Conformational Statistics of Poly(dimethylsiloxane). 1. Probability Distribution of Rotational Isomers from Molecular Dynamics Simulations

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ABSTRACT: The probability distribution of isomeric conformations in poly(dimethylsiloxane) has been investigated both by conformational energy considerations and by molecular dynamics simulations. A comparatively smooth distribution of isomeric states is obtained from both approaches. The molecular dynamics trajectory of a simulated dimethylsiloxane oligomer of eight units is used as a reliable and realistic tool to estimate the probability of occurrence for various rotational isomeric states. Conformations involving bonds in the gauche state produce attractive intramolecular potentials through suitable spatial arrangement of close neighbors, which is contradictory to the unfavorable interactions attributed to them in the model described by Flory, Crescenzi, and Mark. The relative potential energies of the various conformational states are obtained from the probability of those conformations occurring in a molecular dynamics simulation.

I. Introduction

The unique physical properties of poly(dimethylsiloxane) (PDMS) make it an interesting polymer from both a commercial and theoretical point of view. The importance of silicon-containing polymers is outlined in a recent review.[1] PDMS chains are able to occupy many conformations because of their flexibility and molecular geometry.[2] The occurrence of relatively long backbone bonds (1.63 Å) supplemented by the large and highly flexible bond angle of Si–O–Si, plays a major role in relieving most of the unfavorable intramolecular interactions that would otherwise oppose or even inhibit bond rotations. The torsional barrier around the Si–O bond is on the order of a few tenths of a kilocalorie per mole as was first pointed out by Scott and collaborators.[3] Recent detailed studies of the conformational energetics of organosilicon and polysiloxane derivatives by Grigoras and Lane[4,5] corroborate the experimentally measured torsional barriers in hexamethyldisiloxane and the unusually high flexibility of the Si–O–Si bond angle. The O–Si–O bond angle, on the other hand, is much more rigid and almost tetrahedral. The significant difference (>30°) between the two consecutive bond angles leads to a cyclic structure for the planar trans conformation in about 11 units, as may be inferred from Figure 1. This molecular feature gives rise to unusual macroscopic properties such as a contraction of the chain as the number of bonds in the trans state increases.

Although the backbone bonds in PDMS enjoy a high degree of freedom insofar as the torsional mobility and bond bending flexibility are concerned, previous calculations have indicated that the extreme case of a freely rotating chain is not applicable. Intramolecular energetics controlling the distribution of accessible conformations should be incorporated into the theoretical treatment of its conformational statistics. In this respect, the adoption of a discrete set of conformations based on three equally spaced rotameric states, trans (t), gauche$^+$ (g$^+$), and gauche$^-$ (g$^-$), appears to be an acceptable mathematical device to approximate the more or less uniform distribution of backbone torsional angles.[2] From the ab initio molecular orbital computations by Grigoras and Lane,[4,5] it is observed that the first-order interaction energy associated with the occurrence of gauche bonds is comparable in magnitude and even slightly lower in energy than that of bonds in the trans state. This result is in marked contrast to the model introduced by Flory, Crescenzi, and Mark (FCM).[2,6] In fact, a first-order interaction energy of 0.85 kcal/mol for the gauche state above the trans state is estimated in the FCM model. The FCM model predicts a repulsive second-order interaction energy for the pairs of gauche bonds of opposite chirality about the oxygen atom, therefore suppressing the occurrence of g$^+$g$^-$ and g$^-$g$^+$ states. However, the molecular mechanics analysis presented below demonstrates that those unfavorable interactions may be substantially alleviated and even transformed into attractive interatomic potentials by slight distortion of the chain geometry. On the basis of these considerations, a revision of the theoretical treatment of PDMS conformational statistics seems mandatory.

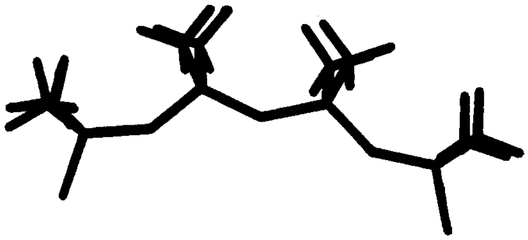

Figure 1. Schematic representation of a portion of a poly(dimethylsiloxane) chain. All internal bonds between O and Si are in the planar (all trans, defined by the torsional angle $\phi_i = 180°$, for a given bond i) configuration.

Although the potential energy for the isomeric states adopted in the FCM model is not in accordance with the conformational energy surfaces used here, their model satisfactorily reproduces the experimentally observed unperturbed mean-square end-to-end distance $\langle r^2 \rangle_0$[7] and its temperature coefficient d ln $\langle r^2 \rangle_0/\mathrm{d}T$.[8] The FCM model also gives a reasonable account of the experimentally measured mean-square dipole moments $<\mu^2>_0$. However, a serious disagreement is present between the experimentally observed[10] cyclization probabilities for oligomers of PDMS and the predictions of the FCM model.[11-13] The cyclization equilibrium constants K_x measured for the oligomers with x = 4–6 repeat units turn out to be about 4 orders of magnitude higher than those computed upon the complete enumeration of the cyclic conformations of the FCM model.[12]

A theoretical fit to the experimental findings is achieved only through the assignment of large statistical weights to specific conformations involving sequences of g^+g^- or g^-g^+ bonds, which are practically precluded in the FCM model. In contrast to the range $4 \geq x \geq 6$, the concentration of cyclic conformers predicted by the FCM model is overestimated in the range x = 10–12, compared to experimental results.[13] This inadequacy is attributed to an overestimation of the statistical weight for the planar all-trans conformation in the FCM model, leading to an overestimate of the probability of cyclic conformers at x = 11, which corresponds to closure of the ring.[11] It is asserted by Semlyen that the experimental values of K_x furnish a good test of a given theoretical model, which can be modified as more structural and conformational data become available.[11] Recent rigorous studies by Grigoras and Lane[4,5] and present computational facilities allow for such a test.

