polymer papers

The low-temperature structure of poly(di-n-hexyl germane)

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The structure of poly(di-n-hexyl germane) has been investigated using X-ray and conformational energy analysis. Wide-angle X-ray diffraction analysis shows that the polymer undergoes an order/disorder transition at about 15°C. The polymer is known to exhibit thermochromism associated with this phase transition. Below the transition temperature, the backbone conformation is all-*trans* and the molecules are arranged in an orthorhombic unit cell. Above the transition temperature, the backbone disorders and the polymer loses long-range ordering. Fixed bonding conformational energy calculations found the lowest energy structure to be a 7/3 helix, very similar to that found for poly(di-n-hexyl silane). Most probably, the observed all-*trans* backbone conformation is due to intermolecular interactions which force the germanium backbone to an all-*trans* conformation. In order to carry out the molecular mechanics calculations, non-bonded energy parameters for germanium atoms were derived.

(**Keywords: crystal structure; phase transition; energy calculations; polysilanes; poly(di-n-hexyl germane); X-ray diffraction**)

INTRODUCTION

Although polysilanes with unusual electronic spectra have been known for some time, the recent discovery of their non-linear optical properties[1,2] has renewed interest in them. These polymers have strong absorption bands in the u.v. region of the spectrum, and their wavelength of maximum absorption, λ_{max}, decreases with a decrease in molecular weight[5]. Some of these materials have found applications as photoresists in microlithography since irradiation causes chain scission and consequent reduction in molecular weight and λ_{max}.

Germanium occurs just below silicon in the periodic table, and the properties of its derivatives are often similar to those of the corresponding silicon derivatives. Recently germanium backbone polymers have generated interest in the context of developing new radiation sensitive polymers and for obtaining a better understanding of polysilanes. Some polygermanes[4], like their silicon counterparts, absorb strongly in the u.v. and exhibit a thermochromic transition, thus showing potential for use in microlithography. Non-linear optical susceptibility measurements have also been reported[5], and polygermanes are emerging as a new class of σ-conjugated polymers.

The backbone conformations of some of the poly(di-n-alkyl silanes) seem to depend strongly on the side-chain length. The most studied polymer of this family, poly(di-n-hexyl silane) (PdnHS), adopts an all-*trans* backbone conformation and is crystalline at room temperature, transforming into a conformationally disordered state above the transition temperature at 41°C (refs 6, 7). The polymer has a λ_{max} of 374 nm at room temperature, shifting to 316 nm above 41°C. Polymers with somewhat shorter side-chains, poly(di-n-pentyl silane) and poly(di-n-butyl silane), which adopt a 7/3 helical backbone conformation in the solid state, absorb at 313 nm and 320 nm, respectively[8,9]. Polymers with somewhat longer side chains, poly(di-n-heptyl silane) and poly(di-n-octyl silane), have an all-*trans* backbone conformation and absorb at about 373 nm (ref. 10). From this, it has been postulated that the long wavelength (373 nm) absorption was associated with the all-*trans* backbone conformation[6] and a side-chain length in the vicinity of six carbon atoms was necessary for the backbone to adopt an all-*trans* conformation. If that were entirely the case, and side-chain length were the sole determining factor, the polymers with still shorter side chains would also be expected to adopt a non-planar backbone conformation. This is not observed. Recent studies have found the backbone conformations of poly(di-ethyl silane) (PdES) and poly(di-methyl silane) (PdMS) to be all-*trans*[11,12]. However, in spite of having all-*trans* backbone conformation, both PdMS and PdES absorb at shorter wavelengths – 339 nm and 316 nm, respectively. It has been suggested[12] that the interactions which drive the backbone into all-*trans* conformation are different for PdMS than for PdnHS. In the case of PdMS, interactions within the silicon backbone determine the molecular conformation, whereas in PdnHS, the backbone conformation is dictated by the interactions between the side chains[12]. The rigidity of the backbone may also affect the electronic absorption. Due to the steric interactions between the long side chains, the PdnHS backbone is much more rigid, leading to absorption at a longer wavelength.

