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Configuration-Dependent Properties of Poly(dimethylsilmethylene) Chains. II. Correlation of Theory and Experiment

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ABSTRACT: Rotational isomeric state theory was used to calculate values of the same configuration-dependent properties of poly(dimethylsilmethylene) (PDMSM) which were determined in the experimental study described in the preceding paper. The analysis of this chain molecule indicates that conformations bringing about pentane-type interferences between bulky $Si(CH_3)_2$ groups are completely suppressed. All other conformations are accessible and, within the approximation that methylene and methyl groups give rise to very similar intramolecular interactions, they are all of the same energy. This lack of any strong conformational preference is the origin of the relatively small value of the unperturbed dimensions of PDMSM, and the insensitivity of both its unperturbed dimensions and dipole moments to changes in temperature. This simplest model for the PDMSM chain gives fairly good quantitative agreement between theory and experiment. The agreement can be improved by taking into account more subtle features of the molecule, such as the fact that the skeletal methylene groups must have larger partial charges than the pendant methyl groups.

The experimental results obtained in the experimental study of poly(dimethylsilmethylene) (PDMSM) reported in the preceding paper[1] are summarized in the first column of Table I. Included for purposes of comparison in the other columns are the corresponding values of the same properties for the two structurally related polymers, poly(dimethylsiloxane) (PDMSO),[2-5] and polyisobutylene (PIB);[1] also included are results on polyethylene (PE),[1] since structurally it is the simplest polymer studied in any detail with regard to chain configuration. For convenience, the structural repeat unit of each of these polymers is given in the first row of the table. As already pointed out,[1] one of the most interesting aspects of the PDMSM chain is its relatively small characteristic ratio $\langle r^2 \rangle_0/nl^2$. As shown in the table, it is 20–30% smaller than the values of the characteristic ratio reported for PDMSO, PIB, and PE. Equally notable[1] is the fact that both the mean-square unperturbed dimensions $\langle r^2 \rangle_0$ and dipole moments $\langle \mu^2 \rangle_0$ of PDMSM are essentially independent of temperature. In this regard, it is quite similar to PIB, which also has values of $\langle r^2 \rangle_0$ almost insensitive to temperature.[2] In contrast, an increase in temperature has the effect of significantly increasing $\langle r^2 \rangle_0$ and $\langle \mu^2 \rangle_0$ in the case of PDMSO[2-5] and significantly decreasing $\langle r^2 \rangle_0$ in the case of PE.[2]

The purpose of the present study is to use rotational isomeric state theory to interpret the properties of the PDMSM chain cited above, in an attempt to elucidate the marked differences in the configurational characteristics of PDMSM, PDMSO, PIB, and PE. Such analysis and comparisons should shed considerable light on the effect of structure on the configurations of chain molecules in general.

Rotational Isomeric State Theory

General Aspects. In the rotational isomeric state approximation, each rotatable skeletal bond in the chain molecule is assigned to one of a small number of discrete rotational states, generally chosen to occur at the minima in the torsional potential or conformational energy for the particular bonds.[2] These minima are, in most cases, situated at rotational angles ϕ of 0, 120, and −120°; such states are designated as trans (t), gauche$^+$ (g$^+$), and gauche$^-$ (g$^-$), respectively. The relative probability or statistical weight of each rotational state is generally represented by a simple Boltzmann factor, exp $(-E_{\zeta\eta;i}/RT)$, where $E_{\zeta\eta;i}$ is the conformational energy characterizing the intramolecular interactions occurring in the associated conformation for a pair of consecutive rotational states with bond $i-1$ in state ζ

Table I
Summary of the Statistical Properties of Poly(dimethylsilmethylene)[a] and Some Other Polymers of Interest

	PDMSM	PDMSO	PIB	PE
Repeat unit	$Si(CH_3)_2-CH_2-$	$Si(CH_3)_2-O-$	$C(CH_3)_2-CH_2-$	CH_2-CH_2-
$\langle r^2\rangle_0/nl^2$	5.3	7.6[b]	6.6[b]	7.6[b,c]
$10^3 d \ln \langle r^2\rangle_0/dT$	0.20	0.75[b]	−0.20[b]	−1.10[b]
$\langle \mu^2\rangle_0/nm^2$	0.39	0.30[d]		
$10^3 d \ln \langle \mu^2\rangle_0/dT$	0.0	0.70[e]		