Two major features led us to a more critical examination of the conformational statistics of PDMS chains: (i) the fact that the potential energy parameters in the currently used theoretical model (FCM) cannot be rationalized on the basis of recent structural and conformational data, and (ii) the existence of a severe discrepancy between experimental and theoretical cyclization equilibria.

The geometrical parameters adopted in the following study will be 1.63 Å for the Si–O bond lengths together with 110° and 145° for the O–Si–O and Si–O–Si bond angles, respectively. The analysis of Grigoras and Lane indicates slightly larger (150°) Si–O–Si bond angles. The use of our structural parameters, which are identical with those of the FCM model, is justifiable in light of experimental evidence including X-ray and electron diffraction measurements. Three rotameric states will be identified by torsional angles of 180° (trans), 300° (gauche$^+$), and 60° (gauche$^-$). The validity of those stable states will be discussed in relation to the energy distribution in conformational space. In contrast to the geometrical parameters, the energy parameters of the FCM model will be subject to substantial modification. The objective is a set of energy parameters that will simultaneously explain the cumulating experimental information on the unperturbed dimensions, their temperature dependence, the dielectric behavior in solution, and the cyclization equilibrium and be compatible with the conformational energetics determined from ab initio computations and conventional molecular mechanics considerations.

The present work consists of a general survey of the short-range intramolecular energetics in PDMS. Two methods will be used to investigate the types and probabilities of accessible isomeric conformers. First, a molecular mechanics approach to determine the conformational potential energy surface associated with the torsions of adjacent skeletal bonds will be undertaken. Second, a molecular dynamics (MD) simulation will be carried out to assess the relative probabilities of occurrence for various conformers from the time period spent by the individual bonds in definite domains of the conformational energy surface. The MD simulation permits the extraction of information about static properties, which should be supplementary if not equivalent to that obtained from conformational energy calculations. It may be supplementary in the sense that the occurrence of specific isomeric states for skeletal bonds is necessarily coupled to the state of neighbors beyond nearest neighbors along the chain, thus automatically incorporating large-scale effects that can be overlooked in the examination of short representative segments.

In the following paper,[14] a brief recapitulation of the RIS formalism will be presented and the predictions of the theory will be analyzed through variation of energy parameters within reasonable ranges inferred from both the conformational probability distribution estimated in section II and the energy functions reported by Grigoras and Lane.[4,5] The applicability of the new energy parameters to PDMS will be assessed through comparison with experimental findings.

II. Conformational Energetics

On the basis of the postulate of pairwise interdependence of skeletal bonds, the change in the short-range intramolecular potential is investigated as a function of the simultaneous rotations of two adjacent skeletal bonds. Two distinct pairs of bonds, one pair centered on the Si atom and the other pair centered on the O atom, are separately investigated. One pair is analyzed as the central pair of bonds in a methoxy-terminated segment of three dimethylsiloxane groups (39 atoms). The other pair is analyzed as the central pair of bonds in a methoxy-terminated segment of four dimethylsiloxane groups (49 atoms). In both cases the conformational energy surface is searched by constraining the torsional angles of the bond pair and minimizing all other contributions to the potential energy. The potential energy evaluated consists of terms for bond bending, bond stretching, interatomic van der Waals interactions, and torsional rotations of bonds in the segment not including the torsional angles of the constrained bond pair. The conjugate gradient energy minimization scheme and the Sybyl force field from Tripos[15] were used. Additional parameters for the silicon atom are adapted from the work of Frierson[16] as indicated in Table I. The torsional angles of bond pairs are then varied in 10° intervals until all combinations of the torsional angles for the pair have been evaluated.

The potential energy surfaces evaluated for both pairs of bonds are found to exhibit a nearly flat potential energy surface, making it difficult to distinguish the precise location of isomeric minima and the saddle heights in between them. The precise locations of the isomeric minima are thus found in another way. A local minimum is found by suitable relaxation of all atoms in the segments investigated starting from a position of torsional angles near a local minimum deduced from the potential energy surfaces found above. The results are listed to Tables II and III for the pairs (O–Si, Si–O) and (Si–O, O–Si), respectively. At the beginning of each minimization all bonds in the segment are assumed to be in the planar trans form except for the two central bonds, whose original torsional angles (ϕ_i, ϕ_{i+1}) are indicated by the first two columns in each table.

A root-mean-square gradient of 0.001 kcal/mol is adopted for the potential energy change as the criteria of

Table I
Energy and Geometry Parameters for PDMS

bond	lengths (l_0), Å	stretching constants (k), kcal/(mol Å^2)	energy function
Si–O	1.63	147.0	$E = k(l - l_0)^2$
Si–C	1.90	107.0	
C–H	1.10	355.0	
Si–H	1.50	500.0	

bond	angles, (θ_0), deg	bending constants (k), kcal/(mol rad^2)	energy function
Si–O–Si	145	5.4	$E = k(\theta - \theta_0)^2$
O–Si–O	110	16.2	
O–Si–C	109.5	3.6	
C–Si–C	109.5	17.2	
H–C–Si	109.5	11.5	
C–O–Si	122.0	5.4	

torsion angles	torsion constants (k), kcal/mol	energy function
X–Si–O–X	0.03	$E = k(1 + \cos 3\phi)$
X–C–Si–X	0.05	

	van der Waals param (e_0), kcal	R_0, Å	energy function
Si	0.040	2.00	
C	0.090	1.80	
O	0.159	1.60	$E = e_0[(R_0/R_{ij})^{12} - 2(R_0/R_{ij})^6]$
H	0.045	1.47	

