A STATISTICAL STUDY OF THE STRUCTURE OF THE DIMETHYLSILOXANE CHAIN AND RINGS

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ABSTRACT

The structural information that has been published on the polydimethylsiloxane chain (mean-square end-to-end dimensions, linear-cyclic equilibria, chain motion from nuclear magnetic resonance, temperature coefficient of the chain dimensions, and x-ray diffraction of the vulcanized elastomer) and on prototype small molecules (internal rotation in hexa-dimethylsiloxane , and heats of formation of lower cyclics) is presented and discussed in detail. The purpose of this section is to establish the framework of information into which is fitted a model for the chain structure.

Equations are developed for the mean-square end-to-end dimensions ($\bar{r}_o^2/nl^2$) of the polydimethylsiloxane chain which are valid at all values of n, the number of links in the chain, and in which first neighbor interactions of independent bonds and pairs of bonds can be included. The structural variables which must be specified are the length of the valence bond in the skeletal structure, bond angles in the skeletal structure, and the energetics and positions of the allowed conformations in the polymer chain. The equations are shown to be convergent for matrix elements $\leq 1/3$. Calculations of $\bar{r}_o^2/nl^2$ as a function of n are made for statistically independent and statistically independent pair models. It is concluded that in order to explain both the small energy differences that must exist between the rotational states available to the chain (certainly less than 1Kcal. mole) and the experimental value of $\bar{r}_o^2/nl^2 = 7.23$, longer range interferences must be included in the theory. All the possible end-to-end vectors of a growing siloxane chain model with three rotational states are generated and examined for n=6 and n=8

for the purpose of gaining insight into the distribution of cyclic molecules in the polydimethylsiloxane equilibrium. The distribution of $\left|\vec{r}\right|$'s is obtained for the three rotational state model for n=6 and n=8. From the fraction of $\left|\vec{r}\right|$'s closing, an equilibrium constant is calculated for the formation of octamethylcyclotetrasiloxane which is in good agreement with the experimental value.

In Appendix I, the formalism for the dimensions of an -M-O-N-O- chain is developed, the equations being valid for all values of n.

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I. INTRODUCTION

Characterization of the spatial configuration of a macromolecular chain consisting of a succession of structural units linearly connected to one another, is prerequisite to the theoretical interpretation of the constitution and properties of polymeric materials. Mathematical methods for treating the configuration of linear chains have been recently greatly advanced through adaptation of the matrix method of orthogonal transformations to the linear chain problem. This method rests on specification of the chain configuration by assigning the valence angles and rotational states of each chain bond. A basis is thus accomplished for establishing a close connection between bond structure and the main characteristics of chain configuration.[1]

Equations for the mean-square end-to-end dimensions of many types of polymers have been developed using the matrix method. These equations are applicable to a real polymer molecule only when this molecule is in an unperturbed state.[2] From the unperturbed dimensions and nuclear magnetic resonance studies of the polyme[illegible]-ray diffraction analysis, and the stress-temperature coefficient of the vulcanized elastomer, parameters are determined which can be related to the potential difference between preferred and non-preferred rotational states.[3]

Most of the equations developed to date are valid only for high molecular weight polymer chains. These equations adequately describe the equilibrium dimensions of many hydrocarbon chains such as polyethylene, polypropylene, and polyisobutylene because only chains of high molecular weight are present.[3,4,5] Small cyclic molecules have not been found to appreciable extents during any of these polymerizations. This is quite a different matter for inorganic polymers, however. In

fact, K. A. Andrianov has said that the most pressing theoretical problem in inorganic polymers today is predicting the cyclic species that are formed in large amounts in many inorganic polymerizations. The most documented example of cyclic formation in an inorganic polymer system is the case of polydimethylsiloxane, in which cyclic molecules containing from six to eighteen atoms in their skeletal structure make up twenty percent by weight of the equilibrated system.[6] No existing theory adequately explains this phenomenon because of approximations which allow equations for a siloxane-type chain to be valid only for chains containing at least 100 links.

The major purpose of this work is to described the structure of the polydimethylsiloxane chain and explain the chain-cyclic equilibrium in terms of this structure as completely as possible within the framework of available experimental information.*

To achieve this result, equations for the mean-square end-to-end dimensions ($\bar{r}_o^2$) have been developed which are valid for any number of bonds in the siloxane chain. These equations will be the means by which the experimental information is fitted to the best model for the chain.

Much experimental information describing the siloxane chain has been published and will be discussed in subsequent paragraphs. Models for polymer chains will then be discussed as a prelude to the presentation of the model chosen to described the polydimethylsiloxane

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* Stockmayer and Jacobson published in 1950 the only attempt to date to predict the molecular size distributions of linear and cyclic molecules for polydimethylsiloxane. This paper is discussed in Section III-D and the results are compared with those obtained from a detailed structural analysis of the chain.

chain. This work is the first attempt to unify all of the available data into a consistent theory for the siloxane polymeric syste .

Experimental data

1. Structural and phenomenological information about the polydimethylsiloxane chain.

A. Determination of the unperturbed root-mean-square end-to-end dimensions $(\overline{r_0^2})$ of the chain from light scattering, osmotic pressure, and intrinsic viscosity measurements.

The important molecular parameter obtained from these measurements is $\overline{r_0^2}/nl^2$, where $\overline{r_0^2} = \vec{r} \cdot \vec{r} = \sum_{i=1}^{n} \sum_{i=1}^{n} \vec{l}_i \cdot \vec{l}_i$ where the end-to-end bond vector $\vec{r}$ is expressed as the sum of the bond vectors $\vec{l}_i$. n = the number of links in the polymer chain, l = the length of the valence bond in the skeletal structure.

The determination of the unperturbed dimensions of polymer molecules from dilute solution viscosity measurements depends first on the specification of a solvent medium in which the net osmotic forces acting on the polymer molecule are exactly zero. It is currently thought that when this condition is fulfilled, the average configuration of the polymer molecule in solution and its average dimensions are "unperturbed" in the sense that these dimensions depend only on the chemical bonds of the polymer chain and include the influences of the hindering potential to rotation about these bonds, the so-called short-range intramolecular effects. Since the intrinsic viscosity depends directly on the volume occupied by the chain, its determination in a solvent at the θ temperature[1] or in bulk[2] provides a method for finding the unperturbed dimensions of the chain.

The first determination of the molecular dimensions of polydimethylsiloxane was made by Flory, Mandelkern, Kinsinger and Schultz.[7] From osmotic pressure and intrinsic viscosity data of fractions in methylethylketone and phenetole at $\theta = 20°$ and 83° respectively the authors found $\overline{r_o^2}/nl^2 = 7.23$. Several authors have subsequently studied the siloxane system and obtained similar results.

Kuwahara, et al.[8] measured osmotic pressure and viscosities over a wide temperature range to obtain second virial coefficients and intrinsic viscosities for various solvents. The authors found $\overline{r_o^2}/nl^2 = 6.89$.

Schultz and Haug[9] made light scattering and intrinsic viscosity measurements on six fractions of polydimethylsiloxane ranging from 33,000 to 1.06×10^6 in molecular weight. Haug and Meyerhoff have also determined the unperturbed chain dimensions from measurements of sedimentation, diffusion and viscosity.[10] Both results agree substantially with those of Kuwahara, et al.[8] and Flory, et al.[7]

For purposes of comparison, the data of chain geometry and structure for polydimethylsiloxane is summarized along with some other organic polymers in Table I.

B. Equilibria between linear and cyclic dimethylsiloxanes.

Hartung and Camiolo[6] have studied the polymerization to equilibrium in xylene solution of octamethylcyclo-

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* At $T = \theta$, there exists an exact balance between the effect of mutual excluded volume of the segments, which tends to enlarge the molecule, and the effect of a positive energy of mixing, which encourages first neighbor contacts between polymer segments and, hence, a more compact configuration for the molecule. Thus the molecular dimensions are unperturbed by intramolecular interactions.

Table I Experimental Polymer Dimensions

Polymer	Chain Bond Length, Å	Chain Bond Angle, °	$\bar{r}_o^2/nl^2$	$(\bar{r}_o^2/\bar{r}_{of}^2)^{\frac{1}{2}}$ *	Reference
Polydimethyl-siloxane	1.65	θ_1=109.5 θ_2=140	7.23	1.60	7,8,9,10
Polyethylene	1.54	110°	6.55	1.81	11
Isotatic Poly-propylene	1.54	114°	7.35	1.93	12
Polyisobutylene	1.54	114°	7.45	1.93	2
Polystyrene				2.3	13
Polymethylmeth-acrylate	Detailed structural information on these polymers is contained in the original references listed in Volkensteins' book.			2.0	13
Polyethylmeth-acrylate				1.9	13
Polybutylmeth-acrylate				2.1	13
Polyhexylmeth-acrylate				2.4	13
Polyvinylacetate				2.3	13
Natural rubber				1.5	13
Gutta percha				1.3	13

tetrasiloxane using KOH as a catalyst and quantitatively reported the weight fraction of cyclic species from trimer through nonamer. Scott[14] studied cyclic formation in polydimethylsiloxane but used large amounts of hexamethyldisiloxane and obtained low molecular materials. A summary of Hartung and Camiolo's data is given in Table II.

C. Molecular motion in the polydimethylsiloxane chain as studied by nuclear magnetic resonance.

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* The mean-square freely rotating dimension of a polymer chain, $\bar{r}_{of}^2$, is the dimension calculated for a chain with fixed bond length and valence angle(s) with no restriction on the rotational angle, ϕ. For this model, therefore, $\langle\cos\phi\rangle = 0$.

Table II Weight Fraction of Cyclic Species in Equilibrated Polydimethylsiloxane $((CH_3)_2SiO)_n$*

n	Weight Fraction	Standard Deviation
3	.0017	.0004
4	.100	.014
5	.0610	.0076
6	.0185	.0042
7	.0038	.0013
8	.0025	.0004
9	.0017	.0003

Only broad line nuclear magnetic resonance spectroscopy has been thus far reported for the siloxane chain. No conformation study of this polymer by high resolution nuclear magnetic resonance spectroscopy has been made.

Honnold, McCaffrey and Mrowca[15] and Rochow and LeClair[16] published the earliest results indicating line width narrowing from 5.0 gauss at 80° to 0.1 gauss at 223°K.

Kusumoto, Lawrenson, and Gutowsky[17] studied a dimethyl-based vulcanized silicone rubber (Silastic 80), a polydimethylsiloxane polymer with molecular weight $>10^6$ (400 gum), and a lower molecular weight fluid polymer (200 fluid). They found a line width of 4.5 gauss from

* The decrease in abundance of dimethylsiloxane rings was discussed earlier by Flory[2] who stated on the basis of less complete data than that of Hartung that the trend is that expected if the decrease is due solely to the statistical decrease in probability of ring closure with increasing chain length, specific steric factors being of minor importance. He concluded that "the greater length of the Si-O bond and the large SiOSi angle may alleviate the repulsions between substituents (in this case $-CH_3$), which in rings consisting of $-CH_2-$ have been suggested as being responsible for both the strong preference for five- and six-membered rings and for the severe difficulty of forming rings of eight- to twelve-members."

77° to 150°K. and a sharp narrowing to >.10 gauss over the range 150° to 180°K. The mean values of the second moments (ΔH_2^2) in the region of 77°K. were found to be 8.4, 8.4, and 7.8 gauss for Silastic 80, 400 gum, and 200 fluid respectively. They attribute a slight narrowing of line width at about 90°K. to translational motion and the major narrowing in the region of 160°K. to the onset of rotation about the Si-O bonds. The minimum in the spin-lattice relaxation time for 400 gum at 190°K. is explained by a torsional oscillation of large amplitude along the Si-O-Si axis.

Huggins, St. Pierre, and Bueche[18] measured the proton magnetic resonance over the temperature range 60°-300°K. of a sample of polydimethylsiloxane with weight average molecular weight 7.5×10^4. The low temperature (60°-80°K.) peak to peak line width was 4.9 gauss, in satisfactory agreement with the results of Gutowsky, et al. The second moment was found to be 7.0 ± 0.2 gauss. It has been shown that an isolated rigid methyl group should exhibit a ΔH_2^2 of about 21.5 gauss. Free rotation about the C-Si bond would reduce this to about 5.4 gauss. The authors presume then that the second moments for silicone polymers at 80°K. consist of contributions of 5.4 gauss due to freely-rotating methyl groups and an inter-group broadening of 1.6 gauss. A sharp line narrowing to .019 gauss was recorded at approximately 190°K. The motion causing this narrowing was assumed to be a rotation about the chain axis made favorable by the low torsional force constant of the Si-O-Si linkage.

The major conclusion of these studies is that the polydimethylsiloxane chain is very flexible with low potential barriers to rotation about the chain axis, Gutowsky, et al., calculated an upper bound of of 3.5 Kcal./mole and shallow potential wells.

D. Temperature coefficient of the siloxane chain from intrinsic viscosity measurements and from stress-temperature measurements of the vulcanized elastomer.

A linear polymer molecule is characterized by the large number of conformations possible through internal rotation around the axis of the chain bonds. For free rotation all these conformations have equal energy and, therefore, the mean-square end-to-end dimension of the polymer is not a function of temperature. If different energy levels exist in the function describing potential energy vs. rotational angle, however, then the unperturbed dimensions of the molecule will be a function of temperature. A study of the temperature variation of the mean-square end-to-end dimension of linear polymer molecules affords a method for studying the nature of the intramolecular interactions in the chain which cause the variations in the potential energy profile of the internal rotational angle. The temperature variation of $\bar{r}_o^2$ is accessible to experiment. Ciferri has determined $d \ln \bar{r}_o^2/dT$ from the equilibrium tension-temperature coefficient at constant volume and length for a cross-linked polydimethylsiloxane network.[19] This result is compared with $d \ln \bar{r}_o^2/dT$ determined by Ciferri for the free polydimethylsiloxane chain through intrinsic viscosity-temperature measurements carried out in athermal polydimethylsiloxane solutions.[20]

These data for the polydimethylsiloxane chain are listed in the table below along with similar data for polyethylene.[21,22] A structural interpretation of this information follows the table.

TABLE III

Temperature Coefficients of the Dimensions of Polymer Chains

Polymer	Method	$d \ln \bar{r}_o^2/dT$, deg.$^{-1}$	Ref.
Polydimethylsiloxane	tension-temp.	$0.46\ (\pm 0.14) \times 10^{-3}$	19
Polydimethylsiloxane	intrinsic vis.-temp.	$0.33\ (\pm 0.05) \times 10^{-3}$	20
Polyethylene	tension-temp.	$-1.16\ (\pm 0.10) \times 10^{-3}$	21
Polyethylene	intrinsic vis.-temp.	$-1.2\ (\pm 0.2) \times 10^{-3}$	22

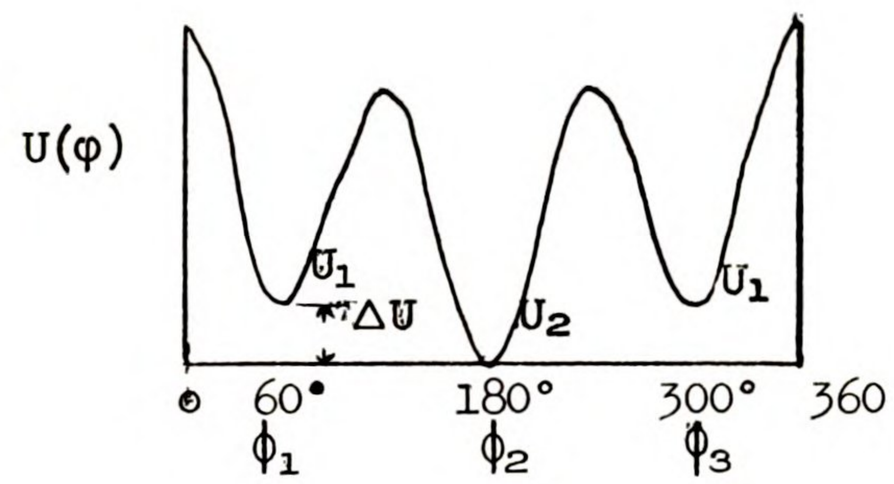
For both polymers there is excellent agreement between the unrelated methods. This lends substantial support to the assumption that the molecular conformation in the amorphous state is not appreciably affected by interactions between neighboring chains.

When the rotational states in adjacent links in the polymer chain are statistically independent (that is, the motion of the groups about the chain axis is not a function of the position of the groups on any following or preceeding chain bonds) and the potential function for each given by a function of the type $V(\phi) = V^\circ/2[x(1-\cos\phi) + (1-x)(1-\cos 3\phi)]$[23], where V° is the value of $V(\phi)$ for $\phi = \pm\pi$, and x is the probability parameter which determines the potential energy differences between the minima, then the sign of $d \ln \bar{r}_o^2/dT$ is easily predicted.

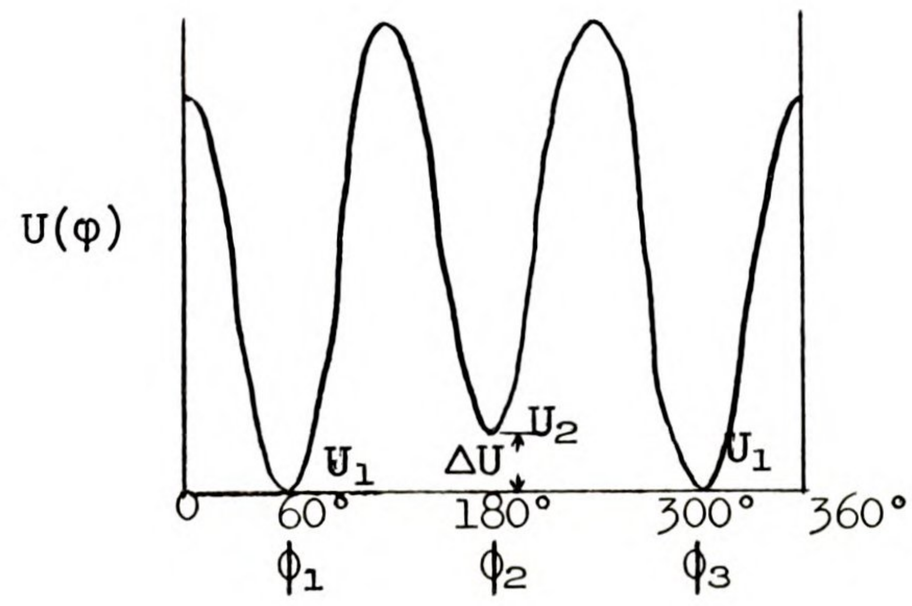
Figure I

Interactions in a Statistically Independent Chain-Represented by a Plot of Potential Energy vs. Rotational Angle

1. Model for the polyethylene Chain



2. Model for the Polydimethylsiloxane Chain



States ϕ_1 and ϕ_3 represent gauche configurations and state ϕ_2 represents the trans configuration. $\Delta U = U_2 - U_1$.

Consider now the case of the polyethylene model. Let a,b,c, be the probability of states ϕ_1, ϕ_2, ϕ_3 respectively. The point of zero potential energy is chosen to be U_2. Then,

$$a = \frac{e^{-\Delta U/kT}}{\sum_{n=1}^{3} e^{-Un/kT}} = \frac{e^{-\Delta U/kT}}{1 + 2e^{-\Delta U/kT}} = c.$$

$$b = \frac{1}{1 + 2e^{-\Delta U/kT}}$$

As T increases, $e^{-\Delta U/kT}$ increases. Therefore, a and c increase while b decreases. Since the all-trans configuration is that of maximum extension of the polymer chain, when b decreases, the mean-square end-to-end dimensions of the chain decrease. Thus, d $\ln \bar{r}_o^2/dT$ is negative.

Since for the model of the polydimethylsiloxane chain, the trans state occurs with lower probability than the gauche states, as T increases b also increases while a and c decrease. Thus, the mean-square end-to-end dimensions of the chain increase and d $\ln \bar{r}_o^2/dT$ is positive.

However, Hoeve has already shown that the dimensions of the polyethylene chain cannot be predicted using a statistically independent model.[24] Later in this work a statistically independent model will prove to be inadequate to interpret all the experimental information on the siloxane chain. Thus, the temperature coefficient of the mean-square end-to-end dimension is a function of more than one variable and cannot be simply interpreted as above,

E. Crystallinity and orientation in silicone rubber studied by x-ray diffraction.

Ohlberg, Alexander, and Warrick in 1958 studied the x-ray diffraction pattern of a silica-filled, vulcanized polydimethylsiloxane polymer at different temperatures and elongations.[25] The crystalline fraction of unstretched and stretched rubber samples was determined.

From this work and a supplemental study of density data, tension-temperature measurements, and normal stress-strain data taken at low temperatures, Warrick[26] concludes that stretched silicone rubber seems to be able to crystallize chain segments in all orientations in space. This contrasts markedly with the behavior of natural rubber which forms crystallites oriented almost exclusively in the direction of stress. He further states that this and all the other differences in crystalline behavior between the two rubbers can be founded upon a much greater chain segment mobility for silicone rubber than found in natural rubber.

