gtrsim 50$ skeletal bonds, the directional correlations between pairs of skeletal bonds approach those calculated for the corresponding open-chain molecules.

(Keywords: cyclic polydimethylsiloxane; linear polydimethylsiloxane; bond vector correlation; scalar products; rotational-isomeric-state model)

INTRODUCTION

Although cyclic oligomers of polymers, particularly those formed during condensation polymerization, have been known for a long time, it is only relatively recently that the potential importance of cyclic polymers has been recognized[1]. Indeed, there is now evidence for the existence of naturally occurring cyclic biopolymers, e.g. cyclic DNA[2]. Recently, Semlyen and coworkers, using gel permeation chromatography, gas–liquid chromatography and fractional distillation, have prepared quantitative amounts of low to medium molecular weight fractions of cyclic polydimethylsiloxane (PDMS), together, in some instances, with similarly prepared fractions of PDMS chains[3,4]. These materials, typically 0.2–2 g in quantity, are distinguished by their narrow distribution of molecular weights, typical heterogeneity indices being in the range 1.05–1.15. The fractions of cyclic PDMS have been the subject of much interest in the polymer community and a series of publications have appeared concerning various aspects of the physical behaviour of cyclic siloxanes in solution and in the pure state, e.g. neutron scattering[5], bulk viscosities[6], solution diffusion[7], thermal properties[8], light scattering[9], photon correlation spectroscopy[10], dipole moments[11] and optical anisotropy[12]. In a recent publication[13] by the present authors, the dipole moments were calculated for cyclic-forming conformations of oligomers of polydiethylsiloxane. These calculations involved a detailed computer analysis of the conformations of chains of PDMS $(\text{–Si(CH}_3)_2\text{O–})_x$ ($x=4$–10) with particular attention being given to the juxtaposition of chain termini and the relative orientation of terminal skeletal bonds. Stringent criteria were used to select cyclic-forming conformations prior to the calculation of molecular dipole moments. Concomitant with these calculations was the production of a structural database from which a number of conformationally dependent quantities may be calculated. One such quantity is the persistence length a, which has been defined[14] as the average sum of the scalar projections of skeletal bonds $j>i$ on skeletal bond i, for a very long chain of n skeletal bonds, such that $1<i<n$. The persistence length may be regarded as a convenient quantitative measure of the flexibility (or rigidity) of a polymer chain. Generally, the smaller the value of the persistence length, the more flexible is the chain, and the more rapid is the decrease of directional correlation between pairs of skeletal bond vectors with respect to an increase in the number of intervening bonds. For a polymer chain containing two different bond angle supplements (e.g. PDMS, for which $\angle(\text{OSiO})=70°$ and $\angle(\text{SiOSi})=37°$), two different persistence lengths may be defined depending on the choice of the reference bond i (i.e. either Si–O or O–Si). This is because the projection of the $(i+1)$th bond, l, on the preceding bond i may be either $l\cos(70°)$ or $l\cos(37°)$. Although the persistence length may be used as a quantitative measure of the orientational correlation between skeletal bonds of an open chain, its application to relatively small cyclic molecules is questionable. In the present study the individual scalar products $\langle \boldsymbol{m}_i \cdot \boldsymbol{m}_j \rangle$, quantities used in the calculation of persistence length of bond vectors $\boldsymbol{m}_i$ and $\boldsymbol{m}_j$, were used as a quantitative measure of orientational correlation between pairs of skeletal bonds in small cyclic structures.

THE ROTATIONAL-ISOMERIC-STATE MODEL

The method used to calculate the average orientations of skeletal bonds, with respect to an arbitrarily chosen reference coordinate system, employs a modified form of the rotational-isomeric-state model (RISM) of Flory, Crescenzi and Mark (FCM)[15], a model that was utilized in a previous publication concerned with the calculation of the electric dipole moments of polydimethylsiloxane chains[13]. The FCM single generator matrix required to describe the geometrical and energetic behaviour

---

*AT&T Bell Laboratories, Whippany Road, Whippany, New Jersey 07981, USA

† To whom correspondence should be addressed

0032-3861/88/010014-04$03.00

associated with each skeletal bond in the siloxane chain cannot be used directly to calculate the properties of cyclic molecules since it is not known at the outset which conformations of the open chain correspond to those adopted by a cyclic molecule with the same number of skeletal bonds. However, the FCM model may still be employed provided that one or two modifications are implemented. Essentially, all possible conformations, defined by a three-state RISM, of the open chain are generated using a computer program and the relative positions and orientations of the terminal skeletal bonds of the chains are carefully examined. If certain geometrical criteria are satisfied, then the conformations are accepted to be those adopted by the corresponding cyclic molecule and the statistically averaged scalar products $\langle \boldsymbol{m}_1 \cdot \boldsymbol{m}_j \rangle$ of bond vectors $\boldsymbol{m}_i$ and $\boldsymbol{m}_j$ are calculated. For details of the criteria used to select cyclic-forming conformers, see ref. 13.

