

Dipole moments and statistical conformations of cyclic and linear dimethylsiloxane oligomers

M. S. Beevers and S. J. Mumby

Department of Chemistry, The University of Aston in Birmingham, Birmingham, B4 7ET, UK

(Received 10 October 1983; revised 7 January 1984)

The statistical conformations of cyclic dimethylsiloxane oligomers $[(\text{CH}_3)_2\text{SiO}]_x$ with x in the range 4–10 have been studied by using rotational isomeric state models to describe the 'cyclic' conformations of the open chain molecules. Stringent criteria were used to select 'cyclic' conformations of the equivalent open chains based on the relative orientations and rotational states of their terminal skeletal bonds. The root-mean-square electric dipole moments $\langle \mu^2 \rangle_0^{1/2}$ and the temperature coefficients $d \ln \langle \mu^2 \rangle_0 / dT$ were calculated using a modified form of the rotational isomeric state model of Flory, Crescenzi and Mark. The calculated dipole moments are compared with some experimental values measured for cyclic oligomers in the undiluted state at 298 K. For the 'cyclic' conformations of the open chains the magnitude of the calculated temperature coefficients for $x=5-9$ were found to be very nearly inversely proportional to the fraction of rotatable skeletal bonds occupying trans rotational states; a functional dependence opposite to that found for the open chains.

(Keywords: cyclic dimethylsiloxanes; dipole moment; average bond conformations; temperature coefficients)

INTRODUCTION

In a recent study¹ the static dielectric permittivities, refractive indices and densities of undiluted low molecular weight cyclic and linear dimethylsiloxanes and narrow molecular weight fractions of cyclic and linear poly(dimethylsiloxanes) were measured for number-average molar masses \bar{M}_n in the range $160 \leq \bar{M}_n \leq 7700$ at temperatures 298–313 K. The experimentally derived dipole moments of cyclic oligomers $[(\text{CH}_3)_2\text{SiO}]_x$ with $x \leq 10$ were observed to be significantly smaller than the experimental dipole moments of the corresponding linear molecules containing the same number of siloxane bonds. Other workers have calculated the dipole moments of poly(dimethylsiloxane) chains using rotational isomeric state models to describe the conformational behaviour of the chains, and have compared these values with those obtained experimentally²⁻⁴.

In this paper, the dipole moments of some cyclic dimethylsiloxanes with $x=4-10$ have been calculated using a modified form of the rotational isomeric state model (RISM) employed by Flory, Crescenzi and Mark in their calculations of the statistical conformations of poly(dimethylsiloxanes)⁵. The matrix representation of this model, which uses a single generator matrix to describe the geometrical and energetic properties associated with each repeat unit, cannot be used directly to calculate the properties of cyclic molecules since it is not known at the outset which conformations of the equivalent open chain correspond to those adopted by a cyclic molecule. However, the FCM model may still be utilized provided that one or two modifications are implemented. Essentially, all possible conformations, defined by a three-state RISM, of the equivalent open chains 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 a cyclic molecule and their statistical weights and dipole moments are calculated. The latter quantities may then be compared with values determined experimentally.

Cyclic conformations of equivalent open chains

The generation of cyclic conformations, using the concept of an equivalent open chain, raises an important question concerning the criteria used for the selection of the conformations of chains that approximate to conformations which could be adopted by the corresponding cyclic molecules. In a previous study it has been suggested that for unperturbed polymer chains a single test, involving only the end-to-end distance of the chains, may be used for this purpose^{6,7}. Thus, for example, if the ends of the chains are separated by less than 0.3 nm (say) then the chain conformations are assumed to be approximately the same as those of the corresponding cyclic molecules. Admittedly this is a subjective approach since it is necessary to choose an apparently arbitrary value for the maximum acceptable end-to-end distance between the terminal atoms of the chains. Nevertheless this simple selection procedure appears to be satisfactory for the calculation of the mean-square radii of gyration⁸ and equilibrium cyclization constants^{7,9-11} of cyclic dimethylsiloxanes. It seems that in these types of calculations it is sufficient to specify the relative positions of the terminal atoms or groups of the open chains solely in terms of the scalar part of the displacement vector of the terminal pair of atoms. However, this approach is not expected to be satisfactory for the calculation of the dipole

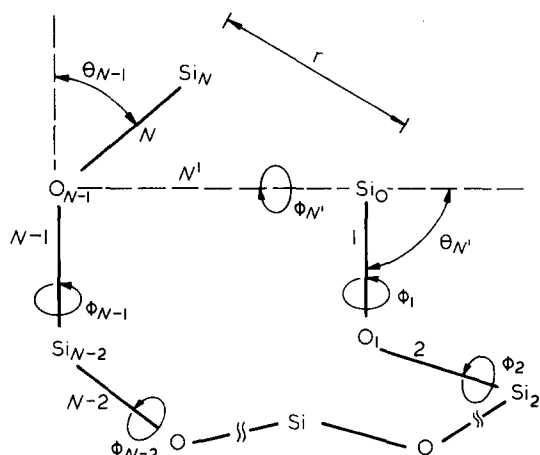


Figure 1 Equivalent open chain of a cyclic dimethylsiloxane $[(\text{CH}_3)_2\text{SiO}]_x (N=2x)$ showing terminal skeletal bonds juxtaposed for a trial cyclic conformation

