

Equilibrium Ring Concentrations and the Statistical Conformations of Polymer Chains

I—Oligomeric Dimethylsiloxanes

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The molar cyclization equilibrium constants K_x of dimethylsiloxanes $[(CH_3)_2SiO]_x$ have been measured in the bulk polymer to within ± 5 per cent at $110^\circ C$ ($x=4-40$) and $145^\circ C$ ($x=4-30$). Values at $110^\circ C$ are compared with those of Brown and Slusarczuk for an equilibrate containing 0.22 g. ml^{-1} siloxane in toluene, and it is concluded that K_4-K_{10} increase markedly with solvent dilution whereas $K_{11}-K_{40}$ remain constant. Using the Jacobson and Stockmayer equilibrium theory of macrocyclization, the dimensions of dimethylsiloxane chains with 40–80 chemical bonds in the bulk polymer at $110^\circ C$ are deduced. They are found to be similar to those in Brown and Slusarczuk's equilibrate and in two θ -solvents of different cohesive energy density. Dilution effects in dimethylsiloxane systems are contrasted with predictions of the Jacobson–Stockmayer theory, and the experimental molar cyclization equilibrium constants of the smallest siloxane rings are discussed in terms of the statistical properties of the corresponding oligomeric chains using Flory, Crescenzi and Mark's rotational isomeric state model of poly(dimethylsiloxane).

IN RECENT years there have been many important advances in the understanding of polymer chain conformations. At Flory's θ -temperature¹, a linear polymer may be considered to be unperturbed by excluded volume effects and its dimensions are characterized by the ratio $\langle r^2 \rangle_0 / nl^2$ (where $\langle r^2 \rangle$ signifies the mean-square distance between the ends of a chain of n bonds each of length l in the limit $n \rightarrow \infty$, and the subscript zero denotes θ -point conditions). The dimensions of many synthetic polymers have been measured by light scattering and viscometric methods, and their temperature coefficients $d \ln \langle r^2 \rangle_0 / dT$ either by stress/temperature measurements on crosslinked networks or by dilute solution measurements². The accumulation of experimental information has been paralleled by important developments in the rotational isomeric state theory of linear macromolecules³⁻⁵. Realistic models of polymer chains have been set up by taking account of the restrictions to rotation about skeletal bonds arising from intrinsic torsional rotational potentials and from intramolecular interactions, and exact mathematical methods have been evolved to calculate the dimensions and dipole moments of chains of any length and sequence of bonds and with interdependent bond rotational states⁵. The rotational isomeric state theory has been used to interpret the conformational-dependent properties of many synthetic polymers.

These advances have encouraged us to embark upon an investigation of chain conformations by the study of ring concentrations in polymeric

systems. Cyclic molecules are present in all condensation polymers and frequently modern analytical methods are available for the determination of their concentrations. Jacobson and Stockmayer⁶ showed that macrocyclization equilibrium constants are directly related to the probabilities of coincidence of the ends of the corresponding acyclic molecules. Hence, a knowledge of the equilibrium concentrations of large rings in condensation polymers will provide information relating to the dimensions and statistical properties of the corresponding chains.

There have been only a few attempts to apply the Jacobson-Stockmayer theory to particular polymeric systems, although there have been many references in the literature to two of its principal predictions, viz. that for ring/chain equilibrium in a condensation polymer (i) the weight fraction of rings will increase with dilution up to a critical point beyond which only rings will be present, and (ii) the concentration by weight of a macrocyclic of x units will be proportional to $x^{-3/2}$.

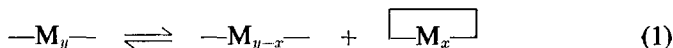
In order to test their theory, Jacobson, Beckmann and Stockmayer⁷ equilibrated polydecamethylene adipate in chlorobenzene at different concentrations, and estimated the total weight fractions of rings and average lengths of the chains viscometrically. As predicted, they found an increase in the weight fraction of rings with dilution and a corresponding decrease in the degree of polymerization of the chain fraction. However, their estimates of the dimensions of polydecamethylene adipate were based on an assumed proportionality between the mean-square end-to-end distances of chains and the number of bonds they contain. In general, this will be true only for very long chains unperturbed by excluded volume effects.

