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## LETTER TO THE EDITOR

# The crystal structure of poly(di-*n*-hexyl-silane) and its orientation in the film

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**Abstract.** This paper describes the reasonable molecular configuration and inter-molecular packing of the poly(di-*n*-hexyl-silane) crystal. The crystal lattice is determined using a wide-angle x-ray diffraction method for the powdered specimen. The experimental diffraction pattern is compared with the theoretical one, in order to clarify the atom positions in the unit cell. The obtained unit cell contains the two polymer chains having an all-*trans* silicon backbone. The hexyl substituents are found to be asymmetrical conformations because of the steric hindrance. The orientation of the prepared thin film is also discussed on the basis of the obtained crystal structure.

Poly(di-*n*-alkyl-silane)s have been investigated with excited interest, because of the characteristic properties relevant to the one-dimensional silicon backbone. For example, these polymers exhibited an ultraviolet absorption peak, the wavelength and intensity of which were strongly related to the conformation of the silicon backbone [1, 2]. It was also reported that the absorption strength depends on the polarization direction of the incident light [2, 3]. Furthermore, electronic properties of some polysilanes were investigated theoretically. In those approaches, the polymers were regarded as one-dimensional silicon systems, and the charge carriers flowed through the delocalized  $\sigma$ -electron molecular orbital on the backbone [4–7]. In the experimental works, it is necessary to prepare the highly oriented specimens in order to pick up the characteristic features of the polymers. Recently, Kuzmany *et al* have prepared the various multilayered polysilane films using the Langmuir–Blodgett (LB) technique [8, 10]. Those oriented characters of the films can be investigated well using a diffraction method, when the crystal structure and the inter-molecular packing are clarified.

In this work, we have examined the crystal structure of poly(di-*n*-hexyl-silane) (PDHS), which exhibits very interesting properties, and has been investigated by many researchers. For example, the phase transition above room temperature with the thermochromism has been attributed to the conformational change in the silicon backbone [9]. In order to prepare the highly ordered materials as well as the highly oriented films, it is necessary to check the crystal structure of the specimens. Concerning the crystal structure of PDHS, Kuzmany *et al* have reported that it has a monoclinic unit cell of  $a = 1.375$  nm,  $b = 2.182$  nm,  $c = 0.407$  nm and  $\gamma = 88.0^\circ$  [10]. The magnitude of the translation vector  $c$  has been determined using a fibre electron diffraction pattern of the uniaxially stretched specimen. In 1992, the model of the molecular configuration and inter-molecular packing was proposed by Patnaik *et al* [11]. The structure was determined by minimizing the difference between the experimental and theoretical structure factors. However, the obtained configuration was

very complex, and the nearest neighbour side-chains were too close to be stabilized. This paper also describes the deduced model of the crystal structure of PDHS. We insist that the molecule has a simple configuration so as to minimize the intra-molecular steric hindrance. In order to determine the inter-molecular packing, we directly compare the experimental x-ray diffraction pattern with the calculated one, because the experimental structure factor is not well defined, when the diffraction peak is assigned the plural indices. The orientation of the prepared thin film is finally discussed on the basis of the obtained crystal structure.

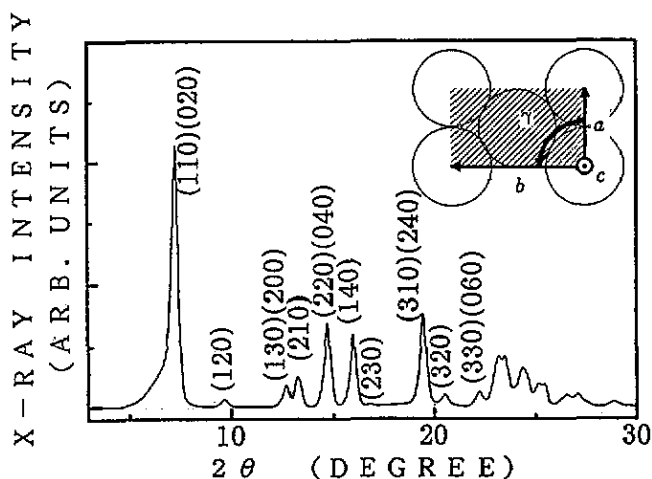


Figure 1. X-ray diffraction pattern of the source powdered specimen. Inset shows the unit cell of the crystal.

The PDHS was chemically synthesized by means of the Waltz method. The colour of the material was pure white. Thin polymer film was prepared from the solution of the PDHS in the heptane solvent. The solution was dropped on the Si(001) wafer substrate, and dried in the air at room temperature. Each sample was investigated using the wide-angle x-ray diffraction method. The wavelength of the x-ray used was 0.154 nm (Cu  $K\alpha$  line), and its power was 50 kV  $\times$  100 mA. The theoretical calculation was performed using the conventional diffraction theory, and its details are described elsewhere [12].