STATISTICAL WEIGHT MATRICES

The original FCM scheme of statistical weight matrices used for describing the conformational energetics of linear PDMS requires modification before it can be used to assign statistical weights to cyclic-forming conformations of PDMS. This is necessary because it is known that there are no severe steric conflicts between non-bonded atoms or groups, separated by four skeletal bonds, for the sequence of bond rotational states $g^{\pm}g^{\mp}g^{\pm}g^{\mp}$ flanking a silicon atom[16,17], whereas the FCM model would assign a statistical weight of zero for such combinations of bond rotational states. Generally, for the calculation of physical properties (e.g. dipole moments) of long chains of polydimethylsiloxane this observation is of little consequence, but it becomes relatively important when considering the very small fraction of chain conformations that correspond to cyclic-forming conformations. In the present study this problem was taken into account by employing two types of statistical weight matrices U' for rotations about pairs of skeletal bonds flanking the silicon atom; one matrix corresponded to that employed for the open PDMS chain, namely:

$$U' = \begin{array}{c} \\ t_{i-1} \\ g_{i-1}^{+} \\ g_{i-1}^{-} \end{array} \left[\begin{array}{ccc} t_i & g_i^{+} & g_i^{-} \\ 1 & \sigma & \sigma \\ 1 & \psi\sigma & 0 \\ 1 & 0 & \psi\sigma \end{array}\right]$$

and was used to determine the statistical weights associated with sequences of rotational states $tg^{\mp}g^{\pm}t$ and $g^{\mp}g^{\mp}g^{\pm}g^{\pm}$; the other matrix was:

$$U' = \begin{array}{c} \\ t_{i-1} \\ g_{i-1}^{+} \\ g_{i-1}^{-} \end{array} \left[\begin{array}{ccc} t_i & g_i^{+} & g_i^{-} \\ 1 & \sigma & \sigma \\ 1 & \sigma & \sigma \\ 1 & \sigma & \sigma \end{array}\right]$$

this statistical weight matrix being used to calculate the statistical weights of conformations containing sequences of bond rotational states $g^{\pm}g^{\mp}g^{\pm}g^{\mp}$ centred about a silicon atom. The corresponding matrix for bond rotations about pairs of skeletal bonds centred about an oxygen atom is:

$$U'' = \begin{array}{c} \\ t_{i} \\ g_{i}^{+} \\ g_{i}^{-} \end{array} \left[\begin{array}{ccc} t_{i+1} & g_{i+1}^{+} & g_{i+1}^{-} \\ 1 & \sigma & \sigma \\ 1 & \sigma & \omega\sigma \\ 1 & \omega\sigma & \sigma \end{array}\right]$$

The quantity σ is the statistical weight assigned to $tg^{\mp}$ and $g^{\mp}g^{\mp}$ bond pairs. The factor ω is necessary to account for interactions in $g^{\mp}g^{\pm}$ conformations not present in $tg^{\mp}$ and $g^{\mp}g^{\mp}$ states. The statistical weights may be represented by the Boltzmann factors, $\sigma = \exp(-E_\sigma/RT)$, $\omega = \exp(-E_\omega/RT)$ and $\psi = \exp(-E_\psi/RT)$ where R is the gas constant, T the absolute temperature and E the energy, associated with the pair of bonds in a particular conformation, relative to the all-*trans* conformation. Analysis of the chain dimensions of polydimethylsiloxane gives $E_\sigma = 3.56\,\mathrm{kJ\,mol^{-1}}$, a positive energy arising from the disruption of favourable methyl–methyl interactions by transitions $t \rightarrow g^{\mp}$ about either Si–O or O–Si bonds. The value of energy E_ω, which characterizes interactions between oxygen atoms engendered in $g^{\mp}g^{\pm}$ conformations about Si–O–Si bonds, was found to be $4.39\,\mathrm{kJ\,mol^{-1}}$ (ref. 15). The energy E_ψ was assumed to be zero on the basis of careful consideration of interactions involved ($\psi = 1$), an acceptable assumption because of the relative insensitivity of chain dimensions to this parameter.

