Structure Elucidation of Crystalline Poly(diphenylsiloxane)

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ABSTRACT: This study shows that the structure of the poly(diphenylsiloxane) (PDPhS) backbone is quasi-planar rather than helical. The nearest-neighbor chains in the crystal are packed in a hexagonal configuration. Using molecular mechanics calculations and analysis of X-ray powder diffraction data, it has been determined that the crystalline structure of PDPhS has $Pbn2_1$ symmetry and the backbone consists of siloxane bonds in a quasi cis–trans sequential conformation. The deviation of each bond from the planar configuration is about 15°. The backbones of the two chains in the unit cell are antisymmetrical. The Si–O–Si bond angle is 145° and the torsional angles of the vicinal phenyl groups relative to each other are 125 and 72°. The orientation of the phenyl groups in the crystal consists of parallel and perpendicular nearest neighbors. The calculated X-ray results are able to explain the main features of the experimental pattern in terms of position and intensity of the peaks. Molecular mechanics calculations suggest that the density of ideal crystals of poly(diphenylsiloxane) at low temperatures should be in the range 1.26–1.3 g/cm^3, whereas the reported experimental value is 1.22 g/cm^3. A new set of molecular mechanics parameters for the UFF method to more accurately describe polysiloxanes in the condensed state is given.

Introduction

Poly(diphenylsiloxane) (PDPhS) has unique thermal and mechanical properties due to its inorganic backbone and its organic side chains. PDPhS is highly crystalline, it has a high thermal stability, and above its melting temperature of 260 °C forms a mesomorphic phase which is intermediate between the crystalline and liquid phases.[1–5] The properties of this material can be related to its structure: its thermal stability is due to the absence of aliphatic groups, which generally decompose above 300 °C, and to the exclusive presence of aromatic groups attached to an inorganic backbone. Its crystallinity results from the siloxane backbone, which allows for the proper alignment of the symmetrical phenyl groups along the polymer. While the siloxane backbone has a large degree of flexibility in the presence of small side groups such as methyl or hydrogen, this feature is removed when rigid and rather bulky phenyl groups are substituted on silicon. The crystalline state of PDPhS is present over a wide range of temperature, and an accurate characterization of its structure would allow for a better understanding of the properties of this polymer.

Based on X-ray powder diffraction data, a helical structure for the backbone of PDPhS has been proposed by Dubchak et al.[6] We will reconsider the structure of PDPhS using a molecular mechanics method with potentials that were refined to describe organosilicon compounds. The experimental X-ray powder diffraction pattern of PDPhS does not have a good resolution in comparison with those of low molecular weight crystals. At the present time, there are insufficient experimental data to allow for a complete account of all peaks in the diffraction pattern. The goal of this work is to provide a structural model for PDPhS capable of explaining the main features of the X-ray powder diffraction pattern.

In principle, the structure of PDPhS can be derived with the knowledge of the X-ray powder diffraction pattern and the unit cell features. While the symmetry and the dimensions of the unit cell determine the positions of the peaks present in an X-ray diffraction pattern, the content of the unit cell determines the intensities of the peaks. The helical model reported previously[6] is in good agreement with the experimental data for the calculated positions of the diffraction peaks, but there is a large discrepancy between the intensities of those peaks as calculated and measured. An assumed helical structure for the siloxane backbone would provide an X-ray diffraction pattern characterized by high-intensity peaks at interplanar distances between 7.2 and 5.2 Å, or at equivalent 2θ values of 12.2–16.7° for $\lambda = 1.5418$ Å. On the contrary, the experimental data indicate a lack of high-intensity peaks in this region. The peaks characterized experimentally by high intensity are located at 10.05 and at 4.48 Å, which correspond to 2θ values of 8 and 20°, respectively.

It has been previously shown by molecular mechanics[7] and molecular dynamics[8] methods that the preferred conformation for the siloxane backbone is planar consisting of a sequence of alternating cis and trans bonds, as opposed to a helical conformation.

