Dipole Moments of Dimethylsiloxane Chains

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A rotational isomeric-state model with neighbor dependence is used to calculate mean-square dipole moments and their temperature coefficients for dimethylsiloxane chains $(CH_3)_3Si[OSi(CH_3)_2]_xOSi(CH_3)_3$ over a wide range of molecular weight. Chain conformational energies required in the calculations are obtained from a previous analysis of the random-coil dimensions of dimethylsiloxane chains in the limit of large x. Calculated dipole moments are in very good agreement with recently reported experimental results for oligomers corresponding to $x=1, 2, 3,$ and 5, at 25°, 40°, and 60°C. A simple physical picture for the predicted values of the dipole moments and their temperature coefficients is provided. As is the case in the interpretation of the dimensions of these chain molecules, the features of paramount importance are the inequality of the bond angles about Si and O atoms and the lower energy of *trans*, relative to *gauche*, states about Si–O and O–Si skeletal bonds.

INTRODUCTION

In the rotational isomeric-state representation of a chain molecule, each skeletal bond is assigned to one of a small number of discrete, rotational "states."[1,2] Since the accessibility of such states almost invariably depends on the rotational states of neighboring bonds, theoretical methods were developed to take into account this interdependence.[2-8] The resulting model for chain molecules has been remarkably successful in interpreting a wide variety of configuration-dependent properties. For example, studies have been carried out on (1) random-coil dimensions,[9-11] (2) dipole moments,[12-14] (3) helix–coil transitions,[15] (4) ring–chain equilibria,[16] (5) stereochemical equilibria,[17] (6) the Kerr effect,[18] and (7) strain birefringence.[19,20]

Studies on α,ω-dibromo-*n*-alkanes,[12] poly(ethylene

oxide),[13] and poly(tetramethylene oxide)[21,22] have demonstrated that conformational energies, or statistical weights, obtained from analyses of the random-coil dimensions of chain molecules of high molecular weight give predicted values of dipole moments and their temperature coefficients in good agreement with experiment over a wide range of molecular weight. Conformational energies have been determined for poly(dimethylsiloxane) (PDMS)[23]; their applicability to dimethylsiloxane (DMS) chains of any length has been demonstrated by the successful calculation of ring–chain equilibrium constants for DMS molecules having degrees of polymerization ranging from 15–200.[16]

Dasgupta and Smyth[24] have reported experimental values of the dipole moments of a number of DMS oligomers at several temperatures. These workers have, however, interpreted their results using a freely rotating chain model. Agreement between theoretical and experimental results was forced by modification of the bond dipole moments for each oligomer studied. The unsuitability of such a model for dimethylsiloxane chains can readily be seen by examination of space-filling molecular models. The abundance of interactions between methyl groups not only causes the various conformations or rotational states to differ in energy but also introduces interdependence, or cooperativeness, between such states.[23] A most compelling demonstration of the untenability of the approximation of free rotation for DMS chains has been given in the case of their random-coil dimensions in the limit of high molecular weight. Such dimensions are conveniently described by the *characteristic ratio* $\langle r^2 \rangle_0 / nl^2$ of the mean-square end-to-end distance $\langle r^2 \rangle_0$ unperturbed by long-range interactions[25] to the product nl^2, where n is the number

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[25] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, N.Y., 1953).

of skeletal bonds in the chain and l^2 is their mean-square length. Use of a freely rotating model for PDMS gives $\langle r^2 \rangle_0/nl^2 = 3.3$, and a temperature coefficient $10^3 d \ln \langle r^2 \rangle_0/dT = 0.0$.[23] The experimental values are 6.3[26] and 0.75,[27] respectively.

