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# SCF-MO AND MONTE CARLO CALCULATIONS OF POLY (DIMETHYLSILOXANE)

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## ABSTRACT

Self-consistent-field molecular orbital calculations are being used more and more extensively in determining the energies and properties of various conformations of polymers. We are using the semi-quantum mechanical procedure MNDO (moderate neglect of differential overlap) to obtain various rotational conformational states of poly(dimethylsiloxane) (PDMS). Before calculation of these states, the molecule is geometrically optimized by using the *ab initio* procedure Gaussian 86 at the 3-21G basis set level. Generations of 144 rotational states by rotating about two bonds simultaneously in increments of 30° were created. A potential energy surface was created from which Monte Carlo generated several polymer characteristics including characteristic ratio and radial distributions.

## INTRODUCTION

Advanced computers and programs are allowing for numerous, very tedious calculations to be done on a variety of applications. One of those applications is the self-consistent-field molecular orbital *ab initio* calculations (SCF-MO) to obtain rotational potential energy surfaces of molecules. Once a rotational potential energy surface is created, a Monte Carlo calculation procedure can predict certain characteristics of polymer chains it grows, using the optimized geometry and energy surface supplied. Some of these characteristics include characteristic ratio and radial distribution. These Monte Carlo simulations can be run at different temperatures to provide another characteristic, temperature coefficient.

The inorganic polymer poly(dimethylsiloxane) (PDMS) is one of several polymers studied in this research over the past year. PDMS was chosen because of its unique structure with an alternating silicon-oxygen backbone, containing methylated silicons, which puts it in the class of polymers called siloxanes. These silicon polymers are used in such applications as lubricants, greases, defoamers, and elastomers (Billmeyer, 1984). PDMS is very important in this class of polymers in that it has applications in gaskets and seals, and has been a subject of controversy lately because of use in prosthetic devices such as breast implants (Billmeyer, 1984; Rochow, 1987).

The configurational properties of poly(dimethylsiloxane) have been studied over the years both experimentally in laboratories, and with calculations. These configurational properties are unique in that PDMS has differing bond angles. The Si-O-Si angle is much greater than that of the O-Si-O angle, giving the accepted preferred conformation of the all-trans form, or cyclic form. These properties were obtained in large part due to calculations based on rotational isometric state theory (Mark and Flory, 1964; Flory *et al.*, 1964; Flory and Chang, 1976; Mark, 1978; Flory, 1969). Due to this cyclic form, the polymer closes upon itself after about 22 bonds (Mark and Flory, 1964; Flory *et al.*, 1964; Flory, 1969).

It is the purpose of this study to continue efforts to upgrade prediction of polymer characteristics using calculations, and in particular, to predict and confirm average poly(dimethylsiloxane) characteristics.

## MATERIALS AND METHODS

The segment of poly(dimethylsiloxane) used for this research consisted of a five member backbone starting with oxygen and is depicted in Figure 1. The size of this segment was determined by calculation, computer, and time constraints. The overall process of this research was to optimize the geometry of the specified segment of PDMS using the Gaussian 86 (Frisch *et al.*, 1988) *ab initio* program, then calculate the rotational potential energies using the procedure MNDO (ChemDraft II, 1989; Dewar and Thiel, 1977), and finally, use the Monte Carlo method (Binder, 1987) to make polymer predictions based on the created potential energy surface. These calculations were carried out on a VAX Station 3100 and various 286/386 computers.

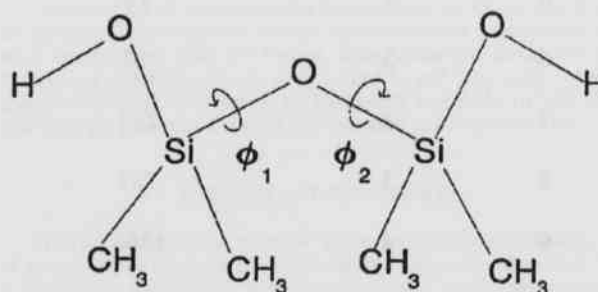


Figure 1. PDMS segment used in calculations with rotation sites.