Experimental Section

Preparation of PDPhS. Poly(diphenylsiloxane) was prepared by the ring-opening polymerization of hexaphenylcyclotrisiloxane in hot diphenyl ether with lithium silanolate as polymerization initiator. The ratio of initiator to diphenylsiloxane unit was 1:500. Due to the insolubility of the polymer at room temperature, the molecular weight of the resultant polymer could not be determined.

X-ray diffraction patterns were recorded with a JEOL JDX-3530 X-ray diffractometer system with Cu Kα radiation at 40 kV, with an amperage of 30 mA, using a 1° dispersive slit and a 0.2 mm window. The X-ray diffraction patterns of powdered PDPhS were recorded for samples that precipitated from a hot solution in diphenyl ether and the annealed precipitate. The sample was annealed at 300 °C for 30 min prior to analysis.

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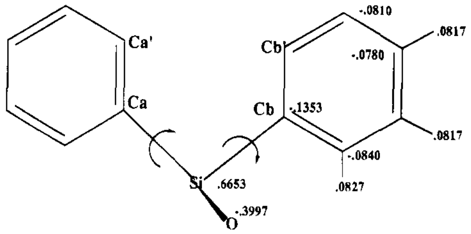

Figure 1. Net atomic charges on PDPhS used to calculate *electrostatic interactions and the notation used to define* torsional angles for the phenyl groups.

Table 1. Modified Parameters from the Original Universal Force Field[10]

atom type	D_i (kcal/mol)	R_i (Å)	natural radius (Å)	natural angle (deg)	eff charge
O−3−z	0.08	3.02	0.618	150	
Si3	0.046	5.4	1.107		0.4
C−R	0.056	3.92			
H	0.02	3.24			

Computational Methods

Molecular mechanics calculations have been performed using Cerius2 software,[9] with the universal force field (UFF).[10] The original UFF parameters were modified to ensure consistent characterization of the siloxane bond. In addition, the van der Waals parameters for the carbon and hydrogen atoms constituting the benzene rings have been taken from Lii and Allinger.[11] These parameters were shown to provide an accurate description of the intermolecular interactions for aromatic compounds, having successfully calculated the correct structure and the heat of sublimation for crystalline benzene. The UFF modified parameters, as used in this study, are given in Table 1. For van der Waals interactions we used the Hill function, which consists of an exponential term for the repulsive component and r^{-6} for the attractive component. The nonbonding interactions have been calculated using the Ewald summation algorithm under periodic conditions.[12] The net atomic charges were obtained by running Extended Hückel calculations[13] for a linear trimer. The net atomic charges, shown in Figure 1, are the charges of the central unit of the diphenylsiloxane trimer, which were averaged and scaled for a corresponding dielectric constant of 1.0. (It has been shown previously[14] that electrostatic interactions for siloxane-containing compounds can be accurately described using charges provided by Extended Hückel MO calculations.) The present modifications of the original universal force field are intended to emphasize the intermolecular interactions for phenylsiloxanes in the condensed state and the effects of such interactions upon the structure of the siloxane units. Therefore, when conformational analysis of isolated systems is needed, the original parameters or alternate force fields given in ref 8 or 14 should be used.

A verification of these potentials was done using molecular structures in the crystalline state that were well characterized by X-ray diffraction. The structures utilized to validate the method were those of pentaphenyldisiloxane and hexaphenyldisiloxane, using as a starting point the experimental structures reported by Wojnowski et al.[15] and Glidewell and Liles,[16] respectively. The structures were optimized to attain the conformation corresponding to minimum energy, allowing the unit cell to relax. The energy-optimized structures were very similar to the original structure, with the root-mean-square between the calculated and experimental coordinates of the structures in the corresponding unit cell of 0.13 for pentaphenyldisiloxane and 0.19 for hexaphenyldisiloxane. The density of the optimized unit cell for pentaphenyldisiloxane increased from 1.162 g/cm^3, which is the experimental value,[15] to 1.191 g/cm^3, and from 1.178 to 1.221 g/cm^3 for hexamethyldisiloxane.[16] A higher density is expected with structures calculated by the molecular mechanics method because the molecules are considered to have rigid conformations in the crystal and because the thermal energies and the entropy resulting from lattice vibrations are assumed to be constant. The calculated Si−O−Si bond angle for pentaphenyldisiloxane is 163.2° and the experimental value is 163.3°, and for the case of hexaphenyldisiloxane, the calculated bond angle is 179.6°, which agrees with the experimental value of 180°.