Table II
Location and Energies of Isomeric Minima for O–Si–O

starting torsions		minimized torsions		
ϕ_i, deg	ϕ_{i+1}, deg	ϕ_i, deg	ϕ_{i+1}, deg	energies, kcal/mol
180	180	196.6	196.6	0.00
180	60	197.0	54.7	–0.35
		193.8	51.8	–0.30[a]
		169.4	53.2	–0.30[a]
		193.0	22.8	–0.26[a]
		196.4	26.6	–0.25
60	60	51.8	34.4	0.14
		97.8	47.1	0.19

[a] Possible only if bond $i - 1$ is such that the resulting conformation for the three successive bonds becomes $g^-g^+g^-$ or $g^+g^-g^+$.

Table III
Location and Energies of Isomeric Minima for Si–O–Si

starting torsions		minimized torsions		
ϕ_i, deg	ϕ_{i+1}, deg	ϕ_i, deg	ϕ_{i+1}, deg	energies, kcal/mol
180	180	197.7	195.8	0.00
180	60	213.7	55.6	–0.29
		170.0	26.1	–0.14
		210.0	54.1	–0.07
		172.1	17.7	–0.04
60	60	69.8	65.9	–0.28
60	300	56.5	314.7	–1.92[a]
		38.5	341.3	–1.19
		17.0	331.9	–0.96

[a] Possible only if bonds $i - 1$ and $i + 2$ assume the state (g^-, t) or t, g^+), so as to lead to the joint configuration $g^-g^+g^-t$ and $tg^+g^-g^+$ (or their mirror images), respectively.

complete minimization. The final rotational states, corresponding to a local minimum energy, are shown in columns 3 and 4 of the tables. The last column gives the conformational energies relative to the tt minimum. For brevity only a reduced set of torsional angles is listed. The conformations corresponding to mirror images and/or opposite rotations may be readily deduced from them.

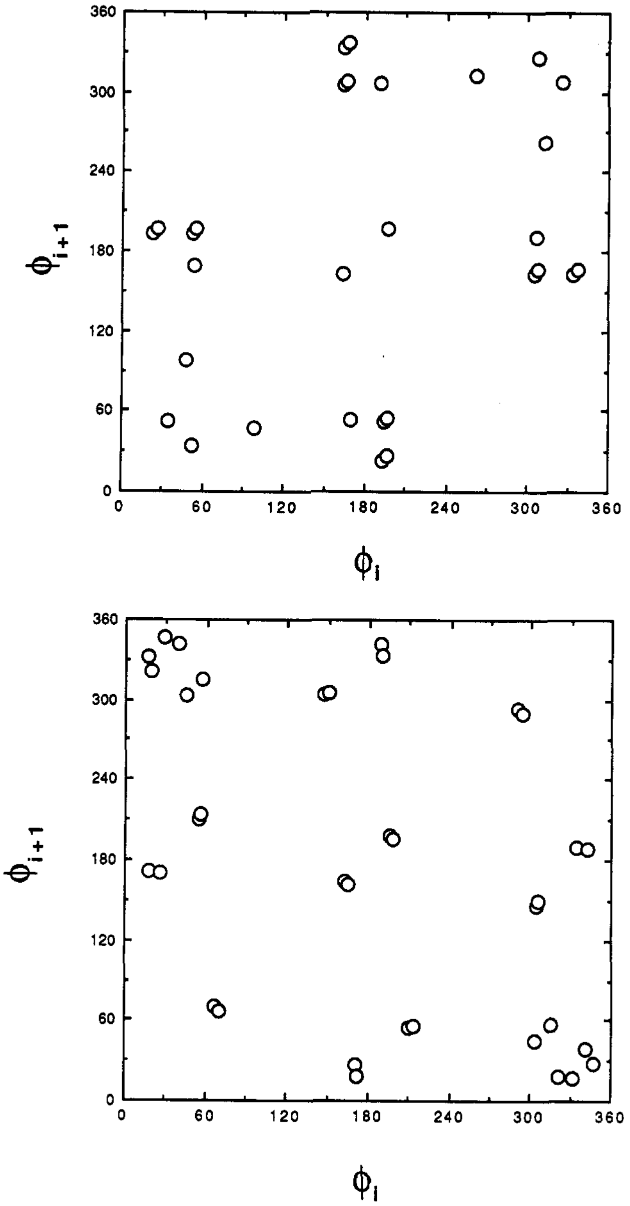

Figure 2. (a) Location of the rotational isomeric minima in the conformational energy map for the pair of bonds (O–Si, Si–O). The ordinate and the abscissa refer to the torsional angles ϕ_i and ϕ_{i+1} of the bonds O–Si and Si–O, respectively. The corresponding energy values are listed in Table II. (b) Location of the rotational isomeric minima in the conformational energy map for the pair of bonds (Si–O, O–Si). The ordinate and the abscissa refer to the torsional angles ϕ_i and ϕ_{i+1} of the bonds Si–O and O–Si, respectively. The corresponding energy values are listed in Table III.

