

Review

Molecular structure and packing of organopolysilanes

Shoji Furukawa *

Faculty of Computer Science and Systems Engineering, Kyushu Institute of Technology, 680-4 Kawazu, Iizuka, Fukuoka 820-8502, Japan

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Abstract

Molecular structure and packing of various organopolysilanes having symmetrical and unsymmetrical side-chains of alkyl substituents, such as poly(dimethylsilane), poly(diethylsilane), poly(methylethylsilane), poly(*n*-butylethylsilane), poly(*n*-propylmethylsilane), and poly(*iso*-propylmethylsilane), are examined by X-ray diffraction, and the characteristic features are obtained for those organopolysilanes. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Organopolysilane; Molecular structure; Packing; Poly(dimethylsilane); Poly(diethylsilane); Poly(methylethylsilane); Poly(*n*-butylethylsilane); Poly(*n*-propylmethylsilane); Poly(*iso*-propylmethylsilane); X-ray diffraction

1. Introduction

Polysilanes consist of one-dimensional Si backbone and alkyl substituents. It has been reported that they have a band structure similar to direct-gap-semiconductor [1]. Therefore, it is expected they will be used for

future optical and electronic devices.

In this paper, molecular structure and packing of various organopolysilanes are examined, and the characteristic features are obtained for those organopolysilanes.

2. Theoretical calculation and experimental procedure

The polysilanes studied in this paper were chemically synthesized by means of the Waltz method. The experimental X-ray diffraction pattern was compared with the theoretical pattern calculated using the computer program written in C language. The packing of the polymer chains was also checked using the computer graphic display.

3. Results and discussion

Fig. 1(a–c) show the previously obtained X-ray diffraction patterns for poly(dimethylsilane) $[\text{Si}(\text{CH}_3)_2]_n$ powder, source-melted film, and theoretical calculation based on the reasonable molecular structure and the packing, respectively [2,3]. Fig. 2 shows the schematic diagram of the obtained crystal structure of poly(dimethylsilane). It has a monoclinic unit cell (sub cell) with $a = 0.745$, $b = 0.724$, $c = 0.389$ nm and $\gamma = 67.1^\circ$. In Fig. 2, the Si atoms are not illustrated, but the

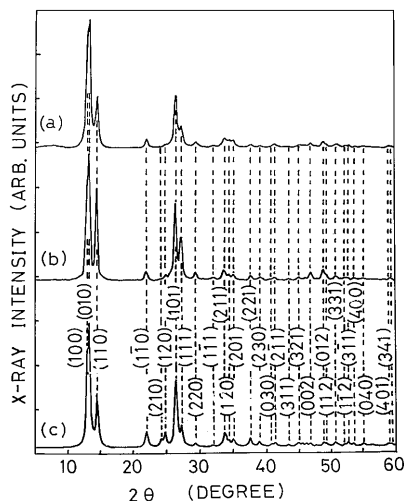


Fig. 1. X-ray diffraction patterns for poly(dimethylsilane) $[\text{Si}(\text{CH}_3)_2]_n$ powder (a), source-melted film (b), and theoretical calculation based on the reasonable molecular structure and the packing (c).

* Fax: +81-948-297683.

E-mail address: furukawa@cse.kyutech.ac.jp (S. Furukawa).

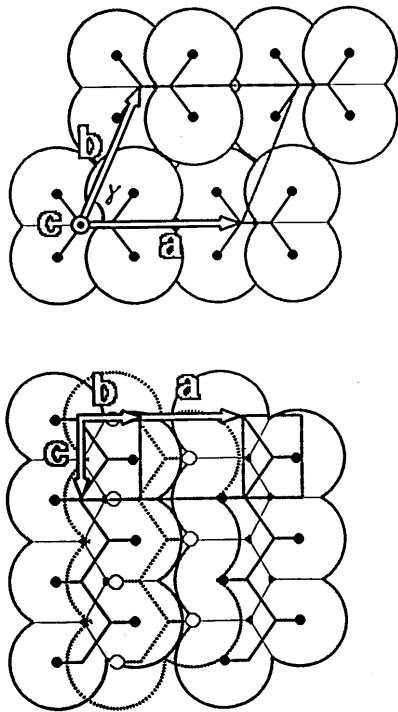


Fig. 2. Schematic diagram of the obtained crystal structure of poly(dimethylsilane). It has a monoclinic unit cell (sub cell) with $a = 0.745$, $b = 0.724$, $c = 0.389$ nm, and $\gamma = 67.1^\circ$