The X-ray powder diffraction patterns for the system to be discussed in this work have been calculated using the standard methods available in the Cerius2 software package.[9]

Results and Discussion

1. Description of the Unit Cell Content and Experimental X-ray Diffraction Pattern for PDPhS. The X-ray powder diffraction pattern shows that the crystalline structure of PDPhS can be characterized by an orthorhombic unit cell having the dimensions a = 20.1 Å, b = 10.51 Å, and c = 10.24 Å.[6] Each unit cell contains two chains, each chain having four repeating units. The reported density[6] of PDPhS is 1.16 g/cm^3. The density calculated from the measured unit cell is 1.22 g/cm^3. No experimental error has been reported. The difference in density can be attributed to amorphous segments of polymer or to the packing of the crystalline domains, which is less efficient than that of the ideal crystalline structure.

The number of reflections which could be resolved experimentally was rather limited, and this factor allows for a large degree of ambiguity in interpreting the data. The low resolution of the pattern might be due to any of several reasons. A first possible reason is that the experimental sample contains crystalline defects. A second possible reason is that the size of the crystalline domains is small; if the size of the crystalline units is less than 400−500 Å, peaks in the X-ray diffraction pattern are broadened. Other possible reasons include polymorphism and the presence of impurities. This will increase the number of peaks which would overlap with the peaks corresponding to the structure of interest. In order to overcome the lack of good resolution of the experimental pattern, the theoretical approach must provide a close simulation of the X-ray diffraction pattern in terms of position of the lines as well as their intensity, and, furthermore, the proposed structure should be energetically stable.

2. Configuration of Chains in the Unit Cell and Chain Conformation. The original structures proposed by Dubchak et al.[6] have been reconstructed, and several arrangements of the helical conformation have been tested in a search of other positions that would account for low-intensity peaks in the X-ray powder pattern between 7.2 and 5.2 Å. During this search, the possibility that the two chains in the unit cell can have either a parallel or antiparallel relationship has been considered as they were shifted along the helical axis. All attempts to shift the chains along the b axis failed to produce low-intensity peaks in the region of interest

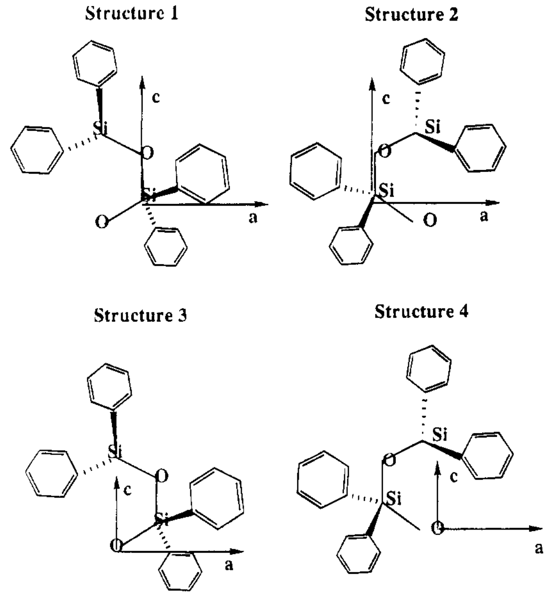

Figure 2. Several orientations for the PDPhS structures relative to unit cell axes *a* and *c* used to evaluate X-ray diffraction patterns.

and did not improve the original results. The same strategy was used with optimized helical structures, but the results again provided a calculated X-ray diffraction pattern having high-intensity peaks in the region between 7.2 and 5.2 Å.

An alternative conformation to the helical backbone is a planar or quasi-planar structure formed by alternating cis–trans sequential torsional angles along the polysiloxane chain. It has been shown previously for poly(dialkylsiloxanes) that this structure is generally more stable than that of the helix.[7,8,18]

A planar structure offers a higher degree of flexibility to orient the chains in the unit cell, and a systematic search has been performed to identify which of these structures will generate a calculated pattern that will match the experimental one. The initial criterion for the structures was to identify those with low-intensity peaks in the region of 7.2–5.2 A. The structures included in the screening process consisted of two chains with the backbones oriented along the *c* axis of the unit cell, with one chain located in the center of the *ab* plane and the other located at one corner of the unit cell.