moments of the cyclic oligomers of dimethylsiloxanes. This is because the model employed in the calculation of the dipole moments is based on the concept of an equivalent open chain and the relative orientations and rotational states of the terminal skeletal bonds of the chain must be accurately defined to permit evaluation of the molecular dipole moment. Consequently, a number of geometrical and conformational constraints must be imposed on the terminal skeletal bonds of the equivalent open chains which have to be satisfied before the conformations are accepted to be those adopted by a cyclic molecule. The structure and nomenclature used in the present calculations are depicted in *Figure 1*. In order to simplify certain aspects of the calculations the exact equivalent open chain of a cyclic x -mer $\{(\text{CH}_3)_2\text{SiO}\}_x$ was extended by an extra silicon atom, Si_N . Thus the equivalent chain used in the present calculations may be represented by $\{(\text{CH}_3)_2\text{SiO}\}_x\text{Si}$. The important geometrical parameters are the angle θ_N , which may be regarded as the bond angle supplement associated with the closing bond denoted by N' , the end-to-end distance r separating the terminal atoms Si_0 and Si_N of the equivalent open chain and the angle ϕ_N ; the latter being defined by the relative orientations of the first and $(N-1)$ th skeletal bonds. It may be seen that for perfect closure to form a cyclic structure the skeletal atom Si_N must be exactly superimposed on the skeletal atom Si_0 and the vector corresponding to the virtual bond denoted by N' must coincide with the N th bond vector (i.e. $r=0$). The supplementary bond angles were fixed at 37° for the oxygen atoms and at 70° for the silicon atoms (except θ_N which is to be calculated). The end-to-end distance r and angles θ_N and ϕ_N were calculated for each conformation generated by successively setting skeletal bonds $i=1, 2, \dots, N-1$ in all possible combinations of rotational states defined by *trans* ($\phi_i=0^\circ$) and *gauche* ($\phi_i=\pm 120^\circ$) conformations. The principal criteria used for the selection of cyclic conformations were that angle θ_N should lie within the range $70^\circ \pm 15^\circ$ and that angle ϕ_N should be close to the values used in the FCM RISM ($0^\circ \pm 15^\circ$ or $\pm 120^\circ \pm 15^\circ$).⁵ To avoid geometrical ambiguities arising from the position of skeletal atom O_{N-1} a check was made to ensure that its y coordinate, expressed in the coordinate system⁵ centred on Si_0 , was negative and that its z coordinate was not greater than ± 0.05 nm. The end-to-

end distance r should be zero for perfect cyclic formation, but this restriction excludes almost all of the generated conformations, many of which require only a small adjustment of the bond rotational angles to complete the closure of the ring. In a later section of this paper it will be demonstrated that fairly minor changes in the rotational states of the skeletal bonds can have a significant effect on the end-to-end distance of the chains without greatly modifying any other calculated parameters. Thus, conformations adopted by the equivalent chains were accepted to be cyclic conformations if their end-to-end distances were ≤ 0.35 nm, provided that they possessed a non-zero statistical weight and that they satisfied the angular restrictions discussed above. The bond rotational angle ϕ_N was evaluated and used (equations (1)–(2) below) in the calculation of the statistical weights of the resultant cyclic conformations.

In *Figure 2* the number, $n(x,r)$, of cyclic conformations accepted as a function of the end-to-end distance of the equivalent open chain are given for $x=4-10$. For $x=4-7$ the imposition of a three-state rotational isomeric state model results in a rather discontinuous functional form for $n(x,r)$ which rapidly becomes effectively continuous (subject to the incremental difference in r used to classify the end-to-end distances) for $x=8, 9$ and 10 . For $x=10$ a statistical weight cut-off procedure was used to reduce computing times by excluding conformations associated with statistical weights of less than 10^{-7} . The effect of this procedure on the calculated dipole moments will be discussed subsequently.

Rotational statistical weight matrices

Following Flory, Crescenzi and Mark's⁵ treatment of the statistical conformations of poly(dimethylsiloxanes)

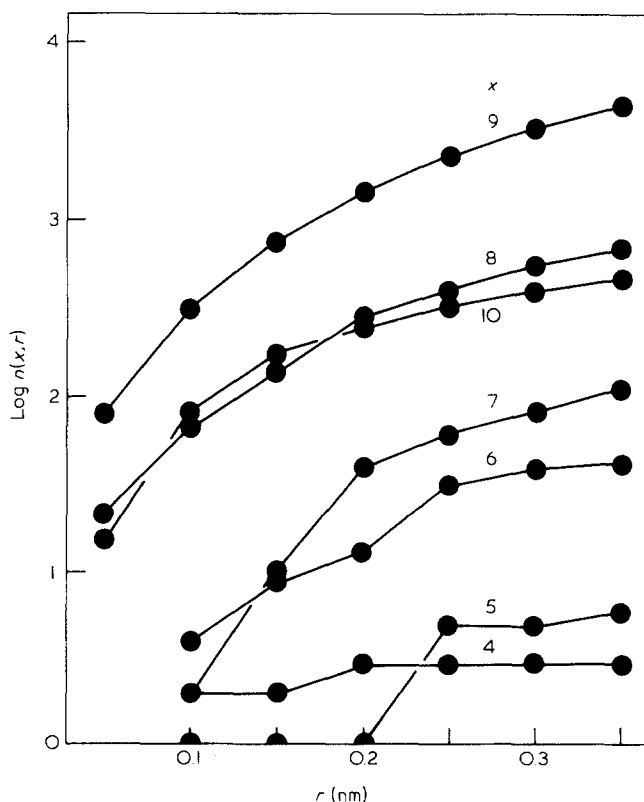


Figure 2 Numbers, $n(x,r)$, of cyclic conformations versus end-to-end distance r for $x=4-10$

statistical weight matrices U' and U'' are employed to take into account the mutual interdependence of the rotational states of pairs of skeletal bonds flanking silicon and oxygen atoms, respectively. The elements in these matrices are the Boltzmann factors $\exp(-\Delta E/RT)$ where ΔE is the difference in energy between the conformations of a pair of bonds and the all-*trans* conformation. Thus, for the dimethylsiloxanes

$$U' = \begin{matrix} & t_i & g_i^+ & g_i^- \\ t_{i-1} & \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & 0 \\ 1 & 0 & \sigma \end{bmatrix} \\ g_{i-1}^+ & \\ g_{i-1}^- & \end{matrix} \quad (1a)$$

and

$$U'' = \begin{matrix} & t_{i+1} & g_{i+1}^+ & g_{i+1}^- \\ t_i & \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \omega\sigma \\ 1 & \omega\sigma & \sigma \end{bmatrix} \\ g_i^+ & \\ g_i^- & \end{matrix} \quad (1b)$$

