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## LETTER TO THE EDITOR

# Crystal structures of poly(di-ethyl silane) and poly(di-*n*-propyl silane)

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**Abstract.** The packings of the poly(di-ethyl silane) and poly(di-*n*-propyl silane) crystals have been examined by comparing the experimental x-ray diffraction pattern with the theoretical pattern. The silicon backbone conformation of both crystals is all *trans*, and the side-chain conformation is mostly determined by the intramolecular steric hindrance. The molecules are closely packed in both cases, and the intermolecular distance is well explained by considering the van der Waals radii of the CH<sub>2</sub> and CH<sub>3</sub> groups.

Organopolysilanes have a one-dimensional silicon backbone and organic side chains. Up to the present, various organopolysilanes have been chemically synthesized, and their physical properties have been examined. They are expected to be used for future electronic and optical devices by controlling the Si backbone conformation, side chains, crystal orientation, and electric conductivity. However, only a few papers have reported on their crystal structure (Kuzmany *et al* 1986, Lovinger *et al* 1986, 1989, 1991, Patnaik and Farmer 1992). Moreover, a reasonable description of the intermolecular packing of the polysilane chains has not been reported, except for the poly(di-methyl silane) [Si(CH<sub>3</sub>)<sub>2</sub>]<sub>n</sub> and poly(di-*n*-hexyl silane) [Si(C<sub>6</sub>H<sub>13</sub>)<sub>2</sub>]<sub>n</sub> crystals (Furukawa *et al* 1993a, b).

In this paper, the packings of the poly(di-ethyl silane) [Si(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>n</sub> and poly(di-*n*-propyl silane) [Si(C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>]<sub>n</sub> crystals have been examined by comparing the experimental x-ray diffraction pattern reported previously with the present theoretical pattern. As a result, it is found that the Si backbone conformation of both crystals is all *trans*, and that the side-chain conformation is mainly determined by the intramolecular steric hindrance. The packings obtained are quite reasonable, and the distance between the molecules is well explained by considering the van der Waals radii of the CH<sub>2</sub> and CH<sub>3</sub> groups.

The theoretical calculation has been performed using conventional diffraction theory (Furukawa *et al* 1993b). The Si-Si, Si-C, C-C, and C-H bond lengths used in this study were 0.235, 0.189, 0.154, and 0.108 nm, respectively. The C-Si-C angle used was 108.0°. The Si-C-C, C-C-C, C-C-H, and H-C-H angles were assumed to be 109.47° (tetrahedral angle). The Si-Si-Si bond angles used for [Si(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>n</sub> and [Si(C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>]<sub>n</sub> were 114.7 and 117.4°, respectively. In order to compare the theoretical result with the experimental pattern, the appropriate half-width and temperature factor were also assumed. The x-ray diffraction patterns of [Si(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>n</sub> and [Si(C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>]<sub>n</sub> reported by Lovinger *et al* (1989) were used as

experimental data. The wavelength of the x-ray used in the theory and experiment was 0.154 nm (Cu  $K\alpha$  radiation).

Figure 1(a) and (b) shows the experimental (Lovinger *et al* 1989) and theoretical x-ray diffraction patterns, respectively, for the powdered  $[\text{Si}(\text{C}_2\text{H}_5)_2]_n$  crystal. In figure 1(a), there are six diffraction peaks in the  $2\theta$  range of 5–30°, five of which were indexed by Lovinger *et al*. They have reported that the interchain-peak  $d$  spacings (determined by the left four peaks in figure 1(a)) were consistent with a two-chain rectangular lattice of  $a = 1.108$  nm and  $b = 1.210$  nm. However, the volume of the rectangular lattice is larger than that occupied by the two closely packed chains. We have, therefore, found the most plausible unit cell and indices, and the result is shown in figure 1(b). Our indices are different from those proposed by Lovinger *et al*. One of the candidates for our unit cell is monoclinic ( $a = 0.820$  nm,  $b = 0.810$  nm,  $c = 0.399$  nm,  $\gamma = 84.8^\circ$ ). These lattice parameters explain well the distance between the chains.

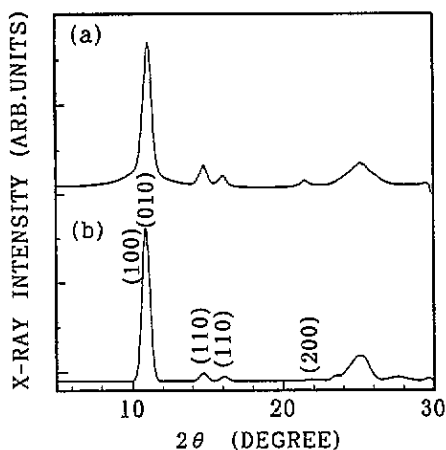


Figure 1. Experimental (a) and theoretical (b) x-ray diffraction patterns for the powdered  $[\text{Si}(\text{C}_2\text{H}_5)_2]_n$  crystal.