The plane of the backbone of each chain can be parallel to the *a* or *b* axis, and for each of the two situations the chains can have two configurations which differ by a rotation of 180° of the plane of the backbone about the *c* axis. Also, the backbone can have Si or O atoms in the *ab* plane. These four cases, where the planar backbone is aligned along the *c* axis and its plane parallel with the *a* axis, are illustrated in Figure 2. A similar arrangement was considered for the *bc* plane. All possible combinations of pairs of structures with one chain in the corner of the cell and the other located in its center have been generated and studied.

In addition, the rotation of these chains around the *c* axis was considered. Each chain was rotated by 30, 45, and 60° around the *c* axis, with the following orientations analyzed: 30–30°, 45–45°, 60–60°, and 30–60°. The first value indicates the rotation of the first chain in the corner of the unit cell, and the second value indicates the rotation of the chain located in the center of the unit cell.

The lowest powder diffraction peaks in the region between 7.2 and 5.2 Å were obtained for the chains having the relative orientation of 30–60°. These chains have been considered as starting points for molecular mechanics minimizations to search for optimum chain conformations which will fit the experimental X-ray powder diffraction pattern.

Table 2

minimization procedure	energy (kcal/mol)	*a* (Å)	*b* (Å)	*c* (Å)	density (g/cm^3)
1	−116.49	20.1	10.51	5.12	1.218
2	−122.24	20.16	9.86	4.91	1.347
3	−122.45	20.14	9.83	4.94	1.345

All configurations of pairs of chains for 30–60° rotations have been minimized under periodic boundary conditions defined by the experimentally determined unit cell, and the simulated X-ray patterns have been screened. The selection criteria for this set were diffraction peak intensities in the region of 10–20° for 2θ.

The selected structures that showed a reasonable profile for the simulated X-ray powder diffraction pattern were screened again in terms of the total energy of the minimized structures under the condition that the unit cell dimensions were fixed. These structures were energy minimized under three different types of constraints for the unit cell:

Procedure 1: the unit cell dimensions are fixed with respect to the values reported from experimental measurements.[6]

Procedure 2: all unit cell parameters were allowed to relax (angles and lengths).

Procedure 3: the angles of the unit cell were maintained at the experimental values of 90°, and the *a*, *b*, and *c* values were allowed to relax.

The unit cell reported in this work has a *c* axis length equal to half of the originally reported value, because the quasi-planar backbone has a shorter repeat length than the helical structure.

The structures which were minimized consisted of a unit cell containing two chains of PDPhS, each chain having two monomers. The minimization was done under periodic boundary conditions.

All selection criteria of the simulated X-ray diffraction pattern have been fulfilled by one structure which had the lowest total energy. For the remainder of this paper, only this particular structure will be discussed. The total energy of this structure was about 30 kcal/mol lower than the corresponding energy for the helical optimized structure. This confirms that the planar backbone provides a better environment to position the bulky phenyl groups in the unit cell with the least steric repulsion.

The results of the optimized structure calculated under the three procedures described above are given in Table 2. The angle values α, β, and γ are all 90°, so they are not listed in Table 2.

3. Molecular Structure of PDPhS. This section will discuss the geometry and orientation of the polymer chains in the configuration determined with the molecular mechanics method.

The structural characteristics of the optimized molecular chains do not differ significantly when subject to the three minimizations procedures. The unit cell maintains its orthogonality when the minimization is done under the condition that the unit cell is allowed to fully relax (procedure 2).

