The conformation and packing of organopolysilane having asymmetric side-chains

LETTER TO THE EDITOR

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Abstract. Conformations and packings of poly(n-butyl-ethyl silane), poly(n-propyl-methyl silane), and poly(iso-propyl-methyl silane) have been proposed on the basis of experimental and theoretical x-ray diffraction patterns. The silicon backbone of poly(n-butyl-ethyl silane) has a helical conformation, whereas the backbones of poly(n-propyl-methyl silane) and poly(iso-propyl-methyl silane) have all-*trans* conformations. Side-chain conformations and packings have also been proposed, and the similarities of and the differences between the structures of the polysilanes having symmetrical and asymmetrical side-chains are pointed out.

Organopolysilane is a candidate for future electronic device material use, because it has many interesting properties. First of all, it is essentially a hybrid material having both organic and inorganic components (West 1988). Second, it shows an interesting thermochromism, which is considered to be due to the conformational change of the silicon backbone (Kuzmany *et al* 1986, Lovinger *et al* 1986). Third, it is anticipated that the conductivity will be very much increased by interstitial doping (Kepler *et al* 1987). Fourth, it is considered to be a direct-gap semiconductor, whose band gap is controlled by changing the dimension of the silicon backbone (Takeda *et al* 1990). In contrast to these points concerning applications, the details of the molecular structures and the packings of the chains are not well understood, because the single-crystal form has not been obtained.

Recently, our group have succeeded in analysing the crystal structures of the polysilanes having symmetrical side-chains (Furukawa and Takeuchi 1993, Furukawa *et al* 1994). The results were based on x-ray diffraction patterns, and the conformation and packing obtained for the poly(di-methyl silane), poly(di-ethyl silane), poly(di-n-propyl silane), poly(di-n-butyl silane), poly(di-n-pentyl silane), and poly(di-n-hexyl silane) were quite reasonable. However, the structures of the polysilanes having asymmetrical side-chains have not been clarified yet.

In this letter, the backbone conformations and the packings of polysilanes having asymmetric side-chains, poly(n-butyl-ethyl silane) $[Si(C_4H_9)(C_2H_5)]_n$, poly(n-propyl-methyl silane) and poly(iso-propyl-methyl silane) $[Si(C_3H_7)(CH_3)]_n$, are examined by comparing the experimental x-ray diffraction patterns with the theoretical patterns. Although the crystallinity of these polysilanes is not very good compared with that of the polysilanes having symmetrical side-chains, the molecular structures and packings can be deduced from the x-ray diffraction data. The similarities of and the differences between the structures having symmetrical and asymmetrical side-chains are clarified by the present analysis for the first time.

We now describe the theoretical calculation. A computer program (C language) for analysing the crystal structure of polysilanes has been developed using the diffraction theory (Furukawa and Takeuchi 1993). A crystallographic unit cell was first assumed, with the structure factor then calculated for each Miller index. The Si–Si and C–H bond lengths were 0.2352 and 0.1090 nm, respectively. The Si–C–C, C–C–H, and H–C–H angles were assumed to be 109.47°, i.e. the same as those in the previous work (Furukawa *et al* 1994).
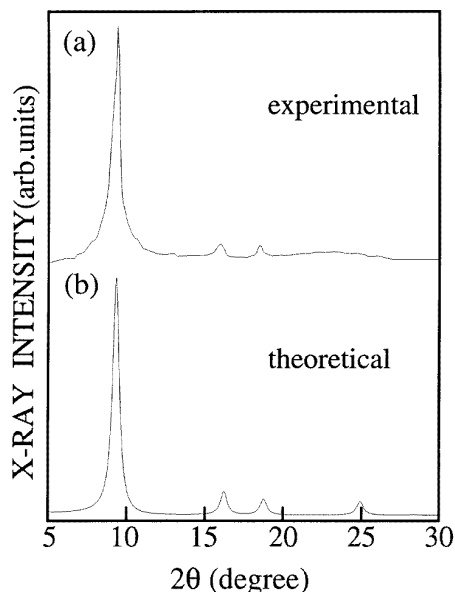

Figure 1. The experimental x-ray diffraction pattern (Asuke and West 1994) (a) and the present theoretical pattern (b) for the poly(*n*-butyl-ethyl silane).