Figure 1 shows the experimental x-ray diffraction pattern of the unprocessed PDHS powder. The lowest angle-peak is considered to correspond to the lattice spacing determined from the smallest triangle consisting of the three PDHS chains. A shoulder also appears in the lowest angle-diffraction peak. This is caused by the conformationally disordered phase of the PDHS [10, 13]. Other diffraction peaks, whose angles,  $2\theta$ , are lower than  $22.2^\circ$ , are similarly attributed to the inter-molecular spacings corresponding to Miller indices of  $(hk0)$ . In this case, the silicon backbone is assumed to have an all-*trans* conformation, whose period causes the diffraction at about  $45.3^\circ$  ( $2\theta$ ) [(002)].

Therefore, we have first investigated the two-dimensional crystal lattice in the  $(hk0)$  plane. We have examined the ten clear peaks on the low-angle side. The primitive unit cell with one kind of conformational and positional state-polymer does not explain the appearance of the ten diffraction peaks. In particular, when the polymers are packed in a quasi-hexagonal lattice, as reported for the high-temperature phase [10], the (120) and (210) peaks do not appear in the diffraction pattern. Therefore, it is considered that the unit cell

contains two polymer chains which are not equivalent, as has been suggested by Kuzmany *et al* [10].

Assuming  $\alpha = \beta = 90.0^\circ$ , the crystal lattice constants are determined to be  $a = 1.38$  nm,  $b = 2.39$  nm,  $c = 0.400$  nm and  $\gamma = 90.0^\circ$  (see the inset of figure 1), from the diffraction angles shown in figure 1. When the crystal has this orthorhombic unit cell having one polymer chain, the peaks should appear at  $3.71$ ,  $6.41$ ,  $11.2$  and  $19.3^\circ$  ( $2\theta$ ), which correspond to the (010), (100), (030) and (300) lattice planes, respectively. However, they do not exist in the diffraction pattern, suggesting again two different polymer chains in the unit cell.

When there is another chain in the centre of the two-dimensional unit cell, the (100) and (010) reflections should almost vanish, because the phase difference between the x-rays diffracted from the centre-chain and the edge-chain is nearly  $\pi$ . In this case, the centre-chain is not equivalent to the edge-chain, in order to explain the large primitive unit cell containing two polymer chains.

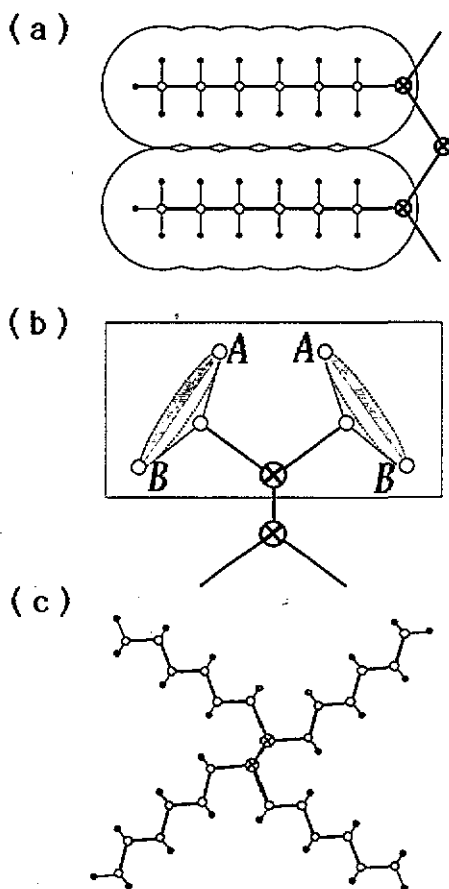


Figure 2. Configuration of the hexyl substituents.  $\otimes$ ,  $\circ$ , and  $\bullet$  indicate silicon, carbon, and hydrogen atoms, respectively. Details are explained in the text.

The volume of the primitive unit cell stated above is a little larger than that reported by Kuzmany *et al*. The origin of the difference is considered as follows: that is, their unit cell

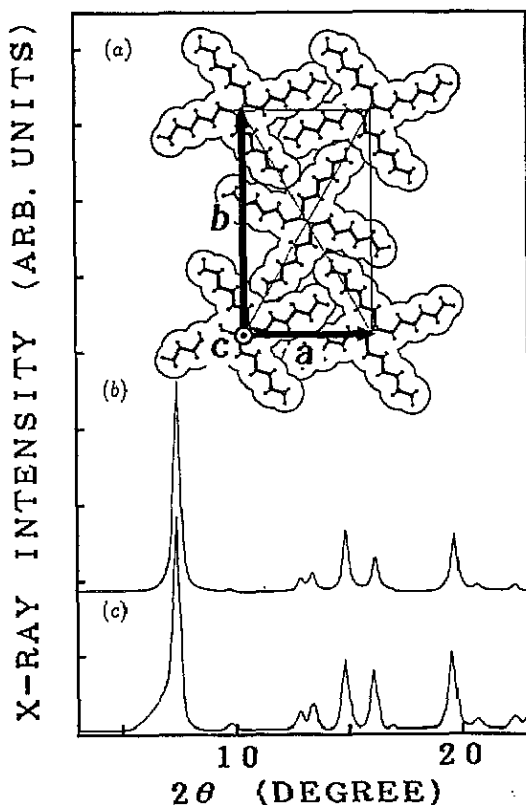


Figure 3. Crystal structure of (a) the PDHS, (b) the theoretical and (c) the experimental x-ray diffraction patterns.

was determined using the data for a uniaxially oriented specimen, and the configuration of the polymer having the silicon backbone might be affected in the stretching process.

