Self-Consistent-Field Conformational Energy Study and Configurational Statistics of Poly(dimethylsiloxane)

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Received February 2, 1989; Revised Manuscript Received May 26, 1990

ABSTRACT: Self-consistent-field molecular orbital ab initio calculations have been performed to obtain the intramolecular rotational potential energy surface for poly(dimethylsiloxane)(PDMS) with simultaneous rotations about successive single bonds. The minimum energy structure is more accurately described as a slightly twisted alternating trans–syn structure as opposed to the more commonly accepted all-trans structure. When an STO-3G basis set was used, it was found that the minimum occurred at $\phi_1 = 156°$ and $\phi_2 = 0°$, (156,0). There is a minimum also at (0,204) because of symmetry. Monte Carlo simulations produced a value for the characteristic ratio of between 3.44 and 3.76 and a value for the temperature coefficient of the mean-square length of 0.511×10^{-3}/deg. More recent efforts using a 3-21G* basis set obtained a minimum at about (144,0) and (0,216) and their symmetric analogues. Incorporating these new values into the Monte Carlo simulations produced a slightly raised characteristic ratio of 4.2 at 423 K. The temperature coefficient of the mean-square length, however, did not change appreciably.

Introduction

Inorganic polymers are becoming an increasingly more important area of polymer science and technology. One of the most important classes of these polymers is the siloxanes, made of alternating silicon and oxygen atoms. These polymers are noted for their stability at temperatures of 150 °C or higher.[1] Silicone polymers are used in a variety of commercial applications including lubricants, defoamers, greases, resins, and elastomers.[1] Poly(dimethylsiloxane) (PDMS) is one of the most important of the silicone elastomers. It has applications in gaskets and seals, wire and cable insulation, surgical and prosthetic devices and is used for caulking, sealing, and encapsulating, especially where high environmental stress may be present.[1,2]

Poly(dimethylsiloxane) has some unique configurational properties due to the differing bond angles Si–O–Si and O–Si–O. The resulting configurational statistics of the PDMS chains have been widely studied by many investigators for many years.[3-12] The most widely used approach for calculations of average statistical properties is based upon rotational isomeric state theory.[3-6,13] It is generally accepted that the preferred conformation of PDMS is the all-trans form. However, because of the inequality of the Si–O–Si and O–Si–O bond angles, which have been experimentally determined to be, respectively, about 143° and 110°, PDMS closes upon itself after about 22 bonds.[3,4,10,13] The resulting structure can be seen in Figure 1. The elasticity and flexibility of this molecule is though to be due to the increase in the number of gauche states occupied upon stretching.[10,13,14] It is the purpose of this study to calculate the full rotational potential energy surface for the simultaneous rotation about the Si–O and O–Si bonds using ab initio SCF theory and to show that there is an alternative minimum-energy structure to the all-trans structure, which can account for several of the average statistical properties measured experimentally.

Method of Calculations

Potential energy calculations on polymers have traditionally been performed via empirical and semiempirical techniques. Recent calculations on PDMS by Bruckner and Malpezzi[7] have used these techniques to calculate potential energy surfaces. Specifically, the energy of a given conformation can be considered to consist of four parts: (i) intrinsic torsional potentials, (ii) van der Waals repulsions between nonbonded atoms and groups, (iii) dispersion attractions between nonbonded atoms and groups and (iv) energy of interaction of dipole moments between consecutive pairs of atoms or groups. The major disadvantage of these calculational techniques is that each different group of atoms must be individually parametrized.[15,16] Often, adjustment of these required parameters has been done arbitrarily[17] and, in the case of Si–O and Si–C bonds, are subject to major uncertainty.[7]

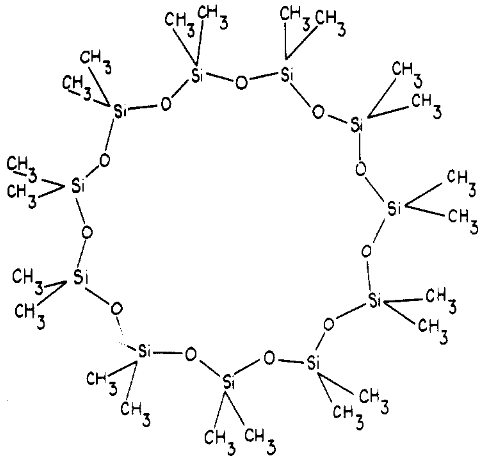

Figure 1. All-trans conformation of an extended chain of the PDMS molecule.