A more searching test of the theory was made possible by Brown and Slusarczuk's⁸ publication of precise values for the molar cyclization equilibrium constants K_x of cyclics $[(\text{CH}_3)_2\text{SiO}]_x$, ($x=4-300$) for a system containing 0.22 g. ml⁻¹ siloxane in toluene at 110°C. Calculations of K_x were based on Flory, Crescenzi and Mark's (FCM) rotational isomeric state model of poly(dimethylsiloxane) (PDMS)⁹. There was close agreement between experimental and calculated values of K_x for $x > ca. 15$, particularly in the range $x=20-50$ ¹⁰.

In Brown and Slusarczuk's equilibration, linear polymer is present in the solution as less than one per cent by weight. Carmichael^{11, 12} has drawn attention to the lower molar cyclization equilibrium constants observed for small siloxane rings in bulk equilibrations, where linear polymer is present as ca. 85 per cent by weight. We have measured the molar cyclization equilibrium constants of cyclics ($x=4-40$ at 110°C, $x=4-30$ at 145°C) in undiluted equilibrates with an experimental error of less than five per cent in order to (i) assess the magnitude and extent of differences in K_x resulting from the presence of inert diluent and (ii) measure the dimensions of dimethylsiloxane chains in the bulk polymer. With these new results, a more detailed comparison of experiment and theory in the PDMS system may be made than proved possible hitherto.

THEORETICAL MOLAR CYCLIZATION EQUILIBRIUM
 CONSTANTS

Consider the equilibrium between dimethylsiloxane rings and polymeric chains



There is a most probable distribution of chain lengths^{12, 13}, so the molar cyclization equilibrium constant K_x of an x -meric ring is given by

$$K_x = [\boxed{M_x}] / p^x \quad (2)$$

where p is the extent of reaction of functional groups in the chain fraction. The Jacobson-Stockmayer theory yields the following expression for K_x (units of moles l^{-1} will be used throughout)^{6, 10}

$$K_x = (3/2\pi \langle r_x^2 \rangle)^{3/2} (1/2N x) \quad (3)$$

where $\langle r_x^2 \rangle$ is the mean-square distance between the ends of the corresponding acyclic and N is Avogadro's number. Equation (3) is based on the following assumptions.

(I) The enthalpy changes for the forward and back reactions of equation (1) are zero. This is true^{14, 15} for $x \geq 4$ but not for $x=3$; K_3 is small and temperature-dependent and will be omitted from consideration.

(II) Chains obey Gaussian statistics, so that the density of end-to-end vectors $W_x(\mathbf{r})$ in the vicinity $\mathbf{r}=\mathbf{0}$ is given by

$$W_x(\mathbf{0}) = (3/2\pi \langle r_x^2 \rangle)^{3/2} \quad (4)$$

(III) Termini in juxtaposition for ring formation are randomly oriented.

Assumptions (II) and (III) will be valid if x is large, thus the molar cyclization equilibrium constants of macrocyclic dimethylsiloxanes can be calculated if $\langle r_x^2 \rangle$ is known as a function of x . Previously $\langle r_x^2 \rangle$ values were identified with $\langle r_x^2 \rangle_0$, the unperturbed mean-square end-to-end distances of siloxane chains in a θ -solvent of cohesive energy density exceeding that of the polymer⁹. Chain dimensions were calculated by the methods of Flory and Jernigan^{16, 17} using the FCM rotational isomeric state model of PDMS⁹.

(NOTE. Identification of $\langle r_x^2 \rangle$ with $\langle r_x^2 \rangle_0$ in the undiluted polymer or in concentrated solution can be supported by theoretical arguments and experimental evidence; but, contrary to a previous statement¹⁰, it cannot be justified under the conditions of Brown and Slusarczuk's equilibration. Although siloxane is present as 0.22 g.ml^{-1} in toluene, the concentration of chain polymer is less than 0.01 g.ml^{-1} . At this polymer concentration, excluded volume effects would be expected to lead to expansion of the chains. Such effects would explain the slope of $-2.86 (\pm 5 \text{ per cent})$ in Brown and Slusarczuk's plot of $\log K_x$ versus $\log x$ over the range $x=40-300$ as they implied⁸.)