For clarity the isomeric minima are displayed in parts a and b of Figure 2. Although the minima are rather scattered over the energy surfaces, it is still possible to distinguish domains, which may be identified with the t, g^+, and g^- rotations. From a close look at the computed energy minima we note that the trans state is always displaced by about 20° from the planar conformation, in parallel with the results from Grigoras and Lane's computations.[4,5] Also in agreement with the shape of the energy curves obtained by Grigoras and Lane, the gauche states for the bonds flanking the O atom are split into two minima centered at about 20° and 60° (gauche$^-$) or 340° and 300° (gauche$^+$). The minima that approximate the cis conformation (20° or 340°) are found to be particularly favorable in the case of a succession of gauche bonds of opposite chirality as may be observed from the set of data at the end of Table III. Attempts to locate a minimum for bonds flanking the Si atom identified as g^+g^- or g^-g^+ states failed inasmuch as the potential surface does not

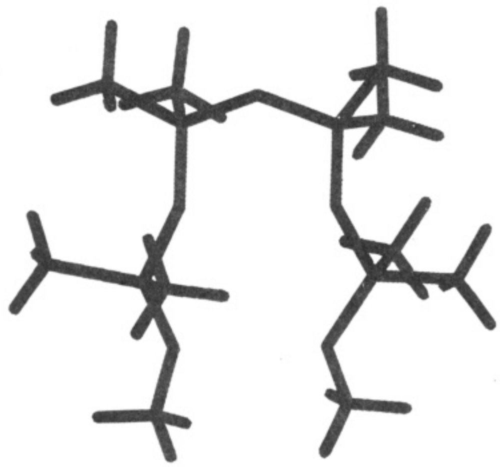

Figure 3. Schematic representation of a low-energy g^-g^+ configuration assumed by the central pair of bonds (Si–O, O–Si) in the segment used in energy minimization. All neighboring Si–O and C–O bonds are in the trans state. The torsional angles of the central bonds are (38.5°, 341.3°), and the prevailing energy is by 1.19 kcal/mol lower than that of the optimal tt state.

present a stable well in that region unless the neighboring bonds are allowed to assume gauche states as indicated in the footnote of Table II.

A general feature determined from the energy minima is the occurrence of favorable intramolecular interactions in the presence of gauche bonds. Thus the more compact conformations lead to interatomic separations suitable for attractive interactions rather than repulsive interferences. We note in particular that for the pair (Si–O, O–Si) the g^+g^- or g^-g^+ state, which was assigned a rather low probability of occurrence in previous theoretical studies,[6] appears, on the contrary, as a rather stable conformation. The spatial distribution of atoms in this case is displayed in Figure 3. In the molecule shown, CH_3O-$[Si(CH_3)_2O]_4CH_3^-$, all O–Si and O–C bonds are in the trans state except for the two central bonds, which assume the torsional angles 38.5° and 341.3°. This conformation is stabilized by the attractive interactions between the tails surrounding the g^-g^+ bonds. Further stabilization of g^-g^+ occurs if the neighboring bonds on either side produce the conformation $g^+g^-g^+t$ as stated in the footnote in Table III.

Before concluding this section it should be mentioned that the comparatively low energies reached in the minimization scheme require cooperative relaxation of all atoms in the investigated segment and may be opposed by chain connectivity in longer polymeric chains. A more realistic estimation of the statistical weights of the respective conformations is provided by MD simulations as will be presented below.

III. Molecular Dynamics Simulations

A. General Approach. Molecular dynamics (MD) simulations have been carried out by using the version of CHARMM[17] supplied by the Polygen Corp.[18] with the energy and geometry parameters given in Table I. In a recent study,[19] CHARMM has proven to satisfactorily reflect the dynamics of polymethylene. The trajectory of a methoxy-terminated chain of eight monomeric units of dimethylsiloxane is analyzed in the present work. A thorough description of the MD technique is given in a recent review by Brooks, Karplus, and Pettitt.[20]

In the present work the equations of motion are integrated every 0.5 fs at a temperature of 300 K. After equilibration at 300 K the temperature is computed every 500 fs, and, if it is found to be out of the range 300 ± 10 K, the velocities of all the atoms are rescaled to preserve isothermal conditions.