The latest x-ray diffraction study reported for polydimethylsiloxane-based rubber was by G. Damaschun in 1962.[27] His study was carried out at -90°C with an extension ratio of 4. The unit cell was reported to be monoclinic with a = 13.0Å, b = 8.3Å, c = 7.75Å, β = 60°. This cell contains six dimethylsiloxane groups with <SiOSi = 140 $\pm$ 10°.

Fig. II is his structural model of the polymer chain. This work gives further evidence for the existence of trans and gauche conformation in the polymer. The sequence of rotational conformations contained in the helical structure above is t,g_r,g_l,t,g_l,g_r. The exact rotational angles at which the gauche states occur cannot be obtained from this two-dimensional diagram and are not reported in the paper.

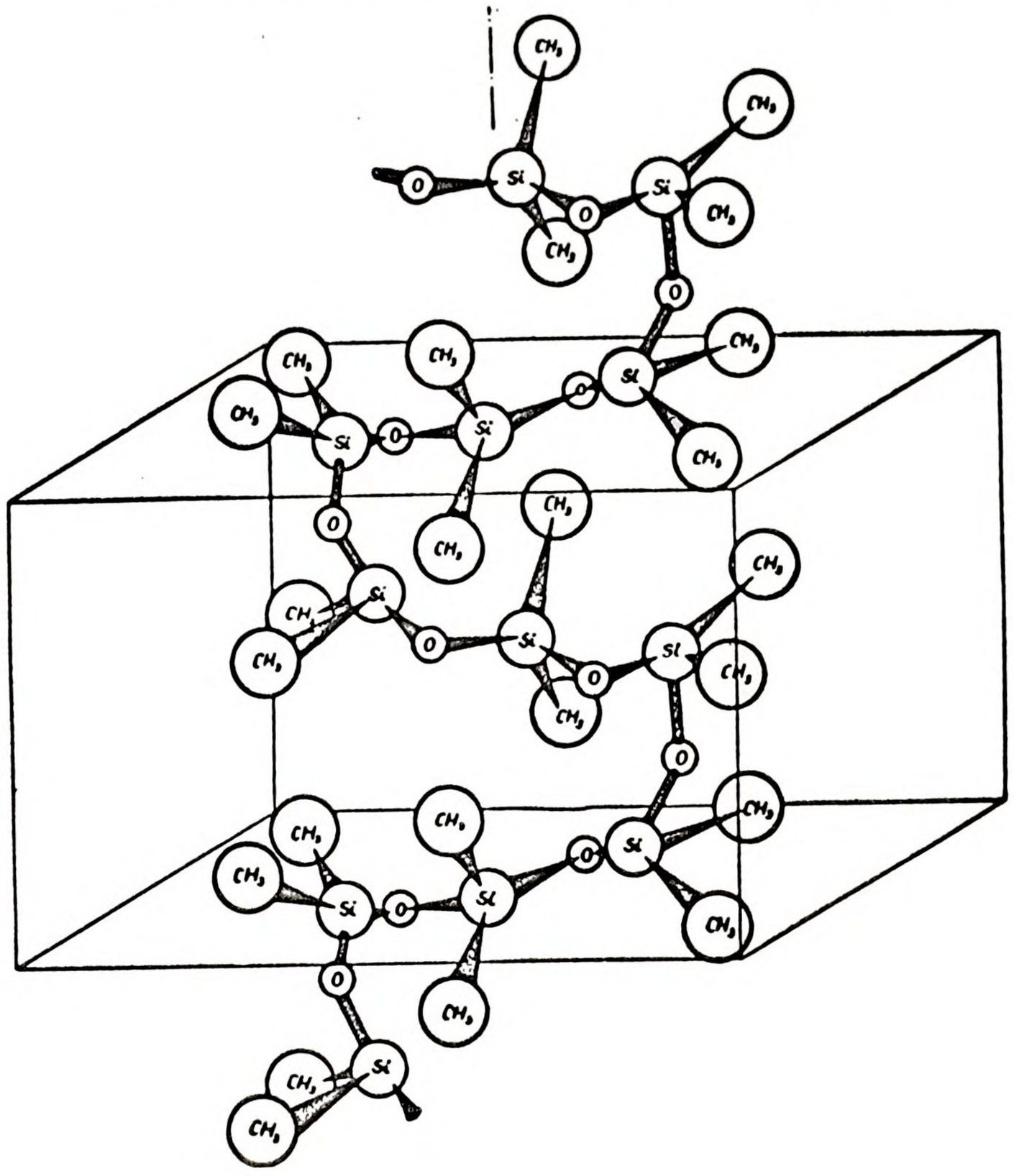
2. Structural information about prototype small molecules.

A. Internal rotation about the siloxane linkage studied in hexamethyldisiloxane.

D. W. Scott and co-workers have done low temperature calori-

Figure II

Structural Model of Crystalline Polydimethylsiloxane[27]



metry, vapor flow calorimetry, and comparitive ebulliometry on hexamethyldisiloxane and have studied the well established infrared and Raman frequencies of the molecule.[28]

When calculated values were used for all unobserved vibrational frequencies, and internal rotation about Si-O bonds was

assumed to be free, both the entropy and the heat capacity were calculated to be greater than the observed values. Agreement between the calculated and observed entropy could be obtained by selection of a suitable barrier height for the siloxane rotation, but only at the expense of a greater discrepancy between the calculated and observed heat capacity. On the other hand, agreement for both entropy and heat capacity could be obtained by suitable adjustment of unobserved vibrational frequencies if the siloxane rotation was assumed to be free.

The authors assert from these observations that there is relatively free rotation about the Si-O-Si axis. For calculating thermodynamic functions, the siloxane rotations were taken to be completely free, although the authors state that the thermodynamic evidence does not rule out a modest barrier height of a few hundred calories per mole.

B. Investigations of the molecular structure of the lower cyclic dimethylsiloxanes.

The planarity of the six-membered ring, hexamethylcyclotrisiloxane, has been demonstrated by x-ray[29,30] and electron[31] diffraction studies. Results of these investigations are summarized in Table IV.

One possible interpretation of the planarity of this ring in terms of the structure of the polymer chain is postulating a cis conformation in the chain[32]. This postulate will be explored later in this work.

The structure of octamethylcyclotetrasiloxane has been studied by Steinfink, et. al.[33] and Yokoi[34]. These results are summarized in Table V.

Table IV

Structure of Hexamethylcyclotrisiloxane

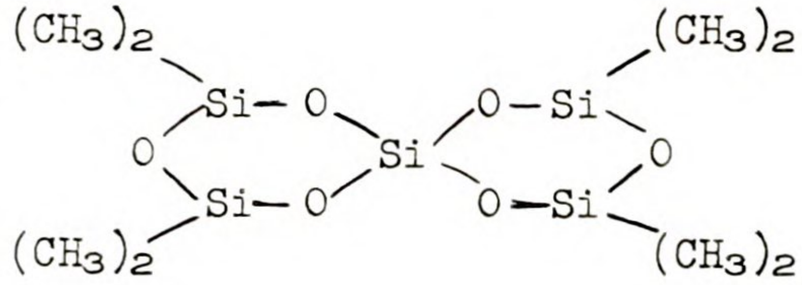
Compound	Si-O (Å)	<OSiO	<SiOSi	Ref.	Comments
	1.64 ± 0.03	109 ± 4°	130 ± 4°	29	Reported the $(Si-O)_3$ ring to be planar.
$((CH_3)_2SiO)_3$	1.61	104°	136°	30	Reported ring to be planar.
$((CH_3)_2SiO)_3$	1.66 ± 0.04	115 ± 5°	125 ± 5°	31	Reported ring to be planar.

Table V

Structure of Octamethylcyclotetrasiloxane

Compound	Si-O Å	<SiOSi°	<OSiO°	Ref.	Comments
$((CH_3)_2SiO)_4$	1.65	142.5	109	33	X-ray diff. ring is puckered.
$((CH_3)_2SiO)_4$	1.63	140 ± 5	109.5 (assumed)	34	Electron diff. Best fit to theoretical intensity curves was cradle form of the ring, B. (See Fig. IV)

Yokoi has constructed several models which give theoretical intensity curves closely approximating that of the experimental curve. Pictured below are diagrams of these structures along with the intensity curves.

Figure III

Conceivable Forms of Octamethylcyclotetrasiloxane[34]

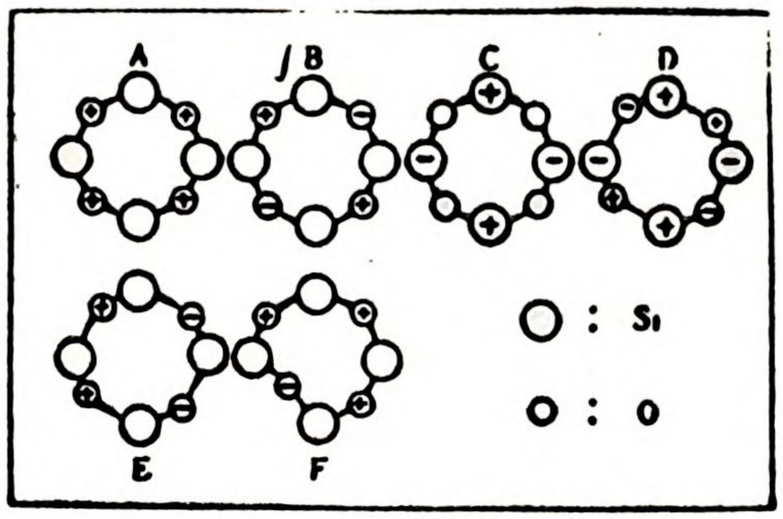
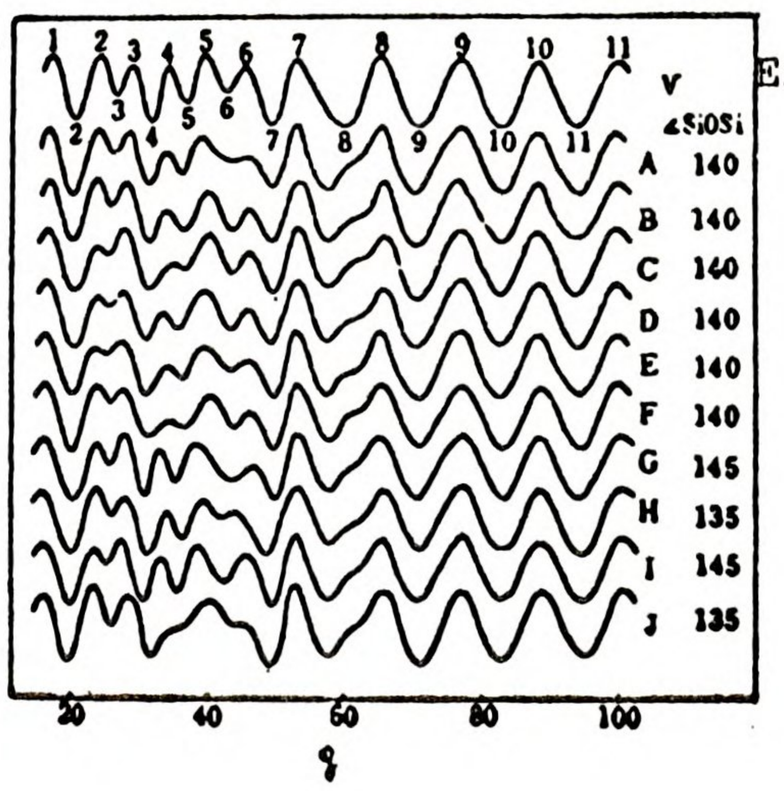


Figure IV

Visual and Theoretical
Intensity Curves of Octamethylcyclotetrasiloxane[34]



Model	Si_O-O(Å)	≤Si-O-Si	<O-Si-C
A	1.63	140°	110°
B	1.63	140	107
C	1.63	140	104
D	1.63	135	107
E	1.63	145	107
F	1.60	140	107
G	1.65	140	107
H	1.63	140	107

Structure B has a cradle form with four silicon atoms in a plane, with one set of opposite oxygen atoms above this plane and the other set of opposite oxygens below this plane. This structure results from the sequence of rotational states $g_r, g_r, g_l, g_l, g_r, g_r, g_l, g_l$.

C. Heats of formation of lower members of dimethyl- and methyl-isopropoxy-cyclopolysiloxanes.

Tanka has measured heats of formation of several of the lower members of the dimethyl- and methyl-isopropoxy-cyclopolysiloxanes and of linear polydimethylsiloxanes.[35,36] Measurements were done at 20° and constant volume. Heats of formation from monatomic gases for the structural units $(^{CH_3}_{CH_3}Si\langle^{O}_{O})$ and $(^{CH_3}_{iC_3H_7}Si\langle^{O}_{O})$ were derived and reported.

On the basis of the assumption that the linear polysiloxanes considered have no strain in their molecular structures, Tanka concludes that the ring structures of the cyclic tetramer and cyclic pentamer are free from strain and the cyclic trimer has strain energy of somewhat less than 9 Kcal./mole.

The conclusion that strain exists in the six-membered ring agrees with the smaller value of <SiOSi found for this molecule as compared with other polysiloxanes.

Since the eight- and ten-membered rings are free from strain, it

seems reasonable to assume that the <SiOSi present is the same as that in the linear chain. Since the earlier reported experimental values for both this ring and the chain agree, the choice of <SiOSi = 140° for the polymer appears sound.

II. THEORETICAL MODELS FOR THE POLYDIMETHYLSILOXANE CHAIN

A. Calculations of the Dimensions of Polymers

Because of the limited free rotation about the bonds forming the "backbone" of a polymer chain, each polymer molecule may assume an enormous number of different ~~conformations~~ configurations. Thus the experimental mean values of various quantities which characterize the polymeric system must be calculated by averaging over all possible configurations of the molecule.

In 1932 Eyring first presented a solution to the problem of calculating the unperturbed mean-square end-to-end dimensions ($\bar{r}_0^2$) of polymers as a function of bond lengths, bond angles, and internal rotations using matrix algebra.[7] Many authors have since improved and extended this method. A comprehensive discussion of many of these techniques is available in M. V. Vol'kenstein, "Configurational Statistics of Polymer Chains."[13] In II-B the matrix technique will be utilized in developing equations for the polydimethylsiloxane chain.

Lifson has presented a statistical theory of chain dimensions of linear polyethylene molecules taking into account interactions between all first and second neighbor $-CH_2-$ groups.[5] The equation is valid only for a high molecular weight polymer. This model will henceforth be termed a second neighbor statistically dependent model and is formally equivalent to a one-dimensional Ising lattice. A summary of the treatment for third and higher neighbor interactions is given. The need for considering higher ordered interactions has been indicated by Ptitsyn and Sharonow who have shown that the interactions of hydrogens in butane are divided between first neighbors, second neighbors, and third neighbors in

the ratio of 40%, 40%, and 20% respectively.[38] Lassettre and Dean have shown an even more pronounced effect of interactions between second neighbor hydrogens in neopentane. Here the equilibrium values of the internal rotation angles are shifted from the position of minimum energy of first neighbors by about 30°.[39]

Hoeve has recently published two papers on the unperturbed dimensions of polymer chains.[40] The first work includes a derivation of the dimensions of a chain $\{CRR'\}_n$ with first and second neighbor interactions paralleling that of Lifson. The method is extended to chains of the type $\{CR_2\text{-}CH_2\}_n$ and isotactic chains of the type $\{CHR\text{-}CH_2\}_n$. Nagai has published a similar treatment for isotactic and syndyotactic vinylic macromolcules.[41] Hoeve's second paper presents the calculation of the dimensions of polyethylene. The model is a three rotational state model with trans, gauche right, and gauche left states. The energy difference between trans and gauche states of 500 cal./mole corresponds to $P_G = P_{G'} = .232$, $P_T = .536$. This statistically independent model yields $\bar{r}_o^2/nl^2 = 3.34$ at 160°C. In order to obtain a value of 6.75 (as compared to 6.55 from intrinsic viscosity measurements), Hoeve used the following statistically dependent model: the energy barrier between the pair GG' was assumed to be 2150 cal./mole. Since the GG' pairs produce the shortest end-to-end vectors of all the possible pairs, increasing the energy required to form GG' lessens the probability of these pairs and increases the average length of the chain. Hence the value of $\bar{r}_o^2/nl^2$ is increased. The coordinate system used in this work is similar to those employed by Lifson and Hoeve.

Several authors have derived expressions for $\bar{r}_o^2/nl^2$ for a polymer chain with any number of bonds. Vol'kenstein and Ptitsyn first

derived a closed mathematical relation for a normal alkane chain with one fixed bond angle using a matrix diagonalization technique.[42] The same derivation was carried through by Smith using the method of difference equations.[43]

In the equations to be developed in the next section for polydimethylsiloxane both fixed valence angle[44] and bond length[45] are assumed. These equations are the first to be developed for a chain with two alternating valence angles that are valid for any number of bonds in the polymer chain by the rotational transformation matrix technique.

Birshtein, Ptitsyn, and Sokolova have developed equations for the dimensions of long chains with symmetric side groups and alternating valence angles.[46] An equation is developed for the mean-square end-to-end dimension of a chain with statistically independent bond pairs i.e., statistically independent pairs of rotational states. The authors chose ∠SiOSi as 150°-160° citing as references the dipole moment measurements of linear and cyclic dimethylsiloxanes by Sauer and Mead[47] (160° ± 15°) and the infrared and Raman absorption spectroscopic investigation of disiloxane of Curl and Pitzer (150°-158°).[48] For the later references cited in this thesis, the best choice for ∠SiOSi is 140° ± 5°.

Birshtein, et al., found that $(\bar{r}_o^2/\bar{r}_{of.p.}^2)^{\frac{1}{2}} = 1.25$ (1), where the designation of $\bar{r}_{of.p}^2$ refers to the unperturbed dimensions of the chain model with freely rotating pairs of rotational state.. Using ∠SiOSi = 160°, Flory and co-workers reported $(\bar{r}_o^2/\bar{r}_{of}^2)^{\frac{1}{2}} = 1.38$ (2), where $\bar{r}_{of}^2$ refers to the unperturbed dimensions of the chain model in which all conformation are allowed to assume free rotation. Since the ratio (1) is less than (2), the chain model of freely rotating pairs must be a closer approximation to the real chain than the model with free rotation of all conformations. The authors state that since the ratio

(1) has a value as low as 1.25, the internal rotation in the polydimethylsiloxane chain is comparatively weakly restricted. These authors do not consider the problem of cyclic formation in the polymerization system.

In the following section a model for the polydimethylsiloxane chain is presented in which all first neighbor interactions of bonds and pairs of bonds can be included.

B. Development of equations for the dimensions of the polydimethylsiloxane chain.

1. Orthogonal transformations

The transformation of a rigid body from a set of coordinates, x, y, z to a set of coordinates x', y', z' can be described by a matrix.[49] For example, a two-dimensional transformation from one cartesian coordinate system to another corresponds to a rotation of the axes in this plane. This rotation can be specified completely by only one quantity, the rotational angle θ.

The transformation equations are:

$$x_1' = x_1\cos\theta + x_2\sin\theta$$

$$x_2' = -x_1\sin\theta + x_2\cos\theta$$

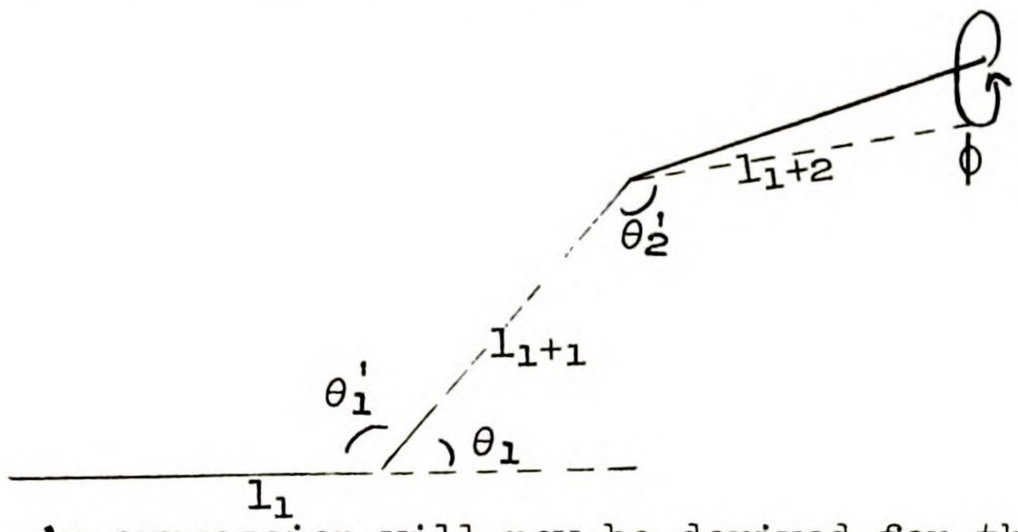
The matrix of the transformation, denoted by θ, is:

$$[\theta] = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix}$$

The matrix equation $\vec{r}' = \theta\vec{r}$ thus represents the transformation of the vector r to the vector $\vec{r}'$ through the angle θ, where $\vec{r}$ corresponds to the original set of coordinates for the rigid body and $\vec{r}'$ corresponds to the set of coordinates for the displaced rigid body.