The segment of PDMS chosen had to be optimized before other calculations could be carried out. First, an internal coordinate data set was created in the Z-matrix form that included bond lengths, bond angles, and dihedral angles, all of which had the appropriate reference atom included. The initial geometrical parameters (Flory, 1969) are listed in Table I. To make sure the Z-matrix geometry was correct, the program ChemDraft II (1989) was used to visually check the geometry. To optimize, the Gaussian 86 program was used first to optimize first the bond lengths, then the bond angles. The basis set used for optimization was the STO-3G level of approximation, followed by a higher basis set, 3-21G, which is a split-valence basis set. Higher basis sets would have been better, but program restraints would not allow for this due to the size of the silicon atoms. Once optimization was completed, the geometry was again visually checked to make sure the optimized parameters looked reasonable.

Table 1. Some initial parameters from Flory (1969).

GEOM. PARAM.	INITIAL	STO-3G	3-21G
Si-O	1.67 Å	1.6422 Å	1.6767 Å
Si-C	1.80 Å	1.8683 Å	1.8952 Å
O-H	0.90 Å	0.9830 Å	0.9712 Å
C-H	1.00 Å	1.0807 Å	1.0863 Å
O-Si-O	108.0°	104.1256°	108.9325°
Si-O-Si	143.0°	143.2753°	143.0753°
C-Si-O	109.5°	110.8980°	110.5136°
H-C-Si	109.5°	111.4374°	111.2324°
H-O-Si	109.5°	108.3012°	126.9710°

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The rotational potential energies were created by rotating about two internal backbone bonds seen as  $\phi_1$  and  $\phi_2$  in Figure 1. While  $\phi_1$  was held,  $\phi_2$  was rotated through  $360^\circ$  by  $30^\circ$  increments; then  $\phi_1$  was rotated  $30^\circ$  and the process repeated until  $\phi_1$  had been rotated through  $360^\circ$ . To reflect these rotations, the dihedrals of the atoms one bond away from the rotation bond were changed according to the rotation amount. These rotations were represented by a total of 144 rotation data sets that were to be used in the actual calculations. The energies of these 144 data sets were calculated by the semi-quantum mechanical procedure MNDO (moderate neglect of differential overlap) in the program ChemDraft II. The reason this calculation procedure was used rather than the Gaussian 86 calculation was because each rotational energy calculation using Gaussian 86 took approximately two to three hours to complete, while the MNDO procedure took two to three minutes. Since there were 144 rotations in each run, the MNDO procedure was very advantageous. These calculations produced a list of 144 rotations with their corresponding energies expressed in Hartree units. These energies were then converted into kilocalories relative to the lowest energy, where the lowest energy was set at 0.0 kilocalories.

The list of relative rotational potential energies was used by Monte Carlo to produce a rotational energy map as depicted by Figure 2. Monte

each chain, from which the characteristic ratio and temperature coefficient were calculated. These characteristics are given by the formulas

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

and

$$d \ln \langle r^2 \rangle_n / dT$$

where  $\langle r^2 \rangle$  is the mean square end-to-end distance of the 10,000 chains,  $l$  is the average bond length, and  $n$  is the number of bonds in the chain. Monte Carlo also gave the radial distributions, which are the number of times two atoms are  $n$  angstroms apart, and it also gave the angular distribution, the number of times a particular rotation set was used.

## RESULTS AND DISCUSSION

The minimal basis set of function, STO-3G, was used to obtain the second set of parameters seen in Table I. The parameters most concerned with were the Si-O bond length, the O-Si-O angle, and the Si-O-Si angle. These three when optimized by the STO-3G basis set were an average of 1.81% off the experimental parameters listed in Table I. To achieve better optimized results, the split level basis set function, 3-21G, was used. Using the 3-21G basis set achieved an average deviation of 0.44% for the three parameters previously mentioned, which was a four fold decrease. As noticed in Table I, the H-O-Si bond angle changes considerably when optimized by the 3-21G basis set. This can be explained by the fact that  $109.5^\circ$  was arbitrarily used as an initial value, as were the C-Si-O and the H-C-Si angles, in accordance to expected  $sp^3$  bonding. The angle of  $126.97^\circ$  is not unexpected in light of its environment in the polymer segment.