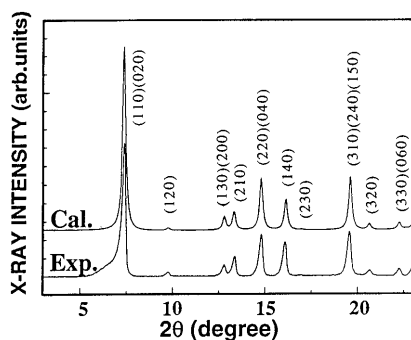


Fig. 3. Experimental and theoretical X-ray diffraction patterns for the powdered poly(di-*n*-hexylsilane) $[\text{Si}(\text{C}_6\text{H}_{13})_2]_n$ crystal.

Si backbones are shown by the zig-zag lines (all-*trans* conformation). The closed circles indicate the center of the CH_3 group. a , b and c denote the primitive translation vectors of the sub-cell.

Fig. 3 shows the previously obtained experimental and theoretical X-ray diffraction patterns for the powdered poly(di-*n*-hexylsilane) $[\text{Si}(\text{C}_6\text{H}_{13})_2]_n$ crystal. The theoretical pattern of Fig. 3 was calculated on the assumption that the crystal has an orthorhombic unit cell with $a = 1.384$, $b = 2.396$, $c = 0.400$ nm (see Fig. 4). The conformation of the Si backbone is all-*trans*, which is the same as those of poly(dimethylsilane), poly(diethylsilane), and poly(di-*n*-propylsilane).

Fig. 5 shows the present experimental X-ray diffraction pattern (a) and the theoretical pattern (b) for the

poly(methylethylsilane). The theoretical pattern is in good agreement with the experimental one. The theoretical pattern in Fig. 5(b) was calculated on the assumption that the backbone conformation is all-*trans* (see Fig. 6). Fig. 6 was obtained by superimposed plural molecular structures (see Fig. 7).

Fig. 8 shows the experimental X-ray diffraction pattern [4] (a) and the present theoretical pattern (b) for the poly(*n*-butylethylsilane). Although there are not many diffraction peaks, the theoretical pattern is in good agreement with the experimental one. The large diffraction peak at $2\theta = 9\text{--}10^\circ$ is due to the main-

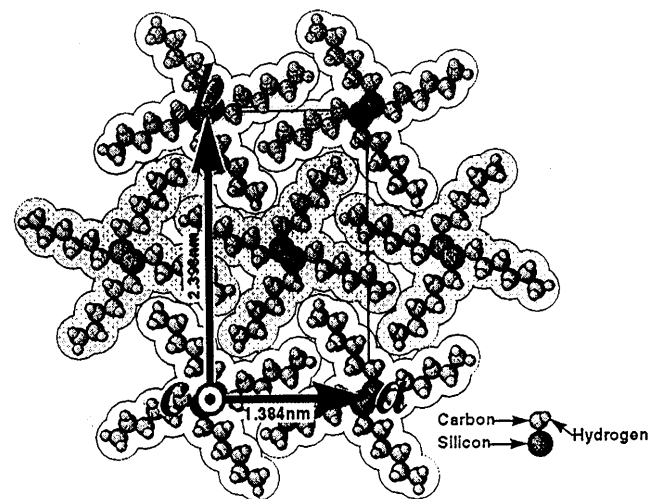


Fig. 4. Crystal structure of poly(di-*n*-hexylsilane). The crystal has an orthorhombic unit cell with $a = 1.384$, $b = 2.396$, $c = 0.400$ nm. The conformation of the Si backbone is all-*trans*.

