Energy calculations of the crystal structure of poly(di-methyl silane)

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Low energy crystal structures of poly(di-methyl silane), which is known to have a *trans* backbone conformation, have been investigated. Energy calculations on isolated molecules show that, like its hexyl counterpart, the lowest energy backbone conformation of the molecule is not all-*trans* but a helix with the backbone bonds rotated 15° away from *trans*. This corresponds approximately to a 15/7 helix. To determine if the observed *trans* conformation results from intermolecular interactions, various packing modes of the *trans* and the 15/7 helix were analysed and their energies compared. Best packing was found for the *trans* conformation. For the all-*trans* molecules arranged in an orthorhombic unit cell, the lowest intermolecular energy was found for $a = 1.19$ and $b = 0.78$ nm, in good agreement with dimensions found experimentally at room temperature.

(Keywords: energy calculations; crystal structure; poly(di-methyl silane); polysilanes)

INTRODUCTION

Di-alkyl substituted polysilanes have recently been the focus of increasing attention due to their potential application as radiation sensitive materials for microlithographic applications, materials with non-linear optical properties, thermal precursors to β-silicon carbide fibres, polymeric photoconductors and oxygen-insensitive photoinitiators for vinyl polymerization, to name a few. The electronic properties of these σ-conjugated polymers are known to be dependent on their backbone conformations.

The solid state molecular conformations and the electronic absorptions of these polymers have been studied extensively. From investigations of homologous polymers with four to eight carbon atoms in their side chains, it was found that polymers with fewer than six carbon atoms in their side chains[1,2] adopt a 7/3 helical backbone conformation and absorb at about 320 nm, whereas polymers with six and more carbon atoms in their side chains[3,4] adopt an all-*trans* backbone conformation and absorb at about 373 nm. From this, it was concluded that the long wavelength absorption was associated with the all-*trans* backbone conformation[3], and that a side-chain length in the vicinity of six carbon atoms was necessary to produce enough steric interactions between molecules to stabilize an all-*trans* backbone conformation, although the lowest energy conformation of an isolated molecule (where intermolecular interactions do not come into play) is a helical one. However, recent studies have found that the backbone conformations of poly(di-methyl silane) (PdMS), poly(di-ethyl silane) (PdES), and poly(di-n-propyl silane) (PdnPrS) are all-*trans*[5,6], although unlike the other group of polysilanes with longer side chains and all-*trans* backbone conformations, these show maximum absorption at about 330–340 nm. In order to explain the unexpected backbone conformation and the electronic transition of these lower homologues, it has been suggested that the force which drives the backbone into all-*trans* conformation is different in the two cases[5]. For the higher homologous polymers, interactions between the side chains determine the molecular conformation, whereas for these lower homologous polymers, interactions within the silicon backbone dominate. The rigidity of the backbone affects the electronic absorption, and these lower homologous polymers absorb at lower wavelengths because of less rigid backbones[5].

The solid-state structures and phase transitions of PdMS have been investigated by Lovinger *et al.*[5]. Differential scanning thermograms reveal two endotherms, one corresponding to a primary transition at about 160°C ($\Delta H \approx 2.5$–2.75 cal g^{-1}), and the other corresponding to a secondary transition at about 220°C ($\Delta H \approx 0.35$–0.8 cal g^{-1}). Below 160°C, the polymer adopts an all-*trans* backbone and packs in a monoclinic unit cell with $a = 1.218$, $b = 0.800$, $c = 0.388$ nm and $\gamma = 91°$. The all-*trans* backbone is preserved through the primary transition at 160°C, although there is intermolecular rearrangement as the molecules arrange themselves in a metrically hexagonal lattice. The second transition at 220°C involves both conformational and orientational disordering and the molecular backbone is no longer all-*trans*. The polymer shows maximum u.v. absorption at 340 nm (at room temperature) and does not show thermochromism.