The approach we chose to take is that of using a modified version of the GAUSSIAN 76,[18] GAUSSIAN 82,[19] and GAUSSIAN 88[26] ab initio programs. We carried out these calculations on the Cyber 180/860 computer located at Tarleton State University (Stephenville, TX) and the IBM 3090-600E supercomputer located at Cornell University (Ithaca, NY). The majority of the ab initio calculations were performed at the STO-3G level of approximation. However, some calculations and geometry optimizations were performed by using a 3-21G* basis set of functions. These choices were necessitated by the size of the molecular segment used in the calculations. This segment is depicted in Figure 2. Using a larger basis set such as 4-31 G* or 6-31G*, which

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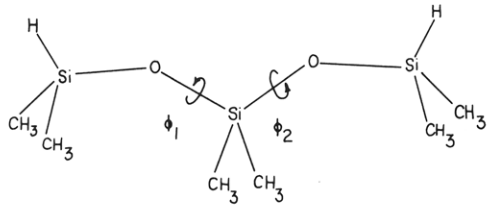

Figure 2. Segment of the PDMS molecule used in the ab initio SCF–MO energy calculations.

would have been more desirable, was impossible with current programs and computers. Potential energies were calculated at intervals of 5–10° for the simultaneous rotations about ϕ_1 and ϕ_2 of Figure 2. In areas around minima, this interval was decreased to 1°. A total of 412 points was calculated, each point requiring between 8 and 42 min of CPU time for a total of approximately 219 h of CPU time. A larger basis set or additional levels of sophistication would add exponentially to this CPU time. It should be noted that because of symmetry, it was not necessary to calculate all points between 0 and 360° for ϕ_1 and ϕ_2.

The great advantage of using these ab initio programs is that they need no arbitrary parameters and yield results, the accuracy of which can be made quite high. Usually the only choice possible in these procedures is the initial geometry of the molecule and the basis functions. This author, in collaboration with many others, has used with great success this approach[15,16,20–22] on polymers. The great disadvantage of this approach is, of course, the tremendous amount of computational time required.

The potential energy surface generated was used to calculate the a priori and conditional probabilities for the molecule to exist in any given configuration. The probability for a molecule to exist in a particular conformation is equal to the statistical weight of that conformation divided by the sum of all statistical weights for all possible conformations. Details of the calculations of statistical weights and various probabilities are available elsewhere.[13,23]

The probabilities were incorporated into a Monte Carlo program, which generated numerous representative chains. Various statistical properties were calculated by averaging over a representative ensemble of chains. In this work, we generated 10 000 chains from 22 to 250 bonds long. The average square end-to-end distance was calculated for each series of 10 000 chains. From this, the characteristic ratio and the temperature coefficient of the mean-square length were calculated. These quantities are, respectively, given by the formulas

$$c_n = \langle r^2 \rangle_n / n l^2$$

and

$$\mathrm{d} \ln \langle r^2 \rangle_n / \mathrm{d}T$$

where $\langle r^2 \rangle$ is the mean-square end-to-end distance of a given chain averaged over the entire ensemble, l is the average bond length (the Si–O bond length), and n is the total number of bonds in a given chain. An ensemble of 10 000 was chosen because several calculations of the characteristic ratio at a given temperature did not vary more that 5% for an ensemble of this size.

Table I
Optimized Values of Various Geometrical Parameters

geometrical param	STO-3G	3-21G*
Si–O	1.633 Å	1.6704 Å
Si–C	1.870 Å	1.9094 Å
C–H	1.096 Å	1.0960 Å
Si–H	1.476 Å	1.4761 Å
Si–O–Si	142.9°	142.9°
O–Si–O	108.0°	109.85°
O–Si–C	110.0°	109.50°
H–C–Si	109.5°	109.45°

[a] Optimized only with STO-3G basis functions.