For the 7/3 helical conformation, the Si–Si–Si–Si dihedral angle and the Si–Si–Si angle were 149.74 and 117.0°, respectively. The Si–C and C–C bond lengths were 0.1946 and 0.1540 nm, respectively. The C–Si–C and C–C–C angles were both assumed to be 110.00°.

For the all-*trans* conformation, the dihedral angle was 180.00°. The Si–Si–Si angle was assumed to be 112.04°. The Si–C bond lengths of the poly(*n*-propyl-methyl silane) and poly(iso-propyl-methyl silane) were 0.1880 and 0.1890 nm, respectively. The C–C bond lengths of the poly(*n*-propyl-methyl silane) and poly(iso-propyl-methyl silane) were 0.1530 and 0.1540 nm, respectively. The C–Si–C and C–C–C angles were assumed to be 112.00 and 110.00°, respectively.

The details of the present method and the other parameters were described in our previous papers (Furukawa and Takeuchi 1993, Furukawa *et al* 1994).

The x-ray diffraction patterns of poly(*n*-butyl-ethyl silane), poly(*n*-propyl-methyl silane) and poly(iso-propyl-methyl silane) reported by Asuke and West (1994, 1995) were used as experimental data. The wavelength of the x-rays used in the theory and experiment was 0.1541 nm (Cu Kα radiation).

We will now give the results and discuss them. Figure 1 shows the experimental x-ray diffraction pattern (Asuke and West 1994) (a) and the present theoretical pattern (b) for the poly(*n*-butyl-ethyl silane). Although there are not many diffraction peaks, the theoretical

pattern is in good agreement with the experimental one. The large diffraction peak at $2\theta = 9$–$10°$ is due to the main chains. The single peak indicates that the lattice distances determined from the triangle constructed from the three nearest-neighbour polymer chains are almost the same, suggesting a hexagonal columnar structure.
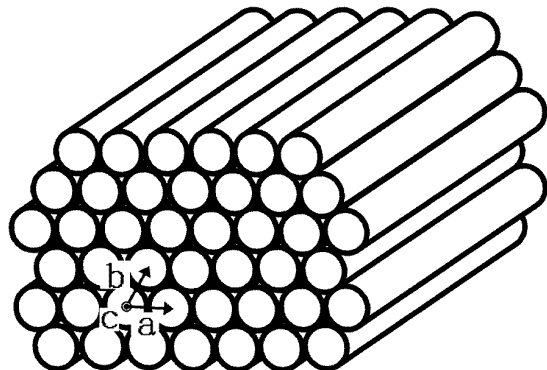

Figure 2. A schematic representation of the structural model for the poly(n-butyl-ethyl silane). The circles indicate the polymers, which are randomly rotated around the c-axis. The backbone conformation is the 7/3 helix.

The theoretical pattern in figure 1(b) was calculated on the assumption that the structure was similar to that of liquid crystal (see figure 2). The vectors a, b, and c in figure 2 are the primitive translation vectors used in the theoretical calculation, whose magnitudes are 1.0865, 1.0865, and 1.3880 nm, respectively ($\gamma = 60°$). In the figure, the polymers are schematically illustrated as circles, which are randomly rotated. The silicon backbone is assumed to have a 7/3 helical conformation. The most important point of the 7/3 helical conformation is that the dihedral angle is determined by the van der Waals interaction between the side-chains attached to the nearest-neighbour silicon atoms. The details of the 7/3 helix were described elsewhere (Furukawa *et al* 1994). In the present calculation, the polymer is rotated around the c-axis (the direction of the polymer chain) in a unit cell, via which procedure the randomness of the rotation angle can be taken into account. This assumption is consistent with the experimental results reported by Asuke and West, and the hexagonal columnar structure of the polysilane has been theoretically confirmed by figures 1 and 2. When the calculation was performed on the assumption that the silicon backbone had other conformations, such as all-*trans* and triangular, the theoretical x-ray diffraction pattern was not in agreement with the experimental one.