CALCULATION OF SCALAR PRODUCTS OF BOND VECTORS

The average scalar products $\langle \boldsymbol{m}_i \cdot \boldsymbol{m}_j \rangle$ were calculated for bond vectors $\boldsymbol{m}_i$ and $\boldsymbol{m}_j$, maintaining $\boldsymbol{m}_i$ fixed (the first skeletal bond in the chain, i.e. $i = 1$) for cyclic-forming conformations generated using linear chains of dimethylsiloxane $(\text{–Si(CH}_3)_2\text{O–})_x\text{Si}$ for $x = 4$–10 repeat units. Ideally, a chain conformation is accepted as a cyclic conformation when the terminal silicon atoms are superimposed (i.e. the end-to-end distance is zero) and the final bond ($i = n$) makes an angle of 110° (the OSiO bond angle) with respect to the first bond ($i = 1$). However, a rigorous adherence to these constraints reduces the number of accepted cyclic-forming conformations to a level that may not be statistically reliable. This problem becomes more important as the size of the cyclic molecule being considered is reduced. Conversely, the acceptance of conformations that possess too great an end-to-end distance will lead to the inclusion of a large proportion of chain-like conformations, which is also undesirable. As a consequence of the method used to generate cyclic-forming conformations from equivalent lengths of chains the calculation of the scalar products of the bond vectors must necessarily involve a consideration of the effect of the non-zero end-to-end distance for chains nominated as 'cyclic' molecules. *Figure 1* shows the average scalar projections of the skeletal bonds on the x-axis of a Cartesian coordinate system attached to the first bond of chains adopting cyclic-forming conformations for two different categories of end-to-end distance, $d < 0.1$ nm and $d < 0.35$ nm.

Also shown in *Figure 1* are the average bond projections for the open chain. Two plots are shown, one plot corresponding to data obtained for a chain that