2. End-to-end distance of a microscopic configuration.

Consider now the polydimethylsiloxane chain, a representative segment of which is pictured below. Here $\theta_1' = \angle OSiO$, $\theta_2' = \angle SiOSi$.



$$\theta' = 180° - \theta$$

An expression will now be derived for the end-to-end distance vector $\vec{r}$ for a given microscopic configuration,

$$\vec{r} = \sum_{i=1}^{n} \vec{\ell}_i$$

as a function of the bond length, ℓ, the complements of the valence angles, θ_1 and θ_2, and the internal rotation angles ϕ_k.

To each bond is attached an orthogonal coordinate system of its own. Then all of these coordinate systems can be transformed to a common system, here chosen to be the system attached to the bond ℓ_1, by a series of successive elementary matrix transformations. The coordinate system attached to the first bond is chosen so that its z axis points in the direction of that bond, its y axis lies in the plane which passes through this bond and the bond preceding it, and its x axis points in the direction of the vector product $\vec{\ell}_1 \times \vec{\ell}_2$ of these two bond vectors.

Consider now the transformation A which transforms the $(k + 1)$th coordinate system into the kth. It may be <u>obtained by two successive elementary transformations</u>. The first, θ, is a rotation of the $(k + 1)$th coordinate system by an angle θ around the x axis. This

transformation leaves the x axis unchanged and rotates y and z in their own plane so that the z axis points in the direction of $\vec{\ell}_k$. This transformation is given by the matrix

$$[\theta] = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & \sin\theta \\ 0 & -\sin\theta & \cos\theta \end{bmatrix}$$

Next the new coordinate system is rotated by an angle ϕ_k around the new z axis (i.e., around $\vec{\ell}_{k-1}$) until it will coincide with the kth coordinate system. Since this transformation leaves z unchanged and rotates y and x in their plane, it is given by the matrix

$$[\phi] = \begin{bmatrix} \cos\phi_k & \sin\phi_k & 0 \\ -\sin\phi_k & \cos\phi_k & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

These two successive transformations, which are represented by the matrix product

$$A = [\theta][\phi] \qquad \begin{bmatrix} \cos\phi_k & \sin\phi_k & 0 \\ -\cos\theta\sin\phi_k & \cos\theta\cos\phi_k & \sin\theta \\ \sin\theta\sin\phi_k & -\sin\theta\cos\phi_k & \cos\theta \end{bmatrix}$$

transform the (k + 1)th coordinate system into the kth coordinate system. The vector $\vec{\ell}_{k+1}$ which in its own coordinate system was given by $\vec{\ell}_{k+1} = (0, 0, \ell)$ is therefore expressed in the kth system by $\vec{\ell}_k = (0, 0, \ell)A$, whereas $\vec{\ell}_k$ is represented in this system by $\vec{\ell}_k = (0, 0, \ell)$. This procedure of elementary transformations may be repeated, transforming the coordinate systems of all bond vectors into that of the first one, $\vec{\ell}_1$.[4]

For the polydimethylsiloxane chain there must be two transformation matrices, corresponding to the two bond angles in the chain.

These matrices are designated A_1 and A_2.

$$A_1 = \begin{bmatrix} \cos\phi_1 & \sin\phi_1 & 0 \\ -\cos\theta_1\sin\phi_1 & \cos\theta_1\cos\phi_1 & \sin\theta_1 \\ \sin\theta_1\sin\phi_1 & -\sin\theta_1\cos\phi_1 & \cos\theta_1 \end{bmatrix}$$

$$A_2 = \begin{bmatrix} \cos\phi_2 & \sin\phi_2 & 0 \\ -\cos\theta_2\sin\phi_2 & \cos\theta_2\cos\phi_2 & \sin\theta_2 \\ \sin\theta_2\sin\phi_2 & -\sin\theta_2\cos\phi_2 & \cos\theta_2 \end{bmatrix}$$

so $\ell_{1+2} = \ell_i A_2 A_1$

Thus, the ℓ_{i+k} bond vector can be expressed back in terms of the ℓ_i vector by the relation: $\ell_{i+k} = \ell_i (A_2A_1)^{k/2}$ k an even integer.

To avoid the troublesome situation of fractional powers of the matrix product A_2A_1, two different expressions for $\vec{r}$ will be written - one for the case of an odd number of links in the polymer chain and the other for the case of an even number of links in the polymer chain.

In the system of coordinates previously described, the end-to-end distance is thus given:

1. for n odd

$$\vec{r} = (0\ 0\ 1)(I + A_1 + A_2A_1 + \ldots (A_2A_1)^{\frac{n-5}{2}} + A_1(A_2A_1)^{\frac{n-5}{2}} + (A_2A_1)^{\frac{n-3}{2}} + A_1(A_2A_1)^{\frac{n-3}{2}} + (A_2A_1)^{\frac{n-1}{2}} .)$$

2. for n even

$$\vec{r} = (0\ 0\ 1)(I + A_1 + A_2A_1 \ldots A_1(A_2A_1)^{\frac{n-6}{2}} + (A_2A_1)^{\frac{n-4}{2}} + A_1(A_2A_1)^{\frac{n-4}{2}} + (A_2A_1)^{\frac{n-2}{2}} + A_1(A_2A_1)^{\frac{n-2}{2}})$$

Note that in both cases, for n links in the chain, the last term in the expression for $\vec{r}$ must be the product of n-1 matrices.

3. Mean-square end-to-end distance of the chain

The square end-to-end distance r^2 of a microscopic conformation changes continually due to the thermal motion which causes the internal rotation angles to vary between the potential energy barriers in the chain. As mentioned in the beginning of this section, the experimentally measurable properties of the macromolecule are related to the average value of r^2, the **mean - square end - to - end** distance, $\bar{r}^2$. **This** distance is obtained by averaging over all values of the trigonometric functions of the angles of internal rotation ϕ_k as they appear in the transformational matrices A_1, A_2, and the product matrices A_1A_2, A_2A_1. In the process of averaging, each microscopic configuration has its statistical weight which depends on the total energy of the system in this configuration. This total energy includes: (1) The potential energy of hindered rotation, that is, the interactions between the various groups attached directly to the two atoms next to each other in the skeletal structure. (2) The energy from the interactions between the neighboring side groups. Models for the chain illustrating both of these energy contributions will be discussed after the equations have been developed. These models will serve as examples illustrating use of the equations for calculations.

The mean-square end-to-end dimension $\bar{r}^2$ is obtained by multiplying $\vec{r}$ by its transpose, $\vec{r}^t$ and inserting averaged values for the trigonometric functions of the rotational angles into the transformation matrices and matrix products.

Consider the case of n odd.

$$(a)\ \overline{r}^2 = \ell^2(0\ 0\ 1)\Big[(I + A_1 + A_2A_1 + \ldots (A_2A_1)^{\frac{n-5}{2}} + A_1(A_2A_1)^{\frac{n-5}{2}} (A_2A_1)^{\frac{n-3}{2}} + A_1(A_2A_1)^{\frac{n-3}{2}} + (A_2A_1)^{\frac{n-1}{2}}\Big] \times \Big[(I + A_1^t + A_1^tA_2^t + \ldots [(A_2A_1)^{\frac{n-5}{2}}]^t + [(A_2A_1)^{\frac{n-5}{2}}]^tA_1^t + [(A_2A_1)^{\frac{n-3}{2}}]^t + [(A_2A_1)^{\frac{n-3}{2}}]^tA_1^t + [(A_2A_1)^{\frac{n-1}{2}}]^t\Big] \begin{pmatrix}1\\0\\0\end{pmatrix}$$

(b) Multiplication yields*

$$\overline{r}^2 = \ell^2(0\ 0\ 1)\Big[(I + A_1 + (A_1A_2)^{\frac{n-5}{2}} + (A_1A_2)^{\frac{n-5}{2}}A_1 + (A_1A_2)^{\frac{n-3}{2}} + (A_1A_2)^{\frac{n-3}{2}}A_1 + (A_1A_2)^{\frac{n-1}{2}} + A_1^t + I + A_2 + A_2A_1 + \ldots A_2(A_1A_2)^{\frac{n-7}{2}} + (A_2A_1)^{\frac{n-5}{2}} + A_2(A_1A_2)^{\frac{n-5}{2}} + (A_2A_1)^{\frac{n-3}{2}} + A_2(A_1A_2)^{\frac{n-3}{2}}A_1 + (A_1A_2)^t + I + A \ldots (A_1A_2)^{\frac{n-7}{2}} + (A_1A_2)^{\frac{n-7}{2}}A_1 + (A_1A_2)^{\frac{n-5}{2}} + (A_1A_2)^{\frac{n-5}{2}}A_1 + (A_1A_2)^{\frac{n-3}{2}} + \ldots [(A_1A_2)^{\frac{n-5}{2}}]^t + [A_2(A_1A_2)^{\frac{n-7}{2}}]^t + [(A_1A_2)^{\frac{n-7}{2}}]^t + \ldots I + A_1 + A_1A_2 + (A_1A_2)A_1 + (A_1A_2)^2 + [(A_1A_2)^{\frac{n-5}{2}}A_1]^t + [(A_1A_2)^{\frac{n-5}{2}}]^t + [(A_1A_2)^{\frac{n-7}{2}}A_1]^t + \ldots A_1^t + I + A_2 + A_2A_1 + A_2(A_1A_2) + [(A_1A_2)^{\frac{n-1}{2}}]^t + [A_2(A_1A_2)^{\frac{n-3}{2}}]^t + \ldots [(A_1A_2)^2]^t + [A_2(A_1A_2)]^t + (A_1A_2)^t + A_2^t + 1)\Big] \begin{pmatrix}0\\0\\1\end{pmatrix}$$

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* Originally the development of r^2 was made from the expression $\vec{r}^t \cdot \vec{r}$ where $\overline{r} = (I + A_1 + A_1A_2 + \ldots)\begin{pmatrix}0\\0\\\ell\end{pmatrix}$. This is identical with the expression $\vec{r} \cdot \vec{r}^t$ where $\vec{r} = (0\ 0\ \ell)(I + A_1 + A_2A_1 + \ldots)$.[3,4]

(c) Collecting terms,

$$\frac{r^2}{\ell^2} = n + (0\ 0\ 1)\Big[(\tfrac{n-1}{2})A_1 + (\tfrac{n-1}{2})A_2 + (\tfrac{n-1}{2})A_1{}^t + (\tfrac{n-1}{2})A_2{}^t + (\tfrac{n-1}{2})A_1A_2 +$$

$$(\tfrac{n-1}{2})(A_1A_2)^t + (\tfrac{n-3}{2})A_2A_1 + (\tfrac{n-3}{2})(A_2A_1)^t + (\tfrac{n-3}{2})(A_1A_2A_1) + (\tfrac{n-3}{2})(A_2A_1A_2) +$$

$$(\tfrac{n-3}{2})(A_1A_2A_1)^t + (\tfrac{n-3}{2})(A_2A_1A_2)^t + (\tfrac{n-3}{2})(A_1A_2A_1A_2) + (\tfrac{n-5}{2})(A_2A_1A_2A_1) +$$

$$(\tfrac{n-3}{2})(A_1A_2A_1A_2)^t + (\tfrac{n-5}{2})(A_2A_1A_2A_1)^t + \ldots.$$

$$2(A_1A_2)^{\frac{n-5}{2}}A_1 + 2A_2(A_1A_2)^{\frac{n-5}{2}} + 2[(A_1A_2)^{\frac{n-5}{2}}A_1]^t + 2[A_2(A_1A_2)^{\frac{n-5}{2}}]^t +$$

$$2(A_1A_2)^{\frac{n-3}{2}} + 1\ (A_2A_1)^{\frac{n-3}{2}} + 2[(A_1A_2)^{\frac{n-3}{2}}]^t + 1\ [(A_2A_1)^{\frac{n-3}{2}}]^t +$$

$$1(A_1A_2)^{\frac{n-3}{2}}A_1 + 1\ A_2(A_1A_2)^{\frac{n-3}{2}} + 1\ [(A_1A_2)^{\frac{n-3}{2}}A_1]^t + 1\ [A_2(A_1A_2)^{\frac{n-3}{2}}]^t +$$

$$1\ (A_1A_2)^{\frac{n-1}{2}} + 0\ (A_2A_1)^{\frac{n-1}{2}} + 1\ [(A_1A_2)^{\frac{n-1}{2}}]^t + 0\ [(A_2A_1)^{\frac{n-1}{2}}]^t\Big]\begin{pmatrix}0\\0\\1\end{pmatrix}$$

Multiplication by the row matrix (0 0 1) reduces each 3 x 3 matrix to a 1 x 3 matrix. Multiplication of the 1 x 3 matrix by the column matrix $(0\ 0\ 1)^t$ reduces to a number. This number is the 3,3 element of the original matrix.

The 3,3 element in $(A^t)^n$ will be the same as the 3,3 element in A^n. This holds when A is any mxm matrix.

$$\frac{r^2}{\ell^2} = n + (n-1)(A_1)_{3,3} + (n-1)(A_2)_{3,3} + (n-1)(A_1A_2)_{3,3} + (n-3)(A_2A_1)_{3,3} +$$

$$(n-3)(A_1A_2A_1)_{3,3} + (n-3)(A_2A_1A_2)_{3,3} + (n-3)(A_1A_2)^2_{3,3} + (n-5)(A_2A_1)^2_{3,3}$$

$$+ \ldots$$

$$+ 4(A_1A_2)^{\frac{n-5}{2}}A_1)_{3,3} + 4A_2(A_1A_2)^{\frac{n-5}{2}})_{3,3} +$$

$$4(A_1A_2)^{\frac{n-3}{2}})_{3,3} + 2(A_2A_1)^{\frac{n-3}{2}})_{3,3} +$$

$$2(A_1A_2)^{\frac{n-3}{2}}A_1)_{3,3} + 2A_2(A_1A_2)^{\frac{n-3}{2}})_{3,3} +$$

$$2(A_1A_2)^{\frac{n-1}{2}})_{3,3} + 0\ (A_2A_1)^{\frac{n-1}{2}})_{3,3}$$

(e) The equation for $\frac{r^2}{\ell^2}$ (n odd) in summation notation is as follow:

$$\frac{r^2}{\ell^2} = n + \sum_{k=1,3,5,\ldots}^{n-2} (n-k)[(A_1A_2)^{\frac{k-1}{2}} A_1]_{3,3}$$

$$+ \sum_{k=1,3,5\ldots}^{n-2} (n-k)[A_2(A_1A_2)^{\frac{k-1}{2}}]_{3,3}$$

$$+ \sum_{k=2,4,6\ldots}^{n-1} (n-k+1)[(A_1A_2)^{\frac{k}{2}}]_{3,3}$$

$$+ \sum_{k=2,4,6\ldots}^{n-3} (n-k-1)[(A_2A_1)^{\frac{k}{2}}]_{3,3}$$

A more compact notation for r^2 will be developed in the following section for the case of n even.

Note that in this derivation all terms have been retained so that the expression for $\overline{r^2}$ is valid for all values of n. Thus, these equations can be used for approaching the cyclic formation problem in the siloxane system.

An expression for r^2 will now be derived for n even.

(a) $$r^2 = \ell^2(0\ 0\ 1)\left[I + A_1 + A_2A_1 + \ldots A_1(A_2A_1)^{\frac{n-6}{2}} + (A_2A_1)^{\frac{n-4}{2}} + A_1(A_2A_1)^{\frac{n-4}{2}} + (A_2A_1)^{\frac{n-2}{2}} + A_1(A_2A_1)^{\frac{n-2}{2}}\right] X$$

$$\left[(I + A_1^t = A_1^t A_2^t + \ldots [(A_2A_1)^{\frac{n-6}{2}}]^t A_1^t + [(A_2A_1)^{\frac{n-4}{2}}]^t + [(A_2A_1)^{\frac{n-4}{2}}]^t A_1^t + [(A_2A_1)^{\frac{n-2}{2}}]^t + [(A_2A_1)^{\frac{n-2}{2}}]^t A_1^t\right]\begin{pmatrix}0\\0\\1\end{pmatrix}$$

(b) Multiplication yields:

$$r^2 = \ell^2(0\ 0\ 1)\left[(I + A_1 + A_1A_2 + \ldots (A_1A_2)^{\frac{n-6}{2}} A_1 + (A_1A_2)^{\frac{n-4}{2}} + (A_1A_2)^{\frac{n-4}{2}} A_1 + (A_1A_2)^{\frac{n-2}{2}} + (A_1A_2)^{\frac{n-2}{2}} A_1 +\right.$$

$$A_1^t + I + A_2 \ldots (A_2A_1)^{\frac{n-6}{2}} + A_2(A_1A_2)^{\frac{n-6}{2}} + (A_2A_1)^{\frac{n-4}{2}} +$$

$$A_2(A_1A_2)^{\frac{n-4}{2}} + (A_2A_1)^{\frac{n-2}{2}} +$$

$$A_2^tA_1^t + A_2^t + I + \ldots (A_1A_2)^{\frac{n-8}{2}}A_1 + (A_1A_2)^{\frac{n-6}{2}} + (A_1A_2)^{\frac{n-6}{2}}A_1 +$$

$$(A_1A_2)^{\frac{n-4}{2}} + (A_1A_2)^{\frac{n-4}{2}}A_1 + \ldots.$$

$$[(A_1A_2)^{\frac{n-6}{2}}A_1]^t + [(A_1A_2)^{\frac{n-6}{2}}]^t + [(A_1A_2)^{\frac{n-8}{2}}A_1]^t + \ldots. I + A_2 +$$

$$A_2A_1 + A_2(A_1A_2) + (A_2A_1)^2 +$$

$$[(A_1A_2)^{\frac{n-4}{2}}]^t [A_2(A_1A_2)^{\frac{n-6}{2}}]^t + [(A_1A_2)^{\frac{n-6}{2}}]^t + \ldots A_2^t + I +$$

$$A_1 + A_1A_2 + (A_1A_2)A_1 +$$

$$[(A_1A_2)^{\frac{n-2}{2}}A_1]^t + [(A_2A_1)^{\frac{n-2}{2}}]^t + [(A_1A_2)^{\frac{n-4}{2}}A_1] + \ldots + [(A_2A_1)^2]^t +$$

$$\left.[(A_1A_2)A_1]^t + [(A_2A_1)]^t + A_1^t + I)\right] \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

Here again the 3,3 element in $(A^t)^n$ will be the same as the 3,3 element in A^n.

(c) For n even,

$$\frac{r^2}{\ell^2} = n + \sum_{k=1,3,5\ldots}^{n-1} [(n-k+1)(A_1A_2)^{\frac{k-1}{2}}A_1]_{3,3}$$

$$+ \sum_{k=1,3,5\ldots}^{n-3} [(n-k-1)\ A_2(A_1A_2)^{\frac{k-1}{2}}]_{3,3}$$

$$+ \sum_{k=2,4,6\ldots}^{n-2} [(n-k)(A_1A_2)^{\frac{k}{2}}]_{3,3}$$

$$+ \sum_{k=2,4,6\ldots}^{n-2} [(n-k)(A_2A_1)^{\frac{k}{2}}]_{3,3}$$

(d) A change in summation notation follows:

Let $A_1A_2 \equiv B$, $A_2A_1 \equiv D$

$$\sum_{k=1,3,5}^{n-1} (n-k+1) \left[B^{\frac{k-1}{2}} A_1\right]_{3,3} = \sum_{k=0,1,2}^{\frac{n-2}{2}} (n-2k) \left[(B)^k A_1\right]_{3,3}$$

$$\sum_{k=1,3,5}^{n-3} (n-k-1) \left[A_2 B^{\frac{k-1}{2}}\right]_{3,3} = \sum_{k=0,1,2}^{\frac{n-4}{2}} (n-2k-2) \left[A_2 B^k\right]_{3,3}$$

$$= \sum_{k=0,1,2}^{\frac{n-4}{2}} (n-2k-2) \left[D^k A_2\right]_{3,3}$$

$$\sum_{k=2,4,6}^{n-2} (n-k) \left[B^{k/2}\right]_{3,3} = \sum_{k=0,1,2}^{\frac{n-2}{2}} (n-2k) \left[B^k\right]_{3,3} - n$$

$$\sum_{k=2,4,6}^{n-2} (n-k) \left[D^{k/2}\right]_{3,3} = \sum_{k=0,1,2}^{\frac{n-2}{2}} (n-2k) \left[D^k\right]_{3,3} - n$$

(e) Dividing each sum by n,

$$\frac{\overline{r}^2}{n\ell^2} = -1 + \sum_{k=0,1,2}^{\frac{n-2}{2}} \left(1 - \frac{2k}{n}\right) \left[B^k A_1\right]_{3,3}$$

$$+ \sum_{k=0,1,2}^{\frac{n-2}{2}} \left(1 - \frac{2(k+1)}{n}\right) \left[D^k A_2\right]_{3,3}$$

$$+ \sum_{k=0,1,2}^{\frac{n-2}{2}} \left(1 - \frac{2k}{n}\right) \left[B^k\right]_{3,3}$$

$$+ \sum_{k=0,1,2}^{\frac{n-2}{2}} \left(1 - \frac{2k}{n}\right) \left[D^k\right]_{3,3}$$

The equations will be used in this form for the determination of the conditions of convergence of the series for $\overline{r}^2/nl^2$ discussed in II D.