The chains are parallel to the c axis, located at the corner and at the center of the unit cell. The orientation of the chains in the unit cell shows the plane of the

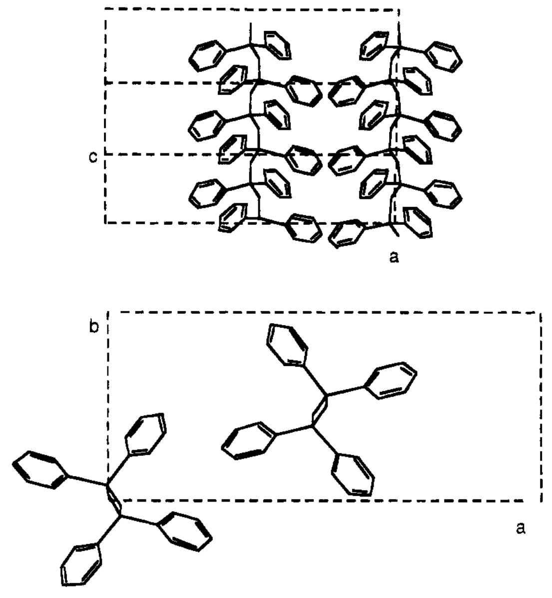

Figure 3. Orientation of PDPhS chains in the crystalline phase: (a) plane *ac*; (b) plane *ab*.

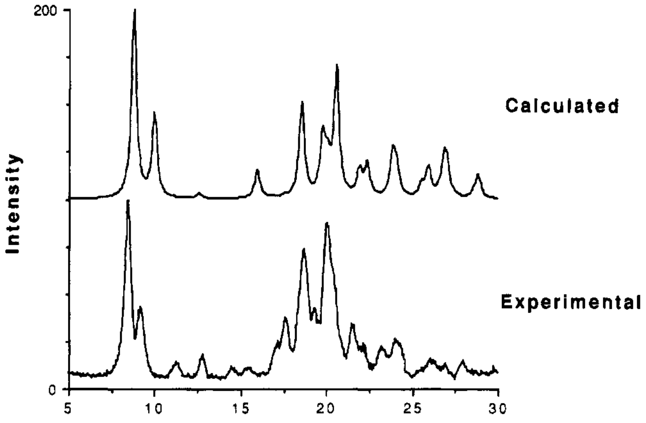

Figure 4. Comparison of experimental and calculated X-ray powder diffraction patterns of PDPhS.

backbone of the chain in the center of the unit cell forming an angle of 22.4° clockwise relative to the 001 plane, and the chain located in the corner of the unit cell forms a corresponding angle of −22.4°. Figure 3 shows the projections of two unit cells in the *ab* and *ac* planes. The backbones of the two chains in the unit cells are oriented along the 510 and −510 planes as defined by Miller indices. The overall packing of the PDPhS chains in the crystalline phase can be considered as being hexagonal. Figure 4 shows one central chain surrounded by the nearest chains in the crystalline phase.

The structure of the backbones of the two chains is not completely planar, and the chain located in the center of the cell is symmetrically inverse to the other chain. There is a deviation from the planar cis−trans structure: the "cis" bond has a torsional angle, τ, with a value of 15.6 ± 3° instead of 0°, and the "trans" bond has a value of 155.6 ± 3°. The deviation from the planar conformation of the two chains is in an opposite sense and is similar with two helices that have opposite rotations.

The minimized structure can be reduced according to crystallographic symmetry operations on the $Pbn2_1$ symmetry group.[19] The repeating unit with normalized coordinates listed in Table 3 can generate the complete structure of the two chains with two monomers per chain using the following equivalent positions:

$$x, y, x; \quad -x, -y, {}^1\!/_2 + z; \quad x + {}^1\!/_2, {}^1\!/_2 - y, {}^1\!/_2 + z; \quad {}^1\!/_2 - x, {}^1\!/_2 + y, z$$

Table 3. Atom Coordinates: Symmetry $Pbn2_1$ (Unit Cell: a = 20.145 Å, b = 9.829 Å, c = 4.944 Å, α = 90.0°, β = 90.0°, γ = 90.0°)

	x	*y*	*z*
Si	−0.01611	0.08612	0.05805
O	−0.01429	0.02826	0.36074
C	−0.10632	0.13002	−0.03809
C	0.03805	0.24221	0.04790
C	−0.14003	0.06570	−0.24636
C	−0.20410	0.10408	−0.31155
C	−0.23514	0.20673	−0.16824
C	−0.20240	0.26930	0.04345
C	−0.13834	0.23064	0.10888
C	0.08786	0.25845	−0.14296
C	0.12837	0.37206	−0.13542
C	0.11968	0.46910	0.06392
C	0.06998	0.45348	0.25364
C	0.02943	0.34020	0.24662