[a] Taken from ref 1. [b] Taken from ref 2. [c] Corrected from the temperature of measurement (140°C) to the vicinity of room temperature by means of $d \ln \langle r^2\rangle_0/dT$. [d] Taken from ref 5. [e] Primarily a theoretical result; see ref 3–5.

and bond i in state η. Since these statistical weights are relative quantities, $E_{\zeta\eta;i}$ may be taken as the energy difference relative to some arbitrarily designated conformation of zero energy.[2]

The entire set of statistical weights required to describe all possible conformations of a pair of consecutive skeletal bonds is conveniently expressed in the form of a statistical weight matrix[2] $\mathbf{U}_i = [u_{\zeta\eta}]_i$ in which states about bond $i-1$ are indexed by ζ = t, g$^+$, g$^-$, and states about bond i by η = t, g$^+$, g$^-$. The $\mathbf{U}_i$ matrix is fundamental to the configurational analysis of a chain molecule since it, in conjunction with structural information (bond lengths, bond dipole moments, bond angles, and locations of rotational states), may be used to calculate theoretical values of $\langle r^2\rangle_0/nl^2$ and the dipole moment ratio $\langle \mu^2\rangle_0/nm^2$.[2,6] Its formulation for the skeletal bonds in PDMSM is given after presentation of the required structural data characterizing the PDMSM repeat unit.

Application to Poly(dimethylsilmethylene)

A. Structural Characteristics of the Polymer Repeat Unit. A portion of the PDMSM chain is shown in Figure 1; for convenience in representation, the chain is shown in its planar, all-trans forms. The C-Si-C bond angle is very nearly tetrahedral according to the tabulated structural data of Bowen and Sutton.[7] Thus the bond angle supplement θ'' in Figure 1 may be assigned the value 70.5°. For the other type of skeletal bond angle, that occurring about the CH_2 groups, there is relatively little information at the present time. An electron diffraction study[8] of disilylmethane $H_3Si-CH_2-SiH_3$ indicates a $Si-CH_2-Si$ bond angle of 114.4°; semiempirical calculations[9] of the energy of the same molecule suggest a minimum energy structure in which this angle is 113.8°. Replacement of the silyl hydrogen atoms by methyl groups in forming the $Si(CH_3)_2-CH_2-Si(CH_3)_2$-sequence may increase this bond angle further beyond the tetrahedral value of 109.5°. In PIB, for example, such an increase, due to steric repulsions between pendant methyl groups,[2] is very marked because the C–C skeletal bonds are relatively short (1.53 Å).[7] The $C(CH_3)_2-CH_2-C(CH_3)_2$ bond angle in PIB is thus found to be in the range 126–128°.[2,10] In PDMSM, the greater length of the Si–C skeletal bonds, 1.90 Å,[7] would significantly decrease such repulsions and the Si–C–Si bond angle in PDMSM may therefore not be very much greater than it is in $H_3Si-CH_2-SiH_3$.[8] We therefore tentatively adopt the value of 115° for this bond angle and thus, the bond angle supplement θ' in Figure 1 is assigned the value 65°. For purposes of illustration, however, calculations of $\langle r^2\rangle_0/nl^2$ and $\langle \mu^2\rangle_0/nm^2$ will also be carried out for Si–C–Si bond angles of 109.5 and 120° (θ' = 70.5 and 60°, respectively).