We have used molecular mechanics methods to study the low-energy crystal structures of PdMS. Our earlier work on poly(di-n-hexyl silane) (PdnHS)[7,8] and poly(di-n-hexyl germane) (PdnHG)[9] suggested that intermolecular interactions are predominantly responsible for the solid-state conformations of these polymers. Although energy calculations have been done on isolated

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molecules of PdnHS[7] and PdnHG[9], packing calculations, which take into consideration intermolecular interactions, could not be undertaken due to lack of information about the side-chain conformations. PdMS, being the simplest di-alkyl polysilane, is an ideal polymer in which to incorporate the effects of packing considerations in determining the molecular conformation of the polymer in the solid state.

Extensive energy calculations have been carried out on single chains of PdMS[10–12]. Full relaxation molecular calculations by Damewood and West[10] found the all-*gauche* conformation to be preferred over the all-*trans* conformation. On the other hand, Mintmire[12], using a LCAO-LDF method, found that the band gap increases as the backbone is twisted from the all-*trans* to an all-*gauche* conformation. In both cases only a few commonly observed conformations were analysed. The calculations did not cover the entire conformational space, and therefore, do not necessarily provide information about the most preferred conformation. Recently Welsh and Johnson[11], using the molecular orbital approach, found the lowest energy conformation to be that with the backbone torsion angle equal to 170° (relative to all-*trans* defined as 180°). This is different from the results found by Cui *et al.*[13]. Using the AM1 approach based on modified neglect of diatomic overlap (MNDO), they found the all-*trans* conformation to be of the lowest energy[13]. However, the torsion angle increments used in the calculations were not specified. AM1 calculations carried out by us indicate that the potential curves are almost flat and, depending on the computational constraints used, off-*trans* conformations can be as low or lower in energy than perfect-*trans* conformations. These conflicting results indicate that the lowest energy conformation of PdMS is far from being resolved.

All the above mentioned calculations were limited to isolated molecules. Energy calculations which consider only intramolecular interactions often predict correct conformations but do not represent a real situation because they ignore intermolecular interactions between molecules. Since we are interested in the solid-state structure and the possible conformations have very similar intramolecular energies, neglect of the intermolecular energies is not reasonable. In the present study, we have calculated crystal packing energies (which consider both intramolecular and intermolecular interactions, unlike calculations on isolated chains which consider only intramolecular interactions). Calculations were also undertaken on isolated chains in order to compare the results with those found by earlier studies.

CALCULATIONS AND RESULTS

Conformational search on isolated molecules

In order to scan large regions of conformational space, a computer program was used[14] which uses the molecular mechanics approach and a force field that considers only steric interactions. Energies of single chains were minimized by varying the torsional rotations about bonds while keeping bond lengths and bond angles fixed. This method offers computational speed and is thus complementary to the more rigorous full relaxation method used for the final analysis of the low energy conformations. The bond lengths and angles used in these fixed geometry calculations are given in *Table 1*. The Si–Si–Si angle was calculated from the layer-line spacing of the fibre diffraction pattern reported by Lovinger *et al.*[5]. Three values of C–Si–C angles were considered: 108.5°, which is the equilibrium angle used for angle bending energy parameters in the SYBYL–Tripos force field[15] (these parameters were later used for the full relaxation calculations); 98° (<108.5°) and 112° (>108.5°), which were chosen to study the effect of different choices of bond angles on the geometry of the minimized structure.

The program calculated the non-bonded energy $E = \sum E_{ij}^{\mathrm{nb}}$ by using the potential function:

$$E_{ij}^{\mathrm{nb}} = A_{ij} \exp(-B_{ij} r_{ij}) - C_{ij}/r_{ij}^6$$

where A_{ij}, B_{ij} and C_{ij} are energy parameters characteristic of the atom pair ij, and r_{ij} is the separation distance between the atoms. Values of the energy parameters are given in *Table 2* and were derived from those given in the polymer module of SYBYL[15]. These parameters describe essentially the same force field as that used by us in earlier calculations[16]. The parameters of the 6–12 form of the potential functions used then[16] were converted from the parameters of the Buckingham potential function in the present case.