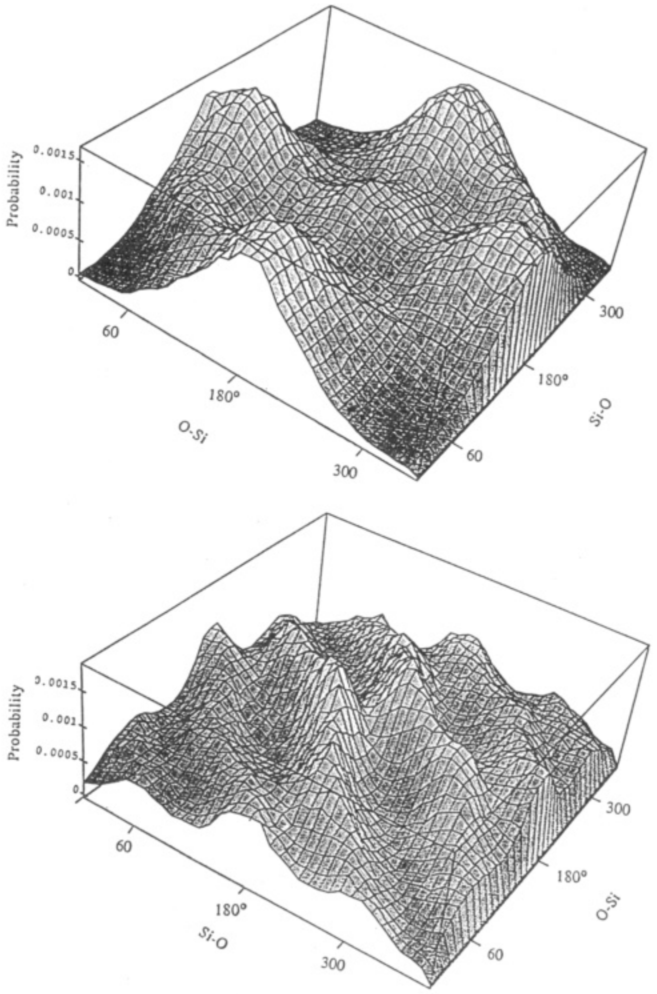

Figure 4. (a) Probability distribution of adjacent torsional angles in the pair of bonds (O–Si, Si–O), at 300 K. The probabilities $P(\phi_i,\phi_{i+1})$ are indicated by the height of the surface at a given combination of torsional angles (ϕ_i, ϕ_{i+1}). (b) Probability distribution of adjacent torsional angles in the pair of bonds (Si–O, O–Si), at 300 K. The probabilities $P(\phi_i,\phi_{i+1})$ are indicated by the height of the surface at a given combination of torsional angles (ϕ_i, ϕ_{i+1}).

Inasmuch as the object of the MD simulations is to gain some information on the probability distribution of rotameric states, we confine our attention to the residence time of each pair of bonds in 36^2 small regions of conformational space. Those regions are defined by the simultaneous torsional angles of two consecutive bonds and are selected with intervals of 10° along each direction. The pairs of bonds (O–Si, Si–O) and (Si–O, O–Si) are independently analyzed to evaluate the probability of each combination of (ϕ_i, ϕ_{i+1}). Data are recorded every 10 fs during a total simulation period of 1.8 ns. Therefore, in each specific region of the probability surface with dimensions $(\Delta\phi_i, \Delta\phi_{i+1}) = (10°, 10°)$, an average of ~1000 samples is recorded, which furnishes statistically reliable results, as will be demonstrated below.

The resulting probability distributions $P(\phi_i,\phi_{i+1})$ are displayed in parts a and b of Figure 4 for the pairs centered on Si and on O, respectively. The *x* and *y* directions in the diagrams refer to the complete revolution of the torsional angles ϕ_i and ϕ_{i+1}, while the *z* direction represents the statistical weight of a given square 10° on a side. Those values are normalized such that the total probability is

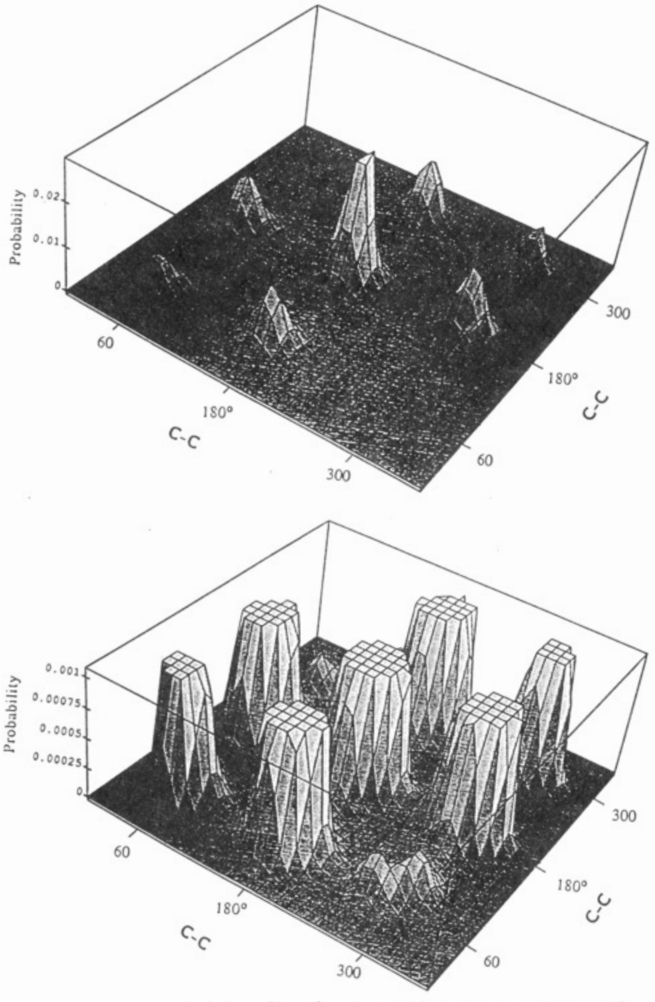

Figure 5. (a) Probability distribution surface for two consecutive internal C–C bonds in polyethylene at 300 K. (b) Same as part a, except that the scale of the probabilities is magnified to show the splitting of the g^+g^- state.

unity. For comparative purposes the same diagram obtained with polymethylene is given in Figure 5a. It may be clearly seen from the peaks in this figure that polymethylene exhibits a strong preference for the tt state. The $tg^\pm$ and $g^\pm t$ states occur less frequently while the g^+g^- (or g^-g^+) state is almost completely suppressed. The closer examination depicted in Figure 5b reveals the splitting of the minimum in the g^+g^- and g^-g^+ regions into two peaks, in agreement with the well-established conformational statistics of polymethylene.[21] In contrast to the structured probability distribution of polymethylene, the bonds in PDMS assume almost any rotation over the whole space and it is harder to discern any rotational state that is predominantly preferred. From Figure 4a it is observed that the g^+g^- (or g^-g^+) states are relatively less frequent, though not totally precluded. It is interesting to note that $tg^\pm$ and $g^\pm t$ states are slightly more probable than the tt state. The breadth of the peaks is such that the probability of tc and ct (where c denotes cis) is nearly as large as the maximum probability at $tg^\pm$ and $g^\pm t$. As to Figure 4b it becomes even harder to locate most probable conformations although an approximate 3-fold symmetry is discernible.