COMPARISON OF THEORY WITH EXPERIMENT

The following conclusions may be drawn from a comparison of the experi-

mental (see *Table 1*) and theoretical¹⁰ molar cyclization equilibrium constants of dimethylsiloxane rings.

Table 1. Experimental measurements of molar cyclization equilibrium constants

Volume % siloxane	Equilibration temperature (°C)	K_x values determined	Uncertainty in K_x values %	References
100	110	K_4 - K_{40}	±5	This study*
100	145	K_4 - K_{30}	±5	This study*
100	25-180	K_4 - K_{10}	†	11
75-25	135	K_4 - K_{25}	‡	18, see also 19
25	110	K_4 - K_{300}	±5	8

*Cyclics were completely separated from high molecular weight polymer and distilled into 30 sharp fractions before analysing by gas-liquid chromatography.

†We have found that gas-liquid chromatographic analysis of cyclics in the presence of large proportions of high polymer leads to underestimates of the concentrations of all but the smallest cyclics. This may explain why the K_x values for $x=7-10$ quoted in ref. 11 are 25-55 per cent lower than our values.

‡No limits of accuracy were placed on these results and they have not been used to derive conformational parameters.

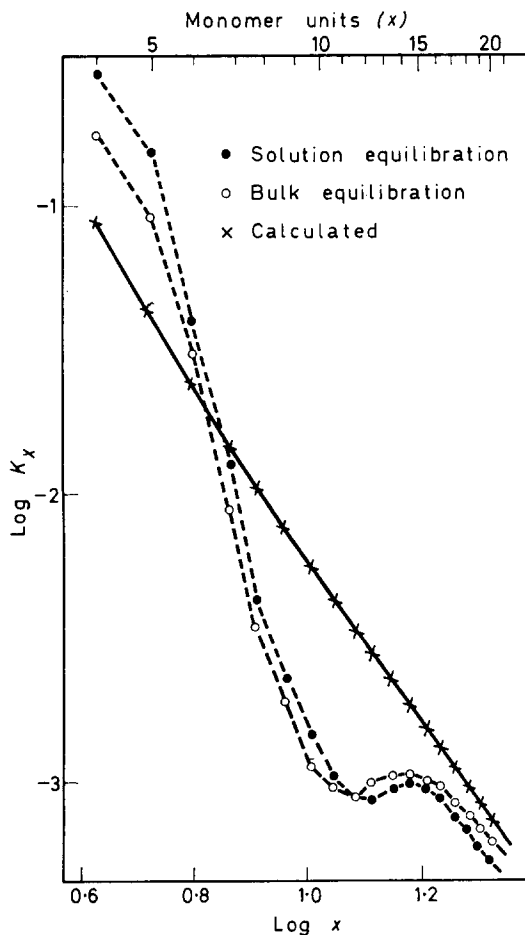


Figure 1—Molar cyclization equilibrium constants of dimethylsiloxanes at 110°C. Values calculated by equation (3) are compared with those measured for an undiluted equilibrate and for Brown and Slusarczuk's⁸ solution equilibrate

(i) Molar cyclization equilibrium constants of cyclics in the range $x=11-40$ are independent of dilution within experimental error. This result is predicted theoretically for chains whose statistical conformations are unaffected by dilution.

In contrast, molar cyclization equilibrium constants of cyclics in the range $x=4-10$ increase with dilution. Brown and Slusarczuk's values for 0.22 g.ml^{-1} siloxane in toluene are higher than our values for a bulk equilibrate at the same temperature by 75 per cent for K_4 , 68 per cent for K_5 and 20-45 per cent for K_6-K_{10} (see *Figure 1*).