The interaction energy of a repeat unit, consisting of two consecutive silicon atoms and attached methyl units, with the rest of the chain (in this case four repeat units) was calculated. A scan of conformational space was made in 30° steps by simultaneously varying the backbone torsion angles and the torsion angles about the Si–C bonds. Each energy minimum was then refined using a grid search method with smaller increments. These calculations show that the lowest energy conformation of an isolated molecule is a helix with torsion angle 15° away from *trans* (see *Table 3*). This is obviously very close to the 170° torsion corresponding to the lowest energy conformation found by Welsh and Johnson[11] using molecular orbital methods. Clearly, the particular minimum energy torsion angle depends upon the computational method, force field, and other aspects of the model. Molecules with a fixed all-*trans* backbone were also analysed by varying only the torsion angles about the Si–C bonds. The calculated intramolecular energies per monomer (one silicon atom and attached methyl units) corresponding to various low-energy

Table 1 Bond lengths and angles

	Bond lengths (nm)		Bond angles (degrees)
Si–Si	0.235	Si–Si–Si	111.3
Si–C	0.188	C–Si–C	98.0, 108.5, 112
C–C	0.153	Si–Si–C	108.6
C–H	0.109	H–C–H	108.0

Table 2 Energy parameters[a]

Interaction	*A*	*B*	*C*
C–C	14 961.4	3.090	640.2
C–H	4315.8	3.415	138.1
H–H	2647.0	3.740	27.3
Si–Si	234 276.0	3.414	2157.9
Si–C	59 198.4	3.252	1175.3
Si–H	24 902.2	3.577	243.1

[a] The units of A, B and C are such as to give E in kcal mol^{-1} when r is in Å

Table 3 Conformational energies of isolated PdMS molecules

	Trans			Helical (15/7)		
C–Si–C (degrees)[a]	112.00	108.50	98.00	112.00	108.50	98.00
Torsion about Si–Si (degrees)[a]	180.00	180.00	180.00	165.00	165.00	165.00
Torsion about Si–C (degrees)[a]	150.00	165.00	165.00	170.00	170.00	170.00
Energy/monomer (kcal mol^{-1})	−2.15	−2.21	−1.95	−2.64	−2.64	−2.34

[a] The torsion angles are defined for all-*trans* as 180°

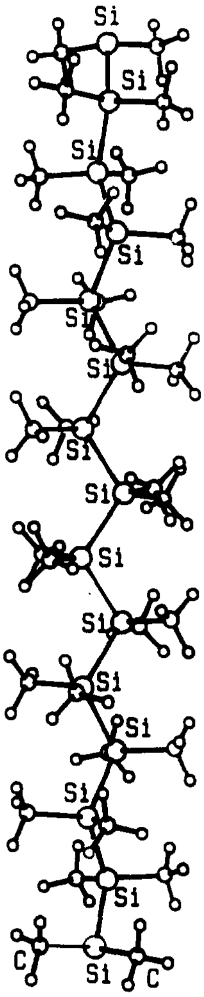

Figure 1 The 15/7 helical conformation of the PdMS molecule shown along the molecular axis

conformations and different C–Si–C angles are given in *Table 3*.

For a helical polymer, the internal rotation angle τ, is related to θ, the angle of rotation about the helix axis, by the equation[17]:

$$\tan(\tau/2) = \frac{d}{r}\tan(\theta/2)$$

where r is the bond length and d is the projection of the bond on the helix axis. For the given backbone bond angle and bond length, values of $\tau = 165°$ and $d/r = 0.826$ correspond approximately to a θ value of 168°, which in turn closely corresponds to a 15/7 helical conformation. For convenience we will refer to this as the 15/7 helix (*Figure 1*), although incommensurate helices having nearly the same torsion angles cannot be ruled out. This is very similar to the backbone conformation of phase I of poly(tetrafluoroethylene), which in its high temperature phase above 19°C exhibits a 15/7 helical conformation.

Energy minimization on isolated molecules

Full relaxation energy minimizations, which adjust bond angles and bond lengths, were also carried out using the SYBYL molecular modelling package[15]. The force field was that used by us in earlier calculations[16]. A similar model to that used for the conformational search, consisting of eight silicon atoms and their attached side chains, was used. Along with the low energy conformations found by conformational search, various other conformations such as *gauche–gauche* and *trans–gauche* were also analysed. Here too, the 15/7 helix was found to be the most preferred conformation.