Our work on PdnHS[13] suggests that intermolecular rather than intramolecular interactions between side chains are predominantly responsible for the all-*trans* backbone conformation. To study this further, we have investigated the low-temperature structure of poly(di-n-

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hexyl germane) (PdnHG), which has a germanium backbone and six methylene units in each side chain. The monomer unit is $((C_6H_{13})_2Ge)$. By comparing its structure with that of PdnHS we expect to gain a better understanding of the role played by intrachain *versus* interchain interactions in determining the backbone conformation. The side chains in PdnHG and PdnHS are of the same length, so the intermolecular interactions between the side chains should be comparable. On the other hand, due to the increase in the bond lengths (Ge–Ge > Si–Si and Ge–C > Si–C), the intramolecular steric crowding near the backbone is expected to be less than that of PdnHS. Like PdnHS, PdnHG exhibits thermochromism. The optical spectrum of PdnHG at room temperature shows a broad absorption peak at 337 nm, which is replaced by a sharp peak at 370 nm upon cooling to about −12°C (ref. 4). D.s.c. studies[4] show that the polymer undergoes a phase transformation at 12.4°C.

In this paper, the structure and conformational energies of PdnHG have been investigated by molecular mechanics calculations. X-ray diffraction analysis was supplemented by density measurements in order to examine the structure. The observed conformation was then compared with that of the lowest energy conformation.

EXPERIMENTAL

Density measurements

Since a very small amount of the material was available, the density measurements were carried out using a specially designed densitometer[14,15]. It employed a hydrostatic weighing technique using Archimedes principle. The sample was weighed in air and in a fluid at various temperatures. The density, as a function of the temperature, was calculated using the equation:

$$d_{\text{sample}} = \frac{d_{\text{fluid}}}{1 - \left(\dfrac{m_{\text{sample in fluid}}}{m_{\text{sample in air}}}\right)}$$

where d = density and m = mass. 2-Methylene-1-pentanol $(CH_3CH_2CH_2CH(CH_3)CH_2OH)$ was selected as the buoying fluid in the densitometer; it is a non-solvent for PdnHG and has the additional advantage of having a high boiling point and a moderate surface tension, both of which are desirable properties in a fluid for this application.

X-ray measurements

Low-temperature wide-angle X-ray data were recorded in vacuum using a specially modified Wahrus camera. Low temperature was attained by passing a flow of methanol from a refrigerated circulating bath through a copper block surrounding the metal disc in which the sample was mounted. Nickel-filtered CuKα radiation was used. The diffraction patterns were recorded on a flat photographic film perpendicular to the direct X-ray beam. The nominal sample-to-film distance was 5 cm. Silicon powder was sprinkled on the sample to calibrate the sample-to-film distance. PdnHG is a soft, viscid polymer at room temperature. This imposes serious limitations on obtaining oriented materials, as the polymer is not able to withstand stress while being stretched. Samples stored at −10°C and stretched showed no preferred orientation. However, slight orientation was achieved by repeatedly rolling and lightly stretching the polymer at room temperature and then cooling it down.

ENERGY PARAMETERS

The non-bonded interactions between atoms i and j were described by the function:

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

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. The energy parameters for carbon and hydrogen were those determined by Williams (set 1)[16]. Values describing the non-bonded interactions involving germanium were not available in the literature, and were derived as described below. The final parameters used for the energy calculations are given in *Table 1*.

The value of C in the attractive term $(-C_{ij}/r_{ij}^6)$ for the Ge–Ge interaction was calculated using a modified form of the Slater–Kirkwood equation as suggested by Scott and Scheraga[17]:

$$C_{ij} = \frac{(3/2)e(h/2\pi m^{1/2})\alpha_i\alpha_j}{(\alpha_i/N_i^{\text{eff}})^{1/2} + (\alpha_j/N_j^{\text{eff}})^{1/2}}$$

where m and e are the electronic mass and charge, respectively, α is the atomic polarizability and N^{eff} is the effective number of electrons surrounding the nucleus when the atom is chemically bound in some compound.