C. Application of the equations to chain models

1. Intramolecular interactions in polymer chains

The interactions between atoms or groups in polymer chains which are not directly joined can be divided into two classes. To the first class belong the interactions between atoms or groups at distances which are, on the average, small and which depend on one or a few internal rotation angles, ϕ_i. These are termed short-range interactions. The interactions have the character of repulsions between atoms or groups with overlapping electron clouds, and lead to the appearance of hindrance of internal rotation since the values of the angles ϕ_i corresponding to greater overlap of the electron clouds ordinarily correspond to greater energies. Short-range interactions are characteristic not only of polymer chains but of small molecules as well, where these interactions lead to the appearance of a hindering potential for internal rotation and to the well-known phenomenon of rotational isomerism. Detailed accounts of the experimental facts and theoretical conceptions of hindered internal rotation in small molecules are located in the book of Mizushima.[50]

When a polymer chain is in the unperturbed state, chain configuration is presumably determined only by short range interactions. Only the unperturbed dimensions of the siloxane chain are considered here so the "excluded volume" effect caused by long range intramolecular interaction does not influence chain dimension.[51]

2. Statistically independent bond model for a polymer chain.

The subject of statistically independent bond models for polymer chains was first discussed in section I-1.0. The essential mathematical feature of this model is that the average of the trigonometric functions of the rotational angle is not a function of the conformations of adjacent links in the chain. That is, $\langle\cos\phi_1\cos\phi_2\rangle = \langle\cos\phi_1\rangle\langle\cos\phi_2\rangle$,

so that there is no correlation between the rotational conformations of adjacent links in the chain.

If all the potential minima in the curve representing the potential energy as a function of rotational angle possess a line of symmetry which passes through the point of minimum potential in the well, then the continuous function can be well approximated by a point function, and the polymer chain can be represented as an equilibrium mixture of discrete rotational isomers. Every link is thus assumed to have a definite state of equilibrium with a discrete value of ϕ_i. [52] Given below are the formulas for calculation of $\langle\cos\phi\rangle$ for the continuous and discrete models. [32] For a chain model having a continuum of rotational states,

$$\langle\cos\phi\rangle = \frac{\int_0^{2\pi} e^{-u(\phi)/kT} \cos\phi \, d\phi}{\int_0^{2\pi} e^{-u(\phi)/kT} \, d\phi}$$

where:

$u(\phi)$ is the rotational potential energy function. For a chain model consisting of a finite number of discrete rotational states,

$$\langle\cos\phi\rangle = \frac{\sum_{i=1}^{n} P_i \cos\phi_i}{\sum_{i=1}^{n} P_i}$$

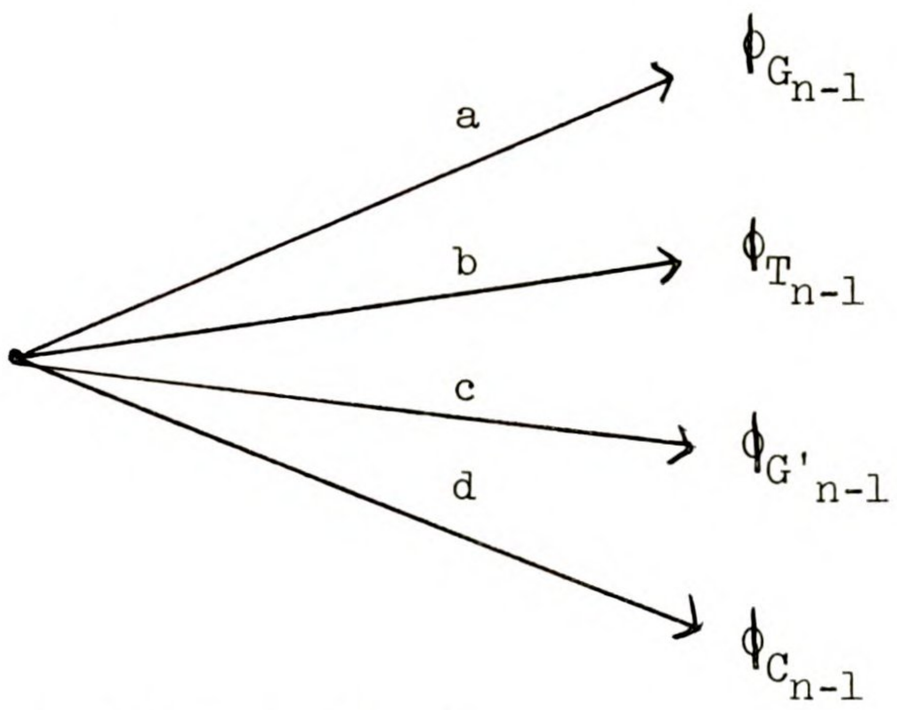
where:

P_i = the probability that the chain assumes the i^{th} rotational state.

The representation of the polymer chain as a mixture of rotational isomers was recently experimentally justified by V. N. Nikitin and B. Z. Volchek[53] who found spectroscopically a transition of certain rotational isomers into others on stretching a polymer.

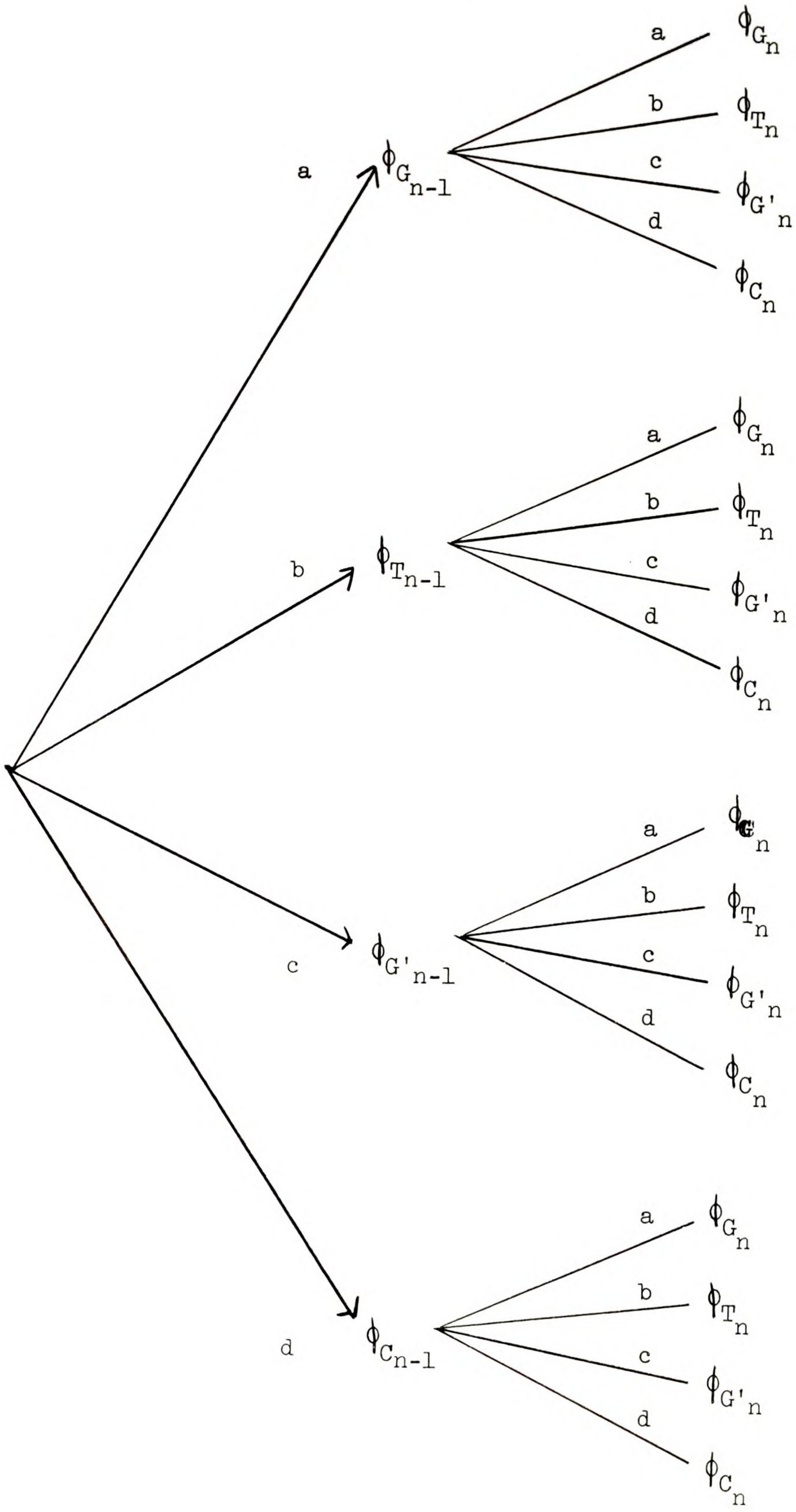
The concept of statistically independent rotational states in polymer chains with discrete states is perhaps most clearly illustrated by the use of probability models.

Consider a polymer chain viewed along the bond axis from the ith atom in the chain to the (i+1)th. This chain will be allowed to assume four possible rotational states (in the case of the siloxane chain these are gauche right, trans, gauche left, cis.) The rotational states will be designated as $\phi_{G_{n-1}}$, $\phi_{T_{n-1}}$, $\phi_{G'_{n-1}}$, $\phi_{C_{n-1}}$ with probability of occurrence a, b, c, d respectively. This model is pictured below.

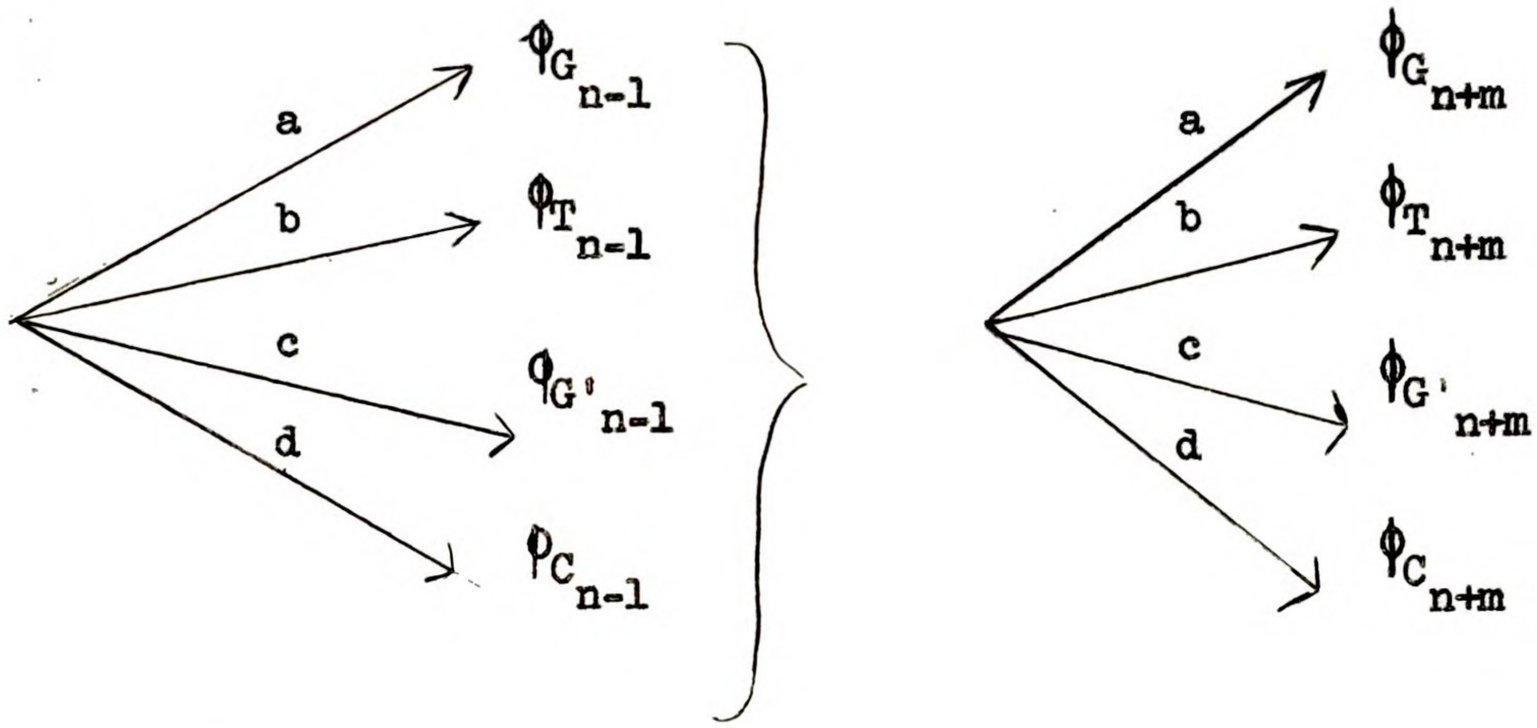


$$a + b + c + d = 1$$

Succeeding links will move outward from whichever of these four states it occurs. If the polymer chain is statistically independent, the probabilities of chain paths do not change with choice of the rotational state. That is, from $\phi_{G_{n-1}}$, $\phi_{T_{n-1}}$, $\phi_{G'_{n-1}}$, $\phi_{C_{n-1}}$ the probabilities of going to ϕ_{G_n}, ϕ_{T_n}, $\phi_{G'_n}$, ϕ_{C_n} are still a, b, c, d respectively. The probability model is illustrated below.


a
$\phi_{G_{n-1}}$
a
ϕ_{G_n}
b
ϕ_{T_n}
c
$\phi_{G'_n}$
d
ϕ_{C_n}
b
$\phi_{T_{n-1}}$
a
ϕ_{G_n}
b
ϕ_{T_n}
c
$\phi_{G'_n}$
d
ϕ_{C_n}
c
$\phi_{G'_{n-1}}$
a
ϕ_{G_n}
b
ϕ_{T_n}
c
$\phi_{G'_n}$
d
ϕ_{C_n}
d
$\phi_{C_{n-1}}$
a
ϕ_{G_n}
b
ϕ_{T_n}
c
$\phi_{G'_n}$
d
ϕ_{C_n}

Since this probability model continues through the polymer chain, a convenient shorthand notation is:



where m = 1,2,3...

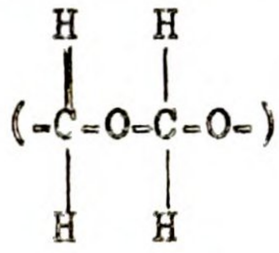
3. Statistically Independent Pairs of Bonds Model for a Polymer Chain

The concept of statistically independent pairs of rotational states in the polymer chain means that the probabilities of the ϕ_{G_n}, ϕ_{T_n}, $\phi_{G'_n}$, ϕ_{C_n} states will depend on the rotational state previously assumed by the polymer chain. That is, the chain will assume a preferential orientation depending on the outcome of previous events. For the most general case, there will be a different probability attached to each rotational state. The restrictions thus imposed are that (1) $\langle\cos\phi_1 \cos\phi_2\rangle \neq \langle\cos\phi_1\rangle \langle\cos\phi_2\rangle$ and (2) $\langle\cos\phi_1 \cos\phi_2\rangle = \langle\cos\phi_3 \cos\phi_4\rangle = \ldots \langle\cos\phi_{n-1} \cos\phi_n\rangle$ for n chain bonds. The arguments of Section II C. 2. regarding statistically independent chain bonds can be applied to this case where now the repeating independent chain unit is a bond pair.

D. The Prediction of Stability of Helical Conformations of Polymer Chains.

DeSantis, Giglio, Liquori, and Ripamonti[54] have approached the problem of predicting the configurations of polymer chains from fundamental principles of non-bonded interactions within the chains. These workers have calculated rotational potential energy curves for several simple polymer chains using a Van der Waal's potential to describe the interactions between pairs of non-bonded atoms. The most stable helical conformations calculated predict the previously known preferred rotational states with surprising accuracy. In several cases less preferred rotational states appear at angles not previously suspected.

No calculations were made on the polydimethylsiloxane chain. Calculations made for the structurally similar polyoxymethylene chain



assuming a one-atom helical chain (statistically independent model) with ∠OCO = ∠COC = 110°53' predict symmetric gauche states at 67° and 293° and a less preferred trans state at 180°. The calculated potential energy curve is pictured on page 38.

In a note added in proof the authors state that no new rotational states were predicted when the conformational potential

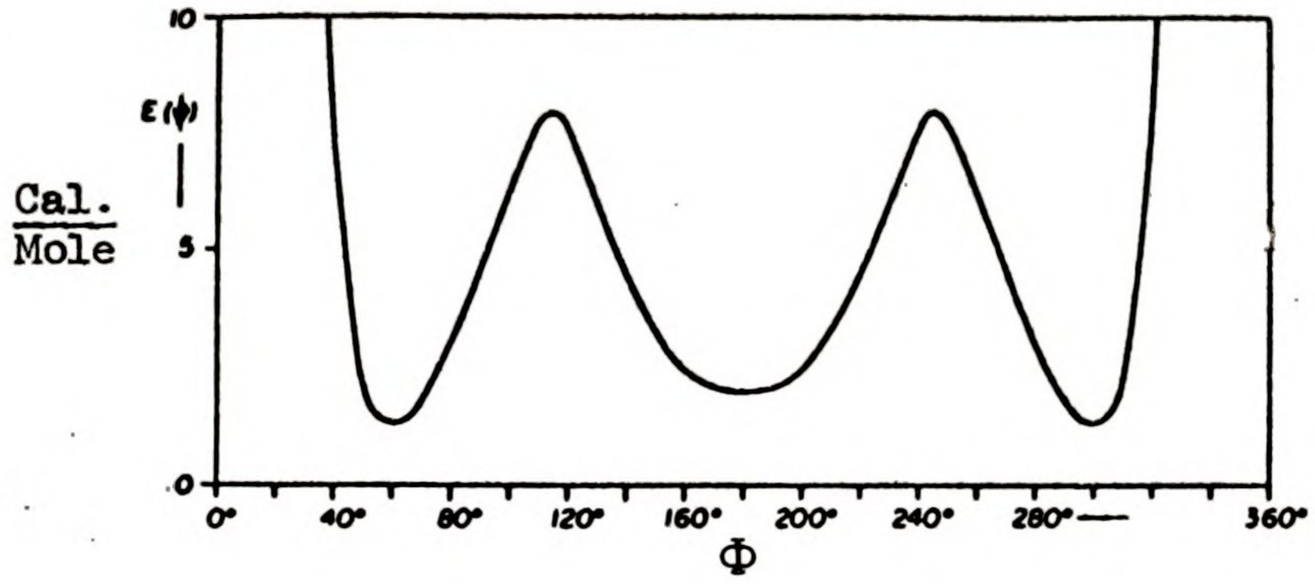


FIGURE V

Conformational potential energy of polyoxymethylene considered as a one-atom helical chain.

energy of the polymer chain was calculated using a statistically dependent, two-atom helical chain model.

The authors state that the lack of side-groups attached to alternate atoms of the chain is responsible for the fact that the gauche conformations are more energetically favorable (have a higher probability of occupancy) than the trans conformation(s) found for both polyethylene and polytetrafluoroethylene, in which side-groups are attached to every atom in the chain backbone.

They apply an analogous reasoning to explain the marked flexibility of the polyoxymethylene chain and the existence of a number of crystalline helical conformations.

The polydimethylsiloxane chain is structurally similar to the polyoxymethylene chain since in both cases the oxygen atom is an alternating atom in the chain and has no side groups attached. In the view of this author the results calculated for polyoxymethylene and the observed structural similarities to polydimethylsiloxane lend weight

to the three state approximation (G, G', T) for the allowed conformations of the polydimethylsiloxane chain.