(ii) Siloxane chains with more than 30 chemical bonds obey Gaussian statistics in bulk and solution equilibrates. The slope of $\log K_x$ with $\log x$ over the range $x=20-30$ is predicted theoretically to be -2.60 at 110° and 145°C . This value is to be compared with the experimental slopes of -2.57 and -2.58 (bulk equilibrates at 110°C and 145°C respectively) and -2.50 (0.22 g.ml^{-1} siloxane in toluene at 110°C).

(iii) The dimensions of siloxane chains of intermediate length (40-80 chemical bonds) are similar in bulk equilibrates (where polymer is present as *ca.*85 per cent by weight), in Brown and Slusarczuk's solution equilibrate (<1 per cent linear polymer) and in two θ -solvents of different cohesive energy density (see *Table 2*). The close correspondence between the dimensions of PDMS chains in the different environments is in striking agreement

Table 2. Dimensions of siloxane chains in different environments at 110°C

Number of [(CH ₃) ₂ SiO] units x in the chain	Chain dimensions as expressed by the ratio $\langle r^2 \rangle / 2xl^2$			
	Undiluted equilibrate*	Solution equilibrate (0.22 g.ml^{-1} siloxane in toluene ⁸)*	Unperturbed dimensions [†] $\langle r^2 \rangle_0 / 2xl^2$ based on measurements in two θ -solvents ⁹	
			(i) methyl ethyl ketone at 20°C	(ii) 1:2 mixture C ₆ F ₁₈ and CCl ₂ F ₂ · CCl ₂ F ₂ at 22.5°C
20	6.7	7.2	5.9	7.2
30	6.9	7.2	6.1	7.5
40	6.9	7.4	6.2	7.6

*Calculated from the experimental values of K_{20} , K_{30} , K_{40} using equation (3). Estimated uncertainty ± 3 per cent.

[†]Unperturbed dimensions were calculated by the methods of Flory and Jernigan (Refs. 15, 16) using the FCM rotational isomeric state model of PDMS. Estimated uncertainty ± 10 per cent.

with current theories of polymer conformations. Contributions to expansion of chain dimensions by excluded volume effects in solution equilibrates are evidently negligible for chains with less than 80 chemical bonds.

It is noted that the study of equilibrium ring concentrations provides a precise method of measuring the dimensions of polymer chains which are too short to be amenable to investigation by light scattering and viscometry. The method also allows for conformational studies in polymer systems (e.g. melts, concentrated solutions) which cannot be investigated using conventional polymer techniques. Furthermore, it is able to provide an

experimental estimate of the lower limit of chain length above which a particular random-coil polymer approximates to Gaussian behaviour.

EFFECT OF DILUTION ON THE TOTAL CYCLIC CONCENTRATION

One of the principal conclusions of the Jacobson–Stockmayer theory is that, for a condensation polymer equilibrated in an inert solvent, there is a critical concentration below which only ring molecules are present. In this section, we calculate the total weight fraction of cyclics in the PDMS system as a function of solvent dilution, making use of the information that is available on the statistical conformations of the linear chains.

An expression for the weight fraction of cyclics w_r in siloxane equilibrates at high extents of reaction ($p=1$) may be obtained by combining equations (2) and (3)

$$w_r = \left(\frac{3}{\pi}\right)^{3/2} \frac{M_0}{2^4 l^3 Nc} \sum_{x=4}^{\infty} (xC_x)^{-3/2} \quad (5)$$

where c is the total siloxane concentration in g.l^{-1} , M_0 is the molecular weight of the unit $(\text{CH}_3)_2\text{SiO}$, l is the length of a siloxane bond, and the small contribution to w_r from the strained, trimeric cyclic is neglected. Equation (5) is based on the assumption that all the chains are unperturbed by excluded volume effects and exhibit Gaussian behaviour, so that $C_x = \langle r^2 \rangle_0 / 2x^2$. For the undiluted system at 110°C , w_r is calculated to be 0.16. This is the same as the experimental value (0.16 ± 0.01) . The agreement is fortuitous. It arises from assumptions underlying the derivation of equation (3), which lead to underestimates of the equilibrium concentrations of the smallest rings ($x=4, 5, 6$) and compensating overestimates for rings with $x \geq 7$ (see *Figure 1*).