Next, the conformations of the backbone and the *n*-hexyl side chains are considered. The previous paper has reported that the silicon backbone had an all-*trans* conformation with a period of 0.400 nm [13]. Therefore, we used this result, and considered the details of the hexyl side groups. The *n*-alkyl runs may take an all-*trans* conformation in the room temperature. Since the Van der Waal's radius of both the methylene and methyl unit is about 0.2 nm, and the half of the silicon *trans* period is about 0.2 nm, the carbons in the same hexyl chain can be on a plane vertical to the direction of the silicon backbone (*c*-axis), as indicated in figure 2(a).

The positions of the second carbons from the silicon atom are very important, because they determine the molecular configuration of the PDHS. The second carbons take only two positions, i.e. A and B in figure 2(b). Considering that the polymer takes the configuration to relieve the steric hindrance, the configuration of the substituents must be asymmetric, as illustrated in figure 2(c). In this figure, the *n*-hexyl substituents and the silicon atom, i.e. C-Si-C-C, have a *cis*-like conformation. Such configuration may be impossible, because the polymers consisted of the carbon backbones hardly have a *cis* conformation. However, in the present case, each *cis* group includes one silicon atom, and the Si-C bond length is longer than that of the C-C bond. Therefore, the effect of the steric hindrance is expected to be much smaller than that of the C-C-C-C *cis* conformation.

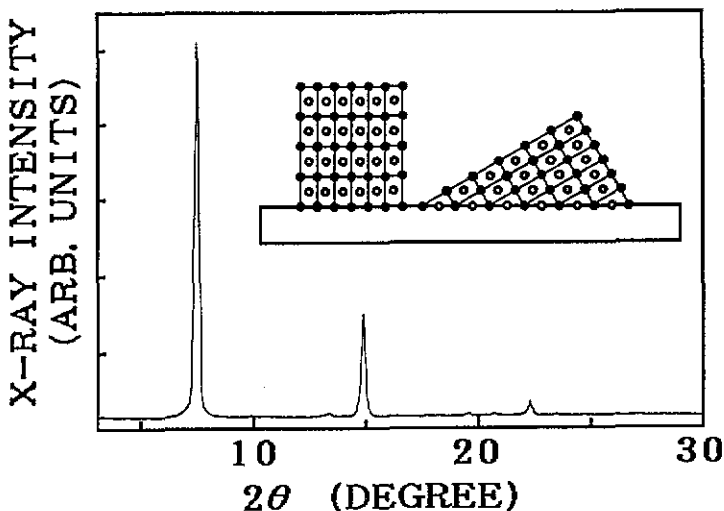


Figure 4. X-ray diffraction pattern of the film prepared from the solution of the PDHS in the heptane solvent. Inset shows the orientation of the film. In the inset, open and closed circles indicate the centre and edge chains, respectively, in the unit cell.

From the above considerations concerning both the arrangement of the PDHS chains in the unit cell and the reasonable configuration of the polymer, the details of the crystal structure are determined as shown in figure 3(a). Figure 3(b) is the theoretical x-ray diffraction pattern calculated using the crystal structure thus obtained. It should be noted that figure 3(b) is in good agreement with the experimentally obtained diffraction pattern shown in figure 3(c).

Figure 4 shows the x-ray diffraction pattern of the film prepared from the solution of the PDHS in the heptane solvent. The observed left peak corresponds to Miller indices of (110) and (020), and the centre and right hand peaks correspond to their higher reflections. Using the obtained unit cell and the inter-molecular packing, it is able to explain the polymer orientation in this thin film. Since only the ( $hk0$ ) peaks appear in the diffraction pattern, it is concluded that the direction of the polymer chains is parallel to the surface of the substrate, as shown in the inset of figure 4.

The above orientation was observed for the specimen prepared from the low-concentration solution. However, the films prepared from the high-concentration solution showed the x-ray diffraction pattern, which was similar to that of the source powdered specimen. Therefore, the force between the extended hexyl substituents and the surface of the substrate may be dominant, rather than the inter-molecular Van der Waal's force, which causes the crystallization of the PDHS polymer, when the molecular concentration of the solution is low.

In conclusion, we have determined the details of the crystal structure of the PDHS in the solid state. The silicon backbone has an all-*trans* conformation, whereas the *n*-hexyl substituents have an asymmetrical conformation. The primitive unit cell contains the two polymer chains which are not equivalent, and these chains are almost closely packed in space. The present result is expected to be used for the analysis of the polymer orientation in the various films.

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