It is, therefore, the purpose of the present study to interpret experimental values of the dipole moments of DMS chains using a physically realistic model and independently determined conformational energies. Comparison of theoretical and experimental results should give an indication of the reliability and range of applicability of conclusions reached from the corresponding analysis of the chain dimensions, an approach restricted to high-molecular-weight materials by the nature of the experimental techniques employed in such investigations. In addition, such calculations may readily be extended to predict the general dependence of the dipole moments of these chains on both temperature and chain length.

THEORY

Rotational Statistical Weight Matrices

Each skeletal bond of the DMS chain is assigned to one of three rotational states: the *trans* (t) state and two *gauche* ($g^\pm$) states, located at bond dihedral angles ϕ of 0 and $\pm 120°$, respectively.[23] Generation of the partition function and the average values of configuration-dependent properties requires statistical weight matrices,[7,8,23,29] the elements of which are the statistical weights for pairs of bond conformations. These matrices have been established for DMS chains by analysis of their random-coil dimensions in the limit of high molecular weight[23]; they should, of course, apply to such chains of any molecular weight.[16] For pairs of bonds meeting at an oxygen atom, the matrix is[23]

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

where rows, associated with states of the Si–O bond, and columns, associated with the following O–Si bond, are indexed in the order t, g^+, g^-. The quantity σ is the statistical weight assigned to $tg^\pm$ and $g^\pm g^\pm$ bond pairs relative to an assignment of unity to tt and $g^\pm t$ pairs.[23] The factor ω is included to account for interactions in $g^\pm g^\mp$ conformations not present in $tg^\pm$ and $g^\pm g^\pm$ states. The corresponding matrix for conformations about

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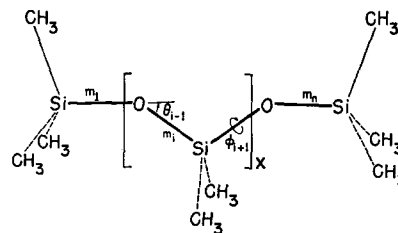[29] G. F. Newell and E. Montroll, Rev. Mod. Phys. **25**, 353 (1953).

FIG. 1. Schematic representation of the all-*trans* conformation of a DMS chain of degree of polymerization $x+1$. Solid, heavy lines represent bond dipole moments, and dotted lines, bonds out of the plane determined by the chain skeletal atoms.

pairs of skeletal bonds meeting at a silicon atom is

$$\mathbf{U}_b = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \psi\sigma & 0 \\ 1 & 0 & \psi\sigma \end{bmatrix}. \qquad (2)$$

The statistical weight ψ appearing therein takes into account the possibility of significant interactions occurring in $g^\pm g^\pm$ states (about O–Si–O bond pairs) which are not present in $tg^\pm$ states. *gauche* pairs $g^\pm g^\mp$ of opposite sign must be assigned statistical weights of zero because of the presence of severe steric repulsions between pendant methyl groups in these conformations.[23]

The statistical weights may be represented as Boltzmann factors in the energy E of the associated conformations:

$$\sigma = \exp(-E_\sigma/RT), \qquad (3)$$

$$\omega = \exp(-E_\omega/RT), \qquad (4)$$

$$\psi = \exp(-E_\psi/RT), \qquad (5)$$

where R is the gas constant and T the absolute temperature. Analysis of the chain dimensions of PDMS gave $E_\sigma = 0.85$ kcal mole^{-1}, this positive energy arising from the disruption of favorable methyl–methyl interactions by transitions $t \rightarrow g^\pm$ about either Si–O or O–Si bonds.[23] The value of the energy E_ω, which characterizes interactions between O atoms engendered in $g^\pm g^\mp$ conformations about Si–O–Si bonds, was found to be 1.05 kcal mole^{-1}.[23] The energy E_ψ was assumed to be zero on the basis of careful consideration of the interactions involved[23]; this assumption was shown to be of little importance because of the relative insensitivity of the chain dimensions to this parameter.