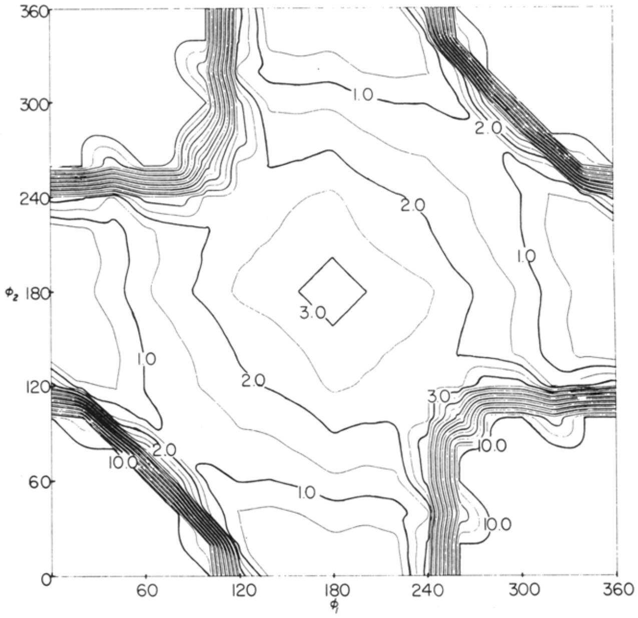

Figure 3. Conformational energy surface of the PDMS molecule using STO-3G.

Results and Discussion

The starting geometry in this study was the experimental geometry used in numerous previous studies.[3–5,7,13] The various geometrical parameters were then subjected to limited optimization within the STO-3G level of approximation. The Si–O bond length was optimized to 1.633 Å. The optimized Si–C bond length was found to be 1.870 Å. The C–H and Si–H bond lengths were, respectively, optimized to 1.096 and 1.476 Å. Bond angles for Si–O–Si, O–Si–O, O–Si–C, and H–C–Si were found to be 142.9, 108.0, 110.0, and 109.45°, respectively.

Subsequent calculations were performed by using a higher level basis set (3-21G*). This is a split-valence basis set with the addition of a complete set of six second-order Gaussian primitives for polarization. The revised optimized bond lengths were calculated with this new basis set of functions to be 1.6704, 1.0960, 1.9094, and 1.4761 Å for the Si–O, C–H, Si–C, and Si–H bonds, respectively. The revised O–Si–O and O–Si–C bond angles were found to be 109.85 and 109.50°, respectively. It was also found that there was effectively little change in the H–C–Si bond angle. The Si–O–Si bond angle was not able to be reoptimized by using the 3-21G* basis set, and therefore the value of 142.9° determined by using the STO-3G basis set was maintained. It should be noted that the optimization was not performed in multidimensional configurational space but as individual geometrical parameters. See Table I for a summary of these results.

Results of energy calculations for the simultaneous rotations about ϕ_1 and ϕ_2 are shown in Figures 3 and 4. These figures show a considerably different minimum-energy structure than the traditionally accepted trans structure. In addition, the energy surface of Figure 3 shows both similarities and some considerable differences from that calculated by Bruckner and Malpezzi[7] using molecular

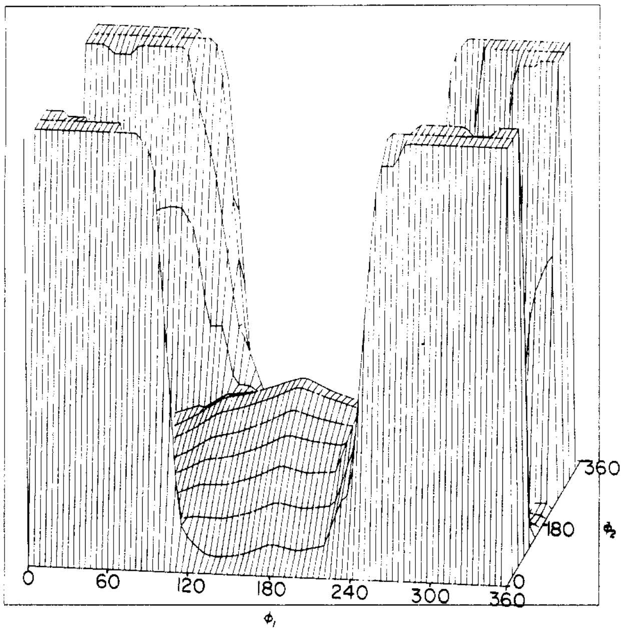

Figure 4. 3-Dimensional conformational energy map of the PDMS molecule using STO-3G.