Crystal packing

In order to investigate whether intermolecular interactions are indeed largely responsible for the observed all-*trans* conformation in the solid state, *trans* and helical backbone structures were packed in various crystalline arrays and the best mode of packing for each conformation was analysed using a program described previously[14]. Chains of 15 monomer units (one monomer being one silicon atom and attached methyl units) were held internally rigid at fixed bond lengths and bond angles (see *Table 1*; the C–Si–C bond angle used was 108.5°). The chains were arranged parallel to each other, and were allowed translations along the x and y cell axes and rotation about the chain axis (z). The interaction energy between the central repeat unit and all neighbouring chains was calculated out to a separation distance of 1.0 nm (beyond this distance the van der Waals interactions are negligible and need not be considered). The non-bonded potential parameters used were the same as in the conformational search (*Table 2*). The initial calculations were made using an array of nine chains for the orthorhombic and monoclinic packing, and an array of seven chains for hexagonal packing. The positions and rotations of the chains were simultaneously varied in large increments. After energy minima were identified, larger arrays of 19 chains were considered and the parameters were varied over a narrow range in very small increments to find the actual minimum. The choice of an array of 19 chains made it possible to directly compare the energies of various packing modes without

Table 4 Intermolecular energies of PdMS molecules

Structure Conformation	Orthorhombic 2/1	Monoclinic(I) 2/1	Monoclinic(II) 2/1	Metrically hexagonal 2/1	Hexagonal 15/7
a (nm)	1.19	0.725	1.45	0.76	0.78
b (nm)	0.78	0.69	1.38	–	–
θ (degrees)	42.00	10.00	10.00	0.00	0.00
γ (degrees)	–	113.60	108.00	–	–
Energy/monomer (kcal mol^{-1})	−6.92	−7.08	−6.91	−5.74	−4.94

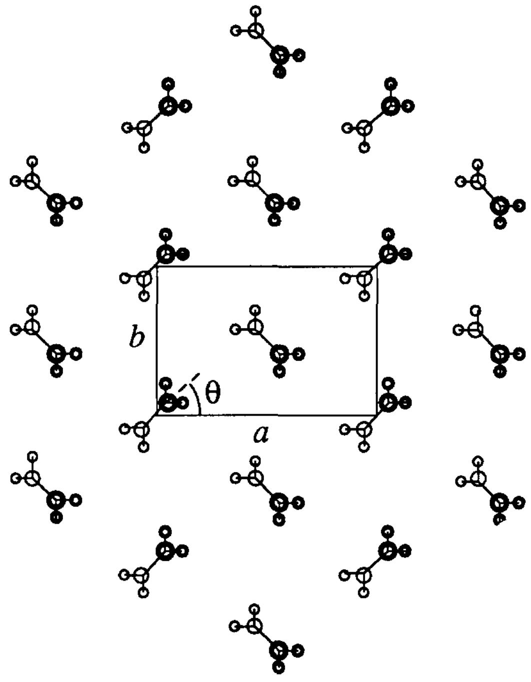

Figure 2 Schematic representation of the orthorhombic array projected parallel to the all-*trans* molecular backbone. The atoms shown by thicker circles are above the plane of the paper while the others are below the plane

over-emphasizing specific interactions in a particular mode of packing[18].

Three cases were considered: case I, orthorhombic and monoclinic packing of all-*trans* backbone structures (similar to that found for polyethylene)[18,19]; case II, metrically hexagonal packing of all-*trans* backbone molecules; case III, hexagonal packing of helical (15/7) backbone molecules. The lowest intermolecular energies per monomer (one silicon atom and attached side chains) found for each case are given in *Table 4*.

Case I. For the orthorhombic packing (*Figure 2*), two chains per unit cell were considered. The interaction energy was minimized by simultaneously varying *a* and *b* and rotating the two molecules independently while keeping *c* fixed at 0.388 nm (the observed layer-line repeat distance). The lowest energy was found for $a = 1.19$ and $b = 0.78$ nm, and with the two molecules oriented at $\theta = \pm 42°$ with respect to the *a* axis (*Figure 3*). These unit cell dimensions are very close to those found at room temperature by X-ray diffraction studies[5] ($a = 1.218$ and $b = 0.8$ nm). Changing the angle between the *a* and *b* axes to the experimentally reported[5] value of 91° did not lower the energy.

