

Macrocyclization Equilibrium Constants and the Statistical Configuration of Poly(dimethylsiloxane) Chains

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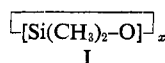
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Abstract: Recent results of Brown and Slusarczuk on the concentrations of macrocyclic dimethylsiloxanes (I) in equilibrium with linear PDMS [*i.e.*, poly(dimethylsiloxane)] are shown to be in good agreement for $x = 15$ to 200 with calculations based on the unperturbed dimensions of PDMS of high molecular weight as found from studies on dilute solutions. The Jacobson-Stockmayer equilibrium theory of macrocyclization, revised to render it applicable to the treatment of real chains, has been used. The prevalence of unperturbed, random-coil configurations for PDMS in bulk and in concentrated solutions is confirmed by the good accord of experiment with theory. An explanation is offered for the formation of small rings ($x = 4$ and 5 for the siloxane system) in amounts in excess of predictions based on the statistical distribution of end-to-end vectors.

The statistical distribution of cyclic species in condensation polymers was given theoretical interpretation some years ago by Jacobson and Stockmayer.^{1b} In contrast to the distribution of acyclic or linear polymers, the weight distribution of macrocyclic constituents at equilibrium was shown to be a monotonically decreasing function of molecular size. The proportion of macrocyclic component consisting of x units in equilibrium with linear chains was related to the probability of coincidence of the ends of a sequence of x units, and hence to the statistics of the spatial configuration of the chains under consideration.

The cyclization equilibrium constants for larger rings may in principle serve as measures of the statistical configuration of chain molecules, or what is loosely referred to as chain "flexibility." This method of approach is applicable at degrees of polymerization much below the range where the familiar light scattering and viscosity methods are effective. Moreover, it is one of the few methods capable of yielding information on the configurations of chains in the bulk state, which is a matter of some controversy at present.

Experimental results admirably suited for a test of the theory of macrocyclization equilibrium, and from which to ascertain the configurational character of chains of intermediate length, have been made available recently by Brown and Slusarczuk² who determined the concentrations of cyclic poly(dimethylsiloxane)s



over the range $x = 4$ to about 200 units by chromatographic methods. The experiments were carried out on polymers equilibrated in toluene solution (200 to 250 g of polymer/l.) and also on polymers equilibrated in absence of diluent.

The theory of Jacobson and Stockmayer^{1b} requires minor amendment in order to achieve a close comparison with recent configuration studies on this polymer (PDMS). Their treatment was set forth in terms of the hypothetical freely jointed, or random flight, chain

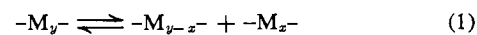
(1) (a) On leave of absence from Christ Church, Oxford, as a Fulbright Scholar. (b) H. Jacobson and W. H. Stockmayer, *J. Chem. Phys.*, **18**, 1600 (1950).

(2) J. F. Brown, Jr., and G. M. J. Slusarczuk, *J. Am. Chem. Soc.*, **87**, 931 (1965).

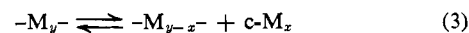
model—a model which has been used extensively despite its unrealistic failure to take account of the correlations of directions of successive bonds imposed by bond angles and by hindrances to bond rotations. Realization of the full potential of their theory as a basis for relating macrocyclization equilibria to chain-configuration statistics requires that it be recast in terms relevant to real molecular chains. This we attempt to do below. The basic assumptions underlying their method will be examined critically as well. Then, the results of Brown and Slusarczuk will be compared with theory, and implications of the comparison will be pointed out.

Theory

Following Jacobson and Stockmayer, we consider the processes



where M denotes the monomer unit, c-M is the cyclic form, and x and y are degrees of polymerization. Terminal groups are omitted in the equations above, their nature being immaterial. For simplicity in developing the following argument, the termini of the intermediate, $-M_x-$, may be regarded as free radicals. The sum of these two processes, namely



is the one whose equilibrium constant is sought.