As already cited, the skeletal bonds in PDMSM are of length 1.90 Å.[7] The magnitude m of the effective skeletal bond moment is harder to fix precisely since it requires analysis of the dipole moment of the PDMSM dimer, as described in the preceding paper.[1] For θ' = 65°, $m_{Si-C} = -m_{Si-C}$ = 0.56 D; for the other illustrative values of θ', 70.5 and 60°, the values are 0.52 and 0.60 D, respectively.[1] The fact that C is more electronegative than Si (~2.5 vs. ~2.0)[11,12] suggests that the negative end of the skeletal bond dipole is on the skeletal carbon atoms. Such deductions based on differences in electronegativity may be misleading,[12] but the direction and even the magnitude of the effective skeletal bond dipole is irrelevant in theoretical calculations of *ratios* such as $\langle \mu^2\rangle_0/nm^2$. All that need be specified in this regard is the fact that, in PDMSM, the Si–C bond moment m_{Si-C} is opposite in sign to the C–Si bond moment m_{C-Si}. The magnitude of m must of course be carefully specified in converting experimental values of $\langle \mu^2\rangle_0$ to values of the dipole moment ratio $\langle \mu^2\rangle_0/nm^2$ to be used in the evaluation of the theoretical results.[1]

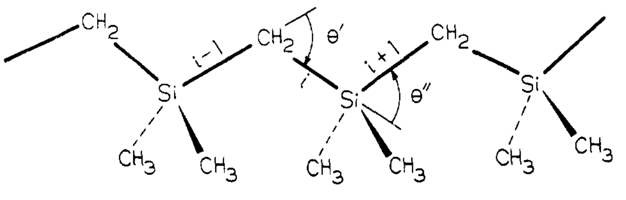

Figure 1. Schematic representation of the poly(dimethylsilmethylene) chain in the all-trans conformation (all rotational angles ϕ = 0°).

B. Construction of Statistical Weight Matrices. Since rotations about Si–C bonds give rise to intramolecular interactions different from those experienced upon rotating about C–Si bonds, the PDMSM chain requires two statistical weight matrices for its characterization. For pairs of consecutive skeletal bonds ($Si-CH_2-Si$) meeting at a CH_2 group, the statistical weight matrix is designated $\mathbf{U}_a$; for pairs ($CH_2-Si-CH_2$) meeting at a Si atom, the designation is $\mathbf{U}_b$.

Rotations about $Si-CH_2-Si$ bond pairs, such as $i-1$ and i of Figure 1, merely serve to interchange CH_2 groups with CH_3 groups and vice versa. Configurational analyses[2] of several other chain molecules have employed the reasonable assumption that CH_2 and CH_3 groups are sterically very nearly equivalent. Strong support for this assumed equivalence has very recently been obtained in epimerization studies[13] of some low molecular weight analogues of polypropylene. The aspect of this work of interest here is the relative energies of these polypropylene oligomers in two conformations which differ only in that the $CH_3\cdots CH$ and $CH_2\cdots H$ gauche interactions occurring in one conformation are replaced by $CH_2\cdots CH$ and $CH_3\cdots H$ gauche interactions in the other. The equilibrium compositions of the diastereomers of these molecules indicate that the energy difference between the two conformations is only ~0.07 kcal mol^{-1}. If, in addition, the CH_2 skeletal groups and the CH_3 pendant groups in PDMSM are temporarily assumed to have essentially the same partial charges, then all conformational pairs about these bonds are of approximately the same energy. In this first-order approximation, therefore, each of these conformations may be assigned a statistical weight of unity, and the statistical weight matrix for the Si–CH$_2$–Si bond pair is then simply

$$U_a = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{bmatrix} \quad (1)$$

For the CH$_2$–Si–CH$_2$ bond pairs, such as i and $i + 1$ of Figure 1, the statistical weights are obviously also unity, except for $g^{\pm}g^{\mp}$ states, where steric conflicts[2] between Si(CH$_3$)$_2$ groups are so severe that the probabilities for these two states are effectively zero. (These interactions are frequently called "pentane-type interactions"[2] because n-pentane is the simplest hydrocarbon in which they occur.) Thus, the statistical weight matrix for CH$_2$–Si–CH$_2$ pairs of bonds in PDMSM is given by

$$U_b = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 0 \\ 1 & 0 & 1 \end{bmatrix} \quad (2)$$