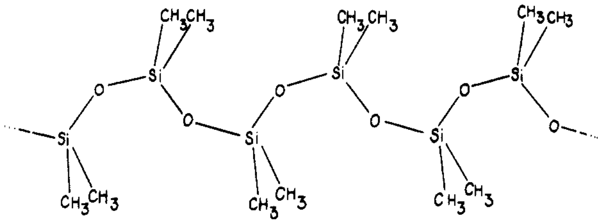

Figure 5. Extended segment of the PDMS molecule in the minimum-energy conformation.

mechanics techniques. The most noticeable difference is in the position of the energy minimum. Bruckner and Malpezzi found this minimum to be located at $\phi_1 = 180°$ and $\phi_2 = 180°$, (180,180). However, our calculations using the minimal basis set indicate two energy minima located at (156,0) and (0,204) and, of course, their symmetric analogues [i.e., (0,156) and (204,0)]. This would correspond to a chain in which one of the dihedral angles is in the syn conformation and the other dihedral angle is +24 or −24° from trans. If a molecule of PDMS propagated this structure for an extended sequence, it would correspond to the structure depicted in Figure 5. It should be noted that if a PDMS molecule had an extended sequence of either (156,0) or (204,0), it would form a helical segment approximately 30 bonds long. Our calculations found that, at (180,180), there is a local energy maximum of 3.254 kcal/mol relative to the energy minima noted previously.

The results using the 3-21G* basis set of functions were very similar to those using the minimal basis set. The minima were found to be at (143.3,0) and (0,216.7) and the other symmetric analogues. This is an additional "twist" angle of about 12°. The local maximum energy at (180,180) was recalculated and found to be slightly lower at 3.16 kcal/mol.

Besides the above-mentioned maximum and minima, there are several additional major structural features needing discussion. An especially noteworthy feature evident in Figure 4 is the huge potential energy barriers against conformations for rotation about ϕ_1 and ϕ_2 between (0,0) and about (120,120) and rotation between (360,0) and about (240,120) and, of course, their symmetric equivalents. These regions can be seen as large white regions in the four corners of Figure 3 and as four "mountainous" regions in the four corners of Figure 4. The "mountains" of Figure 4 look flat due to cutting off of the calculations for energies above 10 kcal/mol. A model of PDMS shows that these large "forbidden" regions are where there is considerable steric repulsion between methyl groups on every second silicon atom. The four minima are located in the "valleys" between these "mountains", as can be seen in both Figures 3 and 4.

Table II
Experimental and Calculated Values of the Characteristic Ratio of PDMS

characteristic ratio	temp, K	characteristic ratio	temp, K
6.2[a]	293	6.2–1.2[g]	350
7.6[b]	295.5	4.62–5.90[h]	298
5.7–6.2[c]	275–363	3.44[i]	298
6.43[d]	383	3.64[i]	348
6.36[e]	383	3.76[i]	423
7.5–4.7[f]	383	4.17[j]	423

[a] Butanone as solvent.[13] [b] $C_8F_{18} + C_2Cl_4F_2$ as solvent.[13] [c] Various solvents.[13] [d] See ref 5. [e] See ref 7. [f] Calculated values of characteristic ratio vs fractional charge of methyl groups.[7] [g] Calculated in rotational isomeric scheme.[11] [h] Monte Carlo calculation of 10, 20, 30, and 40 skeletal bonds.[9] [i] This work, STO-3G basis set. [j] This work, 3-21G* basis set.