The molar free-energy change for the first process can be written

$$\Delta G_{(1)} = \Delta H_{(1)} - RT \ln (4\pi V/N_A \sigma_a \delta r \delta \omega) \quad (4)$$

where N_A is Avogadro's number, V is the volume per mole, and $\Delta H_{(1)}$ is the heat of dissociation according to eq 1; σ_a is the symmetry number for acyclic or chain species ($\sigma_a = 2$ for PDMS chains); δr is the volume element within which termini of the two separated acyclic species must meet in order to reestablish a bond *via* the reverse process, and $\delta \omega$ is, similarly, the permitted range of solid angle for one terminal bond of the fragment (diradical)- M_x- relative to the direction of its partner on the other fragment. Thus, two conditions are required for occurrence of the reverse of reaction 1: (i) the termini must be situated in juxtaposition, and (ii) the directions of terminal bonds, here considered for

convenience to be free radicals, must be colinear within the range $\delta\omega$. Since both the locations and the orientations of the dissociated species are uncorrelated, the probabilities of fulfillment of these respective conditions are $\delta r/V$ and $\delta\omega/4\pi$. We introduce the latter factor, not included explicitly by Jacobson and Stockmayer, for reasons which will be apparent below.

In process 2 an intramolecular bond is formed which is equivalent to the one severed in process 1. Unless the ring is so small as to induce strain, $\Delta H_{(2)} = \Delta H_{(1)}$. Similarly, the termini of $-M_x-$ must meet within the same ranges δr and $\delta\omega$ previously defined. The probability of fulfillment of condition i above is $W_x(\mathbf{0})\delta r$ where $W_x(\mathbf{r})$ is the function expressing the distribution of the end-to-end vector \mathbf{r} , per unit range in \mathbf{r} , for a chain of x units. If x is sufficiently large, the directions of the bonds when condition i is fulfilled will remain uncorrelated; hence, the probability that condition ii also is met will be $\delta\omega/4\pi$ as before. Then

$$\Delta G_{(2)} = -\Delta H_{(1)} - RT \ln [W_x(\mathbf{0})\delta r\delta\omega\sigma_a/4\pi\sigma_{Rx}] \quad (5)$$

where σ_{Rx} is the symmetry number of an x -meric ring. From eq 4 and 5 we have

$$\Delta G_{(3)} = -RT \ln [VW_x(\mathbf{0})/N_A\sigma_{Rx}] \quad (6)$$

Upon equating this expression to zero, we obtain the equilibrium constant for reaction 3

$$K_{(3)} \equiv K_x = W_x(\mathbf{0})/N_A\sigma_{Rx} \quad (7)$$

where N_A is Avogadro's number. As shown by Jacobson and Stockmayer,^{1b} if the reactivity of a terminal functional group can be considered to be independent of the length of the chain, then the cyclization constant K_x is given by

$$K_x \equiv [-M_{y-x-}][c-M_x]/[-M_y-] = [c-M_x]/p^x \quad (8)$$

where p is the extent of reaction of functional groups for the acyclic constituents. Alternatively, p may be defined as the ratio of the concentrations of acyclic species of sizes x and $x-1$. If the average chain length of acyclic species greatly exceeds x , then $p^x \cong 1$ and we have to a sufficient approximation

$$K_x = W_x(\mathbf{0})/N_A\sigma_{Rx} \cong [c-M_x] \quad (9)$$

Equations 6-9 were derived previously by Jacobson and Stockmayer.^{1b}

Cancellation of δr and $\delta\omega/4\pi$ on combining eq 4 and 5 to obtain (6) is contingent upon equivalence of the application of conditions i and ii above to intramolecular cyclization (*i.e.*, to reaction 2) and to intermolecular combination (*i.e.*, to the reverse of reaction 1). In particular, fulfillment of condition i must not vitiate the probability of compliance with ii. This implies in effect that the relative orientation of the terminal bonds of $-M_x-$ must remain random (*i.e.*, uncorrelated) when these bonds are forced into close proximity. It will be readily apparent that this independence of condition ii on i must fail when x is small. If, for example, x approximates the minimum size for ring closure without strain, proximity of the termini is conducive to a regular polygonal conformation, or to the puckered nonplanar analog dictated by preference for bond staggering. The conditional probability of simultaneous fulfillment of condition ii is thus much greater than $\delta\omega/4\pi$. This is doubtless an important factor favoring formation of

cyclic compounds of the minimum size for an unstrained ring. In the PDMS series, for example, the cyclic tetramer occurs in an abundance several times that predicted by calculation according to eq 9 (*cf.* the following).