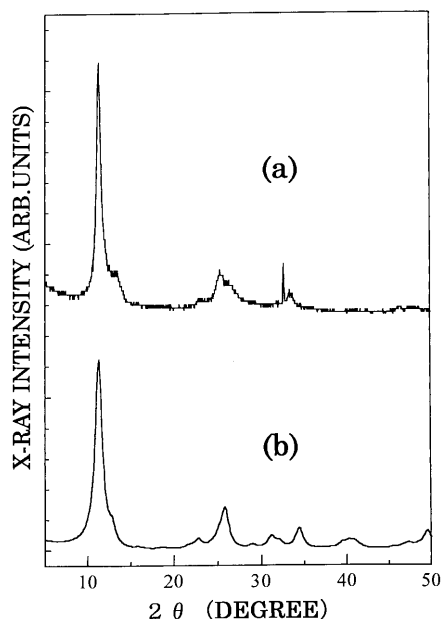


Fig. 5. Experimental X-ray diffraction pattern (a) and the theoretical pattern (b) for the poly(methylethylsilane) $[\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)]_n$.

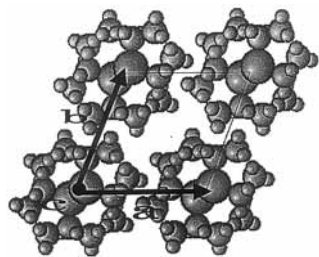


Fig. 6. Molecular structure and packing of poly(methylethylsilane). The large, medium, and small circles indicate silicon, carbon, and hydrogen atoms, respectively. The silicon backbone conformation is all-*trans*. The plural molecular structures shown in Fig. 7 are super-imposed.

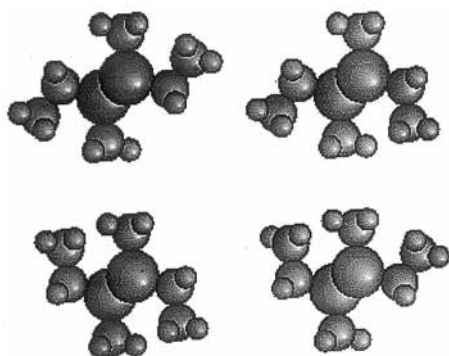


Fig. 7. Plausible molecular structure of poly(methylethylsilane). The large, medium, and small circles indicate silicon, carbon, and hydrogen atoms, respectively. The silicon backbone conformation is all-*trans*.

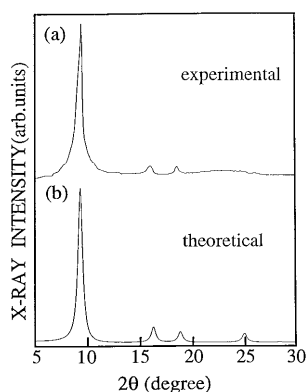


Fig. 8. Experimental X-ray diffraction pattern [4] (a) and the present theoretical pattern (b) for the poly(*n*-butylethylsilane) $[\text{Si}(\text{C}_4\text{H}_9)(\text{C}_2\text{H}_5)]_n$.

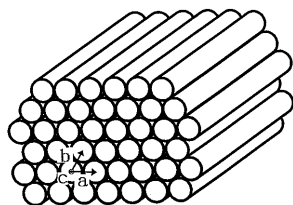


Fig. 9. Packing of poly(*n*-butylethylsilane).

chains. The single peak indicates that the lattice distances, determined from the triangle constructed by the three nearest-neighbor polymer chains, are almost same, suggesting the hexagonal columnar structure.

The theoretical pattern in Fig. 8(b) was calculated on the assumption that the structure was similar to that of liquid crystal (see Fig. 9). The vectors *a*, *b* and *c* in Fig. 9 are the primitive translation vectors used in the theoretical calculation, whose magnitudes are 1.0865, 1.0865 and 1.3880 nm, respectively ($\gamma = 60^\circ$). In the figure, polymers are schematically illustrated by 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-neighbor silicon atoms. The details of the $7/3$ helix were described elsewhere [5]. In the present calculation, the polymer is rotated around the *c* axis (the direction of the polymer chain) in a unit cell, by which the randomness of the rotation angle can be taken into account. The 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 Figs. 8 and 9.

Fig. 10 shows the experimental X-ray diffraction pattern [6] (a) and the present theoretical pattern (b) for the poly(*n*-propylmethylsilane). The appearance of two peaks at around $2\theta = 6-9^\circ$ denies the hexagonal columnar structure similar to Fig. 9, and suggests the orthorhombic or the monoclinic unit cell [3,6].