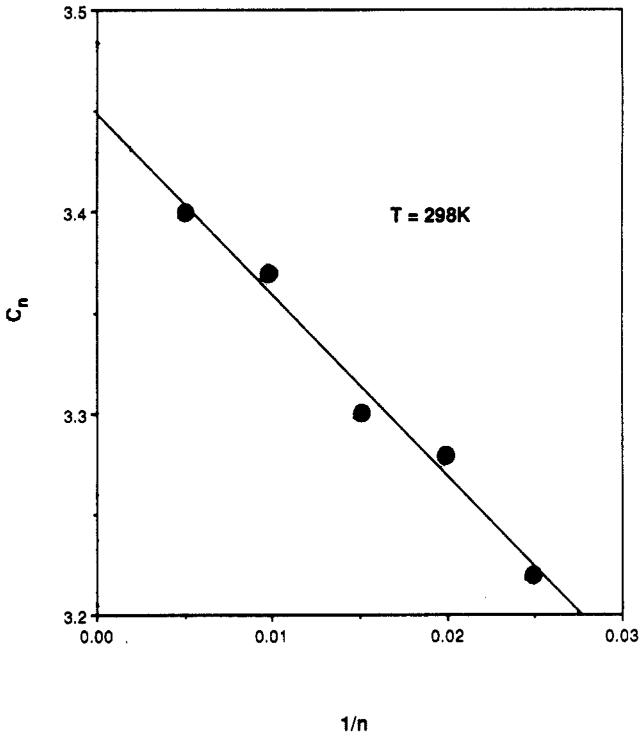

Figure 6. Plot of the characteristic ratio vs 1/*n* where *n* is the number of bonds of a PDMS molecule at 298 K.

Table II summarizes some experimental and theoretical values, including this work, for the characteristic ratio of PDMS. The experimental values range from 5.7 to 7.6.[5,7,10,13] The values obtained for this work using results from STO-3G basis sets are 3.44, 3.64, and 3.75, calculated for the temperatures 298, 348, and 423 K, respectively. Figure 6 shows the results of the calculation of the characteristic ratio at 298 K, where the calculation was performed for molecules ranging in size from 22 bonds to 250 bonds. The extrapolated limit was taken in each case to obtain the values in Table II. The ensemble size used in the Monte Carlo calculations to obtain the characteristic ratios was 10 000 chains. When results from calculations using the 3-21G* split-valence basis sets were used, the characteristic ratio was found to increase to 4.17 at 423

Table III
Experimental and Calculated Values of the Temperature Coefficient of the Mean-Square Length d ln $\langle r^2 \rangle/dT$

10^3d ln $\langle r^2 \rangle/dT$	temp, K	10^3d ln $\langle r^2 \rangle/dT$	temp, K
+0.78[a]	313–373	+0.59[d]	233–398
+0.71[a]	303–378	+0.52[e]	303–373
+0.28–0.46[b]	303–423	+0.511[f]	273–423
+0.75[c]	303–378		

[a] See ref 3. [b] See ref 24. [c] See ref 3. [d] From thermoelastic experiments.[10] [e] From viscosity–temperature experiments.[10] [f] This work.

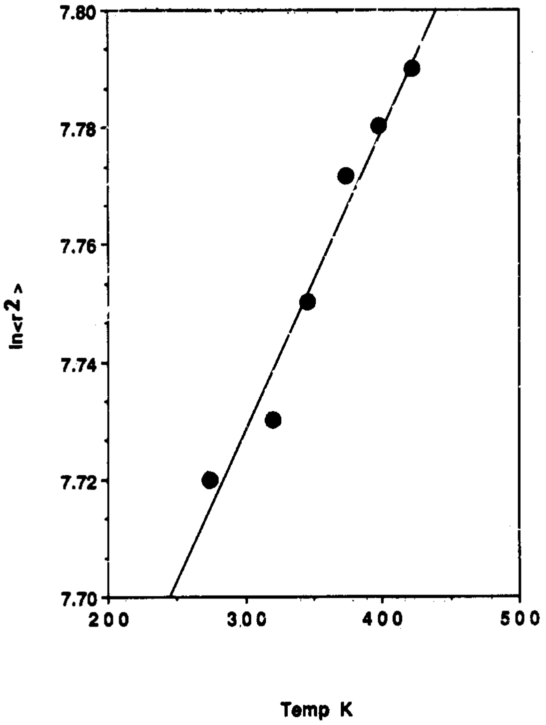

Figure 7. Plot of ln $\langle r^2 \rangle$ vs temperature of a PDMS molecule.