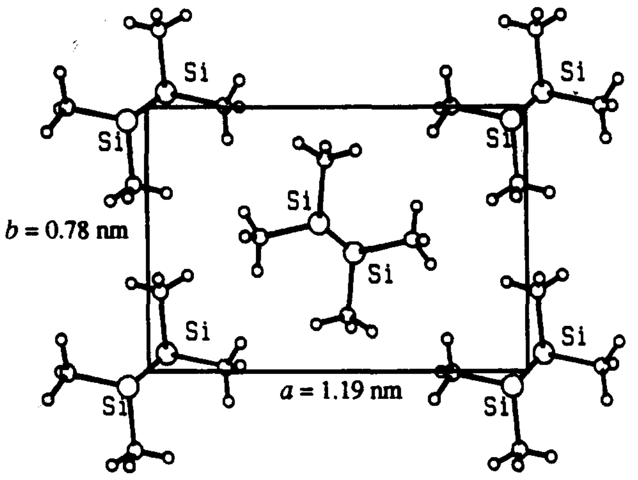

Figure 3 The *ab* projection of the lowest energy orthorhombic unit cell

For the monoclinic unit cell, two kinds of arrangement seemed possible. The first had one molecule per unit cell (*Figure 4a*), while the other had two (*Figure 4b*). In each case the energy was minimized by varying *a*, *b*, *γ* and *θ* simultaneously. The lowest energy was found for the smaller unit cell with $a = 0.725$ nm, $b = 0.69$ nm, $\gamma = 113.6°$ and $\theta = 10°$ (monoclinic I). A slightly higher energy was found for the larger unit cell with $a = 1.14$ nm, $b = 1.38$ nm, $\gamma = 108°$ and $\theta = 10°$ (monoclinic II).

Case II. Since the polymer packs in a metrically hexagonal lattice above 160°C (above the primary transition), a metrically hexagonal packing of all-*trans* molecules was also considered (*Figure 5a*). The energy was miminized by varying *a* and rotating the molecules on adjacent 1 0 0 planes independently (i.e. *p*s and *q*s independently). The lowest energy was found for $a = 0.76$ nm and $\theta = 0.0$ (*Figure 6*). This value of *a* is slightly smaller than that reported[5] from electron diffraction (0.779 nm) at 180°C.

Case III. Chain segments with the 15/7 helical backbone were arranged on a hexagonal lattice (*Figure 5b*), and the energy was minimized by varying the positions and orientations of the molecules. Since left- and right-handed helices are possible, two cases were considered, one with all the molecules of the same hand and the other with molecules of opposite hand on adjacent 1 0 0 planes (i.e. *p*s left-handed and *q*s right-handed). In both cases, along with varying the position of the molecules, adjacent molecules on the same 1 0 0 plane were allowed to rotate independently (adjacent *p*s and adjacent *q*s) in steps of 24° (360/15).

This interval was chosen to allow monomer units on adjacent molecules to be crystallographically equivalent. Unlike the case of poly(tetrafluoroethylene)[20], packing right- and left-handed PdMS molecules on adjacent positions did not decrease the energy significantly, nor did orienting adjacent molecules differently. Therefore, for our final comparison, all the molecules were considered to be right-handed and equivalent. The lowest energy was found for $a = 0.78$ nm.