Calculations of interatomic distances suggest that interactions involving terminal bonds, such as those designated m_1 and m_n in Fig. 1, should not differ markedly from interactions occurring within the chain. Thus, to a good approximation, $\mathbf{U}_a$ and $\mathbf{U}_b$ apply to Si–O–Si and O–Si–O bond pairs, respectively, regardless of their location along the DMS chain.

TABLE I. Experimental dipole moments.[a]

x	$25°$	$40°$	$60°$
1	0.63_7	0.65_3	0.64_2
2	0.80_3	0.82_0	0.81_1
3	0.93_3	0.93_2	0.92_9
5	1.17	1.17	1.18

[a] Calculated from Ref. 24; units are debyes.

The Configuration Partition Function and Mean-Square Dipole Moment

The configuration partition function Z for the DMS chain shown in Fig. 1 is given by[23]

$$Z = \mathbf{J}^*(\mathbf{U}_a\mathbf{U}_b)^x\mathbf{U}_a\mathbf{J}, \qquad (6)$$

where $\mathbf{J}^* = [100]$ and $\mathbf{J}$ is the transpose of $[111]$. The mean-square dipole moment $\langle\mu^2\rangle_0$ of the chain in the absence of long-range interactions[25] will be expressed relative to nm^2, where $n = 2x+2$ is the number of Si–O and O–Si bonds and m^2 is their mean-square moment. The *dipole moment ratio* $\langle\mu^2\rangle_0/nm^2$ thus defined represents the factor by which the mean-square moment of the actual, unperturbed chain differs from that of the same chain in the idealization that all the skeletal bonds are freely jointed. Calculation of this ratio requires construction of right-handed Cartesian coordinate systems about each bond in the chain backbone.[30] If the x axis is taken along bond i and the positive y axis
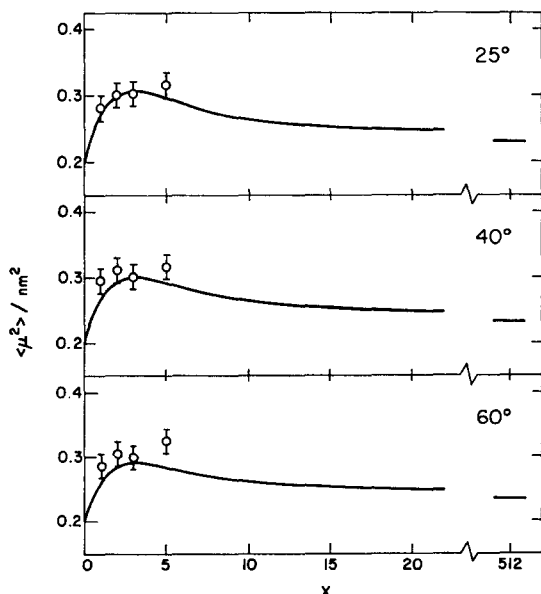
FIG. 2. The dipole moment ratio shown as a function of chain length for 25°, 40°, and 60°C. The experimental results are those of Dasgupta and Smyth.[24]

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in the plane determined by bonds i and $i-1$ and making an acute angle with bond $i-1$, then the matrix $\mathbf{T}$ which transforms a vector in coordinate system $i+1$ into that of system i is[7,8]

$$\mathbf{T}_i = \begin{bmatrix} \cos\theta_i & \sin\theta_i & 0 \\ \sin\theta_i\cos\phi_i & -\cos\theta_i\cos\phi_i & \sin\phi_i \\ \sin\theta_i\sin\phi_i & -\cos\theta_i\sin\phi_i & -\cos\phi_i \end{bmatrix}, \quad (7)$$

where the bond angle supplement θ and the rotational angle ϕ are illustrated in Fig. 1. The dipole moment ratio can then be calculated from[7,8,31]

$$\langle\mu^2\rangle_0/nm^2 = 2(Znm^2)^{-1}\mathbf{I}^*\mathbf{G}_1(\mathbf{G}_a\mathbf{G}_b)^x\mathbf{G}_a\mathbf{I}, \qquad (8)$$