A more elaborate analysis would be required to pursue the contingency of condition ii on i as x increases beyond its value for the optimally favored rings which, depending on the homologous series, usually comprise six to eight bonds. For sufficiently large rings, these two conditions obviously will operate independently, whereupon the Jacobson-Stockmayer equations can be asserted to be rigorous, apart from limitations stemming from inaccuracies in the specification of $W_x(\mathbf{0})$ for a finite chain.

For chains of a length sufficient to comply with the conditions shown to be necessary for validation of eq 6 to 9, $W_x(\mathbf{r})$ should be Gaussian to an adequate approximation. Thus

$$W_x(\mathbf{0}) = (3/2\pi\langle r_x^2 \rangle)^{3/2} \quad (10)$$

where $\langle r_x^2 \rangle$ is the mean-square end-to-end length averaged over all configurations of the *real chain of size* x . Substitution of eq 10 in 7 yields

$$K_x = (3/2\pi\langle r_x^2 \rangle)^{3/2} N_A^{-1} \sigma_{Rx}^{-1} \quad (11)$$

We shall identify $\langle r_x^2 \rangle$ with the unperturbed mean-square end-to-end length $\langle r_x^2 \rangle_0$ as determined for example on a dilute solution of the polymer in a Θ solvent. Expansion (α) of the chain molecule due to exclusion of self-intersections becomes negligible in concentrated solutions and vanishes in the undiluted bulk polymer.

In arriving at eq 11, we make no commitment as to the configurational character of the chain other than to invoke the Gaussian function as a satisfactory approximation for the distribution density $W_x(\mathbf{0})$ at $\mathbf{r} = \mathbf{0}$. We specifically avoid representation of $\langle r_x^2 \rangle_0$ as being proportional to x , except of course in the limit of very large x . In the range of interest $\langle r_x^2 \rangle_0$ may, in light of recent calculations,³ be anticipated to fall appreciably below the value $\nu x l^2 C_\infty$ calculated from the limiting value of the characteristic ratio defined by

$$C_\infty = (\langle r^2 \rangle_0 / n l^2)_{n \rightarrow \infty} \quad (12)$$

where n is the number of skeletal bonds of length l (or its root mean square if the chain comprises bonds of different lengths), ν is the number of bonds per repeat unit, and the subscript zero denotes the unperturbed state. The result of Jacobson and Stockmayer is obtained by substituting $\langle r_x^2 \rangle_0 = \nu' x (l')^2$ in eq 11, where ν' is the number of "equivalent" bonds of length l' per repeat unit. But this implies, of course, a proportionality of $\langle r_x^2 \rangle_0$ to x .

Application to Poly(dimethylsiloxane). Here $\nu = 2$ and $\sigma_{Rx} = 2x$. Hence, eq 11 can be written

$$K_x = (3/\pi)^{3/2} / 2^{3/2} \langle r_x^2 \rangle_0^{3/2} N_A^{-1} x \quad (13)$$

or

$$K_x = (3/\pi)^{3/2} / 2^4 l^3 C_x^{3/2} x^{5/2} N_A \quad (14)$$

where $C_x = \langle r_x^2 \rangle_0 / 2x l^2$ is the characteristic ratio of x -mer. For PDMS, $l = 1.64 \times 10^{-8}$ cm.

(3) P. J. Flory and R. L. Jernigan, *J. Chem. Phys.*, **42**, 3509 (1965).