Table 4. Geometry of PDPhS Obtained with Various Constraints of the Unit Cell

	minimization procedure		
	1	2	3
Si−O−Si−O cis (deg)	18.6	13.4	15.5
Si−O−Si−O trans (deg)	153.1	158.2	155.6
C_a−Si−C_b−$C_{b'}$ (deg)	123.4	124.9	123.3
C_b−Si−C_a−$C_{a'}$ (deg)	68.8	71.6	71.0
Si−O−Si (deg)	150.8	143.2	145.4
C−Si−C (deg)	109.5	111.0	110.9
Si−O (Å)	1.632	1.602	1.601
Si−C (Å)	1.917	1.908	1.905
C−C (Å)	1.386	1.385	1.385

There are small discrepancies between the structures generated with symmetrical equivalent positions and the structures obtained from minimizations. These differences have been removed by shifting each of the four repeating units to the origin of the unit cell through the corresponding symmetry operation and then generating an average structure of the four translated repeating units. The significant geometrical features (torsional and bond angles, bond lengths) of the minimized structures are listed in Table 4.

The type of the unit cell relaxation allowed during the minimization alters the resulting siloxane backbone of the polymer. The structural elements listed in Table 4 show significant differences between the molecular structures obtained by procedure 1 and the other two procedures. On the other hand, the structures obtained by procedures 2 and 3 are similar. Using procedure 1, the unit cell was fixed at the experimental dimensions, which are larger than those of the calculated values of the optimized unit cell, and these conditions lead to a slightly larger deviation of the siloxane backbone from the planar conformation. The "cis" bond has an average torsional angle of ±18.6° and the "trans" bond a torsional angle of ±153.1°. When the unit cell is allowed to relax during optimization (procedure 2), these torsional angles have the corresponding values of ±13.4 and ±158.2°, respectively. The latter set of values for the torsional angles of the siloxane bond lead to a flatter backbone. The Si−O−Si bond angle and the Si−O bond length are larger when minimization is performed under procedure 1. The average value of the Si−O−Si bond angle decreases from 150.8 to 143.2° when the unit cell is allowed to relax. The Si–O bond length also decreases from 1.632 to 1.602 Å.

The changes in the torsional orientation of the benzene rings are small, and only the minimized structure under procedure 2 will be discussed. The orientation of the phenyl groups has been measured in terms of the dihedral angles defined by the $C_a-Si-C_b-C_{b'}$ atoms and $C_b-Si-C_a-C_{a'}$ atoms as shown in Figure 1. The torsional angles for the phenyl rings in the chain located at the corner of the unit cell are 124.9 and 71.6°. The corresponding torsional angles for the phenyl rings attached to the silicon atoms located in the same *ab* plane in the other chain are 55.3 and 111.7°, which can be considered the supplementary angles relative to the first pair of torsional angles and result from the symmetry of the $Pbn2_1$ space group.

We analyzed the relative orientation of the phenyl rings in PDPhS by comparing the interplanar angles of one phenyl ring with its nearest neighbors. For comparison purposes, this analysis was done for PDPhS, hexaphenyldisiloxane, pentaphenyldisiloxane, and crystalline benzene. The nearest neighbors were determined by generating a crystalline domain with three unit cells in each direction and selecting a central phenyl ring with its closest rings. The criterion to select the nearest neighbors was that two rings should have at least one carbon atom at a distance between 3.2 and 4.1Å. The interplanar angles between the central ring and each of its neighbors have been measured.

Crystalline benzene has a central ring surrounded by 12 other rings.[20] Four rings form an interplanar angle with the central ring of 25.9°, another four have an interplanar angle of 83.9°, and the remaining four have an angle of 89.6°.