The calculated weight fraction of cyclics is shown as a function of

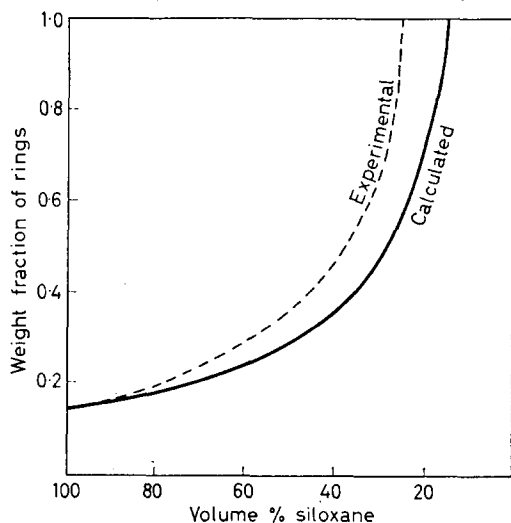


Figure 2—Weight fraction of cyclics in PDMS equilibrates as a function of solvent dilution. Values of w_r at 110°C were calculated for $p=1$ by equation (5). The corresponding experimental plot was constructed from results summarized in *Table 1*, and includes solution equilibrations in toluene at 110°C and xylene at 135°C ; in all cases p is close to unity

solvent dilution in *Figure 2*, where it is compared with the corresponding experimental relationship based on the results summarized in *Table I*. At the present time, the PDMS system is the only one for which there is sufficient information to enable such comparison to be made. The experimental plot applies equally to equilibrations in toluene at 110°C or xylene at 135°C because, for the same volume per cent of siloxane, the total weight fractions of cyclics are within experimental error. Furthermore, we have found K_4 – K_{30} for an undiluted equilibrate at 145°C to be within ten per cent of the corresponding values at 110°C.

Apart from the similarity in the form of the plots shown in *Figure 2*, the most striking feature is the increasing discrepancy between the experimental and calculated weight fractions of cyclics with solvent dilution. This discrepancy is associated entirely with the changes in K_4 – K_{10} , particularly K_4 and K_5 . The molar cyclization equilibrium constants of small dimethylsiloxane rings and their dependence on dilution will now be discussed in terms of the FCM model of PDMS.

MOLAR CYCLIZATION EQUILIBRIUM CONSTANTS OF SMALL SILOXANE RINGS

Non-Gaussian behaviour of finite chain molecules

The Jacobson–Stockmayer expression [equation (3)] is based on the assumption that chains of all lengths obey Gaussian statistics, and that termini of chains in juxtaposition for intramolecular cyclization are randomly oriented. The large differences between experimental and calculated values of K_x for small dimethylsiloxane rings show that one, or both, of these assumptions is not valid for chains with less than *ca.*30 chemical bonds.

It is well known that all random-coil polymers exhibit Gaussian behaviour at moderate extensions provided they are very long, but unfortunately there are no analytical expressions which describe the statistical properties of finite chains. However, the statistical behaviour of such chains may be investigated by direct computation of the end-to-end distance (or other parameter) for every conformation defined by realistic rotational isomeric state models. By this method, it was concluded that unperturbed sulphur chains with seven or more chemical bonds are approximately Gaussian in character^{20, 21}; a similar approach has been taken for dimethylsiloxane chains.

Flory, Crescenzi and Mark's (FCM) rotational isomeric state model⁶

The FCM model of PDMS assumes that each skeletal bond of the chain lies in one of three rotational isomeric states, either *trans* ($\phi=0^\circ$), *gauche+* ($\phi=120^\circ$) or *gauche-* ($\phi=240^\circ$). Statistical weight matrices U' and U'' take account of the interdependence of bond rotational states: U' for rotations about pairs of bonds centred on silicon atoms, and U'' for rotations about pairs of bonds centred on oxygen atoms, thus

$$U' = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & 0 \\ 1 & 0 & \sigma \end{bmatrix}; \quad U'' = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \delta \\ 1 & \delta & \sigma \end{bmatrix} \quad (6)$$

The statistical weight parameters σ [$=\exp(-850/RT)$] and δ [$=\exp(-1900/RT)$] were assigned values based on the unperturbed dimensions of PDMS and its positive temperature coefficient.