The energy of an atom in an external electric field, H, is given by $W = -1/2\alpha H^2$, where α is the electric dipole polarizability of the atom which describes the response of the atom's electron cloud to the field H. In perturbation theory, this external field is treated as a perturbation and W is simply the second-order energy correction[18]. Thus, α can be calculated from W, which is the energy change upon imposition of the external field. The calculated polarizability, α, of germanium atoms, as reported[19], is very high because that calculation ignored the off-diagonal terms in the perturbation Hamiltonian[20]. The polarizability was subsequently corrected. Since the most loosely bound electrons play the largest role in the redistribution of the electron charge in an electric field, the valence electrons generally account for most of the polarizability (at least 90%) of an atom[18]. Since silicon and germanium have the same number of valence electrons, the necessary correction for the off-diagonal terms might reasonably be taken to be the same. The ratio of the corrected polarizability of silicon (implicit in silicon non-bonded parameters[21]) and the uncorrected value[19] is 0.465. This ratio was used to correct the value

Table 1 Energy parameters[a]

Interaction	A	B	C	r_{min} (Å)	E_{min} (kcal mol^{-1})
C–C	86 910	3.6	586	3.85	−0.097
C–H	7800	3.67	112	3.25	−0.043
H–H	2923	3.74	33.5	3.2	−0.013
Ge–Ge	124 623.3	2.87	3905.4	4.75	−0.19
Ge–C	102 734.3	3.21	1512.8	4.3	−0.135
Ge–H	19 390.9	3.28	361.7	3.98	−0.049

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

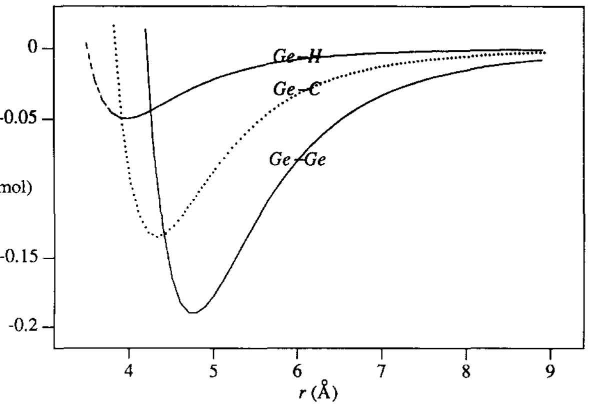

Figure 1 Non-bonded potential energy functions

for germanium[19], giving the value 2.82 × 10^{-24} cm^3. The $N^{\mathrm{eff}}_{\mathrm{Ge}}$ used was 20.76 (ref. 17). For the interactions between pairs of unlike atoms (Ge–C and Ge–H), the value of C was taken to be the geometric mean of the like-atom values.

The role of B in the repulsive term, $A_{ij}\exp(-B_{ij}/r_{ij})$, is to control the shape of the curve representing the repulsive energy. Scott and Scheraga[17] correlated the value of B for an atom with its atomic number. The same method was used here to determine B for germanium: a value of 2.87 was obtained. Geometric mean values were used for Ge–C and Ge–H pairs of unlike atoms.

For each pairwise interaction, the value of A in the repulsive term was calculated using the fact that the potential energy function is minimum at the normal contact distance r_0. Theoretically, r_0 should be equal to the sum of the van der Waals radii, r_w, of the interacting atoms. However, in practice, it has been found that no single set of van der Waals radii can be assigned to a set of atoms so that the correct contact distance is reproduced for every observed pairwise interaction. Thus, r_w has to be modified depending on the situation. In any case, an initial estimate of r_w for the germanium atom had to be made, since it was not available in the literature. The r_w of an atom has been found to be related to the de Broglie wavelength, λ_B, of the outermost valence electron of the atom. For most atoms, r_w is found to be λ_B multiplied by a constant[22]. For silicon, whose r_w was available[22], this constant was calculated to be 0.4884. λ_B for germanium, which can be calculated from the ionization potential, was found to be 0.438 nm (ref. 22). Using the same constant as for silicon, r_w for germanium was calculated to be 0.214 nm.