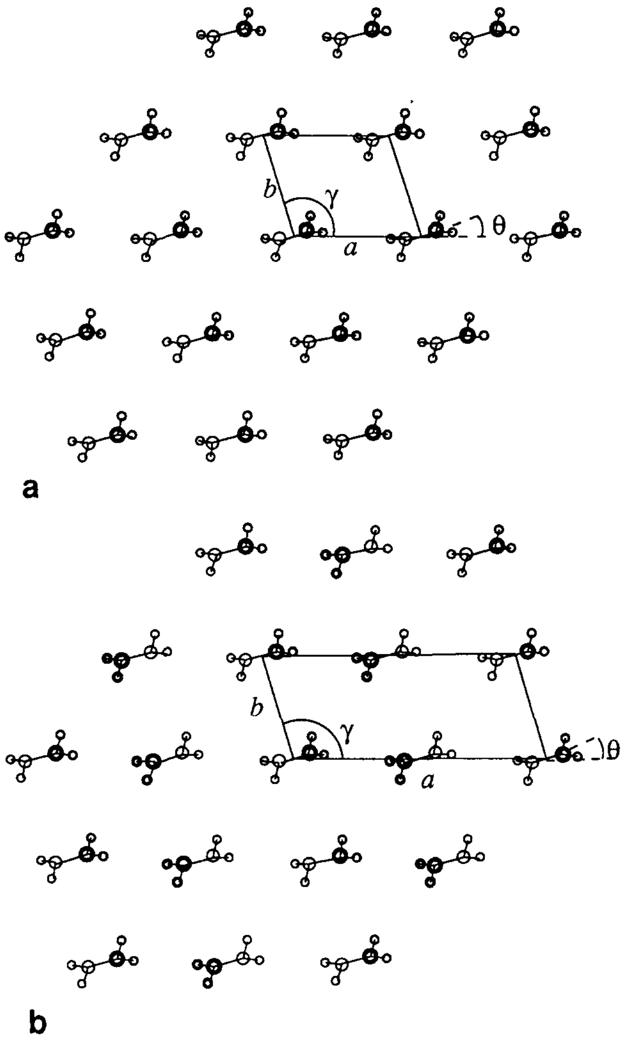

Figure 4 Schematic representation of the monoclinic array projected parallel to the all-*trans* molecular backbone. The atoms shown by thicker circles are above the plane of the paper while the others are below the plane. (a) Monoclinic I. (b) Monoclinic II

DISCUSSIONS AND CONCLUSION

The calculated energies of the experimentally observed[5] crystal structures are tabulated in *Table 5*. All the dimensions for each refined structure were close to those observed experimentally. It can be seen from *Table 5* that although the total conformational energy of an isolated PdMS molecule in a 15/7 helical conformation is a little lower than that in an all-*trans* conformation, the packing energy of molecules in an all-*trans* conformation is

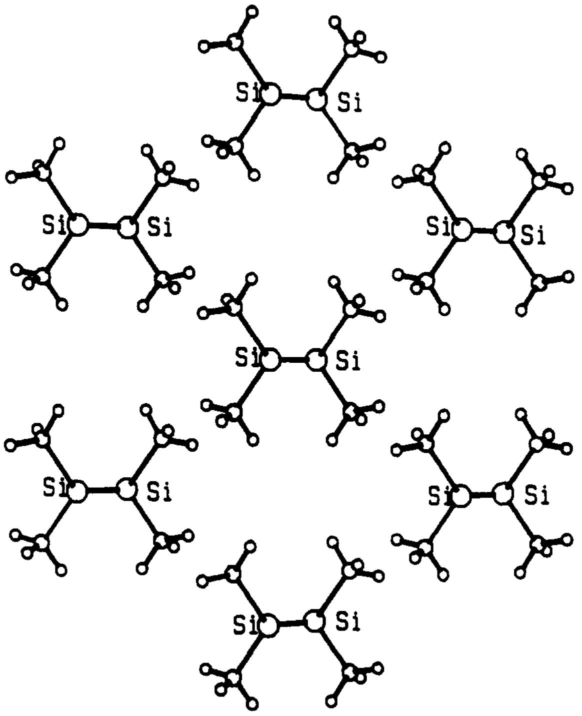

Figure 6 Projection of the low energy metrically hexagonal unit cell parallel to the molecular axis, $a = 0.76$ nm