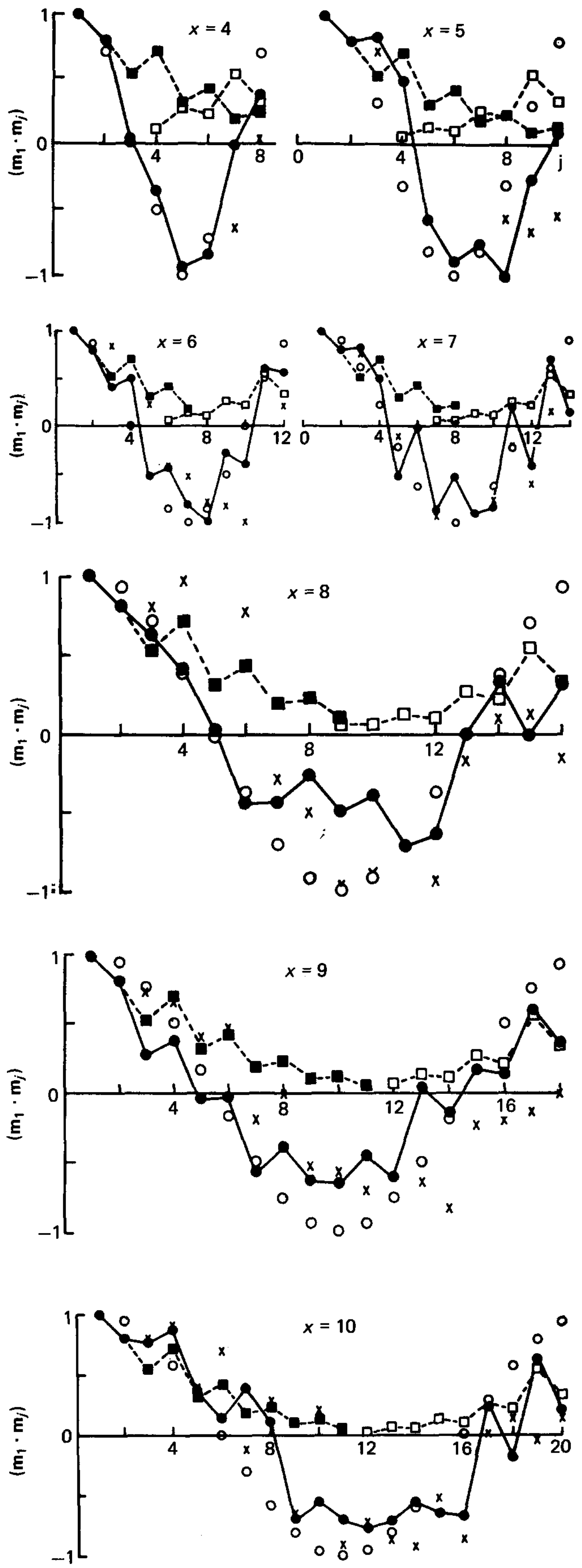

Figure 1 Average scalar products $\langle \boldsymbol{m}_1 \cdot \boldsymbol{m}_j \rangle$ of skeletal bonds j for cyclic-forming conformations of dimethylsiloxanes with end-to-end distances $d < 0.1$ nm (●) and $d < 0.35$ nm (×): (■) open chains terminated with a silicon atom; (□) open chains terminated with an oxygen atom; and (○) the polygon model (see text)

begins with an Si–O bond (full squares) and another plot (open squares) for data obtained for a chain terminated with an O–Si bond. Thus, for cyclic-forming conformations the data for skeletal bonds $i = 1$ (the skeletal bond to which the reference coordinate system is attached) through to skeletal bond $j = x$ may be compared to data obtained for the open chain starting with an Si–O bond. Similarly, the 'cyclic' data for skeletal bonds $j = x + 1$ through to skeletal bonds $j = 2x$ may be compared with data obtained for the open chain possessing a reference coordinate system attached to an O–Si bond. It is necessary to distinguish between Si–O and O–Si bonds, when each is being employed as the x-axis of reference coordinate systems, because of the two different bond angles present in the PDMS chain.

From an examination of the data presented in *Figure 1*, it can be seen that the statistical conformational behaviour of cyclic-forming conformations differs significantly from that associated with conformations generated for the equivalent length of chain. Thus, for cyclic-forming conformations the skeletal bonds opposite the bond associated with the reference coordinate system possess predominantly negative projections, indicative of a closed set of vectors forming a shape approximating to that of a circle. Furthermore, the scalar product $\langle \boldsymbol{m}_1 \cdot \boldsymbol{m}_j \rangle$, a direct measure of orientational correlation, for skeletal bonds separated by approximately x bonds, closely approaches the maximum possible value of -1 for cyclics $x = 4, 5, 6$ and 7. For the cyclic $x = 8$ the value of $\langle \boldsymbol{m}_1 \cdot \boldsymbol{m}_j \rangle$ $(j = x)$ is substantially smaller than that calculated for the smaller cyclics. However, $\langle \boldsymbol{m}_1 \cdot \boldsymbol{m}_j \rangle$ $(j = x)$ increases as x increases over the range $x = 8$ to $x = 10$. The behaviour of $\langle \boldsymbol{m}_1 \cdot \boldsymbol{m}_j \rangle$ $(j = x)$ can be rationalized by recognizing that the statistically weighted fraction of bonds occupying *trans* states increases sharply with increase in ring size, over the range $x = 4$ to $x = 10$ (ref. 13). Since the all-*trans* siloxane chain closes on itself when $x = 11$ and the *trans* states are favourably weighted relative to the *gauche* states the magnitude of $\langle \boldsymbol{m}_1 \cdot \boldsymbol{m}_j \rangle$ $(j = x)$ increases for cyclics $x = 8$ to $x = 10$. However, for sufficiently large cyclic molecules of PDMS it is predicted that, with respect to an arbitrarily chosen reference coordinate system (defined as bond $i = 1$), the directional correlation, indicated by $\langle \boldsymbol{m}_1 \cdot \boldsymbol{m}_j \rangle$, of successive skeletal bonds $j > i$ will gradually diminish and asymptotically approach zero as j approaches x. This is a consequence of the steady decline in the importance of conformations containing large proportions of all-*trans* sequences as x increases beyond 11, the value required for self-closure of the all-*trans* conformation. For values of j greater than x the scalar product $\langle \boldsymbol{m}_1 \cdot \boldsymbol{m}_j \rangle$ gradually increases as j increases since the number of skeletal bonds separating the reference bond $(i = 1)$ and the jth bond may now be considered to be decreasing as a consequence of the cyclic topology. *Figure 2* shows, in an illustrative manner, based on the behaviour of $\langle \boldsymbol{m}_1 \cdot \boldsymbol{m}_j \rangle$ calculated for cyclic molecules in the range $x = 4$–10, how the average bond projections are expected to vary as a function of $j - i$ and size of cyclic x. *Figure 3* shows the difference between the scalar products $\langle \boldsymbol{m}_1 \cdot \boldsymbol{m}_j \rangle$ for cyclics and chains, expressed as $|(\langle \boldsymbol{m}_1 \cdot \boldsymbol{m}_j \rangle_{\mathrm{cyclic}} - \langle \boldsymbol{m}_1 \cdot \boldsymbol{m}_j \rangle_{\mathrm{chain}}| / j$, plotted as a function of j for $x = 4$–10. For the smaller cyclic molecules the difference between the scalar products $\langle \boldsymbol{m}_1 \cdot \boldsymbol{m}_j \rangle$ of chains and cyclic-forming conformations is quite marked. As x increases, these differences decrease significantly, although even for $x = 10$, the largest cyclic considered in