The reported r_w for silicon[22] was deduced from equilibrium crystal structures. This value is therefore subject to the effects of interactions between multiple atoms in the crystal, and is probably smaller than the value that would be observed in the case where only one atomic pair is considered. Thus the constant 0.4884, and consequently r_w for germanium, should be further modified. The calculated r_w for germanium was corrected for the effect of interactions between neighbouring atoms as suggested by Flory[23]. However, an addition of only 0.01 nm (Flory's suggested increment) is typically not sufficient to reproduce the observed unit cell dimensions of known structures[24]. Thus, r_w for germanium was taken to be 0.2375 nm, a value consistent with the fairly hard carbon and hydrogen potentials used.

The various energy functions describing the non-bonded interactions between germanium, carbon and hydrogen atoms are shown in *Figure 1*. The depth of the energy minimum for the Ge–Ge interaction was calculated to be −0.19 kcal mol^{-1}, which is lower than that of Si–Si (−0.16 kcal mol^{-1}). The position of the minimum was found to be at a separation distance of 0.475 nm (greater than that of Si–Si, which is 0.465 nm). This is expected because the germanium atom is larger and has a greater polarizability than silicon.

In addition to the non-bonded energies, for conformations of interest, a torsional energy term was added to the calculated energies. The form of the potential was:

$$E_{\mathrm{tor}} = 0.5E_0(1 + \cos 3\phi)$$

where ϕ is the rotational angle (relative to *trans*, defined as 180°) and E_0 is the intrinsic torsional barrier. Using the torsional barriers from model compounds (Ge_2H_6 for Ge–Ge and $GeCH_3$ for Ge–C), the values of E_0 for rotation about Ge–Ge bond and about the Ge–C bond were taken to be 0.4 kcal mol^{-1} (ref. 25) and 1.24 kcal mol^{-1} (ref. 26), respectively.

RESULTS AND DISCUSSION

Density

The density measurements showed a change of slope in the density *versus* temperature curve (*Figure 2*) between 10 and 15°C, indicating a phase transformation. Below the transition temperature, the volumetric thermal expansion coefficient of PdnHG (3.147 × 10^{-3}°C^{-1}), was found to be greater than that of PdnHS (8.44 × 10^{-4}°C^{-1})[27]. The density of PdnHG at 7°C (1.116 g cm^{-3}), was found to be greater than that of PdnHS (0.936 g cm^{-3}) at the same temperature.

X-ray crystal structure

Both powder and fibre diffraction patterns were recorded. The wide-angle powder diffraction pattern of the polymer sample recorded at −40°C showed sharp reflections out to 0.27 nm (*Figure 3*). The pattern from a slightly oriented fibre sample showed rings tending to localize intensity on the equator and near the meridian on the first-layer line. Four distinct zero-layer and one