Figure 3 shows the experimental x-ray diffraction pattern (Asuke and West 1995) (a) and the present theoretical pattern (b) for the poly(n-propyl-methyl silane). The appearance of two peaks at around $2\theta = 8$–$13°$ tells against a hexagonal columnar structure similar to that of figure 2, and suggests an orthorhombic or monoclinic unit cell (Asuke and West 1995, Furukawa and Takeuchi 1993).

The theoretical diffraction pattern shown in figure 3(b) was calculated on the assumption that the backbone conformation and the unit cell were all-*trans* and monoclinic, respectively (see figure 4). The magnitudes of the primitive translation vectors are 1.1498, 0.9359, and 0.3873 nm, respectively. The value of γ is 52.10°. The large and small circles in figure 4 indicate silicon and carbon atoms, respectively. Hydrogen atoms are not illustrated in figure 4. In the case of asymmetric side-chains, two kinds of side-chain, i.e., n-C_3H_7 and
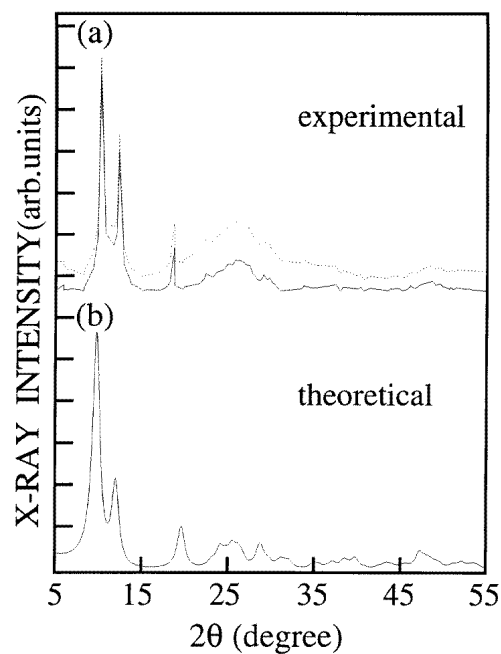
Figure 3. The experimental x-ray diffraction pattern (Asuke and West 1995) (a) and the present theoretical pattern (b) for the poly(*n*-propyl-methyl silane). The background is eliminated in the solid curve of (a).
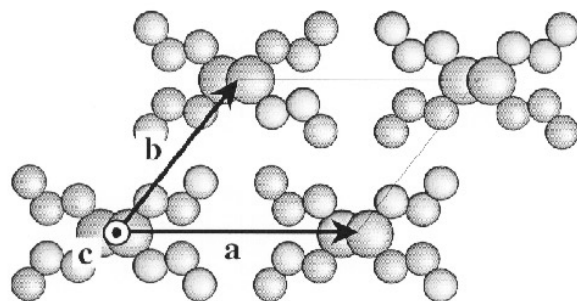

Figure 4. A schematic representation of the structural model for the poly(*n*-propyl-methyl silane). This figure is a view from the direction parallel to the silicon chains. The large and small circles indicate silicon and carbon atoms, respectively. The backbone conformation is all-*trans*.

CH_3 groups, are randomly distributed on both the right-hand and left-hand sides of the chain. In the calculation, this effect is taken into account, so two *n*-propyl groups are seen on both sides of each polymer chain in figure 4.

Because the theoretical x-ray diffraction pattern in figure 3(b) is in good agreement with the experimental one in figure 3(a), the structural model in figure 4 is considered to be reliable. From figure 4, two important results are pointed out. One is that the side-
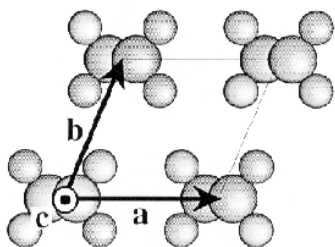
Figure 5. The crystal structure of the poly(di-methyl silane) (Furukawa and Takeuchi 1993).

chains stretch to the right-hand and left-hand sides in figure 4, not upward and downward. Intramolecular steric hindrance does not occur, because one of the two side-chains is a CH_3 group, whose van der Waals radius is small (about 0.2 nm). The other is that the effect of asymmetric side-chains is averaged over due to the randomness of the side-chain configuration, causing the symmetric crystallographic structure (see figure 4).