At 298 K, the temperature chosen for the present calculations, the values of the Boltzmann factors σ and ω are 0.238 and 0.170, respectively; values which correspond to energy differences required to reproduce the experimentally determined characteristic ratio, $\langle r^2 \rangle_0/nl^2$, and the temperature coefficient $d \ln \langle r^2 \rangle_0/dT$ of poly(dimethylsiloxane) in the undiluted state⁵. The above scheme requires modification before it can be used to assign statistical weights to conformations of cyclic dimethylsiloxanes. This is necessary because it is known that there are no severe steric conflicts between non-bonded atoms or groups for the sequence of bond rotational states $g \mp g \pm g \mp g \pm$ centred about a silicon atom, whereas the FCM model would accord a statistical weight of zero for such combinations of bond rotational states^{7,10}. For the calculation of the dipole moments of long poly(dimethylsiloxane) chains this observation is of little consequence, but it becomes relatively important when considering the very small fraction of chain conformations which correspond to cyclic conformations. In the present calculations this problem was taken into account by effectively employing two types of statistical weight matrices U' ; one matrix corresponding to the form already given in equation (1a) which was used to determine the statistical weight associated with sequences of rotational states $t g \pm g \mp t$ and $g \pm g \pm g \mp g \mp$, the other matrix being

$$U' = \begin{matrix} & t_i & g_i^+ & g_i^- \\ t_{i-1} & \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma \\ 1 & \sigma & \sigma \end{bmatrix} \\ g_{i-1}^+ & \\ g_{i-1}^- & \end{matrix} \quad (2)$$

which was used to calculate the statistical weight of conformations containing sequences of bond rotational states $g \mp g \pm g \mp g \pm$ centred about a silicon atom. This amended statistical weight scheme was employed in all the calculations involving cyclic conformations of the open chains, but as anticipated proved to be an unnecessary refinement for calculating the properties of the

linear dimethylsiloxanes free to adopt all possible conformations specified by the FCM model.

Calculation of the dipole moments

The statistical weight Ω and the dipole moment μ of each of the cyclic conformations was calculated assuming a value of 2.0×10^{-30} Cm for the silicon-oxygen bond² and zero dipole moments for all other bonds. After examination of all the 3^{N-1} ($=3^{2x-1}$) conformations generated for the equivalent open chain of a cyclic x -mer the mean-square dipole moment of the cyclic conformations with end-to-end distances in the range $0-r$, was calculated using the expression

$$\langle \mu^2 \rangle_0 = \frac{\sum_{\{\phi\}} \Omega \mu^2}{Z_r} \quad (3)$$

where Z_r is the configurational partition function of the cyclic conformations of the equivalent open chain with end-to-end distances in the range $0-r$ and is defined by

$$Z_r = \sum_{\{\phi\}} \Omega \quad (4)$$

and $\{\phi\}_r$ denotes summation over all conformations possessing end-to-end distances in the range $0-r$.

Table 1 lists values of Z_r for $x=4-10$ calculated using the FCM model and the hard-sphere model ($\sigma = \omega = 1$). The entries in the final column of Table 1 are the total configurational partition functions calculated for the equivalent open chains described by the FCM model. It is noteworthy that the configurational partition function associated with the cyclic conformations of any particular x -mer is several orders of magnitude less than the total configurational partition function of the corresponding equivalent open chain. In Table 2 the root-mean-square dipole moments for cyclics with $x=4-10$ calculated using the FCM model at 298 K, are listed as a function of the end-to-end distance r of the corresponding equivalent open chains. Included in this Table are the experimental values of $\langle \mu^2 \rangle_0^{1/2}$ measured for cyclics with $x=4, 5, 6, 7$ and 10 in the undiluted state at 298 K.

In a rigorously applied RISM the root-mean-square dipole moment should be calculated using only those conformations which possess, (1) a zero end-to-end distance r , (2) fixed bond angles and (3) a non-zero statistical weight. In practice this rigid approach proved not to be very successful because it excluded many potential cyclic conformations. This is a consequence of using a model in which discrete rotational states are assigned to each rotatable skeletal bond. An alternative approach is to consider how Z_r and $\langle \mu^2 \rangle_0^{1/2}$ vary as a function of the accepted end-to-end distance r of the equivalent open chains. Referring to Table 2 it can be seen that if the end-to-end distance is greater than about 0.15 nm then for a given value of x the calculated root-mean-square dipole moment is reasonably constant for different values of end-to-end distance up to a value of at least 0.35 nm (approximately less than 0.15 nm the number of accepted cyclic conformations decreases dramatically (Figure 2) and values of $\langle \mu^2 \rangle_0^{1/2}$ become either inaccurate and/or indeterminate. A more realistic approach would be to generate conformations using bond rotational states additional to those already specified by the FCM model, but such an

Table 1 Configurational partition function Z_r for cyclic conformations of the equivalent open chains dimethylsiloxanes $\text{-(CH}_3\text{)}_2\text{SiO-}_x\text{Si-}$ calculated using the amended FCM RISM at 298 K and the hard-sphere RISM

Number of Si-O bonds		Z_r for cyclic conformations with end-to-end distances in the range 0 to r nm							Z_r (chain)
		$r = 0.05$	$r = 0.10$	$r = 0.15$	$r = 0.20$	$r = 0.25$	$r = 0.30$	$r = 0.35$	
8	$10^8 Z_r =$	0	0.86	0.86	0.89	0.89	0.89	0.89	8.22
8		(0) ^a	(2)	(2)	(3)	(3)	(3)	(3)	
10	$10^6 Z_r =$	0	0.152	0.152	0.152	1.27	1.27	1.27	16.4
10		(0)	(1)	(1)	(1)	(5)	(5)	(6)	
12	$10^5 Z_r =$	0	0.179	0.794	0.884	0.981	1.70	1.70	32.7
12		(0)	(4)	(9)	(13)	(31)	(38)	(41)	
14	$10^4 Z_r =$	0	0.927	0.936	1.09	2.06	2.08	2.20	65.2
14		(0)	(2)	(10)	(39)	(60)	(81)	(110)	
16	$10^4 Z_r =$	0	0.928	7.62	39.7	41.2	41.5	41.5	130.1
16		(21)	(66)	(137)	(279)	(411)	(558)	(695)	
18	$10^4 Z_r =$	0.011	0.078	0.193	0.219	0.286	0.700	1.55	259.6
18		(74)	(289)	(745)	(1472)	(2277)	(3246)	(4333)	
20 ^b	$10^3 Z_r =$	0.518	4.82	13.6	46.8	61.2	122.0	133.0	517.8
20		(15)	(81)	(169)	(246)	(325)	(402)	(468)	

^a Quantities in parentheses indicate hard-sphere model ($\sigma = \omega = 1$)

^b Conformations with statistical weights $< 10^{-7}$ are excluded

Table 2 Calculated root-mean-square dipole moments (10^{-30} Cm) of the cyclic conformations of the equivalent open chain $\text{-(CH}_3\text{)}_2\text{SiO-}_x\text{Si-}$ with end-to-end distances in the range 0 to r and experimental dipole moments for cyclic and linear dimethylsiloxanes in the undiluted state at 298 K

Number of Si-O bonds	r (nm)							Experimental	
	0.05	0.10	0.15	0.20	0.25	0.30	0.35	Cyclics	Linears
8 ^a	—	0.13	0.13	0.33	0.33	0.33	0.33	1.50	3.21
10	—	3.95	3.95	3.95	2.41	2.41	2.41	2.37	3.54
12	—	4.10	2.75	2.71	2.83	2.81	2.81	3.00	3.83
14	—	3.94	3.96	3.90	3.92	3.92	3.89	3.79	—
16	1.73	4.07	4.86	5.25	5.24	5.24	5.24	—	4.24 ^b
18	6.26	6.14	5.68	5.72	5.46	4.69	4.11	—	—
20	5.39	4.67	4.21	4.57	4.79	4.90	4.81	4.64	4.83

^a Refer to text for additional calculations of dipole moment

^b Fraction with an average of 15.54 skeletal bonds

approach would demand a great deal more detail concerning the conformational energies of the skeletal bonds.