where $\mathbf{I}^*$ is the row vector consisting of a single unity followed by fourteen zeros and $\mathbf{I}$ is the column vector consisting of 12 zeros followed by three unities. The
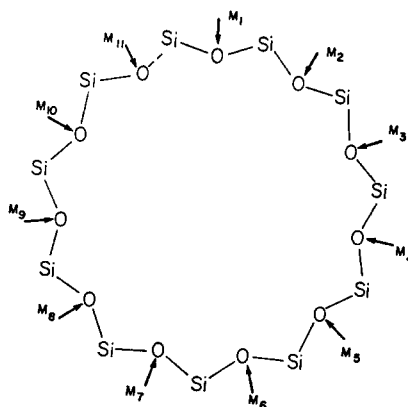
FIG. 3. The DMS chain backbone in the planar, all-*trans* conformation. Heavy lines represent group dipoles M for each Si–O–Si pair of bonds.

matrix $\mathbf{G}$ has the form[31]

$$\mathbf{G}_i = \begin{bmatrix} \mathbf{U} & (\mathbf{U}\otimes\mathbf{m}^T) \,||\, \mathbf{T} \,|| & (\tfrac{1}{2}m^2)\mathbf{U} \\ 0 & (\mathbf{U}\otimes\mathbf{E}_3) \,||\, \mathbf{T} \,|| & \mathbf{U}\otimes\mathbf{m} \\ 0 & 0 & \mathbf{U} \end{bmatrix}_i, \quad (9)$$

where the subscript on the brackets refers to all quantities contained therein; $\mathbf{U}_1$ required in $\mathbf{G}_1$ is simply the unit matrix $\mathbf{E}_3$ of order three. The symbol $\otimes$ denotes the matrix direct product,[7,8] and $\mathbf{m}$ is the bond moment vector

$$\mathbf{m} = \begin{bmatrix} m \\ 0 \\ 0 \end{bmatrix}, \qquad (10)$$

[31] P. J. Flory, *Statistical Mechanics of Chain Molecules* (Interscience Publishers, Inc., New York, 1968).

TABLE II. Calculated results. Dependence of the mean-square dipole moment on the statistical weights and temperature.

x	$\partial \ln \langle \mu^2 \rangle / \partial \ln\sigma$	$\partial \ln \langle \mu^2 \rangle / \partial \ln\omega$	$\partial \ln \langle \mu^2 \rangle / \partial \ln\psi$	$10^3 d \ln \langle \mu^2 \rangle / dT$
1	−0.118	0.000	−0.050	−0.57
2	−0.319	−0.002	−0.074	−1.55
3	−0.337	−0.007	−0.074	−1.66
4	−0.304	−0.008	−0.068	−1.51
5	−0.257	−0.008	−0.066	−1.28
7	−0.185	−0.008	−0.036	−0.94
10	−0.086	−0.004	−0.024	−0.44
20	+0.001	0.000	−0.002	+0.01
32	+0.064	+0.002	+0.010	+0.32
512	+0.138	+0.008	+0.028	+0.71

with $\mathbf{m}^T$ its transpose. The supermatrices $\| \mathbf{T}_i \|$ are defined by[7,8]

$$\| \mathbf{T}_i \| = \begin{bmatrix} \mathbf{T}_i(\phi_i=0°) & & \\ & \mathbf{T}_i(\phi_i=120°) & \\ & & \mathbf{T}_i(\phi_i=-120°) \end{bmatrix}. \quad (11)$$