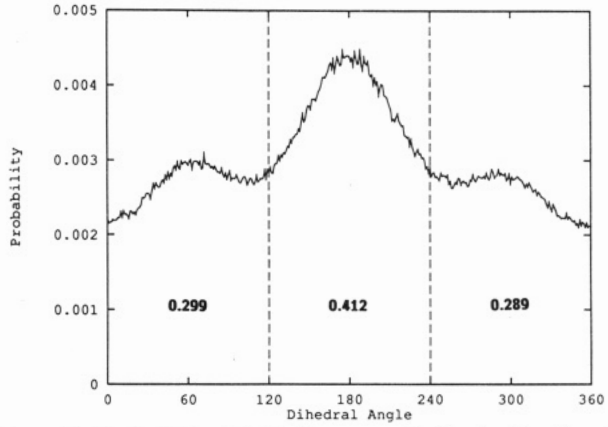

Figure 6. Probability distribution curve for the torsional angle ϕ_i for any randomly chosen internal Si–O bond i in PDMS, resulting from the MD trajectory of the oligomer of eight units, at 300 K.

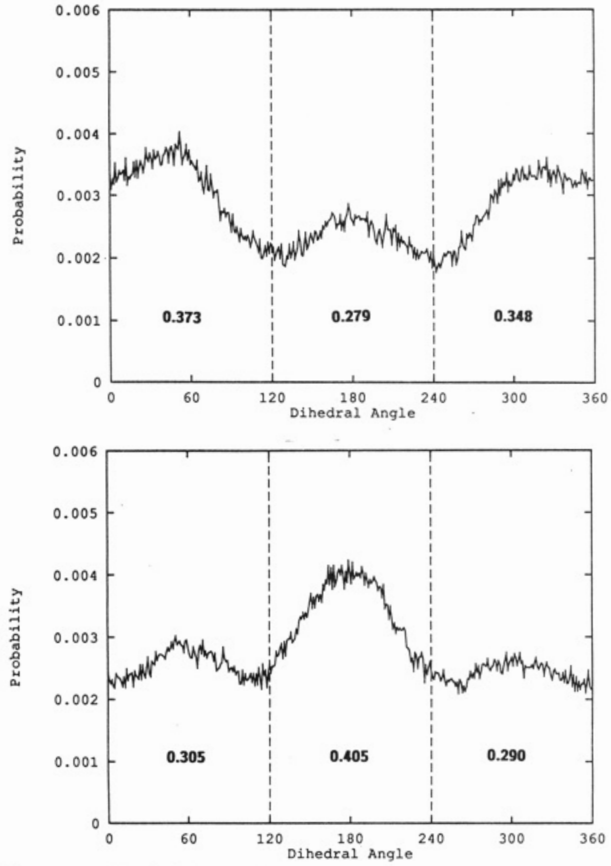

Figure 7. Probability $P(\phi_{i+1}/\phi_i{=}t)$ of occurrence of a given torsional angle ϕ_{i+1} for the $(i + 1)$ skeletal bond (a) Si–O and (b) O–Si in PDMS, at 300 K, provided that the preceding bond assumes the state trans.

B. Probability Distribution of Rotameric States. For a clearer understanding of the types and probabilities of different conformers, we confined our attention to specific slices of the 3D diagrams depicted in parts a and b of Figure 4. As a first analysis the probability of occupancy of each rotameric state has been investigated for any skeletal bond i, regardless of the state of the neighbors. The normalized distribution $P(\phi_i)$ of ϕ_i is displayed in Figure 6. In the approximation where the chain is assumed to be constructed from independent bonds subject to a symmetric 3-fold rotation potential, i.e.

$$Z = (1 + 2\sigma)^{n-2} \tag{1}$$

where Z denotes the conformational partition function, the best value for σ can be obtained directly from Figure 6 as $\sigma = 0.71$.

A quantitative assessment of the influence of higher order interactions on chain statistics necessitates the consideration of conditional probabilities. For each pair

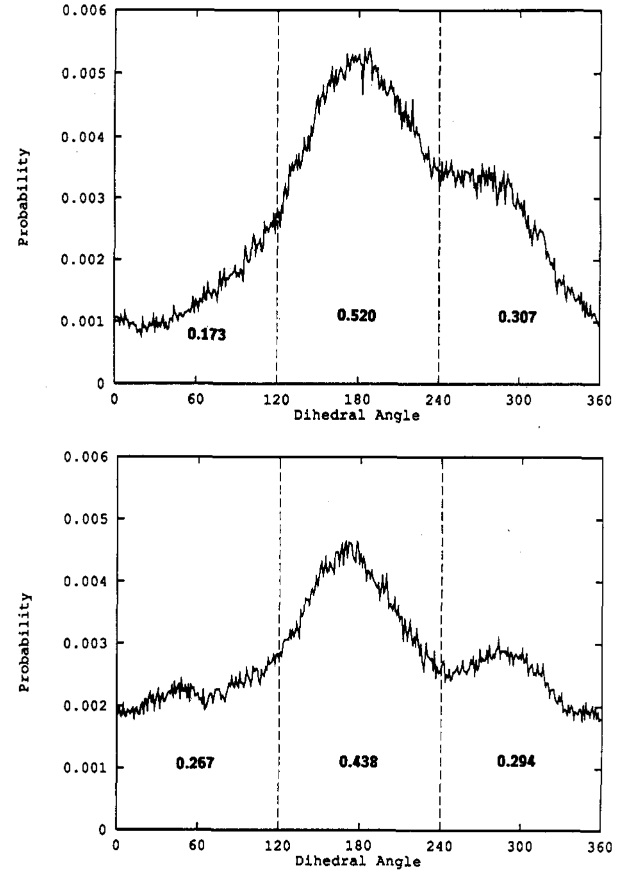

Figure 8. Probability $P(\phi_{i+1}/\phi_i{=}g^+)$ of occurrence of a given torsional angle ϕ_{i+1} for the $(i+1)$ skeletal bond (a) Si–O and (b) O–Si in PDMS, at 300 K, provided that the preceding bond assumes the state gauche$^+$.