Adjustment of the bond rotational states

The number of accepted cyclic conformations with end-to-end distances close to zero can be considerably increased by allowing the rotational states of the skeletal bonds to depart slightly from the rigidly defined states used in the FCM model. Provided that the bond rotational angles do not depart too much from those values used in the FCM RISM then the FCM statistical weight scheme may still be applied without serious loss of rigour since it is known that the rotational potential energy functions for poly(dimethylsiloxanes) are slowly changing functions with respect to the various bond rotational angles⁵. Each of the cyclic conformations of the equivalent open chain, defined by the FCM model, may be used as a starting point for the generation of an additional 3^{2x-1} conformations by permitting each rotatable skeletal bond to adopt nine rotational states instead of the more usual three states. Thus, if a conformation, described by the FCM model, is represented by the sequence of rotational states

$$\phi_1, \phi_2, \dots, \phi_{N-1} \quad (5)$$

then the additional 3^{2x-1} conformations of the equivalent open chain may be represented by the set of bond rotational states

$$\begin{array}{l} \phi_1 = \phi_1, \quad \phi_1 \pm \Delta\phi_1 \\ \phi_2 = \phi_2, \quad \phi_2 \pm \Delta\phi_2 \\ \vdots \\ \phi_{N-1} = \phi_{N-1}, \quad \phi_{N-1} \pm \Delta\phi_{N-1} \end{array} \quad (6)$$

Conformational populations, defined by equation (6) were generated for each of the previously accepted cyclic conformations of the equivalent open chains of the hexamer using a range of values for $\Delta\phi_i$. To prevent excessive computing times all $\Delta\phi_i$ were set equal to one another, i.e. $\Delta\phi_1 = \Delta\phi_2 = \dots = \Delta\phi_{N-1} = \Delta\phi$. The maximum value of $\Delta\phi$ was not allowed to exceed $\pm 15^\circ$ in order to retain the usage of the FCM statistical weight scheme. The magnitude of $\Delta\phi$ was gradually increased from 1° through to 15° , in steps of 1° , and the end-to-end distance was calculated for each resultant conformation. In Figure 3 the end-to-end distances for $x=6$, obtained after adjustment of the FCM conformations in the manner described above, are plotted against the initial end-to-end distances. It was found that over 75% of the starting conformations could be closed to within 0.04 nm and that 45% of the

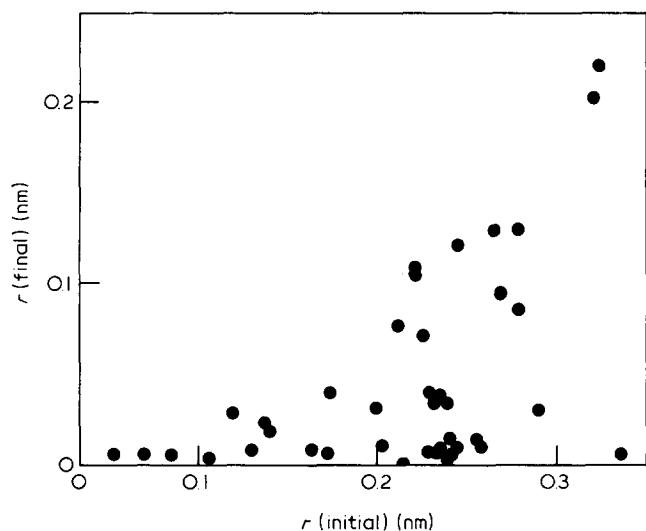


Figure 3 End-to-end distance r before and after adjustment of bond rotational angles for individual conformations of the equivalent open chain with $x=6$

conformations could be closed to within 0.01 nm. Furthermore the dipole moments (Figure 4) of the majority ($\approx 83\%$) of the initial conformations were altered by less than $\pm 10\%$ as a consequence of this ring closing procedure. Thus, the root-mean-square dipole moment of $\approx 2.8 \times 10^{-30}$ cm, calculated for $x=6$ using the FCM bond rotational states ($\phi_i=0^\circ, \pm 120^\circ$) is only slightly below the value of 2.97×10^{-30} cm calculated using the adjusted rotational bond angles and both of these values compare favourably with the experimentally determined value¹ of 3.00×10^{-30} Cm. These calculations indicate that for the range of ring sizes considered in the present study, the maximum acceptable end-to-end distance of the equivalent open chains may be taken to be approximately 0.25 nm. If larger values of r are employed to select cyclic conformations then such conformations cannot be considered suitable for calculating root-mean-square dipole moments of cyclic dimethylsiloxanes using the FCM model, since it is not possible to effect ring closure by making small adjustments to the bond rotational angles of the equivalent open chains.

Statistical weight cut-off procedure

The combinatorial basis for the generation of the statistical weights of the cyclic conformations of the equivalent open chains results in a very wide range of values. This means that a large number of conformations will contribute very little to the calculated root-mean-square dipole moment and may therefore be disregarded without incurring serious loss of accuracy provided that the dipole moments of individual conformations are not large enough to offset the small statistical weights.