EXPERIMENTAL RESULTS

Dasgupta and Smyth[24] have recently reported dielectric constants for DMS oligomers corresponding to $x=1$, 2, 3, and 5, in the undiluted liquid state, over a wide frequency range at 25°, 40°, and 60°C. These workers have demonstrated that these molecules have an unusually high atomic polarization; it is apparently the unjustified neglect of this contribution to the total polarization which is the cause of the inconsistencies in the dipole moments reported for these materials. Dipole moments calculated from their results are presented in Table I. It has been shown theoretically[32] and verified experimentally[33] that long-range interactions do not affect the mean-square dipole moment of a chain molecule in which the group moments lie within the plane bisecting the bond angle of one of the skeletal atoms. Since DMS chains obviously meet this requirement, the subscript zero on $\langle \mu^2 \rangle_0$ may henceforth be deleted; since long-range interactions are certainly of negligible effect in oligomeric chains,[13,25] the direct comparison of the experimental results of Dasgupta and Smyth with the theoretical results would be valid even if this structural requirement were not met. In order to facilitate such comparison, the square of each experimental dipole moment was divided by nm^2. The effective dipole moments m along the Si–O and O–Si bonds were calculated from the dipole moment, 0.38 D,[34] of hexamethyldisiloxane in the undiluted liquid state and the Si–O–Si bond angle, 143°, obtained by critical survey[23] of structural studies on appropriate compounds. The result obtained is $m_{\text{Si–O}} = -m_{\text{O–Si}} = 0.60$ D.[35] Although dipole moments of skeletal bonds within the chain may be expected to differ from those at the ends, the difference should be small,[24] and it is therefore a reasonable approximation to use the same dipole moment, ±0.60 D, for Si–O and O–Si bonds irrespective of their location along the chain molecule.

Experimental values of the dipole moment ratio, arbitrarily assigned an error limit of ±5%, are shown as a function of chain length and temperature in Fig. 2.

THEORETICAL RESULTS

Statistical weights at 25°, 40°, and 60° were obtained from Eqs. (3)–(5) using the conformational energies given above. Bond angles about Si and O atoms were taken to be 110° and 143°, respectively.[23] Equation (8) was then used to calculate values of the dipole moment ratio, at each temperature, for values of x ranging from 1–512; the results are shown in Fig. 2. The agreement between theory and experiment is excellent, the average discrepancy amounting to less than 6%. The dipole moment ratio is predicted to increase as x increases to 3 but should then decrease monotonically, reaching an asymptotic value of approximately 0.23 in the limit of large x. It is unfortunate that the experimental results do not cover a sufficiently wide range of x to indicate whether the predicted maxima shown in the curves of Fig. 2 do in fact occur.

The dependence of the mean-square dipole moment on the statistical weights was determined by extension of the calculations to a range of values of σ and ω. Although it was assumed that $\psi=1$ ($E_\psi=0$) in the calculations described above, other values of ψ were also investigated in order to determine the effect of this parameter on the dipole moments. The results for selected values of x are given in columns two through four of Table II. It is immediately evident that $\langle \mu^2 \rangle$, like $\langle r^2 \rangle_0$,[23] is quite insensitive to ψ. The dipole moment does, however, have a marked dependence on σ, particularly in the range $x=1–5$. The excellent agreement

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[33] J. Marchal and C. Lapp, J. Polymer Sci. 27, 571 (1958).

[34] S. Dasgupta, S. K. Garg, and C. P. Smyth, J. Am. Chem. Soc. 89, 2243 (1967).

[35] Dasgupta and Smyth assume a Si–O–Si bond angle of 150° and obtain $|m| = 0.73$ D. The expression of experimental and theoretical results as the ratio $\langle \mu^2 \rangle_0 / nm^2$ minimizes the effect of this difference.

between theory and experiment therefore strongly supports the previous result that $E_\sigma = 0.85$ kcal mole^{-1}, i.e., that *trans* states in DMS chains are approximately 0.85 kcal mole^{-1} lower in energy than *gauche* states.[23]