Figure 5 shows the crystal structure of the poly(di-methyl silane) reported previously (Furukawa and Takeuchi 1993). It is quite similar to figure 4. However, the distance between the chains is very small compared with that of figure 4. For example, the magnitude of the primitive translation vector a is 0.7450 nm in figure 5, whereas that of figure 4 is 1.1498 nm. This is because the CH_3 group is smaller than the C_3H_7 group.
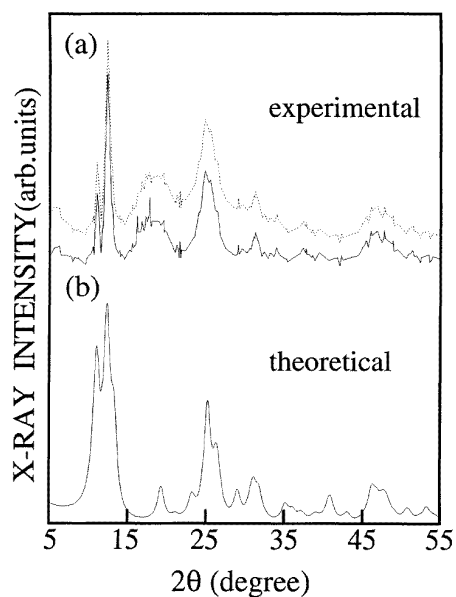

Figure 6. The experimental x-ray diffraction pattern (Asuke and West 1995) (a) and the present theoretical pattern (b) for the poly(iso-propyl-methyl silane). The background is eliminated in the solid curve of (a).

Figure 6 shows the experimental x-ray diffraction pattern (Asuke and West 1995) (a) and the present theoretical pattern (b) for the poly(iso-propyl-methyl silane). There are many diffraction peaks, indicating that the crystallinity is good.
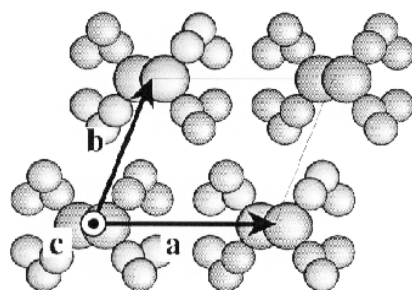
Figure 7. A schematic representation of the structural model for the poly(iso-propyl-methyl silane). The figure is a view from the direction parallel to the silicon chains. The notation is the same as for figure 5.

Figure 7 shows the structural model used in the theoretical x-ray diffraction pattern illustrated in figure 6(b). As in figure 4, the large and small circles indicate silicon and carbon atoms, respectively. The backbone conformation is all-*trans*. a, b, and c in figure 7 indicate the primitive translation vectors, whose magnitudes are 0.8509, 0.7433, and 0.3990 nm, respectively. It has a monoclinic unit cell, whose γ-value is 69.00°. This is similar to that of the poly(*n*-propyl-methyl silane). However, the magnitude of the primitive translation vector a of the poly(iso-propyl-methyl silane) is smaller than that of the poly(*n*-propyl-methyl silane). The broad peak that appeared between 15 and 22° in figure 6(a) may be caused by the randomness of the rotation angle of the iso-propyl groups. When the calculation was performed using other backbone conformations for both the poly(iso-propyl-methyl silane) and poly(*n*-propyl-methyl silane), the theoretical x-ray diffraction pattern was not in agreement with the experimental one.

We now give a summary and our conclusions. The molecular structures and the packings of poly(*n*-butyl-ethyl silane), poly(*n*-propyl-methyl silane), and poly(iso-propyl-methyl silane) have been examined by comparing the calculated x-ray diffraction pattern with the experimental one. The silicon backbone conformation of poly(*n*-butyl-ethyl silane) is the 7/3 helix, whereas those of poly(*n*-propyl-methyl silane) and poly(iso-propyl-methyl silane) are all-*trans*. The backbone conformation is essentially determined by the intramolecular van der Waals interaction between the side-chains, which is similar to that of the polysilanes having symmetrical side-chains.

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