Calculated Results and Discussion

The above statistical weight matrices and the structural information cited earlier were used to calculate values of the mean-square unperturbed dimensions and dipole moments, using the standard equations[2,6] of the rotational isomeric state theory of chain configurations. In the first series of calculations,[14] $\langle r^2\rangle_0/nl^2$ and $\langle \mu^2\rangle_0/nm^2$ were obtained as a function of the degree of polymerization x, using 65° for the Si–C–Si bond angle supplement θ'. These results are shown in Figure 2. As is readily obvious from the curves obtained, both the characteristic ratio and dipole moment ratio essentially reach their limiting values for long chain length at $x \simeq 100$ or $n \simeq 200$ skeletal bonds. These calculated results may thus be directly compared with experimental results obtained on any PDMSM polymer having a molecular weight in excess of approximately 7000 as mentioned in the preceding paper.[1] Since little additional computation is required to raise x from 100 to 512 in the matrix-squaring techniques used in these calculations,[14] all additional calculations were carried out at $x = 512$.

The limiting values of $\langle r^2\rangle_0/nl^2$ and $\langle \mu^2\rangle_0/nm^2$ thus obtained in these calculations on PDMSM are 3.60 and 0.43, respectively. The value calculated for the dipole moment ratio, 0.43, is in quite satisfactory agreement with the experimental result, 0.39 ± 0.03. The calculated value for the characteristic ratio, 3.60, is however in only approximate agreement with the experimental result 5.32 ± 0.01. Since all of the statistical weights are either unity or zero, both $\langle r^2\rangle_0$ and $\langle \mu^2\rangle_0$ are of course predicted to be independent of temperature, in excellent agreement with experiment.[1] Even this simplest model for the PDMSM chain is thus seen to give a good qualitative interpretation of the most striking features of this chain molecule. The characteristic ratio for PDMSM is unusually low because of the large number of conformational states of almost exactly the same energy and therefore of essentially the same probability of occurrence. This lack of preference in PDMSM means of course that there are no strong conformational regularities in this chain molecule, and such conformational regularities generally give rise to high spatial extension as reflected in large values of $\langle r^2\rangle_0/nl^2$.[2,15-19] Relatively simple examples of this effect are polyethylene,[2,16] where the strong preference for extended trans states causes $\langle r^2\rangle_0/nl^2$ to be relatively large, and isotactic vinyl polymers, where the restriction of the chain to helical conformations accounts for the similarly large values of $\langle r^2\rangle_0/nl^2$ in this case.[2,17] Such chain molecules have negative values of the coefficient d ln $\langle r^2\rangle_0/\mathrm{d}T$ since an increase in temperature causes transitions to alternative rotational states which are of higher energy but lower spatial extension.[2,15-19] Poly(dimethylsiloxane) represents a rather different type of chain molecule in that its preferred regular conformation is a closed figure,[2,19] of very small end-to-end distance, because of the inequality of bond angles about the Si and O skeletal atoms. Its characteristic ratio is relatively large because of the frequent occurrence of other states of higher spatial extension. Since such alternative states are of higher energy, their frequency of occurrence increases with increasing temperature, thus giving rise to a positive value of d ln $\langle r^2\rangle_0/\mathrm{d}T$ for PDMSO.

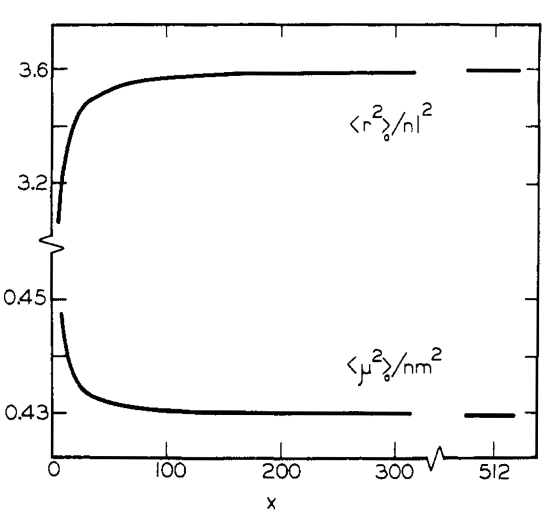

Figure 2. Values of the characteristic ratio and dipole moment ratio of PDMSM chains shown as a function of the degree of polymerization. In this and the following figure, the Si–C–Si bond angle is taken to be 115°.