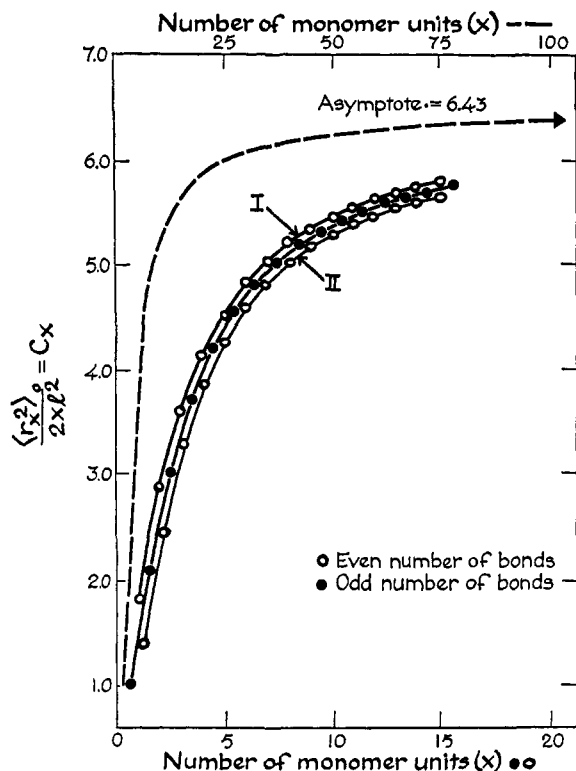


Figure 1. Mean-square end-to-end dimensions of unperturbed PDMS chains: chains terminated with (I) silicon atoms, (II) oxygen atoms.

Values of C_x for PDMS calculated as a function of chain length are shown in Figure 1. The calculations were carried out by the methods of Flory and Jernigan,^{3,4} which are free of mathematical approximations and are applicable to finite chains. The statistical weights used in these calculations ($\sigma = 0.326$ and $\delta = 0.08$) are taken from the analysis of the PDMS configuration by Flory, Crescenzi, and Mark.⁵ These weights have been corrected to 110°, the temperature of Brown and Slusarczuk's experiments.² The correction is trivial, amounting to only about 2% in C_x .

Cyclization equilibrium constants K_x , calculated according to eq 14 and expressed in moles per liter, are represented by the solid line in Figure 2. Other curves represent experimental results from the sources indicated. The most extensive set of results are those of Brown and Slusarczuk covering the range from $x = 4$ to over 200 for polymer equilibrated in toluene solution at a concentration of 222 g/l. and at a temperature of 110°. Gel permeation chromatography was the principal analytical method used by these authors. The results of Hartung and Camiolo⁶ for 25 to 75% by weight PDMS in xylene and of Carmichael and Winger⁷ for the undiluted polymer, also shown in Figure 2, cover the lower range of x only. They tend to support Brown and Slusarczuk's data.

The latter authors refer to less extensive experiments carried out on PDMS equilibrated in the absence of

(4) P. J. Flory, *Proc. Natl. Acad. Sci. U. S.*, **51**, 1060 (1964).

(5) P. J. Flory, V. Crescenzi, and J. E. Mark, *J. Am. Chem. Soc.*, **86**, 138 (1964).

(6) H. A. Hartung and S. M. Camiolo, Abstracts of Papers, 141st National Meeting of the American Chemical Society, Washington, D. C., March 21–29, 1962; see also J. B. Carmichael and J. Kinsinger, *Can. J. Chem.*, **42**, 1996 (1964).

(7) J. B. Carmichael and R. Winger, *J. Polymer Sci.*, **A3**, 971 (1965).

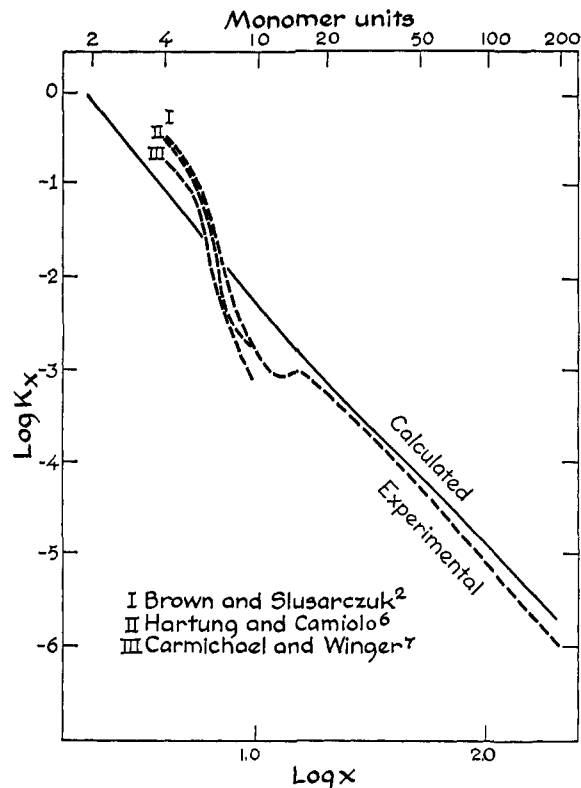


Figure 2. Macrocyclization equilibrium constants of poly(dimethylsiloxanes).