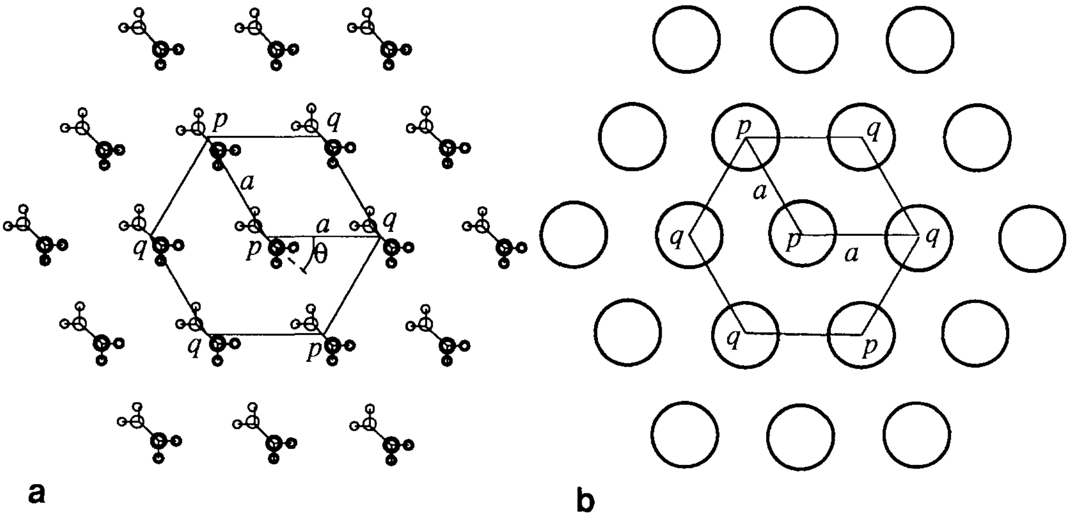

Figure 5 Schematic representation of the basal projection of the molecular arrays. The atoms shown by thicker circles are above the plane of the paper while the others are below the plane. (a) Metrically hexagonal arrangement of all-*trans* molecules. (b) Hexagonal arrangement of helical molecules

Table 5 Crystal packing energy of PdMS

Structure Conformation	Orthorhombic 2/1	Metrically hexagonal 2/1	Hexagonal 15/7
Non-bonded conformational energy (isolated chain) (kcal mol^{-1})	−2.21	−2.21	−2.69
Bonded conformational energy (isolated chain) (kcal mol^{-1})	0.12	0.12	0.04
Total conformational energy (isolated chain) (kcal mol^{-1})	−2.09	−2.09	−2.65
Packing energy (kcal mol^{-1})	−6.92	−5.74	−4.94
Total energy/monomer (kcal mol^{-1})	−9.01	−7.83	−7.59

Table 6 Comparison of *d* spacings

h k l	d_{obs} (nm)	d_{calc} (nm)
1 0 0	0.671	0.675
1 −1 0	0.608	0.605
1 1 0	0.400	0.396
1 0 1	0.338	0.336
2 0 0	0.338	0.337
1 −1 1	0.327	0.327
2 −2 0	0.302	0.302
2 1 0	0.259	0.260
0 0 2	0.194	0.194
0 1 2	0.185	0.186
1 −1 2	0.185	0.185

considerably lower than that of molecules in a helical conformation. The net result is that the total energy (sum of intra- and intermolecular energies) of molecules in an all-*trans* conformation is lower than that of those in a helical conformation.

Since the energy calculations do not take into consideration the effect of atomic vibrations, the computed unit cell dimensions should be compared to the experimental unit cell data extrapolated to a (low) temperature corresponding to the data from which the force field parameters were derived. As expected, the unit cell dimensions for each refined structure were found to be slightly smaller than those observed experimentally.

The lowest energy was found for the all-*trans* conformation packed in orthorhombic or monoclinic lattices. Monoclinic I was actually slightly lower in energy than the orthorhombic and monoclinic II structures (see *Table 4*). However, the lowest energy monoclinic structure (*Figure 4a*) is not observed experimentally whereas the nearly orthorhombic packing (*Figure 3*), with slightly higher calculated energy, is observed[5]. Though surprising, this is not unusual for polymers. The most commonly observed form of polyethylene is orthorhombic, which has slightly higher energy than the monoclinic form[21,22]. Monoclinic polyethylene is observed when the sample is deformed, and has been suggested to be a defect associated with stacking faults.