The MNDO method of calculation was used in determining the rotational potential energies, and the results can be seen in the three dimensional rotational energy map of Figure 2. The X in the energy map marks the lowest energy (map global minimum) rotation set, 180-210. Some other low rotation sets in order of increasing energy include the following: 180-150, 180-180, 150-240, and 180-240. Conversely, the highest rotation sets, in order of increasing energy, include the following: 30-90, 60-90, 90-90, and 300-240. These rotation sets would seem to suggest that a polymer using these preferred sets would be in the cyclic, convoluted conformation, and would shun the unpreferred, which would put methyl groups close to other methyl groups and/or oxygen atoms.

The Monte Carlo method was used to predict PDMS polymer characteristics that included characteristic ratio and temperature coefficient. Table II lists characteristic ratios with the corresponding temperature of this research and other sources. The characteristic ratios

PDMS ROTATIONAL ENERGY MAP

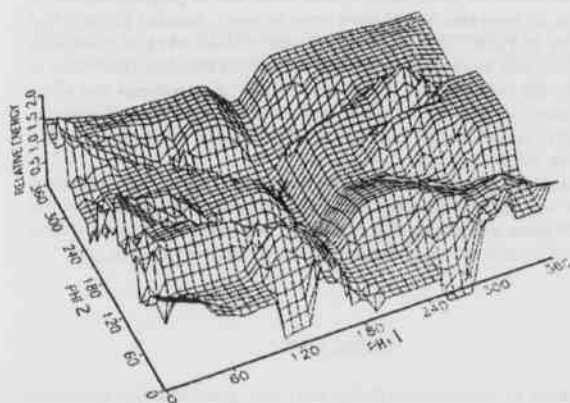


Figure 2. Three dimensional rotational potential energy map, phi 1 vs. phi 2 vs. relative energy in kilocalories.

Carlo used this energy map to mathematically create a probability space. The Boltzman factor is the basis of the mathematics and is given by the following formula:

$$P_{ij} \propto e^{-E_{ij}/kT}$$

Using the probability space created, each rotation set had its own probability of being chosen in a random number generator. The lower the relative energy, the greater chance the rotation set had to be used in a growing polymer chain. The Monte Carlo program was set to grow a set of 10,000 polymers, that were approximately 100 bonds long (put in two at a time), consisting of only the backbone atoms. Only the backbone atoms were used because the methyl groups were taken in account when the probability space was created. The reason that there were 10,000 simulations of 100 bond long polymer chains was because at these parameters, the characteristics calculated didn't change appreciably between repeated runs. Another parameter in the Monte Carlo program was the temperature at which the simulations were to be run. Changing of the temperature allowed the calculation of the temperature coefficient by using data from the temperatures 300, 400, and 500 K. Monte Carlo calculated various average statistical properties by calculating over the 10,000 chains. The mean square end-to-end distance was calculated for

Table 2. Characteristic ratios with corresponding temperatures and temperature coefficients of this work (Monte Carlo) and others. <sup>a</sup>(Curro and Mark, 1984), <sup>b</sup>(Flory and Chang, 1976), <sup>c</sup>(Darsey, 1990), <sup>d</sup>(This work), <sup>e</sup>(Mark and Erman, 1988), <sup>f</sup>(Mark and Erman, 1988), <sup>g</sup>(Darsey, 1990), <sup>h</sup>(This work).

300 K	NUMBER	400 K	NUMBER	500K	NUMBER
180 150	14155	180 210	10730	180 210	8667
180 210	14014	180 150	10509	180 150	8623
180 180	13931	180 180	10235	150 240	8578
150 240	13299	150 240	10149	180 180	8530
180 240	12355	180 240	9175	180 240	7896

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calculated seem in accordance with other values from literature, which vary greatly in some. Using our three characteristic ratios, a temperature coefficient graph was created, Figure 3, from which the PDMS temperature coefficient was calculated and is listed in Table II. The

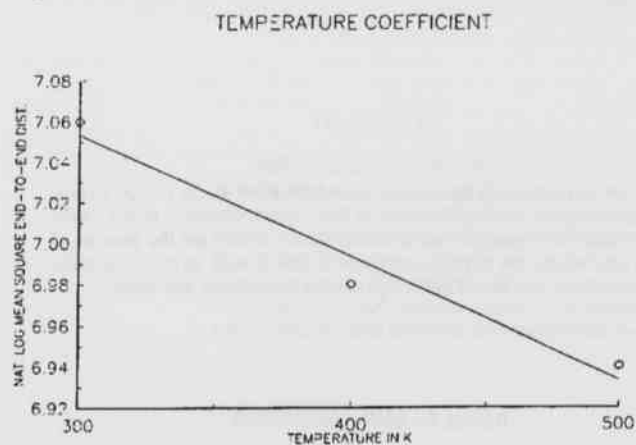


Figure 3. Graph of  $\ln \langle r^2 \rangle$  vs. Temp. in K to produce temperature coefficient.