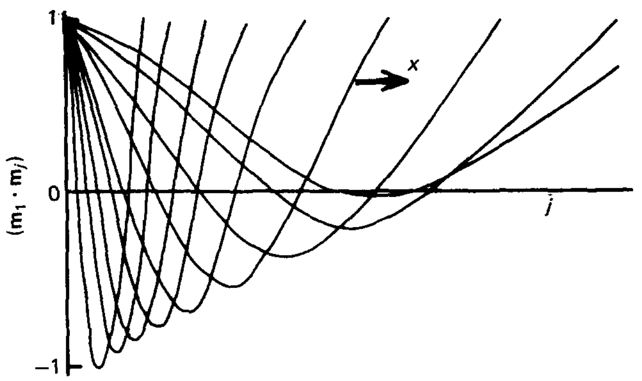

Figure 2 Idealized representation of the average scalar product $\langle \boldsymbol{m}_1 \cdot \boldsymbol{m}_j \rangle$ as a function of cyclic size, x, deduced from results obtained for cyclic-forming conformations of dimethylsiloxane oligomers possessing $n=8$ to $n=20$ skeletal bonds

this study, the directional correlations between the ith and $(i+x)$th bonds are still substantial. Thus, for cyclic-forming chains of PDMS possessing 20 skeletal bonds or less the statistical conformations may not be regarded as chain-like. For siloxane chains the FCM model predicts negligible directional correlation between bonds i and j for values of $j-i$ greater than 15. A least-mean-squares analysis of the differences in the projections of bond $j=x$ for cyclic-forming conformations and chain conformations indicates that at least 50 skeletal bonds are required before there is sufficient conformational flexibility to give values of $\langle \boldsymbol{m}_i \cdot \boldsymbol{m}_j \rangle_{\text{cyclic}}$ comparable to those calculated for the open chains of PDMS. It is instructive to consider a model in which the cyclic molecules of PDMS are each represented by a regular polygon of $2x$ sides. Choosing an Si–O bond, labelled $i=1$, to be the reference direction (the x-axis), the scalar product $\langle \boldsymbol{m}_1 \cdot \boldsymbol{m}_j \rangle$ of any other skeletal bond j may be readily calculated using simple geometry. The results of these calculations for $x=4$–10 are included in *Figure 1* and are represented by the open circles. For $x=4$–7 this polygonal model affords a close description of the average orientational behaviour of the skeletal bonds, although it can be seen that a better description could be achieved by fitting the FCM values of $\langle \boldsymbol{m}_1 \cdot \boldsymbol{m}_j \rangle_{\text{cyclic}}$ for the Si–O bond vectors (j odd) and O–Si bond vectors (j even) to two different polygons of size x, related to each other by a rotational angle $\alpha + 180/x$ about a central axis normal to the plane of the polygons. For a planar cyclic molecule the angle α would equal zero. This simple polygonal model is not able to describe the average projections of skeletal bonds for cyclics $x=8$, 9 and 10, since for these molecules the scalar products $\langle \boldsymbol{m}_i \cdot \boldsymbol{m}_j \rangle$ for skeletal bonds separated by approximately $2x$ skeletal bonds are significantly less than the maximum possible value of -1.

The present study of the conformational behaviour of cyclic-forming configurations of chains of dimethylsiloxane indicates that the cyclic molecules in the size range $x=4$ to $x=10$ are disc-like in shape and relatively rigid. It is also concluded that the statistical conformational behaviour of cyclic and chain molecules of PDMS, when described by the average directional correlation between skeletal bonds, is indistinguishable for molecules possessing $\gtrsim 50$ skeletal bonds. These conclusions are in good agreement with those published by Edwards *et al.*[18,19] in a comparative study of the shapes of cyclic and open-chain dimethylsiloxanes based on radii of gyration calculated using Monte Carlo techniques.