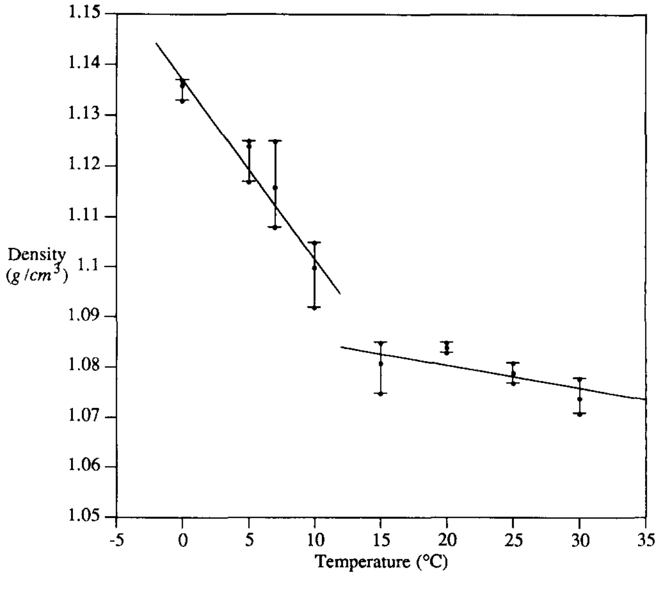

Figure 2 Density *versus* temperature curve of PdnHG

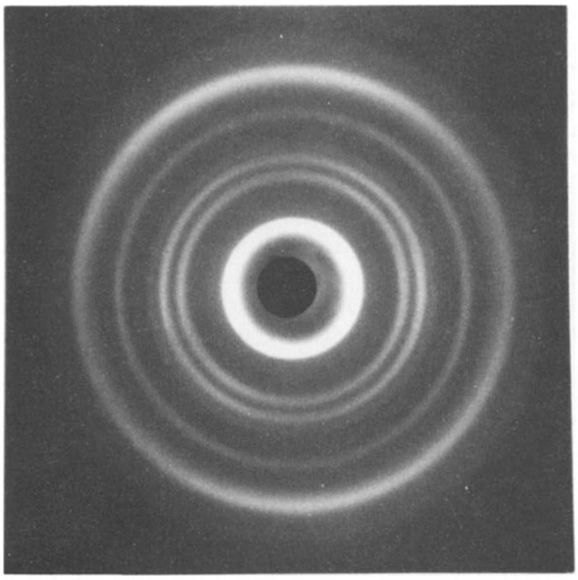

Figure 3 Wide angle X-ray diffraction pattern of PdnHG obtained at −40°C

Table 2 Comparison of calculated and observed *d* spacings

Miller indices	d_{obs} (Å)	d_{calc} (Å)
1 1 0	12.90	12.64
2 1 0	7.30	7.35
2 2 0	6.33	6.32
3 2 0	4.73	4.69
1 1 1	3.86	3.86
1 6 0	3.49	3.49
5 0 0	3.14	3.13
5 3 0	2.86	2.87
5 4 0	2.70	2.70

off-meridional first-layer reflections could be seen. The repeat distance along the fibre axis, calculated from the spacing between the two layer lines on the film, was found to be 0.406 nm. The repeat distance (0.406 nm) can be explained by an all-*trans* planar zigzag backbone with the Ge–Ge bond distance of 0.245 nm and the Ge–Ge–Ge bond angle of 112°. All the rings could be indexed using an orthorhombic unit cell, and after least squares refinement, the unit cell parameters were found to be $a = 1.565, b = 2.146$ and $c = 0.406$ nm. A comparison of the observed and the calculated *d* spacings is given in *Table 2*. Except for one, all reflections could be indexed as *hk*0 reflections, suggesting that there is packing in the lateral directions but not much registry between chains (along *z*). Considering two molecules per unit cell, the density calculated from the X-ray unit cell at 10°C was 1.143 g cm^{-3}, somewhat higher than the measured density of 1.099 g cm^{-3} at the same temperature.

Fibre diffraction patterns taken at 14°C found the polymer to be crystalline, with most of the rings seen at −40°C still present though not as sharp. Patterns taken at 16°C indicated that a disordering process had taken place. At 16°C, three low-angle rings were seen, and the outer rings (present at −40°C) were replaced by an amorphous halo. The presence of the rings indicated that some short range ordering was still present, though extensive three-dimensional ordering was lacking. The disordering temperature of about 15°C found by X-ray diffraction studies, though slightly different from the value of 12.4°C reported from d.s.c. studies of Miller and Sooriyakumaran[4], is consistent with the broad nature of the endotherm corresponding to the transition.