The phenyl rings present in siloxane compounds are either parallel with or perpendicular to the central ring. In hexaphenyldisiloxane the central unit is surrounded by eight rings, out of which two are parallel and the other six have interplanar angles of 85–87°. In pentaphenyldisiloxane one central ring has nine nearest neighboring groups, seven having interplanar angles between 80 and 87°, and the other two are parallel with the central ring. If another central ring is selected, one group is parallel with the central ring and the other forms an interplanar angle of 26°. In poly(diphenylsiloxane), there are ten nearest neighbors. Two phenyl groups are parallel with the central unit, another seven assume interplanar angles between 73 and 80° relative to the central ring, and one forms an interplanar angle of 60°.

The analysis of the interplanar angles indicates that the crystal configuration and the siloxane backbone, in the case of poly(diphenylsiloxane), are trying to accommodate the phenyl rings into an orthogonal configuration, which is the most stable. The siloxane backbone flexibility in PDPhS allows for a more efficient packing of the benzene rings when compared with hexa- or pentaphenyldisiloxane.

Table 5 lists the experimental X-ray diffraction results obtained from two samples of PDPhS. The table includes the original data from ref 6 and the data obtained in our laboratories. It can be seen that the interplanar distances and relative intensities vary from sample to sample, and this may indicate that the crystalline structure of the polymer is sensitive to the thermal history of the sample and perhaps to its preparative method. The most significant differences occur at the first peak, where the interplanar distance varies from 9.905 to 10.418 Å. In addition, the intensity which is the highest in our samples at 10.42 Å, has a lower relative intensity in ref 6, where the maximum intensity peak is located at the distance of 4.42 Å. Our samples also show strong-intensity peaks in that region of the diffraction pattern.

Table 5. Experimental Patterns from X-ray Powder Diffraction for Two Samples

ref 6		present work	
d (Å)	I (%)	*d* (Å)	I (%)
10.050	68.541	10.418	100.0
9.310	38.956	9.605	43.0
7.620	16.600	7.783	14.0
6.810	22.758	6.975	15.0
5.650	6.693	5.700	10.0
5.090	21.553	5.163	24.0
4.960	44.177	5.050	36.0
4.670	89.826	4.736	74.0
4.520	56.359	4.436	86.0
4.420	100.000	4.341	62.0
4.080	38.286	4.111	33.0
3.760	28.380	4.022	22.0
3.660	51.807	3.717	24.0
3.380	32.932	3.424	15.0
3.310	34.806	3.188	15.0
3.150	33.601		

Table 6. Calculated and Experimental X-ray Diffraction Peaks for PDPhS

		calculated		experimental	
hkl	2*θ*	distance (Å)	intensity	distance (Å)	intensity
200	8.779	10.0724	100.00	10.418	100
110	10.013	8.8339	44.29	9.605	43
				7.783	14
210	12.582	7.0348	2.79	6.975	15
310	15.984	5.5447	15.71	5.163	24
400	17.610	5.0362	1.18	5.050	36
101	18.478	4.8016	8.05		
120	18.583	4.7747	44.69	4.736	74
410	19.807	4.4822	31.19		
220	20.102	4.4170	15.99	4.436	86
111	20.586	4.3143	68.56	4.341	62
211	21.973	4.0450	14.07	4.111	33
301	22.329	3.9813	4.45	4.022	22
320	22.417	3.9660	13.18		
510	23.868	3.7280	22.98	3.717	24
311	24.117	3.6901	15.06		
021	25.555	3.4856	6.55		
121	25.941	3.4345	15.89	3.424	15
600	26.547	3.3575	1.32		
411	26.847	3.3207	21.01	3.188	15
221	27.069	3.2939	12.55		
501	28.579	3.1233	1.92		
321	28.859	3.0936	12.52		

We will compare the calculated X-ray diffraction pattern for the structure optimized using procedure 3, where the unit cell was allowed to relax its dimensions but the angles were held orthogonal. The other minimization (procedure 2), where the angles were allowed to relax, provided a pattern that is practically identical to the one obtained under procedure 3; however, the small deviations of the lattice angles by 0.2–0.4° from 90° split some of the peaks between planes with positive and negative Miller indices.