In this simplest model of the PDMSM chain, none of the statistical weights are temperature dependent; two states with very severe steric repulsions are suppressed entirely, with statistical weights constant at zero, and all other states are equally likely, with statistical weights uniformly assigned the reference value of unity. In more physical terms, $\langle r^2\rangle_0$ and $\langle \mu^2\rangle_0$ do not change with changes in temperature because all of the accessible conformational states are of essentially the same energy. On the basis of these arguments, the skeletal bonds of the PIB chain [C(CH$_3$)$_2$–CH$_2$–]$_x$ should also have a number of rotational states of approximately the same energy.[20] This would of course explain the relatively small value −0.20 K^{-1} found for 10^3 d ln $\langle r^2\rangle_0/\mathrm{d}T$ for this chain molecule.[2,21] The configurational analysis of PIB[22] is greatly complicated by the fact, however, that the relatively short C–C skeletal bonds make the intramolecular interactions much more severe in PIB than they are in PDMSM. This causes displacement of rotational states from their normal positions of $\phi = 0, \pm 120°$ and possibly also causes long-range correlations between rotational states, which could be the origin of the moderately large experimental value 6.6 reported for its characteristic ratio.

The above model of the PDMSM chain is very similar to one of the earliest models of a chain molecule, the "freely rotating" chain.[2,23] In such a highly idealized chain, all rotational angles in the continuous range 0–360° are equally likely; its characteristic ratio in the limit of long chain length can be calculated from the simple algebraic equation[2,23]

$$\langle r^2\rangle_0/nl^2 = (1 + \cos\theta')(1 + \cos\theta'')/(1 - \cos\theta' \cos\theta'') \quad (3)$$

Table II
Values of the Characteristic Ratio and Dipole Moment Ratio for PDMSM Calculated Using Two Simple Chain Models

	$\langle r^2\rangle_0/nl^2$		$\langle \mu^2\rangle_0/nm^2$	
θ'[a]	I[b]	II[c]	I[b]	II[c]
70.5	2.00	3.35	0.500	0.494
65.0	2.21	3.60	0.448	0.430
60.0	2.40	3.79	0.400	0.369

[a] $\theta'' = 70.5$, as usual. [b] Freely rotating chain. [c] More realistic model in which $g^{\pm}g^{\mp}$ states about C–Si–C skeletal bonds are entirely excluded.

In rotational isomeric state theory, the same simple equation results if the rotational states are located at $\phi = 0$, 120, and −120° and correspond to the same energy; it is in this sense that the PDMSM chain exhibits some characteristics of the idealized freely rotating chain. It differs of course from the freely rotating PDMSM chain in that $g^{\pm}g^{\mp}$ states about C–Si–C bonds are excluded because of pentane-type interferences. In the present formalism, therefore, the freely-rotating model of the PDMSM chain is obtained simply by the use of the statistical weight matrix containing all unities, as given by eq 1, for both $\mathbf{U}_a$ and $\mathbf{U}_b$. Values of $\langle r^2\rangle_0/nl^2$ and $\langle \mu^2\rangle_0/nm^2$ thus calculated for several illustrative values of the bond angle supplement θ' are given in the columns labeled I of Table II. Values of the same quantities were also calculated using the more realistic model obtained by restoring $\mathbf{U}_b$ to its original form, as given by eq 2, in which $g^{\pm}g^{\mp}$ states about C–Si–C bonds are entirely suppressed. These results are given in the columns labeled II. This important modification of the freely rotating chain is seen to increase $\langle r^2\rangle_0/nl^2$ significantly, because of the compactness[2,14,16] of $g^{\pm}g^{\mp}$ states which are excluded, but to have only a relatively small effect on $\langle \mu^2\rangle_0/nm^2$.