During the computations it is quite easy to calculate the statistical weight of the equivalent open chain before any elaborate, time consuming geometrical calculations have been pursued. By applying a minimum acceptable statistical weight, Ω_{\min} , a large number of conformations may be rejected at an early stage in the calculations. Obviously, if the chosen minimum acceptable statistical weight is set too high then the accuracy of the calculated root-mean-square dipole moment will be reduced. The effect of this time saving device on the Z , and $\langle \mu^2 \rangle_0^{1/2}$ was studied for $x=7, 8$ and 9 using various values for the minimum

acceptable statistical weight Ω_{\min} . The results of these calculations are presented in Tables 3 and 4. For $x=7$ the configurational partition, Z_r ($r=0.35$ nm), is reduced by only 3% when Ω_{\min} is changed from zero to 10^{-6} , but the number of cyclic conformations used to calculate $\langle \mu^2 \rangle_0^{1/2}$ drops sharply from 110 to 7. This reduction is accompanied by a modest saving in the computing time. A similar effect is observed for $x=8$ and $x=9$. For the octamer the imposition of $\Omega_{\min}=5 \times 10^{-5}$ drastically reduces the number of cyclic conformations (with $r \leq 0.35$ nm) from 695 ($\Omega_{\min}=0$) to 9 for only a small decrease ($\approx 3\%$) in the partition function. As x increases the savings in computing time become relatively more important. Thus for $x=9$ the number of cyclic conformations with $r \leq 0.35$ nm was reduced from 4333 to 112 and the computing time was decreased by approximately 7 h.

Since the range of values calculated for the dipole moments of the cyclic x -mers, for any given value of x , is not very great and the configurational partition function remains almost unaffected by the enrichment procedure described above it follows that the calculated values of $\langle \mu^2 \rangle_0^{1/2}$ should be almost constant. The entries in Table 4 support this conclusion.

Examination of selection criteria for cyclic conformations

Since the angular criteria used for selecting acceptable cyclic conformations may appear to be arbitrary several checks were performed to test the dependence of the calculated root-mean-square dipole moments on the limits imposed on the bond angle supplement θ_N and the bond rotational angle ϕ_N . The root-mean-square dipole moments for cyclic conformations of the equivalent open chains for $x=6$ and $x=7$ were calculated for the various ranges of end-to-end distances and for different combinations of θ_N and ϕ_N . Values of $\langle \mu^2 \rangle_0^{1/2}$ were found to be reasonably insensitive to the restrictions imposed on θ_N and ϕ_N . Thus, for both $x=6$ and $x=7$ (Table 5) the

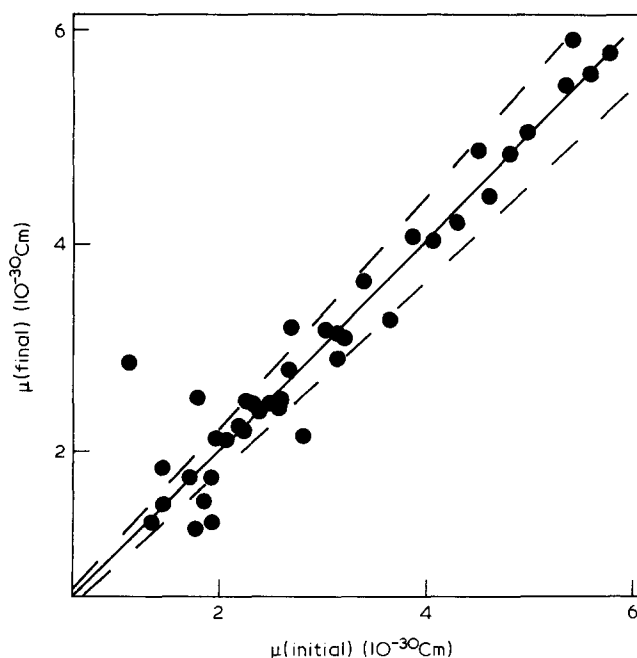


Figure 4 Calculated dipole moments before and after adjustment of bond rotational angles for individual conformations of the equivalent open chain with $x=6$

Table 3 Configurational partition function, Z_r ($\times 10^4$), and number of cyclic conformations of the equivalent chain $\text{-(CH}_3)_2\text{SiO-}_x\text{Si-}$ calculated using the amended FCM model at 298 K for end-to-end distances in the range 0 to r and for various minimum statistical weights Ω_{\min}

x	Ω_{\min}	r (nm)							CPU time ^b (min)
		0.05	0.10	0.15	0.20	0.25	0.30	0.35	
7	0	0.00	0.927	0.936	1.09	2.08	2.08	2.20	8.2
7		(0) ^a	(2)	(10)	(39)	(60)	(81)	(110)	
7	10^{-10}	0.00	0.927	0.936	1.09	2.08	2.08	2.20	8.1
7		(0)	(2)	(7)	(30)	(37)	(43)	(56)	
7	10^{-9}	0.00	0.927	0.936	1.09	2.08	2.08	2.20	7.9
7		(0)	(1)	(5)	(26)	(31)	(37)	(44)	
7	10^{-8}	0.00	0.927	0.963	1.09	2.08	2.08	2.20	7.0
7		(0)	(1)	(3)	(16)	(20)	(21)	(25)	
7	10^{-7}	0.00	0.927	0.936	1.09	2.07	2.07	2.20	6.0
7		(0)	(1)	(2)	(11)	(14)	(14)	(16)	
7	10^{-6}	0.00	0.927	0.927	1.03	2.01	2.01	2.14	5.0
7		(0)	(1)	(1)	(3)	(5)	(5)	(7)	
8	0	0.00	0.928	7.62	39.7	41.2	41.5	41.5	85
8		(21)	(66)	(137)	(279)	(411)	(558)	(695)	
8	10^{-6}	0.00	0.927	7.62	39.7	41.1	41.4	41.4	38
8		(0)	(1)	(4)	(15)	(23)	(24)	(25)	
8	10^{-5}	0.00	0.927	7.62	39.5	40.7	41.0	41.0	28
8		(0)	(1)	(4)	(9)	(11)	(12)	(12)	
8	5×10^{-5}	0.00	0.927	7.31	39.2	40.1	40.1	40.1	23
8		(0)	(1)	(3)	(8)	(9)	(9)	(9)	
9	0	0.011	0.078	0.193	0.219	0.286	0.700	1.55	761
9		(74)	(289)	(745)	(1472)	(2277)	(3246)	(4333)	
9	10^{-7}	0.010	0.068	0.164	0.180	0.228	0.623	1.45	342
9		(2)	(21)	(34)	(38)	(47)	(75)	(112)	
10	10^{-7}	5.18	48.2	136.0	468.0	612.0	1220	1330	3094
10		(15)	(81)	(169)	(246)	(325)	(402)	(468)	