Table 6 compares the calculated X-ray diffraction pattern with experimental data for the sample obtained at Dow Corning. Figure 5 shows the calculated and experimental patterns. The calculated peak positioned at $d = 10.07$ Å is generated by the 200 plane and has the maximum intensity. The calculated pattern does not reproduce the experimental low-intensity peak at 7.783 Å. This might be due to the model or to an impurity or polymorphs. Other sources which might

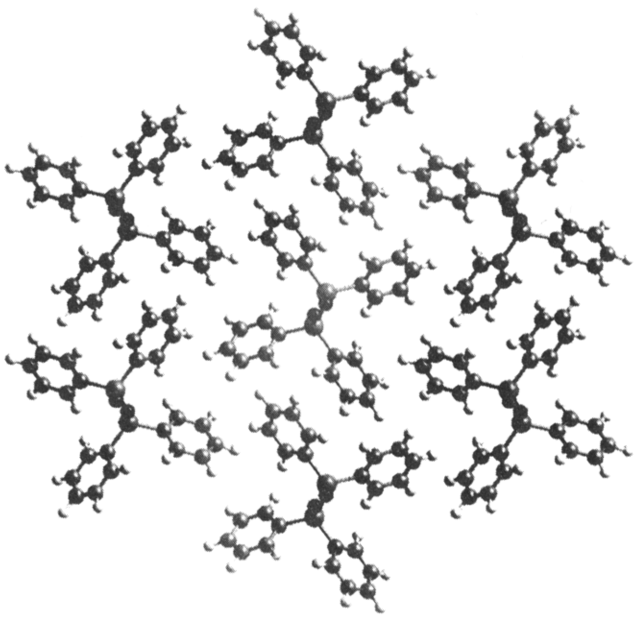

Figure 5. Hexagonal configuration of the nearest-neighbor chains of PDPhS in the crystalline state.

explain some of the discrepancies between the calculated and the experimental patterns are the small size of the crystalline domains and the lattice strain.

The cis–trans conformation of the siloxane backbone is not unusual for polysiloxanes. Using theoretical calculations, it has been shown previously[7,8,14] that the cis–trans conformation is the most stable for siloxanes in general and poly(dimethylsiloxane) (PDMS) in particular. A similar conclusion was reached by Tsvankin et al.[21] who studied poly(diethylsiloxane) (PDES) using crystallographic methods.

The effect of the substituents at silicon upon the organization of the polysiloxane chains can be illustrated by comparing PDMS with poly(dialkylsiloxanes) and poly(diphenylsiloxanes). PDMS does not form a mesomorphic state, and its melting point is below room temperature by 50 °C. In contrast, poly(dialkylsiloxanes) and poly(diphenylsiloxanes) have melting points above room temperature, they have a high degree of crystallinity, and they are forming a mesophase state.[22] We have shown in this study that the tendency of phenyl groups to orient perpendicular to its nearest neighbors is a critical driving force for the orientation of the chains in the crystalline state. Previously, it has been shown[18,23] that in the case of PDES the torsional barrier of the methyl groups at the ethyl side chains has a value for the energy barrier equal to the measured energy required for the isomorphic transitions from the $\alpha 1$ to $\alpha 2$ and from the $\beta 1$ to $\beta 2$ crystalline forms.

Conclusions

Using molecular modeling methods, we have been able to provide a new structure for crystalline PDPhS which is capable of explaining the significant features of the X-ray powder diffraction pattern. The structure of the polymer is not helical but consists of a siloxane backbone in a quasi-planar cis–trans conformation which can be reduced to a unit cell with the $Pbn2_1$ symmetry group. The unit cell is orthorhombic and contains two chains, each chain having two monomers. The chains are symmetrically inverse and are oriented along the *c* axis. The density of the crystalline material as estimated by our study is about 5% greater than the density originally reported. By comparing the calculated and the measured values for the densities of pentaphenydisiloxane and hexaphenyldisiloxane with the density of PDPhS, the molecular mechanics calculations show that at low temperatures the density of the crystalline polymer should be in the range of 1.26–1.3 g/cm^3. This range differs significantly from the measured value of 1.16 g/cm^3 and is higher than the density calculated from the measured unit cell (1.22g/cm^3).

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