Since the discrepancy between theoretical and experimental values of the characteristic ratio (3.6 vs. 5.3) could be partially due to the uncertainty in θ', the dependence of $\langle r^2\rangle_0/nl^2$ and $\langle \mu^2\rangle_0/nm^2$ on θ' shown by the theoretical results given in the columns labeled II are of interest in this regard. They indicate that increase in this bond angle (decrease in θ') increases $\langle r^2\rangle_0/nl^2$ but decreases $\langle \mu^2\rangle_0/nm^2$. At a Si–C–Si bond angle of 120° ($\theta' = 60°$), the calculated value of $\langle r^2\rangle_0/nl^2$ is 3.8, in somewhat better agreement with the experimental value of 5.3. The value of $\langle \mu^2\rangle_0/nm^2$ becomes 0.37 which is also in better agreement with the experimental value 0.34 (calculated using $m = 0.60$ D, as is appropriate for $\theta' = 60°$).[1] Although agreement between theory and experiment is improved by this adjustment, additional structural information on appropriate small molecules would be required to justify the adoption of a Si–C–Si bond angle significantly larger than 115°. We therefore restore the Si–C–Si bond angle to 115° and explore the possibility that not all permitted conformational states in PDMSM chains are of exactly the same energy.

Detailed consideration of the structural characteristics of the PDMSM chain suggests that the difference between the partial charge on a skeletal CH_2 group and that on a pendant CH_3 group may be significant in this regard. Carbon atoms are more electronegative than silicon atoms[11,12] and in the PDMSM sequence $-Si(CH_3)_2-CH_2-Si(CH_3)_2-$ skeletal carbon atoms can withdraw electronic charge from two silicon atoms, but pendant carbon atoms can withdraw charge only from the single silicon atom to which they are appended. If this effect strongly predominates over charge distribution effects involving the single-electron hydrogen atoms, as would be expected, then the skeletal CH_2 groups should have a significantly larger negative partial charge than the pendant CH_3 groups. The effect of this difference in partial charges on the PDMSM conformational energies can probably be ignored except for interactions involving these groups at very small distances of separation. This suggests reconsideration of the statistical weights assigned to the conformations about the Si–C–Si bond pair which give rise to pentane-type interactions. For this elaboration of the model, we retain the statistical weight of unity for the tt state about such pairs of bonds; this conformation involves two pentane-type interactions, both between pendant CH_3 groups. In the $g^{\pm}g^{\mp}$ states, however, one of the pentane-type interactions occurs between skeletal CH_2 groups, of higher negative charge, and the Coulombic repulsions between these more highly charged groups may be sufficient to suppress the associated statistical weights significantly below the value of unity they were assigned in eq 1. Unfortunately, the Coulombic energy of this repulsion is almost impossible to calculate since, even if the partial charges were known, it is extremely difficult to obtain an estimate of the required effective dielectric constant of the medium. We therefore treat this statistical weight for $g^{\pm}g^{\mp}$ states about Si–C–Si bonds as an adjustable parameter $\omega < 1$. In a very approximate way, assignment of values less than unity to ω can be used to account for the fact that interactions between groups separated by more than four bonds could be important in the very compact $g^{\pm}g^{\mp}$ states;[20,24] such interactions may also contribute to the suppression of those states now characterized by the statistical weight ω. In this refinement, $\mathbf{U}_b$ is given by eq 2, and $\mathbf{U}_a$ by

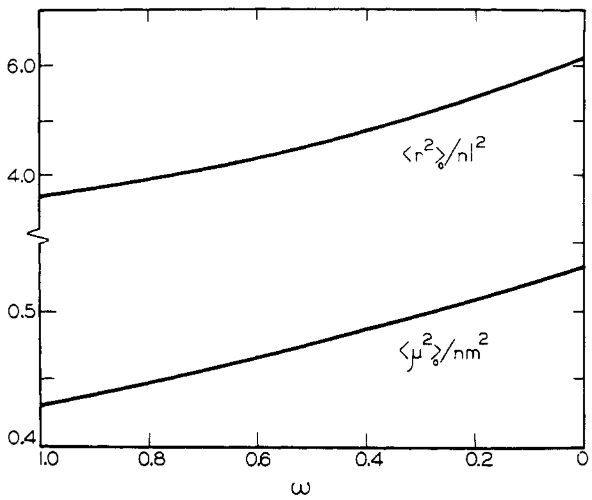

Figure 3. Values of the characteristic ratio and dipole moment ratio of PDMSM chains shown as a function of the statistical weight permitting the occurrence of $g^{\pm}g^{\mp}$ states about Si–C–Si skeletal bonds.