K. Similar increases were calculated at other temperatures. It should be noted that this is still lower than the best experimental numbers available.[10] Since only a limited number of points were recalculated by using 3-21G*, it is felt that further improvement could be obtained if the entire energy surface was recalculated with a more sensitive basis set such as the 3-21G* basis functions or perhaps a 4-32G* basis set of functions. Further improvement could also be obtained if the molecule was allowed to "flex" during the calculations, that is, if the geometry was optimized for each calculated point instead of the bond angles and bond lengths being held rigid. However, with current programs and computers, this would be prohibitively expensive.

Calculations of the temperature coefficient of the mean-square length, i.e., d ln $\langle r^2 \rangle/dT$, are summarized in Table III. The experimental values range from 0.28×10^{-3} deg^{-1}. The most recent experimental values found were 0.59 and 0.52×10^{-3} deg^{-1} measured in thermoelastic and viscosity–temperature experiments, respectively.[10] In this work, we obtained the value 0.511×10^{-3} deg^{-1} for a chain 250 bonds long. No significant difference was noted for simulations using either set of basis functions. Figure 7 shows a plot of ln $\langle r^2 \rangle$ vs T for temperatures ranging from 273 to 423 K. The slope of this line is the temperature coefficient, and our value is very close to the most recent experimental number obtained from viscosity–temperature experiments. It should also be emphasized that we calculated a positive temperature coefficient, a very necessary condition for this molecule, since all experiments obtained a positive number and because a positive temperature coefficient explains so many of the elastic and flexible properties of PDMS. There is one important assumption made in the calculations of the various statistical properties and that is that each set of simultaneous rotations about ϕ_1 and ϕ_2 is taken as independent. Inspection of a model of PDMS shows this to be a very reasonable assumption due to the large steric hindrance to the simultaneous rotation of three or more bonds, mostly because of the presence of large methyl groups.

There are several steps that could be taken to improve on the results of this work. A first, highly desirable, step would be to use a large basis set such as the split-valence 4-31G or 4-31G* basis sets. This would have the effect of providing more sensitivity to small changes in the geometry of the molecule. A second step would be to allow the geometry to optimize at each step, i.e., for each different set of dihedral angles. It would also be very desirable to optimize the geometry in multidimensional configurational space, that is, to allow all bond lengths and bond angles to optimize simultaneously, instead of as individual parameters, as was done in this study. It should be remembered, however, that all of these suggested improvements would add greatly to the computational time with the computers and programs currently available. However, with improvement in the programs and improvement in the computers (such as the new vector processors currently being developed), it may be feasible to attempt these refinements in the near future.

Summary

In this work, we have calculated by using ab initio techniques the conformational energy surface for the simultaneous rotation about two consecutive bonds in a PDMS molecule. From this, we find the minimum-energy conformation for the PDMS molecule to be a slightly twisted alternating trans–syn structure. The twist is ±37° from the trans structure. Monte Carlo calculations found, by using this potential energy surface, that the characteristic ratio was between 3.44 and 4.17, with the latter number calculated by using results from the 3-21G* split-valence basis set at 423 K. The temperature coefficient of the mean-square length had a value of 0.511×10^{-3}/deg. Further improvement could probably be obtained, especially in the characteristic ratio, by recalculating the entire energy surface using a more sensitive basis set of functions such as 3-21G* or 4-31G*. Allowing the molecule to "flex" during calculations would also probably help.

Acknowledgment. I thank Professor Riley Macon of Tarleton State University for reviewing this paper and making very useful suggestions and Professor William Forsman of the University of Pennsylvania for guidance and encouragement during the early stages of this project. Acknowledgment of financial support is given to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Cornell National Supercomputer Facility, a resource of the Center for Theory and Simulation in Science and Engineering, which receives major funding from the National Science Foundation and IBM Corp., with additional support from New York State and members of the corporate Research Institute. Additional financial support was provided by the Organized Research Grant of Tarleton State University and the Robert A. Welch Foundation of Houston, TX.

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