diluent. Cyclic species comprise a smaller fraction of the total polymer under these conditions as must be expected, but in the range $x > 11$ the concentrations of macrocyclic siloxanes agree within ca. 20% with those for polymer equilibrated in toluene solutions. Thus, the equilibrium constants K_x found by Brown and Slusarczuk^{2,8} in solution and in the bulk polymer are in substantial agreement.

Discussion

The calculated curve shown in Figure 2 agrees remarkably well with the results of Brown and Slusarczuk for higher degrees of polymerization. The differences between calculated and experimental curves for $x > 15$ probably do not exceed the experimental error. It is to be noted that the absolute values of K_x are reproduced without adjustment of arbitrary parameters.

Brown and Slusarczuk found the slope of $\log K_x$ with $\log x$ to be $-2.86, \pm 5\%$, for $x > 40$. They cited this as a departure from the Jacobson–Stockmayer theory, which requires a slope of -2.5 . Our calculations support a mean slope of -2.55 over this range, the small departure from -2.5 being due to the change of C_x with x (Figure 1) for $x > 40$.⁹

The cyclic tetramer occurs at a concentration several times that calculated from $\langle r_4^2 \rangle_0$. A plausible explanation for this departure from theory has been given above. It is to be borne in mind, however, that $W_x(0)$

(8) J. F. Brown, Jr., private communication. We are much indebted to Dr. Brown of the General Electric Research Laboratory for kindly providing us with full details on the results published in brief in ref 2.

(9) Expansion of the chain caused by the effect of volume exclusion should be nil for the polymer in concentrated solution (ca. 0.22 g ml.⁻¹) and in the bulk polymer, as pointed out earlier in the text. Hence, an effect on the slope from this source is altogether unlikely.

may not be represented reliably by the Gaussian approximation for chains of so few bonds, and this may contribute in some smaller degree to the disparity between the calculated and observed values for K_4 .

The results of Brown and Slusarczuk² describe a shallow minimum near $x = 12$. Those of Hartung and Camiolo⁶ and of Carmichael and Winger⁷ corroborate the rapid decrease in K_x with x between 4 and 10, and thus tend to confirm an impending minimum for $x > 10$. Superficially similar minima are observed for cyclization of organic compounds, *e.g.*, for homologous cyclic esters and cyclic ketones in the range of 9 to 13 skeletal bonds (in contrast to *ca.* 22 bonds at the minimum for the cyclic siloxanes). These minima have been attributed to crowding of hydrogen atoms within rings of the specified size.¹⁰ The same explanation cannot be supported for the macrocyclic siloxanes. Examination of models for macrocyclic dimethylsiloxanes with $x = 10$ to 14 reveals no indication of crowding of substituents or of other steric interactions which might account for the indicated minimum. No alternative explanation for the minimum is apparent. A detailed examination of various conformations which fulfill condition i above with the object of assessing the

(10) E. W. Spanagel and W. H. Carothers, *J. Am. Chem. Soc.*, **57**, 929 (1935).

conditional probability of meeting condition ii might be instructive in this connection. The task would be formidable, however.

Deviations from the calculations for comparatively small rings, whatever may be their causes, are overshadowed by the excellent agreement at large x . Here the manifest limitations of statistical theory vanish. The sole remaining premise resides in the assumption of unperturbed random-coil configurations for PDMS chains in the bulk state and in concentrated solutions. The comparison of theory and experiment bears ample testimony to the validity of this assumption, which is already supported by a considerable body of evidence.¹¹ A previous suggestion that PDMS chains occur in the form of more or less regularly coiled helices,¹² for example, is refuted unequivocally by the observations presented here.