$$\mathbf{U}_a = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & \omega \\ 1 & \omega & 1 \end{bmatrix} \qquad (4)$$

Values of the characteristic ratio and dipole moment ratio calculated[14] from these statistical weight matrices are shown as a function of ω in Figure 3. Decrease in ω is seen to improve the agreement between the calculated values of $\langle r^2\rangle_0/nl^2$ and the experimental result 5.3, but to increase the difference between the calculated values of $\langle \mu^2\rangle_0/nm^2$ and the corresponding experimental value 0.39. The introduction of a statistical weight different from zero or unity also, of course, gives rise to a temperature dependence for both $\langle r^2\rangle_0$ and $\langle \mu^2\rangle_0$. Therefore values of d ln $\langle r^2\rangle_0/\mathrm{d}T$ and d ln $\langle \mu^2\rangle_0/\mathrm{d}T$, calculated for an average temperature

Table III
The Effect of the Parameter ω on Calculated Values of the Characteristic Ratio and Dipole Moment Ratio, and Their Temperature Coefficients, for the PDMSM Chain[a]

ω	$\langle r^2\rangle_0/nl^2$	$\langle \mu^2\rangle_0/nm^2$	$10^3 \mathrm{d} \ln \langle r^2\rangle_0/\mathrm{d}T$	$10^3 \mathrm{d} \ln \langle \mu^2\rangle_0/\mathrm{d}T$
1.00	3.60	0.430	0.00	0.00
0.86	3.83	0.442	−0.18	−0.09
0.71	4.09	0.456	−0.35	−0.16
0.57	4.40	0.470	−0.49	−0.22
0.29	5.14	0.500	−0.58	−0.23
0.10	5.75	0.520	−0.41	−0.12
0.00	6.21	0.531	0.00	0.00

[a] $\theta' = 65°$ throughout.

of 60°C, are included in the complete set of results shown in Table III. Careful comparisons between these calculated results and the corresponding experimental results[1] indicate that for this model, possibly still somewhat oversimplified, $\omega = 0.75$ gives the best presently attainable agreement between theory and experiment. Further refinements of the chain model for PDMSM must await more definitive information on the Si–C–Si bond angle and the charge distributions in appropriate small molecules. Also of great utility would be reliable interatomic potential functions for interactions involving Si atoms since this would permit direct semiempirical calculations of conformational energies of the PDMSM chain.

Conclusions

In summary, the best model for the PDMSM chain at the present time is one in which most conformational sequences are of identical energy. The only conformational states not of this type are $g^{\pm}g^{\mp}$ states about C–Si–C bond pairs which are totally suppressed because of interferences between very bulky $Si(CH_3)_2$ groups, and $g^{\pm}g^{\mp}$ states about Si–C–Si bond pairs which are partially suppressed, possibly because of Coulombic repulsions between relatively highly charged skeletal CH_2 groups. This model, although rather simplified, is at least semiquantitatively successful in that it explains the most striking configurational characteristics of the PDMSM chain.

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A Generalized van der Waals Equation for Polymers and Other Fluids

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ABSTRACT: A generalized van der Waals partition function is used to derive an equation of state for fluids containing small or large molecules. The derivation uses Prigogine's approximation that at liquid-like densities all external degrees of freedom can be considered as equivalent translational degrees of freedom. The new equation of state is therefore similar to Flory's but differs in three important respects: first, the equation is not restricted to high densities but goes to the ideal-gas limit as the density goes to zero; second, the free volume is given by the Carnahan–Starling expression; and third, the potential field is calculated from Alder's molecular-dynamics results using a square-well potential. The new equation of state represents well volumetric data of liquid polymers at high pressures. Characteristic parameters are given for 14 common polymers.

To obtain an equation of state for real fluids, including polymers, the most successful statistical-thermodynamic treatments are those based on the fundamental ideas of van der Waals: (1) the microstructure of the fluid is determined by the molecules' repulsive forces leading to the concept of free volume; (2) the contribution of attractive forces