of bonds of specific adjoining states the probability of occurrence has been investigated. For that purpose t, g$^+$, and g$^-$ states have been identified with a range of torsion angles (120°, 240°), (0°, 120°), and (240°, 360°), respectively. Those comparatively broad ranges of torsional angles are selected in view of the diffuse distribution of rotations deduced both from parts a and b of Figure 4 and from the energy calculations presented above. To estimate the type and strength of second-order interactions, it is possible to calculate the conditional probability by counting all incidence of bond $i + 1$ when bond i is in a particular torsional angle. This particular analysis applied to the case where bonds i and $i + 1$ are of the type (O–Si, Si–O), and the first bond is in the t state, yields the curve displayed in Figure 7a. Repeating the same procedure for the pair of bonds (Si–O, O–Si) leads to Figure 7b. Similar analysis applied to bonds in the g$^-$ state results in the probabilities in parts a and b of Figure 8 for the two bond pairs. Thus the ordinate in parts a and b of Figure 8 represents the probability $P(\phi_{i+1}/\phi_i{=}g^-)$ of the torsion ϕ_{i+1} indicated by the abscissa. The probabilities are normalized such that the area enclosed by the curve equates to unity in each of the Figures 6–8.

From Figure 6, the probabilities of the three ranges of torsional angles identified here with t, g$^+$, or g$^-$ rotational states above are of comparable magnitude, though the trans state is favored slightly. However, according to Figure 7a, the tg$^+$ or tg$^-$ states for the pair of bonds (O–Si, Si–O) are more probable than the tt state, in agreement with the conformational energy calculations carried out in section II. Although energy minimization yields slightly lower energy values for the tg$^+$ or tg$^-$ states of (Si–O, O–Si) compared to tt, MD result exhibit a weak preference for the tt state as shown in Figure 7b. The MD method is expected to be more reliable inasmuch as the observed behavior results from the cooperative motion of several bonds along the chain and allows bending of the unusually flexible Si–O–Si angle, thus automatically incorporating real chain interactions and constraints. The same argument can be extended to the comparatively low energies reached through energy minimization for the g$^-$g$^+$ or g$^+$g$^-$ states of the pair of bonds (Si–O, O–Si), as listed in Table II. The MD simulations demonstrate that in real chains the contribution of those low-energy states is negligibly small and the majority of conformations that may be classified within g$^-$g$^+$ or g$^+$g$^-$ states possess slightly higher energies than other rotameric pairs. However, the g$^-$g$^+$ and g$^+$g$^-$ states for the pair of bonds (O–Si, Si–O) exhibit finite, nonzero probabilities, which rule out the FCM model that totally prohibits their occurrence.

C. Evaluation of Conformational Energy Parameters. In the above subsection the results from the MD trajectory of a representative oligomeric chain have been qualitatively analyzed and discussed in relation to the results from a more conventional energy minimization approach. The probability distribution curves obtained from MD simulations may be used as a tool to assess the energies of various rotational isomeric states, provided that a Boltzmann distribution of isomers is accepted. We should rigorously start from an expression for Z that uses different statistical weight matrices for the Si–O and O–Si bonds.

$$Z = \mathbf{U}_a\mathbf{U}_b\mathbf{U}_a\mathbf{U}_b \ldots \mathbf{U}_a\mathbf{U}_b \tag{2}$$

However, in view of the relatively weak second-order interactions, the brief development presented here will start from

$$Z = \mathbf{U}\mathbf{U} \ldots \mathbf{U} \tag{3}$$

which is rigorously correct for a simple chain such as polymethylene where all internal bonds have the same statistical weight matrix

$$\mathbf{U} = \begin{bmatrix} \tau & 2\sigma \\ 1 & \sigma(\psi+\omega) \end{bmatrix} \tag{4}$$

with eigenvalues

$$\lambda_{1,2} = \left(\frac{1}{2}\right)\{\tau + \sigma(\psi+\omega) \pm [(\tau - \sigma(\psi+\omega))^2 + 8\sigma]^{1/2}\} \tag{5}$$

The probabilities we seek are

$$p(g^+) = P(g^-) = [2(n-2)]^{-1}(\partial \ln Z/\partial \ln \sigma) \tag{6}$$

$$P(t) = 1 - P(g^+) - P(g^-) \tag{7}$$

$$P(tt) = (n-3)^{-1}(\partial \ln Z/\partial \ln \tau) \tag{8}$$

$$P(g^+g^+) = P(g^-g^-) = [2(n-3)]^{-1}(\partial \ln Z/\partial \ln \psi) \tag{9}$$

$$P(g^+g^-) = P(g^-g^+) = [2(n-3)]^{-1}(\partial \ln Z/\partial \ln \omega) \tag{10}$$

$$\begin{aligned} P(tg^+) = P(tg^-) = P(g^+t) = P(g^-t) = (4)^{-1}(1 - P(tt) - \\ P(g^+g^+) - P(g^-g^-) - P(g^+g^-) - P(g^-g^+)) \end{aligned} \tag{11}$$