At room temperature, the oriented sample showed three broad diffraction rings at 1.314 nm, 0.759 nm and 0.657 nm, concentrated along the equator, and the diffuse amorphous halo concentrated along the meridian. The retention of some of the orientation above the transition temperature indicates that the transition is not a melting process. The intensities of the rings concentrated near the equator indicate that the main chain orientation (such as could be induced) is more or less preserved. The amorphous halo near the meridian suggests that the side chains are not completely random but are arranged preferentially, approximately normal to the main chain. The diffraction rings could be indexed as (1 0 0), (1 1 0) and (2 0 0) planes of a hexagonal lattice with $a = 1.517$ nm. This suggests that at room temperature the polymer molecules behave as rod-like structures, arranged in a hexagonal lattice for effective packing, with the hexyl side-chains randomly arranged about the germanium backbone.

Conformational energy calculations

Conformational calculations were performed using a computer program[28] that allows minimization of energy, $E = \sum E_{ij}^{nb}$, with respect to torsional rotations about bonds, using a force field that considers only non-bonded interactions (given in *Table 1*). Bond lengths and bond angles were fixed (*Table 3*). Various combinations of Ge–Ge–Ge and C–Ge–C angles were considered to study the effect of choosing different angles on the torsion angles of various low energy conformations. Two different Ge–Ge–Ge angles, 112° (agreeing with the layer line spacing of 0.406 nm) and 116°, and two different C–Ge–C angles, 112° (corresponding to that observed for $Ge(CH_3)_2Cl_2$) and 98°, were considered. The repeat unit was defined to consist of two consecutive Ge atoms and their attached side groups. The interactions of one repeat unit with the remainder of the polymer chain (in this case four repeat units) were considered. Initially the torsion angles were varied in steps of 30° to locate energy minima. Each energy minimum was then refined using a grid search method with 5° angle increments.

To analyse the interdependencies between torsion angles of adjacent monomers (consisting of one germanium atom and its attached side chains) in the repeat unit, the two backbone torsion angles and torsion angles about Ge–C bonds were independently varied while keeping the rest of the side-chain torsion angles fixed at *trans*. Two side-chain cases were considered:

(1) Both Ge–C bonds from the same germanium atom (Ge_1–C_1 and Ge_1–C_2) were assigned the same torsion angle. Torsion angles about adjacent Ge–C bonds (Ge_1–C and Ge_2–C'_1) were varied

Table 3 Bond lengths and angles

Bond lengths (nm)		Bond angles (degrees)	
Ge–Ge	0.245	Ge–Ge–Ge	112.0, 116.0
Ge–C	0.198	C–Ge–C	98.0, 112.0
C–C	0.153	Ge–Ge–C	108.6
C–H	0.109	C–C–C	111.0
		H–C–H	108.0