^a Entries in parentheses indicate number of accepted conformations

^b Central processing unit times for a CDC 7600 computer

Table 4 Root-mean-square dipole moments $(\mu^2)_0^{1/2}$ (10^{-30} Cm) for cyclic conformations of the equivalent chain $\text{-(CH}_3)_2\text{SiO-}_x\text{Si-}$ calculated using the amended FCM model at 298 K for end-to-end distances in the range 0 to r and for various minimum statistical weights Ω_{\min}

x	Ω_{\min}	r (nm)						
		0.05	0.10	0.15	0.20	0.25	0.30	0.35
7	0	0.00	3.94	3.96	3.90	3.92	3.92	3.89
7	10^{-10}	0.00	3.93	3.96	3.91	3.92	3.92	3.89
7	10^{-9}	0.00	3.93	3.96	3.91	3.92	3.92	3.89
7	10^{-8}	0.00	3.93	3.96	3.91	3.92	3.92	3.89
7	10^{-7}	0.00	3.93	3.96	3.91	3.93	3.93	3.89
7	10^{-6}	0.00	3.93	3.93	3.80	3.87	3.87	3.83
8	0	1.73	4.07	4.86	5.25	5.24	5.24	5.24
8	10^{-6}	0.00	4.07	4.87	5.24	5.24	5.24	5.24
8	10^{-5}	0.00	4.07	4.87	5.24	5.24	5.24	5.24
8	5×10^{-5}	0.00	4.07	4.84	5.27	5.24	5.24	5.24
9	0	6.26	6.14	5.68	5.72	5.46	4.69	4.11
9	10^{-7}	6.29	6.41	5.92	6.02	5.76	4.77	4.12
10	10^{-7}	5.39	4.67	4.21	4.57	4.79	4.90	4.80

Table 5 Dependence of $(\mu^2)_0^{1/2}$ on the bond angle supplement $\theta_{N'}$ and bond rotational angle $\phi_{N'}$ for the cyclic conformations of the equivalent chain $\text{-(CH}_3)_2\text{SiO-}_x\text{Si-}$ with $x = 6$ and $x = 7$ for end-to-end distances in the range 0 to r nm

	$\Delta\theta_{N'}$	$\Delta\phi_{N'}$	r (nm)						
			0.05	0.10	0.15	0.20	0.25	0.30	0.35
$x = 6$	$\pm 10^\circ$	$\pm 15^\circ$	—	4.10	2.77	2.70	2.80	2.80	2.80
	$\pm 15^\circ$	$\pm 15^\circ$	—	4.10	2.77	2.70	2.84	2.80	2.80
	$\pm 20^\circ$	$\pm 15^\circ$	—	4.10	2.77	2.74	2.84	2.80	2.80
	$\pm 15^\circ$	$\pm 10^\circ$	—	4.10	2.54	2.50	2.67	2.70	2.70
	$\pm 15^\circ$	$\pm 20^\circ$	—	4.10	2.77	2.70	2.84	2.80	2.80
$x = 7$	$\pm 10^\circ$	$\pm 15^\circ$	—	3.94	3.97	3.87	3.87	3.87	3.87
	$\pm 15^\circ$	$\pm 15^\circ$	—	3.94	3.97	3.90	3.94	3.94	3.90
	$\pm 20^\circ$	$\pm 15^\circ$	2.77	3.87	3.90	3.87	3.90	3.90	3.87
	$\pm 15^\circ$	$\pm 10^\circ$	—	3.40	2.90	4.64	3.97	3.97	3.97
	$\pm 15^\circ$	$\pm 20^\circ$	—	3.94	3.97	3.77	3.87	3.70	3.67

Table 6 Conformations and calculated dipole moments (10^{-30} Cm) of the cyclic tetramer of dimethylsiloxane

Conformer	Bond rotational angles								$\langle \mu^2 \rangle_0^{1/2}$
	1	2	3	4	5	6	7	8	
A	247.5°	112.5°	247.5°	112.5°	247.5°	112.5°	247.5°	112.5°	3.80
B	128.9°	231.1°	231.1°	128.9°	128.9°	231.1°	231.1°	128.9°	0.00
C	214.7°	214.7°	145.3°	145.3°	214.7°	214.7°	145.3°	145.3°	0.00
D	142.3°	260.1°	180.0°	142.3°	142.3°	260.1°	180.0°	142.3°	0.80
E	127.1°	259.3°	120.2°	204.2°	233.1°	100.6°	240.0°	155.5°	0.03
F	127.6°	242.4°	96.6°	232.4°	232.4°	127.6°	127.6°	263.4°	2.00

dipole moments calculated for the cyclic conformations of the equivalent open chains were found to be approximately constant, for any given end-to-end distance, provided that the tolerances imposed on the angles θ_N and ϕ_N are not less than $\pm 10^\circ$.

Dipole moment of the cyclic tetramer

The conformations of the cyclic tetramer, $x=4$, are not adequately described by the FCM RISM since it is known that this molecule exists in conformations other than those defined by the bond rotational states of *trans* ($\phi_i=0^\circ$) and *gauche* ($\phi_i=\pm 120^\circ$). Structures corresponding to the crystalline¹² and vapour phase¹³ have been previously reported and discussed by Carmichael and Kingsinger¹⁴ (structures B and E in Table 6). Additional conformers for the cyclic tetramer have also been proposed (A, C, D and F in Table 6)¹⁵. The bond rotational angles of these conformations depart substantially from the values ($0^\circ, \pm 120^\circ$) assigned by the FCM RISM for the linear dimethylsiloxanes. After making a visual estimate of the bond rotational angles an interactive computer program was used to adjust the bond rotational angles to obtain an exact ring closure while maintaining the same bond angle supplements as the open chain [$\theta(\text{oxygen})=37^\circ, \theta(\text{silicon})=70^\circ$]. The conformation, E, corresponding to that found in the solid phase was analysed in a different manner. Since the relative positions of all the atoms in this conformer have been determined using X-ray crystallography¹ the bond rotational angles may be readily calculated. The results of these calculations for conformers A–F are presented in Table 6. Also included in this Table are the corresponding molecular dipole moments for each of the conformers calculated assuming a Si–O bond dipole moment of 2.0×10^{-30} Cm and zero dipole moments for all other bonds. The calculation of the root-mean-square dipole moment of the cyclic tetramer in the liquid state requires a knowledge of the statistical weights of the various conformers, but this demands an analysis of the non-bonded interactions across the ring which is not available at the present time. Calculation of distances between pairs of non-bonded atoms of the various conformers of the cyclic tetramer suggests that their statistical weights should be set approximately equal to one another with the exception of conformer C where it is apparent that there are severe steric overlaps of opposite pairs of methyl groups. Assuming equal statistical weights for the conformers A–F, with the exception of conformer C which is assigned a zero statistical weight, enables the root-mean-square dipole moment to be calculated. The value obtained (1.93×10^{-30} Cm) compares favourably with the experim-