E. Long Range Interferences in Polymer Chains

The average configuration of real polymer molecules in the unperturbed state is markedly influenced by the requirement that two elements of the polymer chain are forbidden from occupying the same location in space. This requirement is often implicitly neglected in calculations of chain dimensions and has been neglected in all prior derivations of this work. The long range interference effect means that a given configuration calculated from a period one or period two model will be acceptable only in the case that none of its segments is assigned to a site occupied by another segment. Only a small fraction of the calculated configurations may be realized by the actual chain molecule[55]. Thus, even if one uses an accurate assignment of rotational states and their occupancy and correct bond angles and lengths, the calculated dimensions will be smaller than the actual dimensions because unallowed configurations have been included in the calculations.

G. W. King has provided much insight into the theoretical considerations necessary to take account of the long range interference effect[56]. King reiterated the generally accepted principle that the thermodynamical properties of long chain molecules depend only on the configurations of segments of the chain very short compared with the whole molecule. The geometrical complexion of a segment, say, 20 atoms long are independent to a very large extent of segments more than 20 atoms away. The smallest tolerable subsystem necessary to accurately

describe such a system is thus a sliding segment of $Z_1 \sim 20$ chain links, whose configurations are independent of atoms outside the segment but dependent on those within it. Each chain link occurs in $Z_1 + 1$ different segments obtained by sliding.

What King proposed is, in the terminology of this work, a chain of period Z_1. Let $F_1(Z_1)$ be the number of configurations of a segment of Z_1 atoms. Then the Markov matrix, P, necessary to describe the chain is of order $F_1(Z_1)$. Consider now a property **P** which has a value p_i in the ith. segment. **P** could be the vectorial distance between the ends of the segment weighted by the Boltzmann factor of the energy of the combined configuration. The elements of the Markoff matrix are $p_{i,j} = p_i x p_j$. An element p_{ij} is the value of the property **P** of the segment of length $2Z_1$ obtained by the concentration of a segment of Z_1 atoms of configuration i with a segment of Z_1 atoms of configuration j. The most important feature of this model to note is that long range interferences are dealt with explicitly and directly. An element $p_{i,j}$ always has a factor which is 0 if the combined segments cannot exist, 1 if the combination is allowed.

The immense complexity of the formalism necessary to describe the period Z_1 chain makes calculations prohibitive. The important feature is the insight which the model offers into the long range interference problem. If the chain can be represented by a sliding segment of twenty atoms, the model of King would account for long range interference effects.

Tractible solutions to the long range interference problem lie in finding approximate methods to eliminate unallowed chain config-

urations. In a classic paper, E. W. Montroll has treated a chain on a square lattice in which right and left steps are required at each lattice point, and short range overlapping is eliminated[57]. Those overlaps which occur when a monomer four removed from a given monomer returns to the position of the given monomer are called first-order overlaps (⌊⌋). Overlaps of monomers 12 removed are called second-order overlaps (⌜⌝⌞⌟), etc. The first order overlaps are much more probable than those of higher order and Montroll has chosen as his approximate treatment the elimination of interferences in the chain due to first order overlaps. Montroll is able to obtain in closed form, the difference equation for the number of configurations for this very restrictive model. When n(the number of links in the chain) = 10, the fraction of configurations without first order overlap = 0.18.

When Montroll's method is applied to a real polymer chain off a lattice, as, for example, the polydimethylsiloxane chain, the number of configurations available to the chain is increased many times over the number available to the square-lattice chain and predicting a priori those configurations which lead to overlap becomes a much more difficult matter. A numerical approach is taken in this work as follows:

The siloxane chain is assumed to have G, T and G' rotational states available. The value of the end-to-end bond vector is calculated for all possible configurations for small values of n to numerically obtain the paths that lead to interferences. The number of configurations available to this chain model is 3^{n-1}. A further interest of this calculation is to gain insight

into the necessity of postulating a cis state to explain the formation of hexamethylcyclotrisiloxane.

F. Chain Configuration and Motion

Grubb and Osthoff[58] have studied the kinetics of the KOH-catalyzed polymerization of octamethylcyclotetrasiloxane as a function of catalyst concentration and polymerization temperature. In all cases, the reaction was found to be first order in monomer concentration. At 152.6°C and 0.043% by weight KOH, equilibrium is reached in approximately 90 minutes.

The frequency of intramolecular rotations in the polydimethylsiloxane chain has been studied by nuclear magnetic resonance. Huggins and co-workers[18] found that the transition temperature, arbitrarily defined as the point at which the line width has changed by one-half the total change in log ΔH, is 180°K. The temperature-dependence of N.M.R. line narrowing has been explained in terms of the onset of intramolecular rotations by Slichter[59]. The frequency of chain-twisting and torsional oscillation is concluded from line narrowing data, to be greater than several tens of kilocycles per second.

Since the rate of intramolecular rotations is many orders of magnitude greater than the rate of monomer addition to a chain, the chain configuration is taken up independently of the reaction mechanism and rate.

G. Convergence of $\bar{r}^2/nl^2$ -- Investigation of the Convergence of the Matrix Power Series

The conditions under which the equation for $\bar{r}^2/nl^2$ converges will be determined.

Consider now the following matrix power series*:

* Multiplying each term in a matrix series by a constant matrix does not alter the conditions of convergence. Two of the matrix series in $\bar{r}^2/nl^2$ are multiplied by a constant matrix, but are otherwise identical with 1a) and 1b). Therefore, establishing the conditions of convergence of 1a) and 1b) is sufficient to establish the conditions of convergence of $\bar{r}^2/nl^2$.

1a) $\sum_{k=0,1,2}^{\frac{n-2}{2}} (1 - 2k/n)B^k$; 1b) $\sum_{k=0,1,2}^{\frac{n-2}{2}} (1 - 2k/n)D^k$; where $B = A_1A_2$, $D = A_2A_1$

Both of these series can be expressed as:

2) $S = \sum_{6=0} c_6A^6$, where A is an m x m matrix and the c_6 are numbers.

The power series of S can be shown to converge for each element of S if $\sum_6 |c_6| (na)^6$ converges, where $|a_{ij}| \leq a$; i, j = 1, 2.....n [60].

The subject of interest thus becomes that of the convergence of ordinary number power series [61].

For the case of series 1a):

3) $Z = \sum_{k=0,1,2}^{\frac{n-2}{2}} |1 - \frac{2k}{n}| (3a)^k$, where $n \longrightarrow \infty$.

We examine the ratio of any two arbitrary terms in the series. Consider the terms where k = m, m+1:

4) $\dfrac{1 - \frac{2(m+1)}{n}}{1 - \frac{2m}{n}} \times \dfrac{(3a)^{m+1}}{(3a)^m} =$ test ratio.

Simplification of 4) gives:

5) $\dfrac{n - 2m - 2}{n - 2m} \times 3a =$ test ratio.

We wish to consider the $\lim_{n \longrightarrow \infty} \left(\frac{n-2m-2}{n - 2m}\right) = L$

6) $$\left(\frac{n-2m-2}{n-2m}\right) = 1 - \frac{2}{n} - \frac{4m}{n^2} - \frac{8m^2}{n^3} - \ldots\ldots\ldots$$

7) $$\lim_{n \to \infty} \left[1 - \frac{2}{n} - \frac{4m}{n^2} - \frac{8m^2}{n^3} \ldots\ldots\right] = 1 = L$$

The series 3) will converge wherever:[62]

8) $$-\frac{1}{|L|} < 3a < \frac{1}{|L|} \quad \Rightarrow \quad -1 < 3a < 1$$

Therefore the series will converge whenever:

9) $$-\frac{1}{3} < a < \frac{1}{3}$$

Therefore, the convergence of 1a) is assured whenever $|a| < \frac{1}{3}$, where a is the largest matrix element in B. This means that the series will converge for every element in the matrix. However, for the case of $\bar{r}^2/nl^2$, only the 3,3 element of B contributes to the final value. Consider now the form of the matrix B and the effect on the convergence of the 3,3 element in the sum. For a symmetrical potential; i.e., $< \sin \phi > = 0$:

10) $$B = \begin{bmatrix} a_{11} & 0 & 0 \\ 0 & a_{23} & a_{23} \\ 0 & a_{32} & a_{33} \end{bmatrix}$$

The 3,3 element in B^k is made up of the third row in B^{k-1} times the third column in B^{k-1}. Since zeros appear at the 3,1 and 1,3 positions in B^{k-1}, the 3,3 element in B^k will be of the forms:

11) $$a_{32} \times a_{23} + a_{33} \times a_{33})_{B^{k-1}} = a_{33})_{B^k}$$

Since only two row elements and two column elements make up $a_{33})_{B^k}$, the condition for convergence of a_{33} in 1a) subject to 10) is:

12) $$-1 < 2a < 1$$

13) $$|a| < 1/2$$

Therefore, if all of the matrix elements in B, D, A_1, and A_2 are < 1/2, $\bar{r}^2/nl^2$ is guaranteed to converge. This is not a very strict test for convergence, since there are cases where some of the elements can be greater than 1/2 and $\bar{r}^2/nl^2$ will converge. Several examples can be seen in Table VII and the accompanying Figure VIII. Two other examples are: 1) The case of a statistically independent polyethylene type chain. Here $\bar{r}^2/l^2 = n + 2\sum_k (n-k)A^k|_{33}$. The condition for convergence of $\bar{r}^2/nl^2$ is again $|a| < 1/2$. By evaluating the series in closed form, Volkenstein[13] has shown that if $|a| < 1$, the series will converge. In other words, Volkenstein's proof for the polyethylene case is more general than the one offered here. 2) Similarly, Tokita + Krigbaum[63] have shown that for a three choice cubic lattice chain, $\bar{r}^2/nl^2$ will converge if $|a| < 1$.

III. Results

A. Verification of the Equations

1. Correct computation of the ring formation at n = 6 for hexamethylcyclotrisiloxane.

An independent corroboration of the equations for $\overline{r^2}/nl^2$ is the computation of $\overline{r^2}/l^2$ under the conditions of formation of hexamethylcyclotrisiloxane and the prediction of ring closure at n = 6.

As discussed in Section I, the six-membered ring is known to be planar. If the calculated chain is allowed to assume the cis conformation with probability = 1 and if the bond angles assigned are those experimentally observed for the ring, the calculated value of $\overline{r^2}/l^2$ vs. n should become zero at n = 6. This behavior is illustrated in Figure VI. The maximum at n = 3 corresponds to the maximum distance between two chain atoms across the ring.

2. Computation of $\overline{r^2}/nl^2$ for the freely rotating model.

Flory has shown[2] for a chain of large n with bond angles θ_1 and θ_2 and free rotation ($\langle\cos\phi\rangle = \langle\sin\phi\rangle = 0$) that

$$1)\quad \frac{\overline{r^2}}{nl^2} = \frac{(1 - \cos\theta_1)(1 - \cos\theta_2)}{(1 - \cos\theta_1 \cos\theta_2)}$$

Results from 1) are compared in Table VI with the computor results for the freely rotating model.

For the calculation of $\overline{r^2}/nl^2$ vs. n for a period 2 chain the matrix elements in A_1, A_2, A_1A_2, and A_2A_1 are the data from which calculations are made. Figure VII is a plot of $\overline{r^2}/nl^2$ vs. n for the freely rotating model.

From the plot in Figure VII one can see that the computor value of $\overline{r^2}/nl^2$ at large n approaches that value calculated in 1).

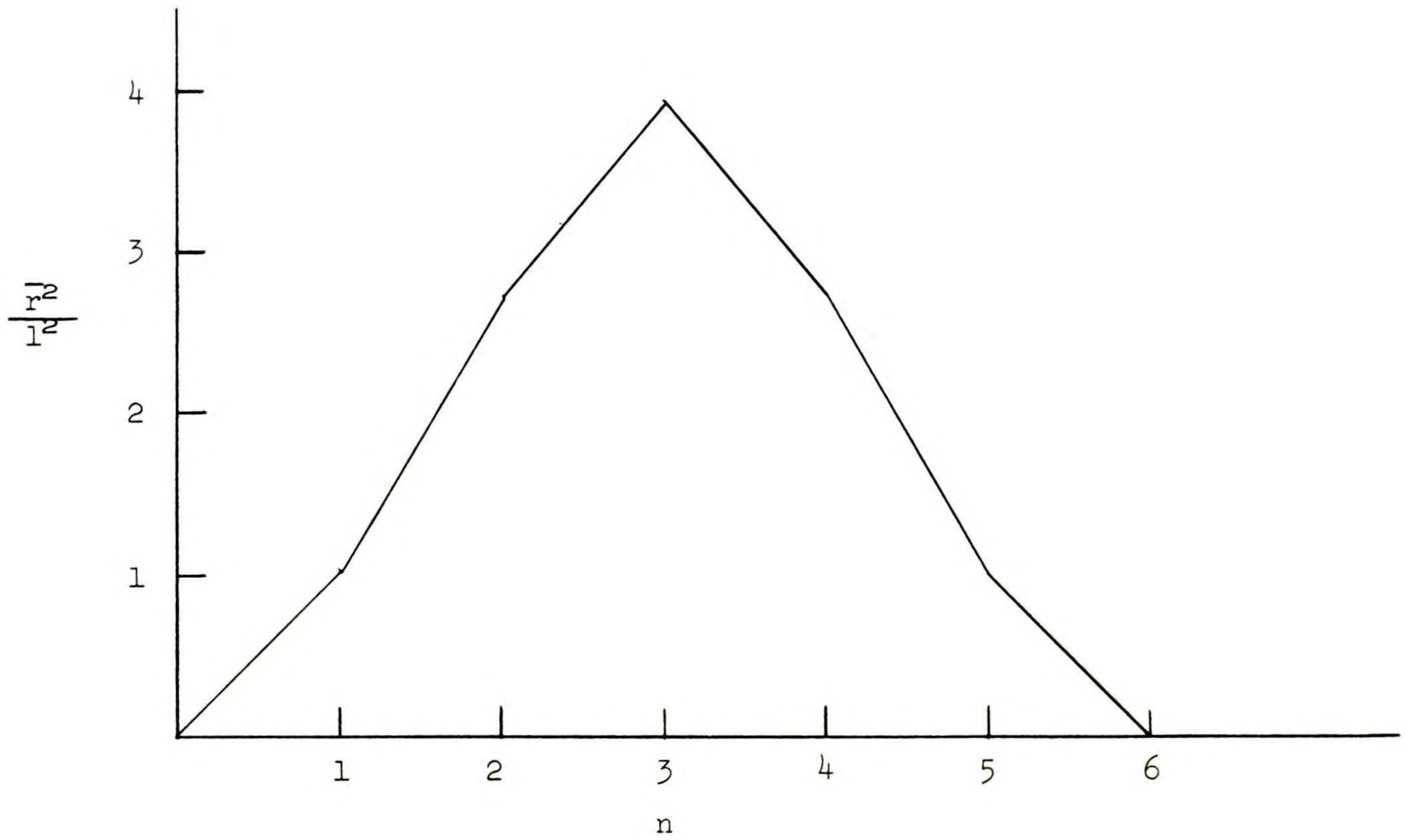
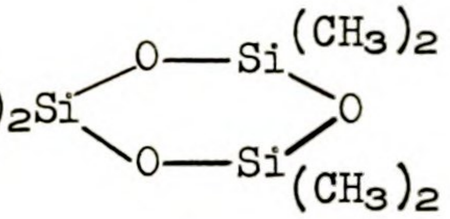


Figure **VI.** Verification of the Equations

Calculation of $\frac{\overline{r^2}}{l^2}$ vs. n for $(CH_3)_2Si$ 

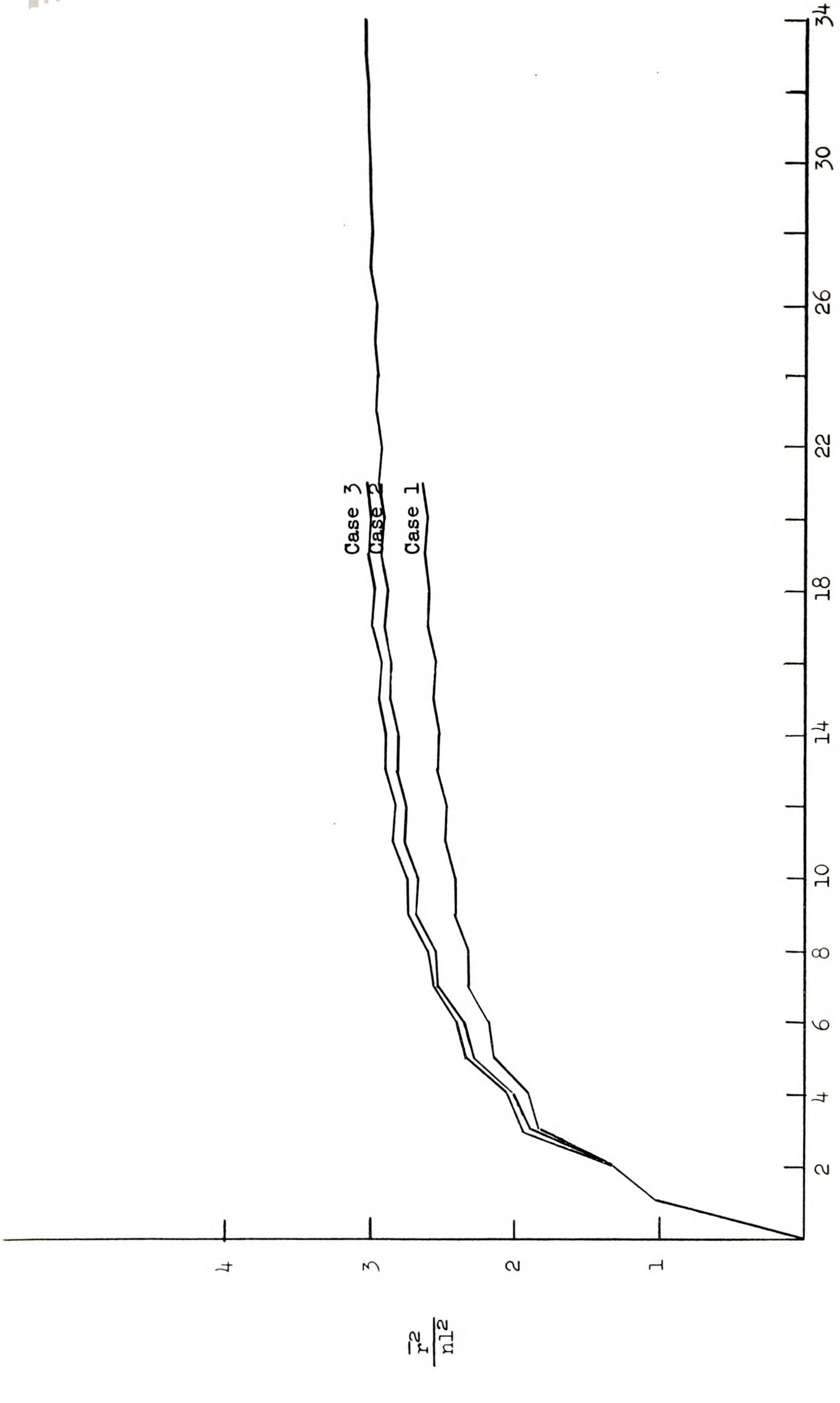


FIGURE VII. $\frac{r^2}{nl^2}$ vs. n for Flory's freely rotating model as a function of ∠SiOSi
See Table 8

Table VI. $\overline{r^2}/nl^2$ as a function of ∠SiOSi for $\langle\cos\phi\rangle = 0$.
Comparison with values calculated from Flory's approximate equation*

	∠SiOSi	$\frac{\overline{r^2}}{nl^2}$)n=21	$\frac{\overline{r^2}}{nl^2}$)n=40	$\frac{\overline{r^2}}{nl^2}$)Flory's eq.	% deviation of Flory's results from computor value
Case 1	1.30°	2.630	2.71**	2.79	2.9
Case 2	140°	2.96	3.07	3.16	2.9
Case 3	142.5°	3.02	3.14**	3.25	3.5

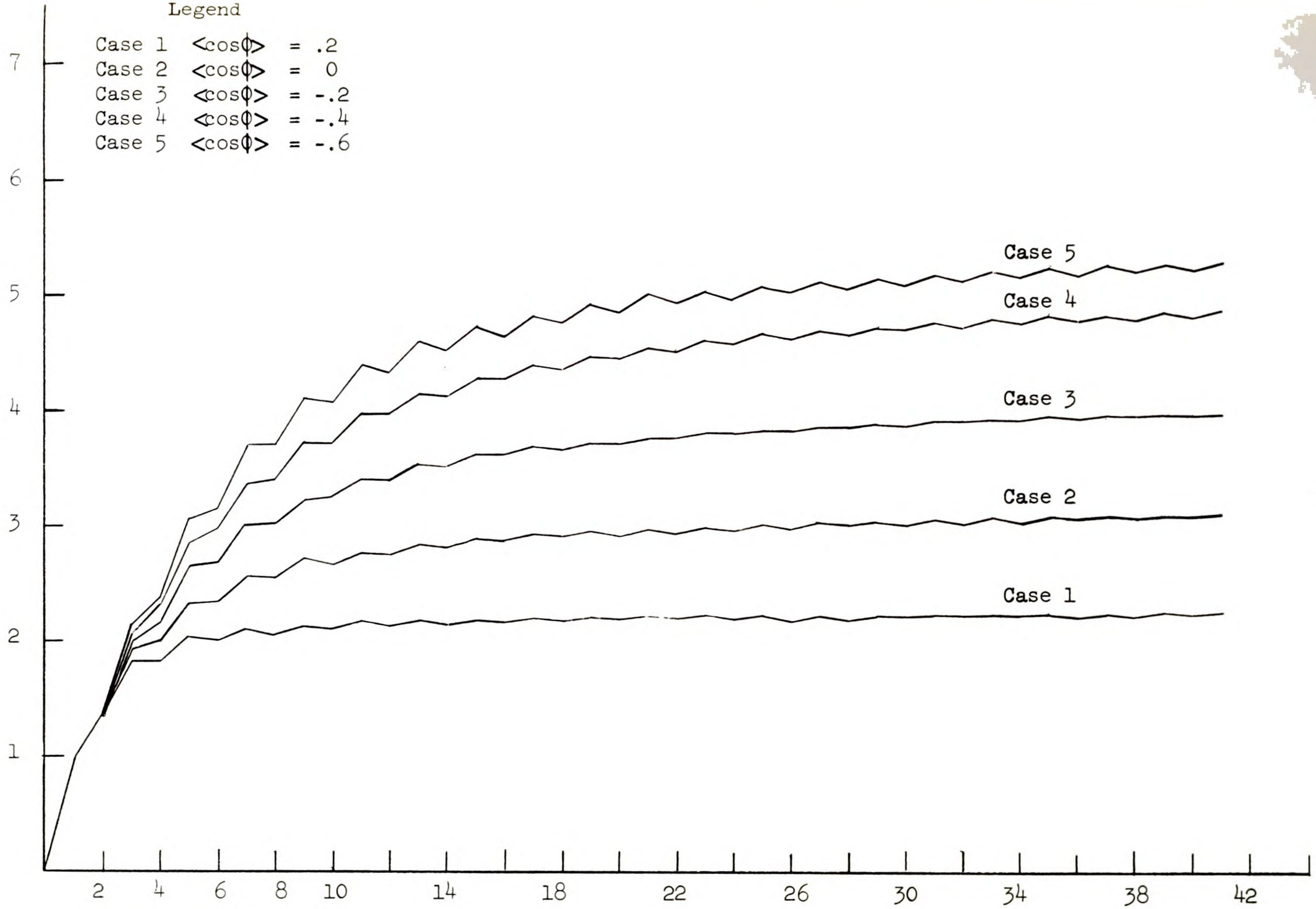
* ∠OSiO = 109°28' for all cases
** Extrapolated from n = 21.