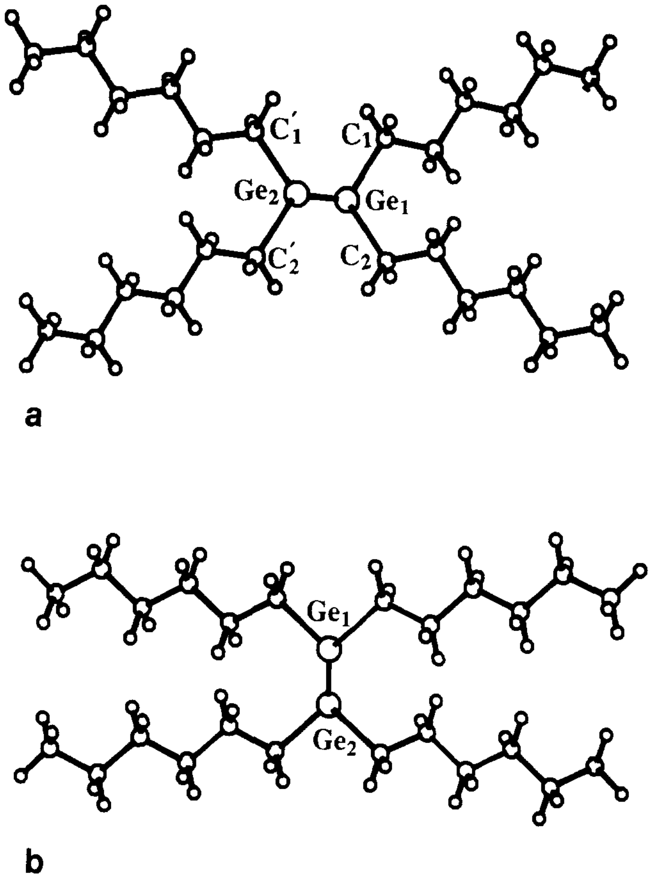

Figure 4 Ball and stick representation of two low energy conformations of the all-*trans* PdnHG molecule (projected onto a plane normal to the backbone axis). The medium circles represent carbon atoms and the smallest circles represent hydrogen atoms. (a) Near-*cis* conformation; (b) near-*trans* conformation

independently (the atom labels are shown in *Figure 4a*).

(2) Torsion angles about adjacent Ge–C bonds were assigned the same value (Ge_1–C_1 = Ge_2–C_1', and Ge_1–C_2 = Ge_2–C_2') and Ge–C bonds from the same germanium atom (Ge_1–C_1 and Ge_1–C_2) were varied independently.

It was found that for the lowest energy conformation, the two backbone torsion angles were the same, as were all the Ge–C torsion angles. Thus, for further analysis, torsion angles in one asymmetric unit (consisting of one germanium atom and its attached side chains), were varied, and the corresponding torsion angles in the adjacent monomer unit were assigned the same values.

The lowest energy conformation was found to be helical with the backbone bonds at 210° (i.e. 30° away from *trans*, defined as 180°), and Ge–C bonds at about 60° (i.e. 120° away from *trans*). This helix (*Figure 5*) is similar to the one found to have the lowest energy for PdnHS by molecular mechanics calculations[29]. The backbone torsion angle corresponds to the 7/3 helical conformation found for several polysilanes[8,9].

For the helical conformation, all possible combinations of rotations about the Ge–C and the first C–C bond were also examined. The energy was further minimized with respect to the side-chain bonds by letting two consecutive C–C bonds rotate independently. The lowest energy was found when all the torsion angles about the C–C bonds were *trans* (see *Figure 5*). Due to the twist about the backbone bonds, the side chains on successive repeat units are comfortably separated, and rotation about the C–C bonds is not needed to relieve any severe steric interaction.

Side-chain torsion angles were analysed in a similar manner for a backbone conformation fixed at all-*trans*. Two low energy side-chain arrangements were identified:

(1) Ge–C bonds rotated about 30° from *cis* (*Figure 4a*)
(2) Ge–C bonds rotated about 20° from *trans* (*Figure 4b*).

Some of the steric interactions between the side chains decreased further when the rest of the side-chain torsion angles were allowed to vary. The lowest energy conformation for the side chains has rotations about the first two C–C bonds slightly away from *trans* (*Table 4*). However, if the torsional energy contributions were included, they would be expected to favour *trans* rotations. Since the intrinsic torsional barrier for rotation about a C–C bond is relatively high (2.8 kcal mol^{-1} – more than twice that of Ge–C), the decrease in steric energy by allowing non-*trans* outer side-chain torsion angles would be overshadowed by the increase in torsional energy. *Figures 4a* and *b* show the near-*cis* (torsion about Ge–C bond = 335°) and near-*trans* (torsion about Ge–C bond = 200°), side-chain con-