In the limit as $n \to \infty$, when $Z \to (\text{constant})\lambda_1^{n-2}$, eqs 5–11 lead ultimately to[22]

$$\sigma = (\tau - \lambda_2)^2[P(g^+)/P(t)] \quad (12)$$

$$\tau = (\tau - \lambda_2)[P(tt)\,P(g^+)/P(tg^+)\,P(t)] \quad (13)$$

$$\psi^2 = (\tau - \lambda_2)^{-1}[P(g^+g^+)\,P(t)/P(g^+t)\,P(g^+)] \quad (14)$$

$$\omega = (\tau - \lambda_2)^{-1}[P(g^+g^-)\,P(t)/P(g^+t)\,P(g^-)] \quad (15)$$

The numerical labor required for the evaluation of σ, τ, ψ, and ω from the probabilities via eqs 12–15 depends on the importance of $\tau - \lambda_2$. In general, this term becomes increasingly important as the interdependence of the bonds becomes stronger. Conversely, if the interdependence is weak, it may be appropriate to simply assign the value of 1.0 to $\tau - \lambda_2$. For example, in PDMS the value of $\tau - \lambda_2$ is about 1.05. Therefore, we will employ an analysis here that is based on the replacement of $\tau - \lambda_2$ by 1.0 in eqs 12–15. This approximation would be inappropriate for chains with more strongly interdependent bonds. In the case of polymethylene at 400 K, for example, $\tau - \lambda_2 = 1.27$, and σ would be seriously underestimated if it were simply identified with $P(g^+)/P(t)$ instead of being calculated from eq 12 with the inclusion of $(\tau - \lambda_2)^2$.

With the approximation $\tau - \lambda_2 = 1.0$ the analysis may be carried out in three steps on the premise of a pairwise interdependence between skeletal bonds: (i) Inasmuch as the curve in Figure 6 is obtained on the basis of single bonds irrespective of the states of adjoining bonds, it may be used with eq 12 to derive the representative first-order intramolecular interaction energy E_σ distinguishing gauche from trans states for any backbone bond. The generalized statistical weight ω is converted to energy via

$$E_\omega = -RT \ln \omega \quad (16)$$

where R is the gas constant and T is the temperature. From symmetry considerations this energy has to be identical for both Si–O and O–Si bonds. (ii) The fact that parts a and b of Figure 7 exhibit distinct qualitative features is indicative of the presence of second-order interactions operating even in the presence of bonds in the trans state. Those figures and eq 13 will yield the second-order interaction energy E_τ associated with bond pairs in the tt state, relative to tg$^\pm$ or g$^\pm$ states. Clearly E_τ assumes different values for the two respective pairs (O–Si, Si–O) and (Si–O, O–Si). (iii) The second-order interaction energies E_ψ and E_ω, arising when adjacent bonds are in the respective states g$^\pm$g$^\pm$ and g$^\pm$g$^\mp$, are evaluated from the probability distribution curves depicted in parts a and b of Figure 8 and eqs 14 and 15. The latter yield distinct energy parameters for the pairs (O–Si, Si–O) and (Si–O, O–Si), respectively.

From the arguments presented above, it is clear that two sets of energy parameters consisting each of four elements as (E_σ, E_τ, E_ψ, E_ω) and (E_σ, $E_{\tau'}$, $E_{\psi'}$, $E_{\omega'}$) govern the conformational statistics of the chain. Here the primed parameters will be adopted for the pair of bonds (Si–O, O–Si) while the former set corresponds to the pair (O–Si, Si–O). For a quantitative evaluation of those energies, the probability distribution curves in Figures 6–8 are numerically integrated over the three portions (0°, 120°), (120°, 240°), and (240°, 360°) separated by the vertical dashed lines. The results from integration, i.e., the fractional area enclosed by the curves over the three intervals, are explicitly indicated in each figure.

From Figure 6, it is observed that $P(\phi_i{=}t) = 0.41$ while $P(\phi_i{=}g^+) = P(\phi_i{=}g^-) = 0.29$, at 300 K. For brevity the symbol ϕ_i will be omitted from the probability expressions in the following discussion. With selection of the energy of the t state as zero, E_σ is evaluated as 0.20 kcal/mol. From parts a and b of Figure 7, E_τ and $E_{\tau'}$ are calculated as 0.37 and 0.02 kcal/mol. Application to the pair of bonds (O–Si, Si–O) and (Si–O, O–Si) yields, using the information given in parts a and b of Figure 8, the respective energies $E_\omega = 0.45$ kcal/mol and $E_{\omega'} = 0.13$ kcal/mol. Similarly, the same figures are used to determine $E_\psi = 0.12$ and $E_{\psi'} = 0.06$ kcal/mol. These parameters will be validated upon comparison of the experimental results with the predictions of a RIS formalism incorporating the new set of energy parameters obtained here.

IV. Conclusion

It is concluded from both energy minimizations and molecular dynamics simulations that the gauche states in PDMS backbone bonds are not as unfavorable as previously predicted in the FCM model but effectively compete with the trans states to yield a rather uniform distribution of rotational isomeric states. In particular, the probability of consecutive gauche bonds of opposite chirality is not at all negligibly small and therefore cannot be overlooked in a statistical treament of the chain conformational behavior. That the PDMS chain enjoys a high degree of flexibility that hardly distinguishes between different rotameric states was evident from the work of Grigoras and Lane and from previous experiments. It is necessary to test and validate the applicability of a RIS formalism based on energy parameters in conformity with the presently obtained smooth distribution of isomers, and this task will be undertaken in the following paper.

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