temperature coefficient,  $-0.61 \times 10^{-3} \text{ K}^{-1}$ , as seen with others in Table II, has approximately the same magnitude, but is a negative value rather than a positive one, which predicts that the polymer actually tightens rather than relaxing with increased temperature. Some insight into our value can be given if the radial distribution (Figure 4) and the angular distribution (Table III) are studied. As the energy was increased from 300K to 500K, the characteristic ratio, a measure of the "tightness" of a polymer, decreases, which means the polymer became more convoluted. As seen in Table III, as energy was increased the polymer tended to not spend as much time in the normal conformation denoted by the angles listed, but occupied higher energy rotational sets which convolutes the polymer to a more globular shape. The radial distribution, Figure 4, shows that at 300K, the number of atoms apart by 22Å to 55Å is more than at 400K or 500K, and at 0Å to 22Å is less than the other temperatures. Looking at 500K, just the opposite is true, and 400K falls in between. This graph supports the findings that as the temperature increases, thus the energy, the polymer conforms to a state where it is more compact.

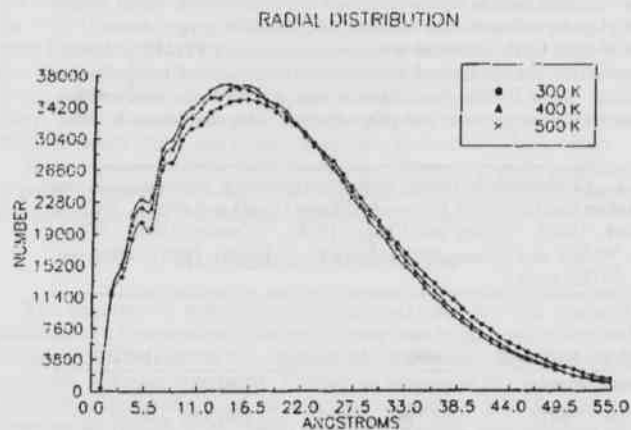


Figure 4. Graph of radial distributions produced by Monte Carlo at three temperatures from 0 to 55Å further points cut off due to graphing purposes).

Table 3. Five most used angular distributions for each temperature from Monte Carlo calculations.

CHAR. RATIO	TEMP K	TEMP. COEFF. $\times 10^{-3}/\text{K}$
4.62-5.90 (a)	298.0	+0.59 (e)
6.43 (b)	383.0	+0.52 (f)
4.17 (c)	423.0	+0.511 (g)
4.1025 (d)	300.0	-0.61 (h)
3.7783 (d)	400.0	
3.6466 (d)	500.0	

Several factors could have influenced the data obtained in this research. First, and most important, since MNDO had to be used in the calculation of the rotational potential energies, they were not as accurate as with using a Gaussian split valence basis set. We believe this has the greatest affect on the results. In optimizing, we were also restrained in that a higher basis set level could not be used due to program ability. A higher basis set here also would have been an asset. Another factor is that our segment of PDMS that was utilized started with oxygen rather than silicon, which had been used in earlier studies. In the data referenced in Table II, for the experiments, PDMS was dissolved in solvents that affect characteristics that can not be taken into account when using theoretical calculations. All of these factors in differing importance, probably represent the differences seen in our data.

This research has been invaluable in that future projects can be refined using what was learned here, and hopefully theoretical calculations of this type can be done with increasing certainty. This research is also valuable in that it will be used in a neural network project that is ongoing.

## SUMMARY

A segment of poly(dimethylsiloxane) was geometrically optimized using a split valence level, 3-21G, Gaussian program. A set of 144 rotational potential energies was created using the MNDO method to calculate. The optimized geometry and the rotational potential energies were used in a Monte Carlo method to create a probability space that simulated 10,000 polymer chains at three different temperatures. The characteristics determined suggest that PDMS is in a cyclic form, preferring to use the angles  $180^\circ$  and  $210^\circ$ , and convolutes to a greater extent when energy is increased, thus giving a negative temperature coefficient.

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