Since the publication of this model, the dipole moments of some liquid oligomeric dimethylsiloxanes $(\text{CH}_3)_3\text{Si}(\text{OSi}(\text{CH}_3)_2)_y\text{OSi}(\text{CH}_3)_3$ ($y = 1, 2, 3, 5$) have been measured at 25°C by Dasgupta and Smyth²³. If all the siloxane bonds are assumed to have the same moments as those in hexamethyldisiloxane²³, experimental dipole moments are in excellent agreement with those calculated using the FCM model*. However, it is noted that the calculated dipole moments are sensitive to the choice of siloxane bond moments and relatively insensitive to the statistical weight parameters, particularly δ . Indeed, if free rotation is assumed about every siloxane bond, calculated values are still within 25 per cent of the experimental dipole moments. A more demanding test of the model is provided by stress/optical data of PDMS networks, where it has been reported that a close correspondence between theory and experiment is more difficult to achieve²⁴.

(N.B. Rotational isomeric state models of PDMS which assume independent bond rotational states²⁵⁻²⁸ ignore intramolecular steric and Coulombic interactions. Such models are incapable of interpreting the unperturbed dimensions of PDMS and its temperature coefficient, and cannot properly be used to describe the statistical properties of real dimethylsiloxane chains.)

Statistical properties of oligomeric dimethylsiloxanes and the molar cyclization equilibrium constants of small siloxane rings

The distances between the terminal silicon atoms of unperturbed oligomeric dimethylsiloxanes $(\text{CH}_3)_3\text{Si}(\text{OSi}(\text{CH}_3)_2)_y\text{OSi}(\text{CH}_3)_3$ ($y = 3, 4, 5$) have been calculated for the 9^y conformations defined by the FCM model. In Figure 3 the weighted fraction of conformations with their end-to-end distances between 0 and r (where r increases in steps of 1Å) are plotted as functions of r . They are compared with the corresponding integrated and normalized Gaussian radial distributions for which mean-square end-to-end distances were calculated by the methods of Flory and Jernigan^{16,17}. The distributions were computed at 110°C. Asymptotic limits correspond to the conformational partition functions Z of the chains, where

$$Z = [1 \ 0 \ 0] (\mathbf{U}''\mathbf{U})^y \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \end{bmatrix} \quad (7)$$

There are very large differences between the distributions found by direct computation and those calculated assuming Gaussian statistics, particularly in the region of interest for ring studies where r is small (cf. model sulphur chains with 8-12 chemical bonds²¹). Similar results were obtained for siloxane chains terminated in oxygen atoms.

The relative directions of the terminal bonds of siloxane chains with 8, 10 and 12 skeletal bonds have been examined for those conformations

*Similar calculations have been carried out by Professor J. E. Mark of the University of Michigan (private communication).

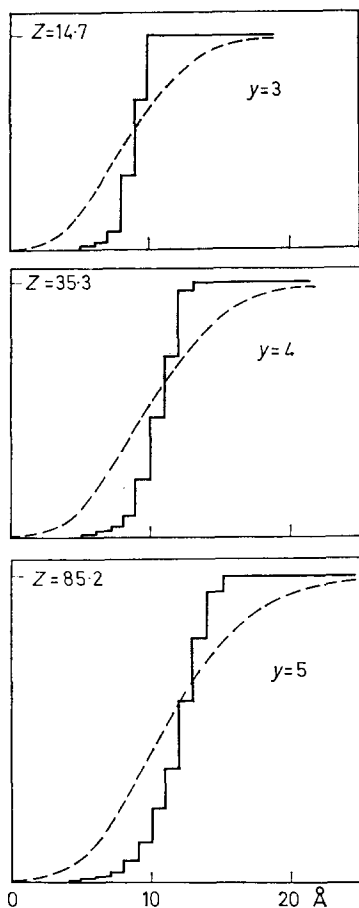


Figure 3—Weighted fraction of conformations of unperturbed oligomeric dimethylsiloxanes $(\text{CH}_3)_3\text{Si}(\text{OSi}(\text{CH}_3)_2)_y\text{OSi}(\text{CH}_3)_3$ ($y=3, 4, 5$) with their end-to-end distances in the range $0-r$ plotted against r . The corresponding integrated and normalized Gaussian distributions are shown as broken lines