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(11) See, for example, P. J. Flory, A. Ciferri, and R. Chiang, *ibid.*, **83**, 1023 (1961); J. E. Mark and P. J. Flory, *ibid.*, **87**, 1423 (1965); C. A. J. Hoeve and M. K. O'Brien, *J. Polymer Sci.*, **A1**, 1947 (1963); and P. J. Flory, "Lectures in Materials Science," P. Leurgens, Ed., W. A. Benjamin, Inc., New York, N. Y., 1963, pp 37-42.

(12) A. J. Barry and H. N. Beck, "Inorganic Polymers," F. G. A. Stone and W. A. G. Graham, Ed., New York, N. Y., 1962, p 266 ff.

The Reaction of Hydrogen Sulfide and Atomic Oxygen¹

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Abstract: A study of the mechanism for $\text{H}_2\text{S} + \text{O}$ atoms showed that the initial reaction was $\text{H}_2\text{S} + \text{O} \rightarrow \text{HS} + \text{OH}$ (5), followed by the chain reactions $\text{HS} + \text{O} \rightarrow \text{SO} + \text{H}$ (6) and $\text{H} + \text{H}_2\text{S} \rightarrow \text{H}_2 + \text{HS}$ (3). Since a mixture of D_2S and $\text{H}_2\text{S} + \text{O}$ atoms produced equilibrated HD, the reaction $\text{H}_2\text{S} + \text{O} \rightarrow \text{H}_2 + \text{SO}$ (4) has to be disregarded. The reaction rate for the initial reaction, k_5 , was found to be $4 \pm 2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.

This investigation involves the study of the reaction of $\text{H}_2\text{S} + \text{O}$ atoms using a time-of-flight mass spectrometer to detect the species formed and to measure the over-all rate constant of the reaction. The reaction of O atoms with H_2S occurs readily producing a blue luminescence^{2a} with yields of SO_2 , SO_3 , H_2O , H_2SO_4 ,^{2b} H_2 , S_2O , and S_2O_2 both at room temperature³ and at low temperature.⁴ However, the rate of the $\text{H}_2\text{S} + \text{O}$ atom reaction, and the mechanism of the over-all process for the oxidation and the formation of final products, has not been established.

The thermal oxidation of H_2S in the 100-mm range has been studied by several investigators (see ref 5 for

an account of the previous literature). Marsden⁵ studied the H_2S combustion using a mass spectrometer and identified the intermediates: H_2S_2 , H_2SO_2 , S_2 , and SO and S_2O . Norrish and Zeelenberg,⁶ studying the flash photolysis of $\text{H}_2\text{S} + \text{O}_2$, identified the species (HS , OH , SO , and S_2O_2 and SO_2) whose concentration strongly depended upon reaction time and initial composition of the $\text{H}_2\text{S}-\text{O}_2$ mixture. Recently, MacDonald and Goll^{7,8} obtained the electronic paramagnetic resonance spectra of radicals such as HS and SO by passing water vapor through a microwave discharge and permitting the products to react with H_2S (total pressure less than 1 mm).

The over-all mechanism of the oxidation depends strongly upon conditions. From the literature it appears that in the oxidation of H_2S , HS is primarily

(1) This research was supported by the U. S. Atomic Energy Commission under Contract AT(30-3)-321.

(2) (a) P. Harteck and U. Kopsch, *Z. Physik. Chem.*, **B12**, 327 (1931); (b) *Z. Elektrochem.*, **26**, 714, (1930).

(3) G. Liuti, S. Dondes, and P. Harteck, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 1963, Abstract 40T.

(4) P. N. Schenk and H. Jablowowski, *Z. Elektrochem.*, **95**, 650 (1939).

(5) D. G. H. Marsden, *Can. J. Chem.*, **41**, 2607 (1963).

(6) R. G. W. Norrish and A. D. Zeelenberg, *Proc. Roy. Soc. (London)*, **A240**, 293 (1957).

(7) C. C. MacDonald, *J. Chem. Phys.*, **39**, 2587 (1963).

(8) C. C. MacDonald and R. Z. Goll, *J. Phys. Chem.*, **69**, 293 (1965).