Temperature coefficients of $\langle\mu^2\rangle$ at 25°C were calculated using[23]

$$\frac{d\ln\langle\mu^2\rangle}{dT} = -T^{-1}\left(\ln\sigma\frac{\partial\ln\langle\mu^2\rangle}{\partial\ln\sigma} + \ln\omega\frac{\partial\ln\langle\mu^2\rangle}{\partial\ln\omega}\right) \quad (12)$$

and the entries of Columns 2 and 3 of Table II. (The assignment of $\psi = 1$ nullifies, of course, any contribution from this parameter.) The results are given in the final column of Table II. The predicted temperature coefficient is negative for small values of x, reaching a maximum magnitude at $x = 3$; thereafter, it increases monotonically, reaching a moderately large, positive value in the limit of large x. As can be seen from Table I and Fig. 2, the experimental results are of insufficient precision to permit comparison of experimental and predicted values of $d\ln\langle\mu^2\rangle/dT$.

DISCUSSION

Consideration of conformational energies and structural features of the DMS chain provides a simple physical picture of the configurational behavior described in the preceding section and illustrated in Fig. 2 and Table II. As has already been pointed out,[23,36] the most important structural aspect of such chains is the regular alternation of skeletal bond angles. As a direct consequence, the hypothetical, planar, all-*trans* conformation of these molecules traces out a series of closed polygons.[23] For chain molecules in which bond angle supplements at consecutive skeletal atoms alternate between θ_a and θ_b, the number of pairs of bonds per closed figure is $2\pi\,|\,\theta_a - \theta_b\,|^{-1}$. Thus, approximately 11 repeat units are required to form a closed structure in the case of DMS; it is shown diagramatically in Fig. 3. Since the *trans* state is of lower energy than the *gauche*, the preferred conformational sequences will be such closed figures, or portions thereof. The effect of this preference on the dipole moments can best be seen by considering the group dipoles M for each Si–O–Si bond pair. The considerable attenuation of the dipole vectors which occurs in such closed or partially closed conformations is the basis for the relatively low values, 0.2–0.3, found for $\langle\mu^2\rangle/nm^2$. Nonstatistical vectorial calculations indicate that for the all-*trans* conformation, addition of group dipoles beyond the fourth $(x = 3)$ *diminishes* the dipole moment ratio until the figure is completely closed. The effect is qualitatively apparent in Fig. 3 and is of course the basis for the maximum predicted for $\langle\mu^2\rangle/nm^2$ at $x = 3$ in Fig. 2.

As is evident from Table II, the sign and magnitude of $d\ln\langle\mu^2\rangle/dT$ depend primarily on the effect of transitions $t\rightarrow g^\pm$ about Si–O and O–Si bonds, the effect of transitions involving $g^\pm g^\mp$ states about Si–O–Si bond pairs being of minor importance. The magnitude of the effect of the $t\rightarrow g^\pm$ transitions depends of course on the extent to which attenuation of dipole vectors occurs in the oligomer under consideration. At $x = 3$ such attenuation is at a minimum, and it is therefore reasonable that the magnitude of $d\ln\langle\mu^2\rangle/dT$ be a maximum at this point. The moderately large, positive value predicted for this coefficient in the limit of large x is undoubtedly due to the decrease in this attenuation caused by $t\rightarrow g^\pm$ transitions as the temperature is increased. The same transitions, since they represent departure from a conformation having a very small end-to-end distance, are also the basis for the positive temperature coefficient of $\langle r^2\rangle_0$ observed for PDMS.[23,27]

The above predictions may perhaps be best tested by dielectric constant measurements on solutions of DMS oligomers, rather than by measurements on the pure liquids. It should be noted, however, that a large specific solvent effect on $\langle r^2\rangle_0$ has been observed for PDMS.[26,37] This complication could cause some uncertainty in the interpretation of such measurements.

ACKNOWLEDGMENT

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[37] Such effects are most pronounced for polar chain molecules, suggesting that they are due at least in part to the dependence of the Coulombic contribution to the conformational energy on the dielectric constant of the solvent medium.