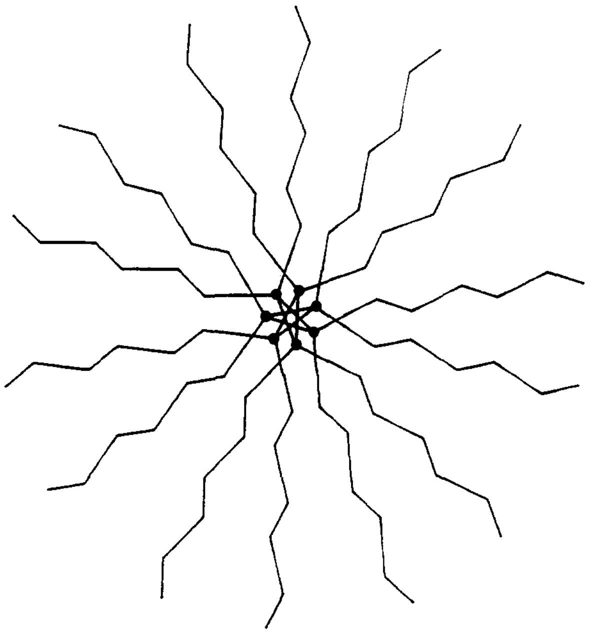

Figure 5 Schematic representation of the 7/3 helical conformation of PdnHG (shown normal to the helical axis). The filled circles represent germanium atoms. Hydrogen atoms have been removed for clarity

Table 4 Conformational energies of PdnHG molecules: comparison of *trans* and helical conformations at two C–Ge–C angles

	Trans		Helical	
	112°	98°	112°	98°
Torsion about Ge_1–Ge_2 (degrees)	180	180	210	210
Torsion about Ge_1–C_1 (degrees)	335	200	55	65
Torsion about C_1–C_2 (degrees)	203	172	180	180
Torsion about C_2–C_3 (degrees)	193	180	180	180
E^{nb} (kcal mol^{-1})	2	7	−9	−8
Relative E_{tor} (kcal mol^{-1})	16	5	1	1

formations respectively. Here, the outer side-chain torsion angles have been shown to be all-*trans*. The near-*trans* conformation was very similar to the conformation found to have low energy for PdnHS[6]. It was later found that a conformation similar to the near-*cis* conformation was also possible for PdnHS[30].

A comparison of the energies of the 7/3 helix and the all-*trans* conformations with a backbone bond angle of 112° and two different C–Si–C bond angles is given in *Table 4*. The relative energies of different conformations depend on the values chosen for the C–Ge–C bond angle. The larger bond angle decreases the steric interactions between the side-chain atoms, resulting in a lower energy. The difference in energy between the helical and the *trans* conformations increases further when, along with contributions from non-bonded interactions, contributions from torsional rotations are also considered. The relative torsional energies of the *trans* and helical conformations are given in *Table 4*. For the all-*trans* backbone conformation, there is no contribution from rotation about the Ge–Ge bonds. However, the Ge–C bonds are away from the minimum. In the helix, although there is some contribution from the Ge–Ge torsional energy, the Ge–C bonds are near the minimum. The intrinsic torsional barrier for rotation about the Ge–C bond being greater than that about the Ge–Ge bond, the Ge–C torsional energy overshadows the Ge–Ge contribution. The net result is a greater torsional energy for the all-*trans* conformation.

CONCLUSION

Like its silicon counterpart, PdnHG undergoes a transformation from a crystalline phase with an all-*trans* backbone to a disordered phase. PdnHG in its low temperature crystalline phase is less ordered than PdnHS, which exhibits an unusually well developed diffraction pattern. The phase transformation between the crystalline all *trans* backbone conformation and the disordered phase could give rise to the observed shift in u.v. absorption maxima. The lower transition temperature of about 12°C compared to that of PdnHS at 41°C can be attributed to the slightly longer bond lengths (Ge–Ge > Si–Si and Ge–C > Si–C), which separate the side chains somewhat more. Thus, PdnHG has more flexibility near and about its backbone and disorders at a lower temperature.

The lowest energy structure for an isolated PdnHG molecule (i.e. considering only intramolecular interactions) was found to be a 7/3 helix. This supports the premise that the all-*trans* conformation found by the X-ray diffraction studies below 15°C is most probably due to the intermoleculear interactions between the side chains. For a single molecule with an all-*trans* backbone, a near-*cis* side-chain arrangement was found to have the lowest energy.

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