which correspond to the close approach of chain ends. For the chain with 12 bonds, termini in juxtaposition were found to be approximately randomly oriented; thus the molar cyclization equilibrium constant of $[(\text{CH}_3)_2\text{SiO}]_6$ may be written

$$K_6 = W_6(\mathbf{0})/12N \quad (8)$$

where $W_6(\mathbf{0})$ is the density of end-to-end vectors in the region $\mathbf{r}=\mathbf{0}$. Using the experimental values of K_6 at 110°C , $W_6(\mathbf{0})=0.24 \times 10^{24}$ molecules l^{-1} for siloxane chains in an undiluted equilibrate, and $W_6(\mathbf{0})=0.30 \times 10^{24}$ molecules l^{-1} for chains in an equilibrate containing 0.22 g. ml^{-1} siloxane in toluene. These values are far greater than those calculated by the FCM model, which gives densities of end-to-end vectors in the range $0-r$ of $0.005, 0.004, 0.009, 0.015, 0.017 \times 10^{24}$ molecules l^{-1} for $r=1, 2, 3, 4, 5 \text{ \AA}$ respectively. Even greater differences are found between values of $W_4(\mathbf{0})$ and $W_5(\mathbf{0})$ derived from experimental molar cyclization equilibrium constants and those calculated by the FCM model.

It should be emphasized that the inability of the FCM model to furnish values of $W_x(\mathbf{0})$ for these very small siloxane rings in no way renders the model invalid. The model was set up to calculate the average properties of long linear chains and not to estimate the probabilities of coincidence of the termini of short chains. For this latter purpose, certain of the FCM statistical weights associated with particular sequences of bond rotational states are clearly inapplicable. For example, the tetrameric cyclic $[(\text{CH}_3)_2\text{SiO}]_4$ adopts a low-energy, puckered conformation in the crystalline state which is free of unfavourable intramolecular interactions. As has been pointed out²⁶ this conformation corresponds to sequences of bond rotational states with neighbouring bonds in *gauche* states of opposite sign (e.g. $g^+g^+g^-g^-g^+g^+$ gives a cradle form, $g^+g^-g^+g^-g^+g^-$ a crown form). Thus a sequence of states $g^+g^-g^+g^-g^+g^-$ is correctly accorded a statistical weight of zero in calculations of the average properties of siloxane chains, but such a statistical weight is quite inappropriate for estimates of the probability that the ends of a tetrameric chain will meet to form a bond. In principle, the molar cyclization equilibrium constants of small siloxane rings could be carried out by the method suggested for cyclo-octasulphur and cyclo-octaselenium²⁹; each conformer being examined for intramolecular interactions before assigning an appropriate statistical weight. Such calculations should give values of K_x of the right order of magnitude, but they would not be expected to provide a rationale for the large increases in the molar cyclization equilibrium constants of small siloxane rings with solvent dilution. These changes cannot be interpreted satisfactorily at present. They imply increases in the densities of end-to-end vectors in the regions corresponding to the close approach of chain ends; but, in the absence of an analytical expression relating $W_x(\mathbf{0})$ and $\langle r_x^2 \rangle$ no conclusions can be drawn regarding the corresponding changes in chain dimensions. Similar increases in the molar cyclization equilibrium constant of ϵ -caprolactam in nylon-water equilibrates with increase in water concentration also await quantitative theoretical interpretation³⁰. Further experimental and theoretical studies on the concentrations of rings in polymeric siloxane and other systems are in progress.

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