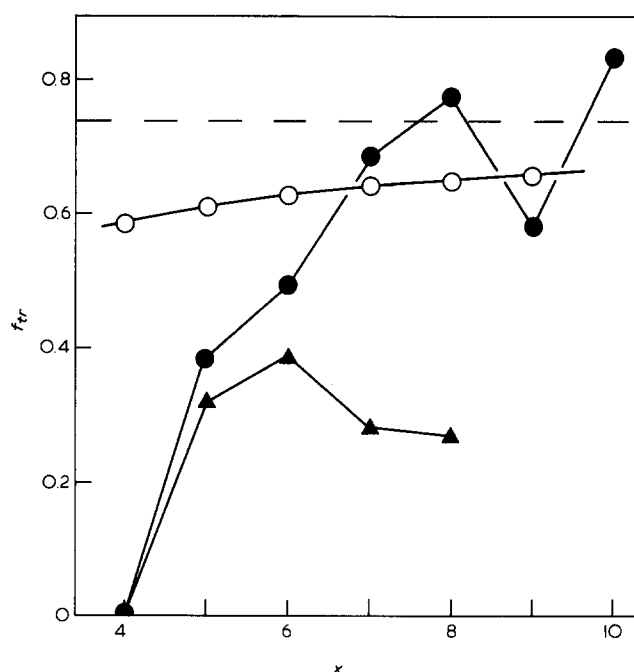


Figure 5 Statistically weighted fraction of skeletal bonds occupying *trans* states for linear dimethylsiloxanes (○) and for cyclic conformations ($r \leq 0.35$ nm) of the equivalent open chain calculated using the amended FCM model (●) and the hard-sphere model (▲) at 298 K

ental value of 1.5×10^{-30} Cm measured for the cyclic tetramer in the liquid state at 298 K.

Average bond conformations

It is well known that as a consequence of the alternating bond angles the siloxane chain will close to form a cyclic structure when the backbone is placed in the all-*trans* conformation. Since the *trans* rotational states are energetically more favoured relative to the *gauche* states this behaviour leads to a maximum in the experimentally determined dipole moment ratio $\langle \mu^2 \rangle_0 / nm^2$ for the linear dimethylsiloxanes¹ in the region of $x=8$. However, for the cyclic dimethylsiloxanes the functional form of $\langle \mu^2 \rangle_0 / nm^2$ is substantially modified because the backbone is constrained to be disc-like¹⁶, when averaged over all possible conformations, and a maximal behaviour of the experimental dipole moment ratio is not observed¹.

For the conformations of the open chain described by the FCM FISM the fraction, f_{tr} , of skeletal bonds occupying *trans* states steadily increases with increasing chain length (Figure 5) and approaches the value of 0.74 calculated for the infinitely long chain. The behaviour of

Table 7 Partial derivatives $\partial \ln \langle \mu^2 \rangle_0 / \partial \ln \sigma$ and $\partial \ln \langle \mu^2 \rangle_0 / \partial \ln \omega$ for cyclic and linear dimethylsiloxanes calculated at 298 K using the amended FCM and unamended FCM models, respectively

Number of Si—O bonds	$\partial \ln \langle \mu^2 \rangle_0 / \partial \ln \sigma$		$\partial \ln \langle \mu^2 \rangle_0 / \partial \ln \omega$	
	Cyclics	Chains	Cyclics	Chains
8	—	-0.335	—	-0.008
10	0.038	-0.312	0.438	-0.009
12	0.009	-0.268	0.347	-0.008
14	-0.014	-0.218	0.032	-0.008
16	-0.188	-0.173	-0.041	-0.008
18	-0.061	-0.136	0.130	-0.007
20	-0.048	-0.106	-0.021	-0.006

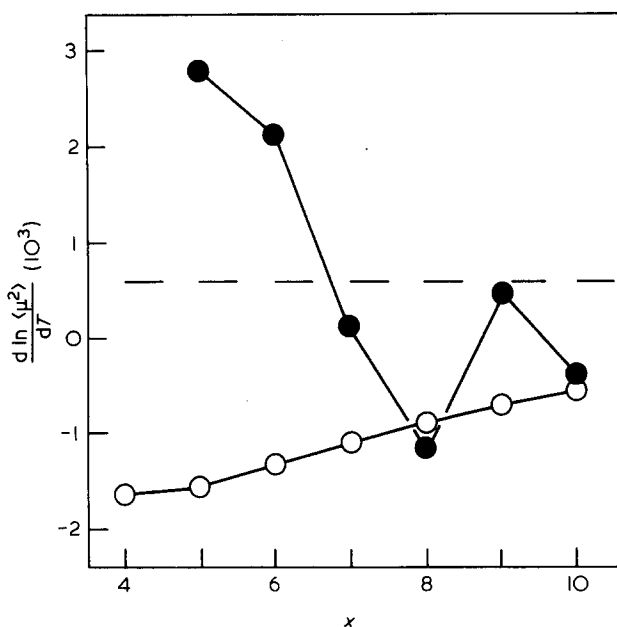


Figure 6 Calculated temperature coefficients for linear dimethylsiloxanes (○) $(\text{CH}_3)_3\text{SiO}[(\text{CH}_3)_2\text{SiO}]_{x-1}\text{Si}(\text{CH}_3)_3$ and cyclic conformations of the equivalent open chains $\{(\text{CH}_3)_2\text{SiO}\}_x\text{Si-}$ (●) at 298 K based on the unamended and amended FCM models, respectively. The broken line is the value calculated for infinitely long open chains

the corresponding cyclic conformations of the equivalent open chains is quite different. For the smaller cyclics ($x=4, 5$ and 6) the statistically weighted fractions of skeletal bonds in *trans* states, calculated using the amended FCM model, are markedly less than those of the corresponding equivalent open chains. Furthermore, the rate of change of f_{tr} as x increases from $x=4$ to $x=8$ is very rapid for the cyclic conformations whereas for the chains f_{tr} changes by only about 10% over the same range of x . Prohibitively long computing times prevented the calculation of f_{tr} for values of x greater than 10 but it is anticipated that the fraction of bonds occupying *trans* states would be a maximum at $x=11$ for reasons previously discussed.