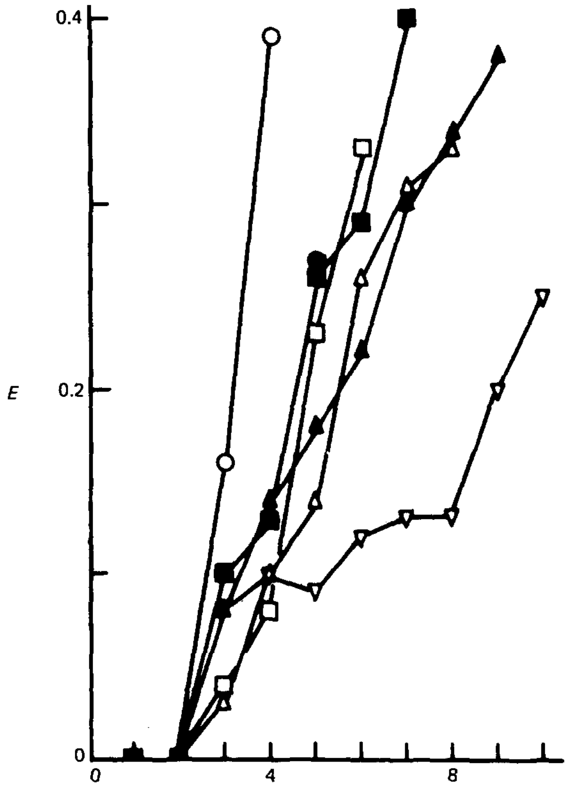

Figure 3 $E = |(\langle \boldsymbol{m}_1 \cdot \boldsymbol{m}_j \rangle_{\text{cyclic}} - \langle \boldsymbol{m}_1 \cdot \boldsymbol{m}_j \rangle_{\text{chain}})|/j$ for cyclic-forming conformations and open-chain conformations of dimethylsiloxane oligomers possessing $n=8$ (○), 10 (●), 12 (□), 14 (■), 16 (△), 18 (▲) and 20 (▽) skeletal bonds

ACKNOWLEDGEMENTS

The authors would like to thank the Science and Engineering Council for a research grant (SJM) and the Departments of Computing at the Universities of Aston and Manchester.

REFERENCES

1 Semlyen, J. A. (Ed.), 'Cyclic Polymers', Elsevier Applied Science, London, 1986

2 Freifelder, D. and Sinheimer, R. L. *Science* 1964, **146**, 254; and references cited in Ch. 7 of 'Cyclic Polymers' (ref. 1)

3 Dodgson, K. and Semlyen, J. A. *Polymer* 1977, **18**, 1265

4 Dodgson, K., Sympson, D. and Semlyen, J. A. *Polymer* 1978, **19**, 1285

5 Higgins, J. S., Dodgson, K. and Semlyen, J. A. *Polymer* 1979, **20**, 553

6 Dodgson, K., Bannister, D. J. and Semlyen, J. A. *Polymer* 1980, **21**, 663

7 Edwards, C. J. C., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1980, **21**, 781

8 Bannister, D. J. and Semlyen, J. A. *Polymer* 1981, **22**, 377

9 Edwards, C. J. C., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1982, **23**, 869

10 Edwards, C. J. C., Bantle, S., Burchard, W., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1982, **23**, 873

11 Beevers, M. S., Mumby, S. J., Clarson, S. J. and Semlyen, J. A. *Polymer* 1983, **24**, 1565

12 Mumby, S. J. and Beevers, M. S. *J. Chem. Phys.* 1985, **83**, 5260

13 Mumby, S. J. and Beevers, M. S. *Polymer* 1984, **25**, 1122

14 Flory, P. J., 'Statistical Mechanics of Chain Molecules', Interscience, New York, 1969

15 Flory, P. J., Crescenzi, V. and Mark, J. E. *J. Am. Chem. Soc.* 1964, **86**, 146

16 Semlyen, J. A. and Wright, P. V. *Polymer* 1969, **10**, 543

17 Beevers, M. S. and Semlyen, J. A. *Polymer* 1972, **13**, 385

18 Edwards, C. J. C., Rigby, D., Stepto, R. F. T., Dodgson, D. and Semlyen, J. A. *Polymer* 1983, **24**, 391

19 Edwards, C. J. C., Rigby, D., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1983, **24**, 395