We refined our lowest energy monoclinic unit cell dimensions (monoclinic I) using the reported *d* spacings from X-ray measurements[5]. Interestingly, the agreement between the observed[5] and calculated *d* spacings (*Table 6*) is very good for the refined unit cell of dimensions $a = 0.737$ nm, $b = 0.707$ nm and $\gamma = 113.6°$. The average discrepancies in the values of the *d* spacings and the diffraction angles were found to be 0.02 Å and 0.11°, respectively. This is slightly better than those for the unit cell reported by Lovinger[5] ($\Delta d = 0.024$ Å and $\Delta\theta = 0.157°$).

All-*trans* molecules packed in a metrically hexagonal fashion have a higher energy than in the orthorhombic packing, but lower energy than hexagonally packed helical molecules. This fits very well with what is known about the polymer structure. PdMS undergoes a primary transition from an orthorhombic packing of all-*trans* molecules to a metrically hexagonal packing of all-*trans* molecules above 160°C and then to a hexagonal packing of non-*trans* molecules above 220°C (ref. 5).

It can be seen from *Table 5* that the change in energy for packing rearrangement (i.e. the energy difference between all-*trans* molecules arranged in an orthorhombic packing and those arranged in a metrically hexagonal packing, $\Delta E = 1.18$ kcal mol^{-1}), is greater than the change in energy for a conformational change (i.e. the energy difference between all-*trans* molecules arranged in a metrically hexagonal packing and molecules with 15/7 helical conformation arranged in hexagonal packing, $\Delta E = 0.24$ kcal mol^{-1}). This was also found by Lovinger *et al.*[5] from thermal analyses where the change in enthalpy corresponding to the first transition is much larger than that of the second transition. It has also been suggested[23] that the second transition at about 220°C could not be due to conformational disordering because the enthalpy of transition is too small. However, since there is a very small difference in energy between the all-*trans* and the 15/7 helix, supplying a little energy might change the backbone conformation. It is thus possible for the second transition to involve conformational disordering. Further, the calculations suggest that the enthalpic change for the first transition could be attributed largely to the relative inefficiency of hexagonally packed all-*trans* molecules.

Even when the backbone is planar zigzag, the methyl groups in the side chains are relatively free to rotate and there is very little steric interaction between the side groups. Therefore, conformational disordering does not influence greatly the interactions between side groups of a molecule, and ΔE for conformational disorder is small. This is unlike the findings for poly(di-n-hexyl silane) where, due to the presence of longer side chains, there is considerable steric interference between the side chains when the backbone is planar zigzag, and its relief produces a large ΔE for conformational disorder.

In conclusion, we have found the intermolecular interactions to be primarily responsible for the all-*trans* conformations in PdMS although, when only intramolecular interactions are considered, a 15/7 helical conformation has lower energy than the all-*trans*. This is very similar to results found for PdnHS[8], although in the latter case the intermolecular interactions arise mostly between the side chains. The all-*trans* conformation of PdMS packs more efficiently than the helical conformation, thus leading to the best packing mode.

One of the questions that still remains unanswered is, if indeed the all-*trans* molecules pack more efficiently than the helical molecules (as in PdMS), why do poly(di-n-pentyl silane) and poly(di-n-butyl silane), whose lowest energy isolated chain conformations are helical, not adopt an all-*trans* backbone in the solid state? Most probably, since their side chains are longer than those of PdMS, there are significant steric interactions between adjacent side chains of a molecule in the all-*trans* backbone conformation, making it energetically favourable for the isolated chains to be in a helical conformation and causing a large energy requirement for going from a helical to a *trans* conformation (unlike in PdMS). The intermolecular interaction energy for all-*trans* packing, compared to that of helical packing, is not sufficient to compensate for the difference in intramolecular interactions (between all-*trans* and helical conformations). Unlike in PdnHS, the side chains are not sufficiently long for intermolecular interactions between them to offset the intramolecular cost of the planar zigzag molecule and dictate the molecular conformation. Crystal packing calculations of PdnHS and PdnPS should be undertaken to provide more insight into the role of side-chain length in determining the crystal structures of polysilanes.

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