B. Calculation of $\overline{r^2}/nl^2$ for statistically independent models of the polydimethylsiloxane chain.

Because of the symmetry due to all identical substituents (the same symmetry as exists in the previously discussed polyisobutylene chain), $U(\phi_i) = U(\phi_{i+1})$. In all models considered here the rotational states are symmetrically disposed about the trans state. Therefore, $\langle\sin\phi_i\rangle = 0$. From the chain symmetry, $\langle\cos\phi_i\rangle = \langle\cos\phi_{i+1}\rangle$. For statistically independent models $\langle\cos\phi_i\cos\phi_{i+1}\rangle = \langle\cos\phi_i\rangle\langle\cos\phi_{i+1}\rangle$.

In the series of curves of $\overline{r^2}/nl^2$ vs. n in Figure X, $\langle\cos\phi\rangle$ decreases from Case 1 through Case 5. It should be recalled at this point that $\langle\cos\phi\rangle$ is a function of two kinds of variables - the rotational states available and their respective probabilities. For the four state model of G, T, G' and C states with respective probabilities a, b, c, d (and a=c from chain symmetry),

$$1) \quad \langle\cos\phi\rangle = 1/2(1-3b+d)$$



∠SiOSi = 140°
∠OSiO = 109°28'

FIGURE VIII. $\frac{\bar{r}^2}{nl^2}$ vs. n for statis. ind. siloxane models. See Table VII.

However, the gauche rotational states might actually be shifted several degrees from their ideal values in hydrocarbons of 60° and 300°. Liquori's calculations indicate minima shifted in polyoxymethylene (G=67°, G'=293°).[60] Two other sets of assignments for the gauche states in the siloxane chain will be presented to discuss the implications of shifted gauche states on the parameter of the chain dimensions.

(2) G=50°, G'=310°

$$\langle\cos\phi\rangle = .6428 - 1.6428b + .3572d$$

(3) G=70°, G'=290°

$$\langle\cos\phi\rangle = .3420 - 1.3420b + .6580d.$$

For a given value of $\langle\cos\phi\rangle$, the magnitude of the probabilities b and d will depend on the choice of rotational angles for G and G'. The normal set of gauche states G=60° and G'=300° are chosen so that the curves may be considered to be a function of only probability variables, thus making interpretations simpler. But the choice is somewhat arbitrary and further experimental work may indicate that those of (2) or (3) better approximate the real chain.

None of the curves in Figure VIII approach the experimental value of $\bar{r}^2/nl^2 = 7.23$. In addition, the energy difference between the trans and gauche potential well (ΔE) in each of the Cases 3-7 in Table VII far exceeds the allowable few hundred calories per mole commensurate with the data of Scott, et. al.[28] From these two results it is concluded that the dimensions of the polydimethyl siloxane chain cannot be described using a statistically independent model. One explanation for the difference between $\bar{r}^2/nl^2$ obtained from a model with a reasonable ΔE and the experimental value of 7.23 is that included in dimensions of the model

are many configurations of the entire chain that are physically unallowed due to long range interferences. These interferences are from a segment of the chain occupying a space previously occupied by another chain segment. Chains in which this occurs have dimensions much lower than chains which do not have long range intramolecular interferences. Thus, the effect of including "unallowed" total chain configurations is to lower the calculated chain dimensions.*

The nature of the long range interference effect in the siloxane chain will be examined in detail in III-D for chains with six and eight chain bonds.

Table **VII.**

$\overline{r^2}/nl^2$ as a function of $\langle\cos\phi\rangle$ ∠SiOSi=140°, ∠OSiO=109°28'

	$\langle\cos\phi\rangle$	$\frac{\overline{r^2}}{nl^2})n=40$	Probability of trans *	ΔE^+, 25°
Case 1	.2	2.22	.200	750
Case 2	0	3.07	.333	0
Case 3	-.2	3.95	.467	-650
Case 4	-.4	4.83	.600	-1250
Case 5	-.6	5.21	.733	-1950

* Assuming prob. of cis = 0. Then $\langle\cos\phi\rangle = \frac{1}{2}(1-3b)$.
\+ Measured with E increasing upward from reference point of E=0 at deepest gauche minima at 60° and 300°.

The purpose of the graph in Figure **IX** is to investigate the necessity for postulating the availability of a cis state to the siloxane chain in order to explain the planarity of the hexamethylcyclotrisiloxane ring. The model for this graph is ∠SiOSi = 140°, ∠OSiO = 109°28' (the

* In the case of polyethylene, the experimental $\overline{r^2}/nl^2 = 6.55$. Using a statistically independent model with rotational states, G, T, G' and ΔE = 500 cal/mole (the energy difference between trans and gauche obtained from spectral data of normal paraffins), $\overline{r^2}/nl^2 = 3.34$. Perhaps here as well as in the siloxane case one of the major contributory factors to the low model value is the inclusion of configurations which are unallowed due to long range interaction.

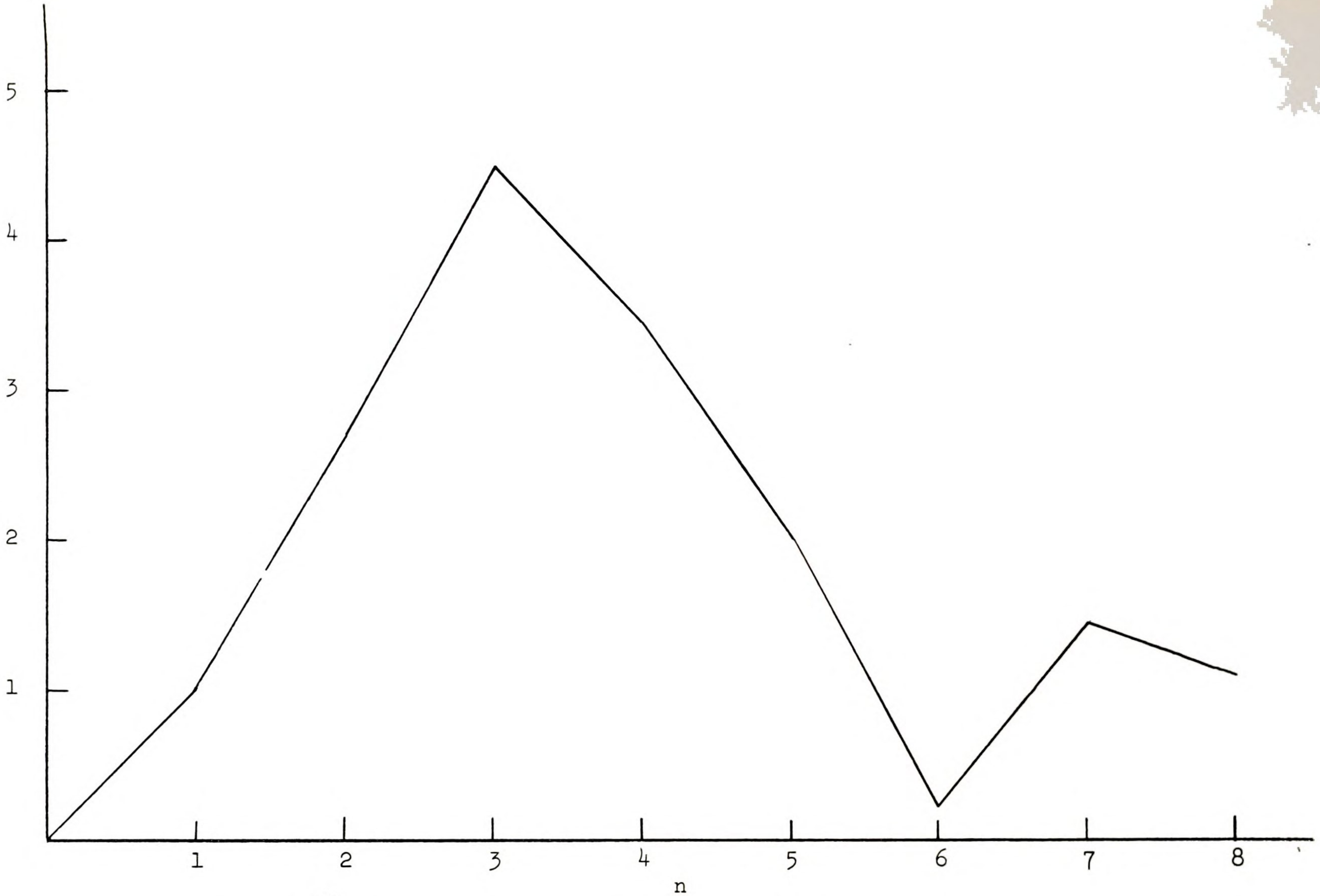


FIGURE IX. $\frac{\overline{r^2}}{l^2}$ vs. n for all cis chain, ∠SiOSi = 140°.
∠OSiO = 109°28'

bond angles accepted in this work as valid for the polymer chain) and $\langle\cos\phi\rangle = 1$ (corresponding to the cis state being occupied with probability =1). At n=6, the value of $\sqrt{\bar{r}^2/l^2}$ represents how far the chain ends are apart giving a direct indication of how readily they might be expected to join to form the planar ring.

From the graph, $\sqrt{\bar{r}^2/l^2} = .49$. Thus the chain ends are slightly less than half bond length apart at n=6. If the cis state is available to the chain then the sequence of cis conformations seems to be a plausible mechanism for the formation of hexamethylcyclotrisiloxane.

C. A comparison of statistically dependent and statistically independent models for the polydimethylsiloxane chain.

In Table VIII the values of $\langle\cos\phi_i\rangle$ and $\langle\cos\phi_i\cos\phi_{i+1}\rangle$ are listed for statistically independent pair and statistically independent models for the polydimethylsiloxane chain. The purpose of these models is to illustrate that two rather widely differing models can be employed to generate approximately the same value of $\bar{r}^2/nl^2$ at large n. Case 1 is a statistically independent model of the same form as presented in Fig. VIII. In Case 2, $\langle\cos\phi_i\rangle_{\text{case 2}} < \langle\cos\phi_i\rangle_{\text{case 1}}$. This has the effect of increasing the chain dimensions of Case 2 over Case 1. However, $\langle\cos\phi_i\cos\phi_{i+1}\rangle_{\text{case 2}} > \langle\cos\phi_i\rangle^2_{\text{case 2}}$. Introducing this statistical dependence into the chain has the effect of reducing the dimensions from what they would be if the chain were statistically independent. At large n the two changes in Case 2 nearly balance giving the result that for Case 1, $\bar{r}^2/nl^2)_{n=40} = 4.24$, for Case 2, $\bar{r}^2/nl^2)_{n=40} = 4.28$.

Note from Figure X that the curves begin rather closely together, spread apart in the region of n = 6-20 and become closer together

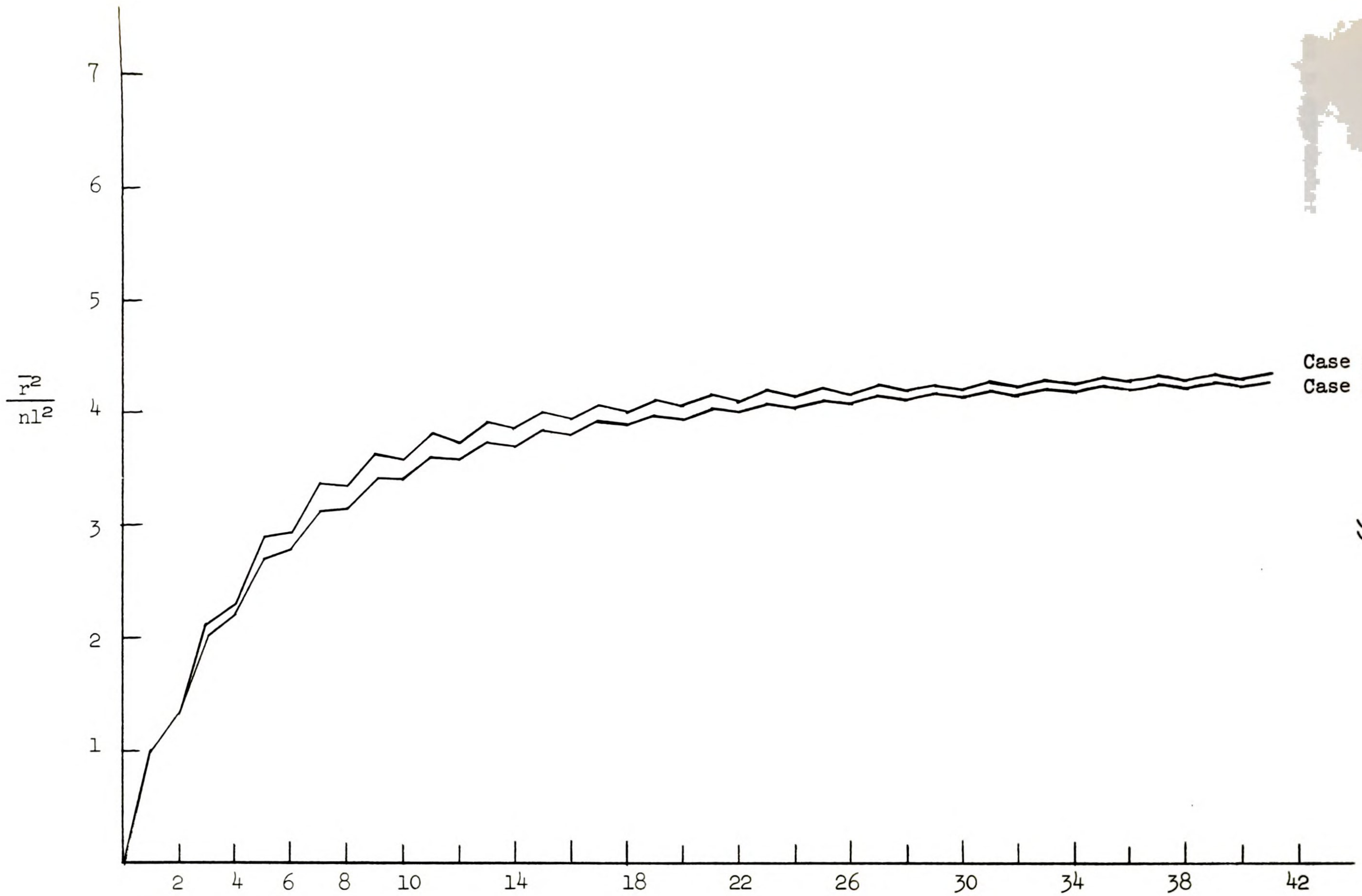


FIGURE X. Use of stat. ind. and stat. dependent models to obtain the same $\frac{\overline{r^2}}{nl^2}$) n=4.0
See Table VIII

as n approaches 40. The greater spread in the curves from n = 6-20 is a possible indication that the statistically dependent model of Case 2 more accurately reflects the cyclic formation in the polydimethylsiloxane chain which takes place predominately in the region of n = 6-20.

Table VIII.

Application of statistically independent and statistically dependent models for calculating the same $\bar{r}^2/nl^2$.
$\angle SiOSi = 142.5, \angle OSiO = 109°28'$

	$\langle\cos\phi\rangle$	$\langle\cos\phi_i\cos\phi_{i+1}\rangle$	$\frac{\bar{r}^2}{nl^2})n=8$	$\frac{\bar{r}^2}{nl^2})\ n=40$
Case 1	-.259	+.0671	3.15	4.24
Case 2	-.504	+.386	3.33	4.28

D. Calculation of ring-chain equilibria in polydimethylsiloxane.

In 1950, Stockmayer and Jacobson[64] published a theoretical paper in which they predicted the equilibrium molecular size distributions of linear and cyclic molecules for polymers. A major assumption of this work was that the distribution of end-to-end distances (r) of a randomly coiled chain, (W(r)dr), is Maxwellian. That is, $W(r)dr = \frac{\beta^3}{\pi^{3/2}} \exp(r^2\beta^2)\ 4\pi r^2 dr$, where $\beta = \frac{3}{2\langle r_o^2\rangle}$ and $\langle r_o^2\rangle$ represents the unperturbed mean-square end-to-end distance of the polymer. From this, a formalism was developed for the chain-cyclic distribution. However, no calculations based on this formalism were undertaken for polydimethylsiloxane.

Calculations were performed on the ring-chain equilibrium in polydecamethylene adipate and compared with experimental results. More ring structures were predicted than actually observed.

The treatment here parallels that of Stockmayer and Jacobson except that the probability of ring closure is obtained from a discrete rotational state model.

The equilibrium constant for the formation of octamethylcyclotetrasiloxane is calculated from the discrete rotational state model and from the Gaussian distribution.

1. The distribution of $|\vec{r}|$'s for a three rotational state chain.

We consider now the entire set of $|\vec{r}|$'s for the case of a growing three rotational state chain. The total number of chain conformations increases as 3^{n-1}, where n = number of links in the chain. Many of the $|\vec{r}|$'s thus produced are degenerate. The cases of n = 6 and n = 8 will be examined in detail.

Consider the interval tabulation for the 243 $|\vec{r}|$'s at n = 6 in Table IX.

Table IX.

Distribution of $|\vec{r}|$'s for n=6

Range of $\lvert\vec{r}\rvert$	No. of $\lvert\vec{r}\rvert$'s in the interval	Fraction of $\lvert\vec{r}\rvert$'s in the interval
0-.5ℓ	0	0
.5ℓ-ℓ	0	0
ℓ-1.5ℓ	6	.0247
1.5ℓ-2ℓ	6	.0247
2ℓ-2.5ℓ	0	0
2.5ℓ-3ℓ	42	.1728
3ℓ-3.5ℓ	36	.1481
3.5ℓ-4ℓ	60	.2469
4ℓ-4.5ℓ	51	.2099
4.5ℓ-5ℓ	42	.1728
	243	.9999

Note that no $|\vec{r}|$ falls within the range of 0-ℓ. If the three state model were an exact description of the potential energy profile in the chain and if the requirement for ring closure were $|\vec{r}| < \ell$, no six-membered ring would form in the siloxane system. As pointed out, however, the six-membered ring does form and is planar. Two possible mechanisms for the formation of this ring are offered. Mechanism A: (1) A puckered six-membered ring is formed by a sequence of gauche rotational states, some or all of which are shifted from 60° and 300° so that for this sequence, $|\vec{r}| < \ell$. (2) The ring rearranges from the puckered form into the planar form. Since specific steric factors are thought not to influence ring configurations, due to the large SiOSi angle and the comparatively long SiO bond, a shift from a puckered to a planar ring form would probably require energy (since any puckered ring that could form would be expected to be rather stable.) (3) In order to accommodate

the geometrical requirements of the planar ring, the SiOSi bond angle shifts from 140° to 130°. This change in bond angle will require absorption of energy.