Temperature coefficients of the dipole moments

The partial derivatives $\partial \ln \langle \mu^2 \rangle_0 / \partial \ln \sigma$ and $\partial \ln \langle \mu^2 \rangle_0 / \partial \ln \omega$ were calculated at 298 K for the cyclic conformations of the equivalent open chains $\{(\text{CH}_3)_2\text{SiO}\}_x\text{Si-}$ with $x=5-10$ using the amended FCM

statistical weight scheme. Similar calculations were also performed for the equivalent open chains for $x=4-12$ using the original FCM model⁵. The temperature coefficients of the mean-square dipole moments were then obtained using the relationship^{2,5}

$$\frac{d \ln \langle \mu^2 \rangle_0}{dT} = -T^{-1} \left(\ln \sigma \left[\frac{\partial \ln \langle \mu^2 \rangle_0}{\partial \ln \sigma} \right] + \ln \omega \left[\frac{\partial \ln \langle \mu^2 \rangle_0}{\partial \ln \omega} \right] \right) \quad (7)$$

The calculated partial derivatives are listed in Table 7 for the linear chains and the cyclic conformations thereof. It is noted that for the cyclic conformations the partial derivatives $\partial \ln \langle \mu^2 \rangle_0 / \partial \ln \sigma$ are generally smaller in magnitude than the values calculated for the corresponding equivalent open chains. The converse relationship was found for the partial derivative $\partial \ln \langle \mu^2 \rangle_0 / \partial \ln \omega$. Temperature coefficients $d \ln \langle \mu^2 \rangle_0 / dT$ (Figure 6) obtained for cyclic conformations with $x=5$ and $x=6$ were similar in magnitude to those calculated for the corresponding equivalent open chains but were opposite in sign. For $x=7$ and $x=9$ the temperature coefficients of the cyclic conformations were small and positive. Negative temperature coefficients, close in magnitude to those obtained for the open chains, were found for cyclic conformations with $x=8$ and $x=10$.

In Figure 7 the calculated temperature coefficients $d \ln \langle \mu^2 \rangle_0 / dT$ are plotted against the statistically weighted fraction, f_{tr} , of skeletal bonds occupying *trans* rotational states for cyclic and open chain conformations. For the cyclic conformations an approximately inverse relationship was found between $d \ln \langle \mu^2 \rangle_0 / dT$ and f_{tr} for $x=5-9$; a functional dependence quite dissimilar to that

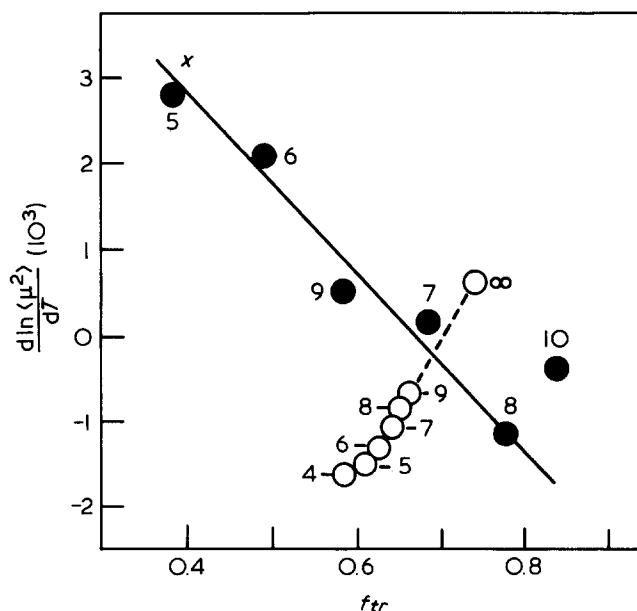


Figure 7 Calculated temperature coefficients of the mean-square dipole moments of linear dimethylsiloxanes $(\text{CH}_3)_3\text{SiO}[(\text{CH}_3)_2\text{SiO}]_{x-1}\text{Si}(\text{CH}_3)_3$ (○) and cyclic conformations (●) of the equivalent open chains $\{(\text{CH}_3)_2\text{SiO}\}_x\text{Si-}$ versus the statistically weighted fraction, f_{tr} , of skeletal bonds occupying *trans* states at 298 K. The solid line was fitted to data obtained for $x=5-9$

found for the total conformational populations of the corresponding equivalent open chains. The variation of the temperature coefficients with x for the cyclic conformations is quite irregular when compared with the very regular trend exhibited by the chains, no doubt reflecting to some extent the drastic differences in the number of conformations taken for the averaging processes as well as reflecting the intrinsically different bond correlations of cyclic and linear molecules. However, the general dependence of the temperature coefficients of the cyclic conformations on x indicates that they are converging to a value similar to the asymptotic limit attained by the chain molecules.

ACKNOWLEDGEMENTS

We would like to thank the Science and Engineering Research Council for a research grant (S.J.M.), the University of Aston in Birmingham and the University of

Manchester for the provision of computing facilities and Ms C. Cade for drawing the Figures.

REFERENCES

- 1 Beevers, M. S. and Mumby, S. J. *Polymer* 1983, **24**, 1565
- 2 Mark, J. E. *J. Chem. Phys.* 1968, **49**, 1398
- 3 Liao, S. C. and Mark, J. E. *J. Chem. Phys.* 1973, **59**, 3825
- 4 Sutton, C. and Mark, J. E. *J. Chem. Phys.* 1971, **54**, 5011
- 5 Flory, P. J., Crescenzi, V. and Mark, J. E. *J. Am. Chem. Soc.* 1964, **86**, 146
- 6 Jacobson, H. and Stockmayer, W. H. *J. Chem. Phys.* 1950, **18**, 1600
- 7 Semlyen, J. A. and Wright, P. V. *Polymer* 1969, **10**, 543
- 8 Edwards, C. J. C., Rigby, D., Stepto, R. F. T., Dodgson, K. and Semlyen, J. A. *Polymer* 1983, **24**, 391
- 9 Beevers, M. S. and Semlyen, J. A. *Polymer* 1971, **12**, 373
- 10 Beevers, M. S. and Semlyen, J. A. *Polymer* 1972, **13**, 385
- 11 Beevers, M. S. and Semlyen, J. A. *Polymer* 1972, **13**, 523
- 12 Steinfink, H., Post, B. and Fankuchen, I. *Acta Cryst.* 1955, **8**, 420
- 13 Yokoi, M. *Bull. Chem. Soc. (Jpn.)* 1957, **30**, 100
- 14 Carmichael, J. B. and Kinsinger, J. B. *Can. J. Chem.* 1964, **42**, 1996
- 15 Kurita, Y. and Kondo, M. *Bull. Chem. Soc. Jpn.* 1954, **27**, 160
- 16 Edwards, C. J. C., Rigby, D., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1983, **24**, 395