The theoretical diffraction pattern shown in Fig. 10(b) was calculated on the assumption that the backbone conformation and the unit cell were all-*trans* and monoclinic, respectively (see Fig. 11). 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 Fig. 11 indicate silicon and carbon atoms, respectively. Hydrogen atoms are

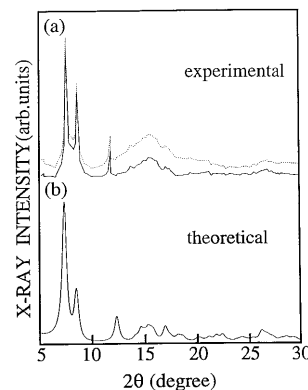


Fig. 10. Experimental X-ray diffraction pattern [6] (a) and the present theoretical pattern (b) for the poly(*n*-propylmethylsilane) $[\text{Si}(\text{C}_3\text{H}_7)(\text{CH}_3)]_n$.

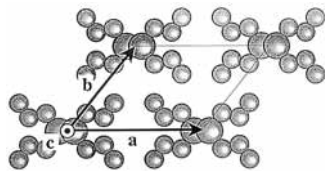


Fig. 11. Molecular structure and packing of poly(*n*-propylmethylsilane).

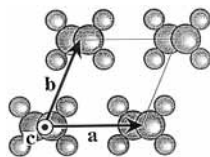


Fig. 12. Crystal structure of the poly(dimethylsilane) $[\text{Si}(\text{CH}_3)_2]_n$.

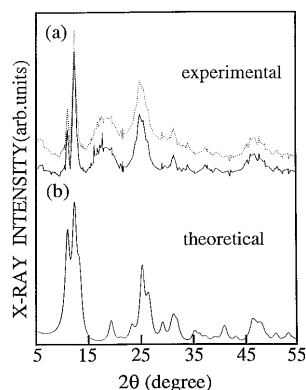


Fig. 13. Experimental X-ray diffraction pattern [6] (a) and the present theoretical pattern (b) for the poly(iso-propylmethylsilane) $[\text{Si}(\text{C}_3\text{H}_7)(\text{CH}_3)]_n$.

not illustrated in Fig. 11. In the case of two different side-chains, i.e. *n*-C₃H₇ and CH₃ groups, they are randomly distributed on both the right and left hand sides of the silicon 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 Fig. 11.

Because the theoretical X-ray diffraction pattern in Fig. 10(b) is in good agreement with the experimental one in Fig. 10(a), the structural model in Fig. 11 is considered to be reliable. From Fig. 11, two important results are pointed out. One is that the side-chains stretch on the right and left sides in Fig. 11, not upward and downward. The intramolecular steric hindrance is not present, because one of the two side-chains is a CH₃

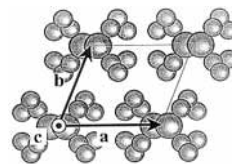


Fig. 14. Structural model used in the theoretical X-ray diffraction pattern illustrated in Fig. 13(b).

group, whose van der Waals radii are small (about 0.2 nm). The other is that the effect of unsymmetrical side-chains is averaged over due to the randomness of the side-chain conformation, causing the symmetric crystallographic structure (see Fig. 11).

Fig. 12 shows the crystal structure of the poly(dimethylsilane) reported previously [3]. It is quite similar to Fig. 11. However, the distance between the chains is very small compared with that of Fig. 11. For example, the magnitude of the primitive translation vectors, *a* is 0.7450 nm in Fig. 12, whereas that of Fig. 11 is 1.1498 nm. This is because the CH₃ group is smaller than the C₃H₇ group.

Fig. 13 shows the experimental X-ray diffraction pattern [6] (a) and the present theoretical pattern (b) for the poly(iso-propylmethylsilane). There are many diffraction peaks, indicating that the crystallinity is good.

Fig. 14 shows the structural model used in the theoretical X-ray diffraction pattern illustrated in Fig. 13(b). Similar to Fig. 11, the large and small circles indicate silicon and carbon atoms, respectively. The backbone conformation is all-*trans*. *a*, *b* and *c* in Fig. 14 show 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*-propylmethylsilane). However, the magnitude of the primitive translation vector, *a*, of the poly(iso-propylmethylsilane) is smaller than that of the poly(*n*-propylmethylsilane).

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