Mechanism B: (1) A cis rotational state is available to the chain (probably with much lower probability of occupancy than the gauche and trans states). (2) The chain grows to a length of six links occupying all cis states. A graphical representation of this chain follows in Figure 5. Plotted is r^2/ℓ^2 vs. $n(r^2 = |\vec{r}|^2)$. Calculation from the graph shows $|\vec{r}| = 0.49\ell$. Thus, the chain ends are slightly less than half a bond length apart at n = 6. For the ring to form, the bond angle SiOSi must compress from 140° to 130°.

The energy required to form the six-membered ring is probably least for Mechanism B, so that if the cis state is available to the polymer chain, Mechanism B may represent the most likely route to the formation of hexamethylcyclotetrasiloxane.

Consider now the interval tabulation for the 2187 $|\vec{r}|$'s at n = 8 in Table X.

Table X.

Distribution of $|\vec{r}|$'s for n=8

Range of $\lvert\vec{r}\rvert$	No. of $\lvert\vec{r}\rvert$'s in the interval	Fraction of $\lvert\vec{r}\rvert$'s in the interval
0-.5ℓ	12	.00548
.5ℓ-ℓ	0	.0000
ℓ-1.5ℓ	58	.0265
1.5ℓ-2ℓ	44	.0201
2ℓ-2.5ℓ	84	.0384
2.5ℓ-3ℓ	152	.0695
3.0ℓ-3.5ℓ	102	.0466
3.5ℓ-4ℓ	294	.1344
4ℓ-4.5ℓ	320	.1463
4.5ℓ-5ℓ	316	.1445
5ℓ-5.5ℓ	367	.1678
5.5ℓ-6ℓ	372	.1701
6ℓ-6.5ℓ	66	.0302
	2187	.9999

There are 12 $|\vec{r}|$'s in the range of 0-1ℓ. All of these are less than 0.5ℓ and are probably within the range of cyclic forming molecules. We recall that Yokoi[34] postulated six reasonable structures for the eight-membered ring, octamethylcyclotetrasiloxane. Structure B, the structure which gives the best fit to the experimental radial distribution function, is formed by all the following sequences of configurations:

G,G,G',G',G,G,G'
G',G',G,G,G',G',G
G,G',G,G,G',G',G
G',G,G',G',G,G,G'
T,G,G',G',G,G,G'
T,G',G,G,G',G',G

For structure B, $|\vec{r}| = 0.303\,\ell$.

Structure A has a crown form with the four silicon atoms in one plane and the four oxygen atoms lying in a plane above the silicons. This ring is formed by the sequences of configurations:

G,G',G,G',G,G',G
G',G,G',G,G',G,G'
G,G,G',G,G',G,G'
G',G',G,G',G,G',G
T,G,G',G,G',G,G'
T,G',G,G',G,G',G

These 12 sets correspond to the 12 $|\vec{r}|$'s found to be less than $0.5\,\ell$ and are those most likely to form rings. These 12 $|\vec{r}|$'s represent .0584% of the total number of 2187 chains that are generated. The experimental evidence which must be reconciled is that 10% of an equilibrated polymer is octamethylcyclotetrasiloxane. The experimental data and theoretical calculation are compared through the equilibrium constant for the formation of octamethylcyclotetrasiloxane.

2. Equilibrium constant for R_4 formation.

Following the treatment of Stockmayer and Jacobson, we consider a siloxane chain of (n + 4) -Si-O units in equilibrium with a chain of n units and a cyclic of four units.

(1) $C_{n+4} \rightleftharpoons C_n + R_4$

(2) $K = \dfrac{[C_n][R_4]}{[C_{n+4}]}$

Because the chains C_{n+4} and C_n lie very close to one another on the molecular weight distribution curve for the high polymer, $[C_{n+4}] \simeq [C_n]$.

(3) Therefore $K \simeq [R_4]$

A. Calculation of experimental equilibrium constant.

Density of R_4 = 0.9558 g./cm^3 at 20°C

Density of polydimethylsiloxane = 0.9660 g./cm^3 at 25°C

Molal volume of R_4 = $\frac{312 \text{ cm}^3}{\text{mole}}$

Consider 1000 grams of mixture 100g. = R_4

900g. = C_n

$$\text{cm}^3 \text{ of } R_4 = \frac{100\text{g.}}{0.9558 \text{ g./cc.}} = 104.2 \text{ cc.}$$

$$\text{cm}^3 \text{ of } C_n = \frac{900\text{g}}{0.9660 \text{ g./cc.}} = \underline{931.0 \text{ cc.}}$$

Total volume 1035 cc. Assuming volume additivity

$$(4)\quad K_{experimental} = \frac{100\text{g. } R_4}{\text{cm}^3} = \frac{100/74.13 \text{ moles of -SiO- units}}{\text{cm}^3}$$

$$K_{experimental} = 13.2 \times 10^{-4} \frac{\text{moles of -SiO- units}}{\text{cm}^3}$$

3. Calculation of theoretical equilibrium constant.

The general development here closely follows that of Stockmayer and Jacobson.[64] Important departures are noted in the text.

Since reaction (1) involves no change in number of chemical bonds, we may assume it takes place with a negligible change of internal energy.* With this assumption, the prediction of K in (3) requires the calculation of the entropy change in the equilibrium reaction. For this purpose, reaction (1) is broken up into steps.

$$(5)\quad C_{n+4} \rightleftharpoons C_n + C_4$$

$$(6)\quad C_4 \rightleftharpoons R_4$$

For reaction (5), the entropy change is:

$$(7)\quad S_s = k\ln(V/2v_s)$$

where v_s is volume of the constrained skeletal atom under consideration, and V is

* For R_4 the assumption seems valid based on the freedom from bond angle strain in octamethylcyclotetrasiloxane. However, for R_3 where strained bond angles are present, such an assumption would be invalid.

the volume of the system as a whole which is available to this atom once the bond is broken. The symmetry number of a chain molecule is 2. In the Stockmayer-Jacobson development, v_s cancelled with the same term in the denominator of S_8 and calculation of v_s was unnecessary. In this development, v_s remains in the final expression for K and is calculated separately.

The entropy change in reaction (6) is:

$$(8) \quad S_6 = k\ln(P/4)$$

where P is the fraction of chains which will close. The symmetry number of an n-membered ring is 2n. (The fact that the symmetry number os a siloxane chain is two means that either end has an equivalent opportunity to close back on itself to form a ring. For a ring containing n siloxane units, a symmetry number of 2n means that there are 2n equivalent bonds that can be broken when the ring reacts with a chain to form a larger chain.)

Combining the results of equations (7) and (8), the equilibrium constant is:

$$(11) \quad K = \frac{PV}{8v_s}$$

In the Stockmayer-Jacobson development, P was obtained by assuming a Gaussian distribution of end-to-end distances and integrating over the volume element v_s. Here P is obtained from the set of chains generated from the three-rotational state model and found to be 0.00548.

Calculation of v_s will complete the specification of variables from which K can be calculated. The approach is that of Mayer and Mayer. The one-dimensional length available to an atom (along the reaction coordinate giving its distance) from another atom to which it is bound is twice the average amplitude, $\frac{1}{2}\xi$, of vibration. The value of ξ as a function of temperature is given to a good approximation by the emperical equation:

$$(10) \quad \xi = (RT/D)^{\frac{1}{2}} \text{ Å}$$

where D is the energy necessary to break the chemical bond.

The two-dimensional surface available to an atom rotating about another is:

$$(11) \quad A = 4\pi r_o^2$$

where r_o is the distance between the two atoms.

The constrained atom of the molecule (the chain of n + 4 segments) moves in a shell of radius r_o and thickness ξ about the atom regarded as free. Therefore, the volume, v_s, is:

$$(12) \quad v_s = 4\pi r_o^2 \xi$$

For the Si-O bond, r_o = 1.65 Å

D = 93 Kcal./mole

at 135 C, ξ = 0.094 Å

Inserting these data into (12),

$$(13) \quad v_s = 3.2 \text{ Å}^3.$$

Substituting the values of v_s and P into (9) and assuming a system volume, V, of 1 cm.^{3} we find:

$$(14) \quad K = 3.6 \times 10^{-4}$$

4. Discussion

This result is tabulated with two values of K calculated from the Stockmayer-Jacobson theory and the experimental K in Table XI.

Table XI.

Comparison of Experimental and Theoretical Calculations of the Equilibrium Constant for R_4.

Worker	K x 10^{-4} moles/liter
Hartung and Camiolo[6]	13.2
[a]Stockmayer-Jacobson[64]	1.2
[b]Ibid	0.42
[a]This work	3.6

[a]Calculated assuming equally probable rotational states. For the Stockmayer-Jacobson calculation, $\langle r_{o_f}^2 \rangle / nl^2 = 3.2$, where $r_{o_f}^2$ refers to the mean square dimensions of a freely rotating siloxane chain with three rotational states at 60°, 180°, and 300°.

[b]Calculated using experimentally determined $\langle r_o^2 \rangle / nl^2 = 6.3$

In no case is there good agreement between theory and experiment. However, K calculated in this work represents an improvement over the earlier Stockmayer-Jacobson result. The only difference between the two derivations is in obtaining P and v_s. Stockmayer and Jacobson assumed a Gaussian distribution with an effective link length parameter, b, and we obtain P from a conformation model with equally probable rotational states. Also, we find it necessary to calculate v_s whereas Stockmayer and Jacobson found K independent of v_s.

We must remember that Hartung's data, upon which the calculation of $K_{experimental}$ was based, is data extrapolated for the undiluted polymer from solvent polymerizations. Certainly, Hartung meant this extrapolation as a guide to be used for predicting cyclic contents at solvent concentrations beyond the limits of those he used. We are, no doubt, subjecting the extrapolated concentration of R_4 to undue scrutiny in Table XI.

Certainly the model developed here is a primitive beginning to the ring closure problem. Evaluating preferred conformations and relating these to ring formation in siloxanes with other organic side groups could help provide fundamental groundings in this hitherto undeveloped area. No mention has been made here of specific solvent effects which are, at present, impossible to evaluate theoretically. No published data is available on the effect of media viscosity on cyclic concentration. It is hoped that this re-examination of the ring closure problem will lead to further critical experimental studies.

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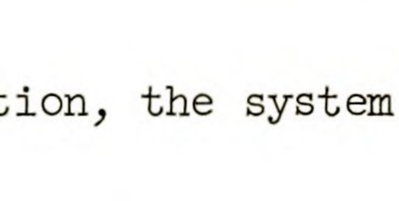
APPENDICES

APPENDIX I

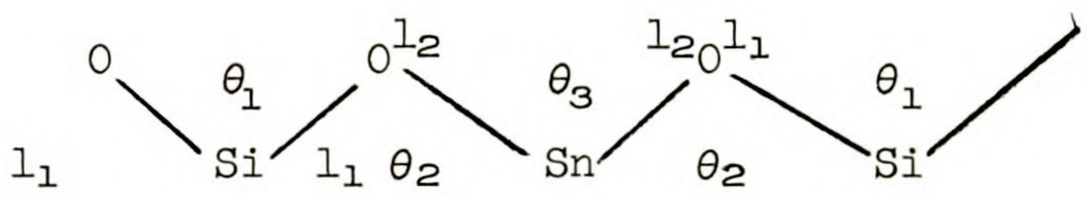
CALCULATION OF $\overline{r}^2$ FOR -M-O-N-O- CHAIN

Presented here is a derivation of an expression for $\overline{r}^2$ for a polymer chain with two different bond lengths of the form -M-O-N-O-M.

For purposes of illustration, the system



will be used:



Let $l_1)_1$ be the first bond of length l_1

$l_1)_{\underline{n-2}}$ be the (n-1)th bond of length l_1

$l_1)_{n/2}$ be the nth bond of length l_1

$l_2)_1$ be the first bond of length l_2

$l_2)_{n-2/2}$ be the (n-1)th bond of length l_2

$l_2)n-2$ be the nth bond of length l_2

A_1 = Matrix associated with bond angle θ_1 and rotational states $\phi_1)i$.

A_2 = Matrix associated with bond angle θ_2 and rotational states $\phi_2)i$.

A_3 = Matrix associated with bond angle θ_3 and rotational states $\phi_3)i$.

Each bond vector is written now in terms of the preceeding bond vector using the associated transformation matrix. Matrix relations are then written for the first eight bonds in the chain in terms of all

prior bonds.

$l_1)_1 = l_1$ — 1st bond

$l_1)_2 = A_1 l_1)_1$ — 2nd bond

$l_2)_1 = A_2 l_1)_2 + l_2 - l_1$

$= A_2 A_1 l_1)_1 + (l_2 - l_1)$* — 3rd bond

$l_2)_2 = A_3 l_2)_1$

$= A_3 A_2 A_1 l_1)_1 + A_3(l_2 - l_1)$ — 4th bond

$l_1)_3 = A_2 . l_2)_2 - (l_2 - l_1)$

$= A_2 A_3 A_2 A_1 l_1)_1 + A_2 A_3(l_2 - l_1) - (l_2 - l_1)$ — 5th bond

$l_1)_4 = A_1 l_1)_3$

$= A_1 A_2 A_3 A_2 A_1 l_1)_1 + A_1 A_2 A_3(l_2 - l_1) - A_1(l_2 - l_1)$ — 6th bond

$l_2)_3 = A_2 l_1)_4 + (l_2 - l_1)$

$= A_2 A_1 A_2 A_3 A_2 A_1 l_1)_1 + A_2 A_1 A_2 A_3(l_2 - l_1) - A_2 A_1(l_2 - l_1)$

$+ (l_2 - l_1)$ — 7th bond

$l_2)_4 = A_3 l_2)_3$

$= A_3 A_2 A_1 A_2 A_3 A_2 A_1 l_1)_1 + A_3 A_2 A_1 A_2 A_3(l_2 - l_1) -$

$A_3 A_2 A_1(l_2 - l_1) + A_3(l_2 - l_1)$ — 8th bond

For n = 4, 8, 16, 20, ...

$$l_2)_{n/2} = (A_3 A_2 A_1 A_2)^{\frac{n-4}{4}} A_3 A_2 A_1 l_1 + (A_3 A_2 A_1 A_2)^{\frac{n-4}{4}} A_3(l_2 - l_1) - (A_3 A_2 A_1 A_2)^{\frac{n-8}{4}} A_3 A_2 A_1(l_2 - l_1) + \ldots\ldots\ldots$$

---

* The difference in bond lengths, $l_2 - l_1$, must be included for the matrix equality to hold. This is the salient mathematical feature of this chain model.

$$l_2)_{n-2/2} = (A_2A_1A_2A_3)^{\frac{n-4}{4}} A_2A_1l_1$$
$$+ (A_2A_1A_2A_3)^{\frac{n-4}{4}} (l_2 - l_1)$$
$$- (A_2A_1A_2A_3)^{\frac{n-8}{4}} A_2A_1(l_2 - l_1)$$
$$+ .....$$

$$l_1)_{n/2} = (A_1A_2A_3A_2)^{\frac{n-4}{4}} A_1l_1$$
$$+ (A_1A_2A_3A_2)^{\frac{n-8}{4}} A_1A_2A_3(l_2 - l_1)$$
$$- (A_1A_2A_3A_2)^{\frac{n-8}{4}} A_1(l_2 - l_1)$$
$$+ .....$$

$$l_1)_{n-2/2} = (A_2A_3A_2A_1)^{\frac{n-4}{4}} l_1$$
$$+ (A_2A_3A_2A_1)^{\frac{n-8}{4}} A_2A_3(l_2 - l_1)$$
$$- (A_2A_3A_2A_1)^{\frac{n-8}{4}} (l_2 - l_1)$$
$$+ .....$$

Consider the summations for the four types of bonds.

$$\sum_{k = 4,8,12...}^{n} l_2)_{n/2} = \sum_{k=4,8,12...}^{n} (A_3A_2A_1A_2)^{\frac{k-4}{4}} A_3A_2A_1(l_1)$$
$$+ \sum_{k=4,8,12...}^{n} (n/4 - k/4 + 1)(A_3A_2A_1A_2)^{\frac{k-4}{4}} A_3(l_2-l_1)$$
$$+ \sum_{k=8,12,16...}^{n} (n/4 - k/4 + 1)(A_3A_2A_1A_2)^{\frac{k-8}{4}} A_3A_2A_1(l_1 - l_2)$$

$$\sum_{k=4,8,12...}^{n} l_2)_{n-2/2} = \sum_{k=4,8,12...}^{n} (A_2A_1A_2A_3)^{\frac{k-4}{4}} A_2A_1(l_1)$$
$$+ \sum_{k=4,8,12...}^{n} (n/4-k/4 + 1)(A_2A_1A_2A_3)^{\frac{n-4}{4}} (l_2 - l_1)$$

$$+ \sum_{k=8,12,16\ldots}^{n} (n/4 - k/4 + 1)(A_2A_1A_2A_3)^{\frac{n-8}{4}} A_2A_1(l_1 - l_2)$$

$$\sum_{k=4,8,12\ldots}^{n} l_1)_{n/2} = \sum_{k=4,8,12\ldots}^{n} (A_1A_2A_3A_2)^{\frac{k-4}{4}} A_1l_1$$

$$+ \sum_{k=8,12\ldots..}^{n} (n/4 - k/4 + 1)(A_1A_2A_3A_2)^{\frac{k-8}{4}} A_1A_2A_3(l_2 - l_1)$$

$$+ \sum_{k=8,12\ldots..}^{n} (n/4 - k/4 + 1)(A_1A_2A_3A_2)^{\frac{k-8}{4}} A_1(l_1 - l_2)$$

$$\sum_{k=4,8,12\ldots}^{n} l_1)_{n-2/2} = \sum_{k=4,8,12\ldots}^{n} (A_2A_3A_2A_1)^{\frac{k-4}{4}} l_1$$

$$+ \sum_{k=8,12\ldots}^{n} (n/4 - k/4 + 1)(A_2A_3A_2A_1)^{\frac{k-8}{4}} A_2A_3(l_2 - l_1)$$

$$+ \sum_{k=8,12\ldots}^{n} (n/4 - k/4 + 1)(A_2A_3A_2A_1)^{\frac{k-8}{4}} (l_1 - l_2)$$

The expression for $\vec{r}$ is the sum of the contributions from each of the four types of bonds.

$$\vec{r} = (1\ 0\ 0)\left[\sum_{k=4,8,12\ldots}^{n} l_2)_{n/2} + \sum_{k=4,8,12\ldots}^{n} l_2)_{n-2/2} + \sum_{k=4,8,12\ldots}^{n} l_1)_{n/2}\right.$$

$$\left. + \sum_{k=4,8,12\ldots}^{n} l_1)_{n-2/2}\right]$$

Substitution yields:

$$\vec{r} = (l_1\ 0\ 0)\left[\sum_{k=4,8,12\ldots}^{n} (A_3A_2A_1A_2)^{\frac{k-4}{4}} A_3A_2A_1 + \sum_{k=4,8,12\ldots}^{n} (A_2A_1A_2A_3)^{\frac{k-4}{4}} A_2A_1\right.$$

$$\left. + \sum_{k=4,8,12\ldots}^{n} (A_1A_2A_3A_2)^{\frac{k-4}{4}} A_1 + \sum_{k=4,8,12\ldots}^{n} (A_2A_3A_2A_1)^{\frac{k-4}{4}}\right]$$

$$+ (l_2 - l_1\ 0\ 0)\Bigg[\sum_{k=4,8,12\ldots}^{n} (n/4 - k/4 + 1)(A_3A_2A_1A_2)^{\frac{k-4}{4}}\ A_3$$

$$+ \sum_{k=4,8,12\ldots}^{n} (n/4 - k/4 + 1)(A_2A_1A_2A_3)^{\frac{k-4}{4}}$$

$$+ \sum_{k=8,12\ldots}^{n} (n/4 - k/4 + 1)(A_1A_2A_3A_2)^{\frac{k-8}{4}}\ A_1A_2A_3$$

$$+ \sum_{k=8,12\ldots}^{n} (n/4 - k/4 + 1)(A_2A_3A_2A_1)^{\frac{k-8}{4}}\ A_2A_3\Bigg]$$

$$+ (l_1 - l_2\ 0\ 0)\ \Bigg[\sum_{k=8,12\ldots}^{n} (n/4 - k/4 + 1)(A_3A_2A_1A_2)^{\frac{k-8}{4}}\ A_3A_2A_1$$

$$+ \sum_{k=8,12\ldots}^{n} (n/4 - k/4 + 1)(A_2A_1A_2A_3)^{\frac{k-8}{4}}\ A_2A_1$$

$$+ \sum_{k=8,12\ldots}^{n} (n/4 - k/4 + 1)(A_1A_2A_3A_2)^{\frac{k-8}{4}}\ A_1$$

$$+ \sum_{k=8,12\ldots}^{n} (n/4 - k/4 + 1)(A_2A_3A_2A_1)^{\frac{k-8}{4}}\Bigg]$$

Rearrangement yields:

$$\vec{r} = (l_1\ 0\ 0)\ \Bigg[\sum_{k=4,8,12\ldots}^{n} (A_3A_2A_1A_2)^{\frac{k-4}{4}}\ A_3A_2A_1 + \sum_{k=4,8,12\ldots}^{n} (A_2A_1A_2A_3)^{\frac{k-4}{4}}\ A_2A_1$$

$$+ \sum_{k=4,8,12\ldots}^{n} (A_1A_2A_3A_2)^{\frac{k-4}{4}}\ A_1 + \sum_{k=4,8,12\ldots}^{n} (A_2A_3A_2A_1)^{\frac{k-4}{4}}$$

$$- \sum_{k=4,8,12\ldots}^{n} (n/4 - k/4 + 1)(A_3A_2A_1A_2)^{\frac{k-4}{4}}\ A_3$$

$$- \sum_{k=4,8,12\ldots}^{n} (n/4 - k/4 + 1)(A_2A_1A_2A_3)^{\frac{k-4}{4}}$$

$$
[C] \equiv \left\{
\begin{aligned}
&- \sum_{k=8,12\ldots}^{n} (n/4 - k/4 + 1)(A_1A_2A_3A_2)^{\frac{k-8}{4}}\, A_1A_2A_3 \\
&- \sum_{k=8,12\ldots}^{n} (n/4 - k/4 + 1)(A_2A_3A_2A_1)^{\frac{k-8}{4}}\, A_2A_3 \\
&+ \sum_{k=8,12\ldots}^{n} (n/4 - k/4 + 1)(A_3A_2A_1A_2)^{\frac{k-8}{4}}\, A_3A_2A_1 \\
&+ \sum_{k=8,12\ldots}^{n} (n/4 - k/4 + 1)(A_2A_1A_2A_3)^{\frac{k-8}{4}}\, A_2A_1 \\
&+ \sum_{k=8,12\ldots}^{n} (n/4 - k/4 + 1)(A_1A_2A_3A_2)^{\frac{k-8}{4}}\, A_1 \\
&+ \sum_{k=8,12\ldots}^{n} (n/4 - k/4 + 1)(A_2A_3A_2A_1)^{\frac{k-8}{4}} \Bigg]
\end{aligned}
\right.
$$

$$
+ (l_2\ 0\ 0) \left\{
\begin{aligned}
&\Bigg[\sum_{k=4,8,12\ldots}^{n} (n/4 - k/4 + 1)(A_3A_2A_1A_2)^{\frac{k-4}{4}}\, A_3 \\
&+ \sum_{k=4,8,12\ldots}^{n} (n/4 - k/4 + 1)(A_2A_1A_2A_3)^{\frac{k-4}{4}} \\
&+ \sum_{k=8,12\ldots}^{n} (n/4 - k/4 + 1)(A_1A_2A_3A_2)^{\frac{k-8}{4}}\, A_1A_2A_3 \\
&+ \sum_{k=8,12\ldots}^{n} (n/4 - k/4 + 1)(A_2A_3A_2A_1)^{\frac{k-8}{4}}\, A_2A_3 \\
&- \sum_{k=8,12\ldots}^{n} (n/4 - k/4 + 1)(A_3A_2A_1A_2)^{\frac{k-8}{4}}\, A_3A_2A_1 \\
&- \sum_{k=8,12\ldots}^{n} (n/4 - k/4 + 1)(A_2A_1A_2A_3)^{\frac{k-8}{4}}\, A_1A_2 \Bigg]
\end{aligned}
\right. \equiv [D]
$$

$$\left.\begin{array}{l} - \sum_{k=8,12\ldots} (n/4 - k/4 + 1)(A_1A_2A_3A_2)^{\frac{k-8}{4}} A_1 \\ \\ - \sum_{k=8,12\ldots} (n/4 - k/4 + 1)(A_2A_3A_2A_1)^{\frac{k-8}{4}} \end{array}\right]$$

With the notation introduced above,

$$\vec{r} = (l_1\ 0\ 0)\ [C] + (l_2\ 0\ 0)\ [D]$$

$$r^2 = \vec{r} \cdot \vec{r} = \vec{r} \times \vec{r}^t$$

$$\vec{r}^2 = \left[(l_1\ 0\ 0)[C] + (l_2\ 0\ 0)[D]\right] x \left[(l_1\ 0\ 0)[C] + (l_2\ 0\ 0)[D]\right]^t$$

$$\vec{r}^2 = \left[(l_1\ 0\ 0)[C] + (l_2\ 0\ 0)[D]\right] x \left[[C]^t \begin{pmatrix} l_1 \\ 0 \\ 0 \end{pmatrix} + [D]^t \begin{pmatrix} l_2 \\ 0 \\ 0 \end{pmatrix}\right]$$

$$\vec{r}^2 = l_1^2\ [C][C]^t_{1,1} + l_2^2\ [D][D]^t_{1,1}$$

$$+ l_1 l_2 \left([D][C]^t_{1,1} + [C][D]^t_{1,1} \right)$$

As an illustration of these equations consider a chain with eight links.

$$\vec{r} = (l_1\ 0\ 0)[1 + A_1 + A_2A_1 + A_3A_2A_1 + A_2A_3A_2A_1 + A_1A_2A_3A_2A_1 +$$

$$A_2A_1A_2A_3A_2A_1 + A_3A_2A_1A_2A_3A_2A_1]$$

$$+ (l_2 - l_1\ 0\ 0)[1 + A_3 + A_2A_3 + A_1A_2A_3 + A_2A_1A_2A_3 + 1 + A_3A_2A_1A_2A_3 + A_3]$$

$$+ (l_1 - l_2\ 0\ 0)[1 + A_1A_2A_1 + A_3A_2A_1]$$

$$\vec{r} = (l_1\ 0\ 0)\ [1 + A_1 + A_2A_1 + A_3A_2A_1 + A_2A_3A_2A_1 + A_1A_2A_3A_2A_1 +$$

$$A_3A_2A_1A_2A_3A_2A_1 - 1 - A_3 - A_2A_3 - A_1A_2A_3 - A_2A_1A_2A_3 - 1 - A_3A_2A_1A_2A_3$$

$$- A_3 + 1 + A_1 + A_2A_1 = A_3A_2A_1]$$

$$+(l_2\ 0\ 0)\ [1 + A_3 + A_2A_3 + A_1A_2A_3 + A_2A_1A_2A_3 + 1 + A_3A_2A_1A_2A_3 + A_3 - 1 -$$

$$A_1 - A_2A_1 - A_3A_2A_1]$$

Simplification gives:

$$\vec{r} = (l_1\ 0\ 0)\,[\,2A_1 - 2A_3 + 2A_2A_3 + 2A_3A_2A_1 - A_1A_2A_3 + A_2A_3A_2A_1$$
$$- A_2A_1A_2A_3 + A_1A_2A_3A_2A_1 - A_3A_2A_1A_2A_3 + A_2A_1A_2A_3A_2A_1 +$$
$$A_3A_2A_1A_2A_3A_2A_1\,]$$
$$+(l_2\ 0\ 0)\,[1 + 2A_3 - A_1 + A_2A_3 - A_2A_1 + A_1A_2A_3 - A_3A_2A_1 + A_2A_1A_2A_3$$
$$+ A_3A_2A_1A_2A_3\,]$$

APPENDIX II

160A FORTRAN Programs for Calculation of $\overline{r^2}$ for -M-O-M- Chain

Case one - n even

```
0001 format (I^2, (E^8.4))
0002 format (^12HN; even; case; i2)
0003 format (E^15.7)
00040dimension ala2(^3,3),
0004lal(^3,3),a2(^3,3),a2al(^3,3),d(^3,3),w(^10),x(^10),y(^10),z(^10)
0005 subroutine matpow (B,c)
0006 nonlocal d
0007 do 10 i=^1,3
0010 d(I,j)=B(I,1)'C(^1,j)+B(I,2)'C(^2,j)+B(I,3)'C(^3,j)
     return
     end
0011 subroutine matmul (B,c,e)
0012 e=B(^1,1)'C(^1,1)+B(^1,2)'C(^2,1)+B(^1,3)'C(^3,1)
0013 return
     end
0014 read 1,ncase, ala2, al, a2, a2al
0015 pause 0005
0016 do 30 j=^1,3
0017 do 30 i=^1,3
0030 d(I,j)=A^1A^2(I,j)
     do 35k=^2,10
0031 call matmul (D,al,e)
     x(K)=E
0032 CALL MATMUL (A^2d,e)
     y(K)=E
0033 CALL MATPOW (A^1A^2,d)
0035 w(K)=D(^1,1)
     do36 j=^1,3
     do36i=^1,3
```

```
0036 d(I,j)=A^2A^1(I,j)
     do 370 k=^2,10
0037 call matpow (A^2A^1,d)
0370 z(K)=D(^1,1)
0038 punch 2, ncase
     pause 0006
     x(^1)=A^1(^1,1)
0140 y(^1)=A^2(^1,1)
0041 w(^1)=A^1A^2(^1,1)
0042 z(^1)=A^2A^1(^1,1)
0039 punch3(W(I),x(I),y(I),z(I),i=^1,10)
0043 do46 n=^2,20,2
     m=N-^1
     RATIO=^0
     I=^1
0044 DO ^45 K=^1,m,2
     ratio=RATIO+(N-K+^1)'X(I)+(N-K-^1)'Y(I)+(N-K-^1)'W(I)+(N-K-^1)'Z(I)
0045 i-I+^1
     RATIO=RATIO+N
0046 PUNCH^3,ratio
     pause0007
     end
     end
```

Case two - n odd

```
      0001 format (I^2, (E^8.4))
      0002 format (^11HN;odd;case; i2)
      0003 format (E^15.7)
      00040dimension ala2(^3,3),
      0004lal(^3,3),a2(^3,3),a2al(^3,3),d(^3,3),w(^10),x(^10),y(^10),z(^10)
      0005 subroutine matpow (B,c)
      0006 nonlocal d
      0007 do 10 i=^1,3
      0008 do 10 j=^1,3
      0010 d(I,j)=B(I,1)'C(^1,j)+B(I,2)'C(^2,j)+B(I,3)'C(^3,j)
           return
           end
      0011 subroutine matmul (B,c,e)
      0012 e= B(^1,1)'C(^11)+B(^1,2)'C(^2,1)+B(^1,3)'C(^3,1)
      0013 return
           end
      0014 read 1, ncase, ala2, al, a2, a2al
      0015 pause 0005
      0016 do 30 j=^1,3
      0017 do 30 i=^1,3
      0030 d(I,j)=A^1A^2(I,j)
           do 35k=^2,10
      0031 call matmul (D,al,e)
           x(K)=E
      0032 CALL MATMUL (A^2,d,e)
           y(K)=E
      0033 CALL MATPOW (A^1A^2,d)
      0035 w(K)=D(^1,1)
           do 36 j=^1,3
           do 36 i=^1,3
      0036 d(I,j)=A^2A^1(I,j)
           do 370 k=^2,10
```

```
 0037 call matpow (A2A1,d)
 0370 z(K)=D(1,1)
c      now we have all the xs ys zs ps
 0038 punch 2, ncase
      pause 0006
      x(1)=A1(1,1)
 0140 y(1)=A2(1,1)
 0041 w(1)=A1A2(1,1)
 0042 z(1)=A2A1(1,1)
 0039 punch3(W(I),x(I),y(I),z(I),i=1,10)
 0043 do46 n=3,21,2
      m=N-1
      RATIO=0.
      i=1
 0044 DO 45 K=1,m,2
      ratio=RATIO+(N-K)'X(I)+(N-K)'Y(I)+(N-K)'W(I)+(N-K-2)'Z(I)
 0045 i=I+1
      RATIO=RATIO+N
 0046 PUNCH3,ratio
      pause 0007
      end
      end
```

Program for generating all end-to-end vectors of a growing three-rotational state chain.

```
C0811 CHEMISTRY PROGRAM
      3 FORMAT(E14.8)
      1 FORMAT(I2)
    310 FORMAT (/)
      4 FORMAT(14HR$DOT$R$FOR$N=,I2)
      2 FORMAT(E8.5)
        DIMENSION THETA(3,3,2),PHI(3,3,3),A1(3,3,3),A2(3,3,3),A2A1(3,3,9),
       1 TEMP1(3,3,1),TEMP2(3,3,1),TEMP3(3,3,1),A1A2A1(3,3,27),SUM(1,3,1)
        SUBROUTINE MULT(X,N,Y,M,Z,L)
      1 DO4 I=1,3
      2 DO4 J=1,3
      3 DO4 K=1,3
      4 Z(I,J,L)=X(I,K,N)*Y(K,J,M)+Z(I,J,L)
        RETURN
        END
        SUBROUTINE ADD (X,L,Y,M,Z)
      1 DO2 I=1,3
      2 Z(1,I,1)=X(3,I,L)+Y(3,I,M)
        RETURN
        END
        DO 300 I=1,3
        DO 300 J=1,3
        DO 300 K=1,3
        IF (I-1) 301,301,302
    301 TEMP1(J,K,I)=0.0
        TEMP3(J,K,I)=0.0
    302 A1(I,J,K)=0.0
        A2(I,J,K)=0.0
        A2A1(I,J,K)=0.0
    300 A1A2A1(I,J,K)=0.0
        DO 303 I=1,3
        DO 303 J=1,3
        DO 303K=4,9
        A2A1(I,J,K)=0.0
    303 A1A2A1(I,J,K)=0.0
        DO 304 I=1,3
        DO 304 J=1,3
        DO 304 K=10,27
    304 A1A2A1(I,J,K)=0.0
        READ1,NUMBER
        READ2,(((THETA(I,J,K),I=1,3),J=1,3),K=1,2)
        READ2,(((PHI  (I,J,K),I=1,3),J=1,3),K=1,3)
     18 DO5 M=1,3
      5 CALL MULT (THETA,1,PHI,M,A1,M)
     19 DO6 M=1,3
      6 CALL MULT (THETA,2,PHI,M,A2,M)
        K=0
        DO7 N=1,3
        DO7 M=1,3
```

```
      K=K+1
   20 CALL MULT(A2,M,A1,N,A2A1,K)
   21 CALL ADD(A1,N,A2A1,K,SUM)
      PUNCH3,(SUM(1,J,1),J=1,3)
    7 CONTINUE
      PAUSE 0003
      K=1
      DO8 M=1,9
      DO8 N=1,3
   22 CALL MULT (A1,N,A2A1,M,A1A2A1,K)
      IF(N-1)16,15,16
   15 READ3,(TEMP2(3,J,1),J=1,3)
   16 CALL ADD (A1A2A1,K,TEMP2,1,SUM)
   23 PUNCH3,(SUM(1,J,1),J=1,3)
      K=K+1
    8 CONTINUE
      PAUSE 0004
      DO9 N=1,9
      DO9 M=1,9
      DO500 J=1,3
      DO 500 I=1,3
  500 TEMP1(I,J)=0
   24 CALL MULT (A2A1,M,A2A1,N,TEMP1,1)
      IF(M-1)112,25,112
  112 IF(M-4)113,25,113
  113 IF(M-7)26,25,26
   25 READ3,(TEMP2(3,J,1),J=1,3)
   26 CALL ADD(TEMP1,1,TEMP2,1,SUM)
      PUNCH3,(SUM(1,J,1),J=1,3)
    9 CONTINUE
      IF(NUMBER-5)102,101,102
  102 PAUSE 0005
      DO10 N=1,9
      DO10 M=1,9
      DO10 L=1,3
      DO501 I=1,3
      DO501 IJ1,3
      TEMP1(I,J,1)=0.0
  501 TEMP3(I,J,1),0.0
      CALL MULT (A1,L,A2A1,M,TEMP1,1)
      CALL MULT(TEMP1,1,A2A1,N,TEMP3,1)
      IF(L-1)31,30,31
   30 READ3,(TEMP2(3,J,1),J=1,3)
   31 CALL ADD(TEMP3,1,TEMP2,1,SUM)
   27 PUNCH3,(SUM(1,J,1),J=1,3)
   10 CONTINUE
      IF(NUMBER-6)103,101,103
  103 PAUSE 0006
      DO11 N=1,9
```

```
      DO11 M=1,9
      DO11 L=1,9
      DO 502 J=1,3
      DO 502 I=1,3
      TEMP1(I,J,1)=0.0
  502 TEMP3(I,J,1)=0.0
   28 CALL MULT(A2A1,L,A2A1,M,TEMP1,1)
   29 CALL MULT(TEMP1,1,A2A1,N,TEMP3,1)
      IF(L-1)116,40,116
  116 IF(L-4)117,40,117
  117 IF(L-7)41,40,41
   40 READ3,(TEMP2(3,J,1),J=1,3)
   41 CALL ADD (TEMP3,1,TEMP2,1,SUM)
      PUNCH3,(SUM(1,J,1),J=1,3)
   11 CONTINUE
      IF(NUMBER-7)104,101,104
  104 PAUSE 0007
      DO12 N=1,9
      DO12 M=1,9
      DO12 L=1,9
      DO12 K=1,3
      DO 503 I=1,3
      DO 503 J=1,3
      TEMP1(I,J,1)=0.0
  503 TEMP3(I,J,1)=0.0
      CALL MULT(A1,K,A2A1,L,TEMP1,1)
      CALL MULT(TEMP1,1,A2A1,M,TEMP3,1)
      CALL MULT(TEMP3,1,A2A1,N,TEMP1,1)
      IF(K-1)51,50,51
   50 READ3,(TEMP2(1,J,1),J=1,3)
   51 CALL ADD(TEMP1,1,TEMP2,1,SUM)
      PUNCH3,(SUM(1,J,1),J=1,3)
   12 CONTINUE
      IF(NUMBER-8)105,101,105
  105 PAUSE 0010
      DO13 N=1,9
      DO13 M=1,9
      DO13 L=1,9
      DO13 I=1,9
      DO 504 I=1,3
      DO 504 J=1,3
      TEMP1(I,J,1)=0.0
  504 TEMP3(I,J,1)=0.0
   35 CALL MULT(A2A1,I,A2A1,L,TEMP1,1)
   36 CALL MULT(TEMP1,1,A2A1,M,TEMP3,1)
   37 CALL MULT(TEMP3,1,A2A1,N,TEMP1,1)
      IF(I-1)120,60,120
  120 IF(I-4)121,60,121
  121 IF(I-7)61,60,61
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   60 READ3,(TEMP2(3,J,1),J=1,3)
   61 CALL ADD (TEMP1,1,TEMP2,1,SUM)
   45 PUNCH3,(SUM(1,J,1),J=1,3)
   13 CONTINUE
      IF(NUMBER-9)106,101,106
  106 PAUSE 0011
      DO 14 N=1,9
      DO14 M=1,9
      DO14 L=1,9
      DO14 I=1,9
      DO14 K=1,3
      DO 505 I=1,3
      DO 505 J=1,3
      TEMP1(I,J,1)=0.0
  505 TEMP3(I,J,1)=0.0
      CALL MULT(A1,K,A2A1,I,TEMP1,1)
      CALL MULT(TEMP1,1,A2A1,L,TEMP3,1)
      CALL MULT(TEMP3,1,A2A1,M,TEMP1,1)
      CALL MULT(TEMP1,1,A2A1,N,TEMP3,1)
      IF(K-1)71,70,71
   70 READ3,(TEMP2(3,J,1),J=1,3)
   71 CALL ADD(TEMP3,1,TEMP2,1,SUM)
   44 PUNCH3,(SUM(1,J,1),J=1,3)
   14 CONTINUE
      IF(NUMBER-10)107,101,107
  107 PAUSE 0012
  101 PAUSE 1234
      L=27
      NU=NUMBER-4
      DO90 I=1,NU
   90 L=3*L
   55 PUNCH4,NUMBER
      DO200 N=1,L
   47 READ3,(TEMP2(1,J,1),J=1,3)
      TEMP2(1,3,1)=TEMP2(1,3,1)+1.0
      RDOT=0.0
   49 DO100 M=1,3
   99 A=TEMP2(1,M,1)
      B=A*A
      RDOT=B+RDOT
  100 CONTINUE
   48  PUNCH3,RDOT
      PUNCH310
  200 CONTINUE
      PAUSE 1111
      END
      END
```

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