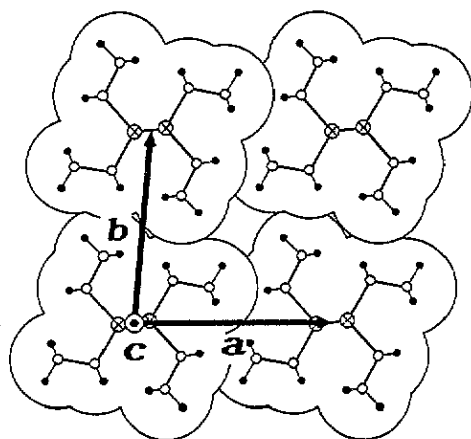


Figure 2. Structure of the  $[\text{Si}(\text{C}_2\text{H}_5)_2]_n$  crystal. The large circles marked by a cross, the medium circles, and the small filled circles indicate Si, C, and H atoms, respectively. The envelope shows the van der Waals radii of the  $\text{CH}_2$  and  $\text{CH}_3$  groups.  $a$ ,  $b$ , and  $c$  denote the primitive translation vectors.

Figure 2 shows the intermolecular packing obtained, in which the large circles marked by a cross, the medium circles, and the small filled circles represent Si, C, and H atoms, respectively. The envelope shows the van der Waals radii of the  $\text{CH}_2$  and  $\text{CH}_3$  groups. The side chains extend asymmetrically, causing the close intramolecular packing. These molecules are also closely packed in the present unit cell.

The theoretical calculation was performed using the configuration shown in figure 2. As a result, the diffraction peaks indexed by  $(hk0)$  were explained by the model, whereas the peaks  $(hkl)$ ,  $l \neq 0$ , were not. As shown in figure 1(a), the peak near  $2\theta = 25^\circ$  is broad, suggesting that the unit cell is not well defined. One of the origins of the ambiguity is the phase shift of the nearest-neighbour chain along the  $c$  axis. Therefore, the calculation was performed on the assumption that there were 12 configurations in which the shift of the nearest-neighbour chain along the  $c$  axis was different. The theoretical x-ray diffraction pattern thus obtained is shown in figure 1(b). The pattern is in good agreement with the

experimental pattern shown in figure 1(a). This indicates that the unit cell is not uniquely determined, because of the variety of the packing along the  $c$  axis. However, the molecules are almost closely packed in the planes perpendicular to the  $c$  axis, as shown in figure 2. These circumstances are similar to those of  $[\text{Si}(\text{C}_6\text{H}_{13})_2]_n$  (Furukawa *et al* 1993a).

Figure 3(a) and (b) shows the experimental (Lovinger *et al* 1989) and theoretical x-ray diffraction patterns, respectively, for the powdered  $[\text{Si}(\text{C}_3\text{H}_7)_2]_n$  crystal. Similarly to figure 1(a), there are six diffraction peaks in figure 3(a), and these were indexed by Lovinger *et al*. Their most recent paper (Lovinger *et al* 1991) has pointed out that the interchain-peak  $d$  spacing (determined by the left five peaks in figure 3(a)) were consistent with a one-chain tetragonal lattice of  $a = b = 0.980$  nm,  $c = 0.399$  nm. The volume of this unit cell is in good agreement with that occupied by the closely-packed single  $[\text{Si}(\text{C}_3\text{H}_7)_2]_n$  chain.

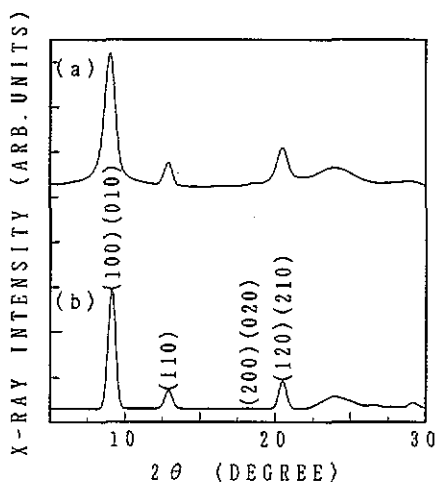


Figure 3. Experimental (a) and theoretical (b) x-ray diffraction patterns for the powdered  $[\text{Si}(\text{C}_3\text{H}_7)_2]_n$  crystal.

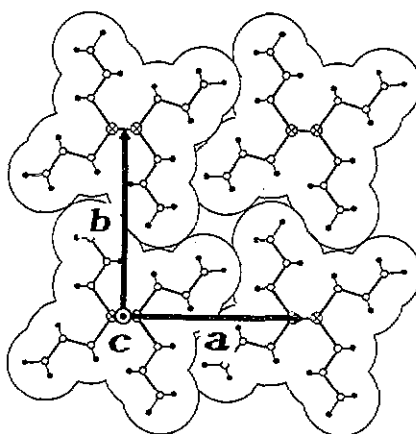


Figure 4. Structure of the  $[\text{Si}(\text{C}_3\text{H}_7)_2]_n$  crystal. The notations are the same as those of figure 2.

We therefore considered the packing of the chains using the above unit cell, and the result is shown in figure 4. The Si backbone conformation is all *trans*. However, the side chains do not extend symmetrically due to the steric hindrance, similarly to those of the  $[\text{Si}(\text{C}_2\text{H}_5)_2]_n$  and  $[\text{Si}(\text{C}_6\text{H}_{13})_2]_n$  crystals (Furukawa *et al* 1993a). The magnitudes of the primitive translation vectors  $a$  and  $b$  are well explained by the intermolecular distance deduced from the model shown in figure 4.

The theoretical x-ray diffraction pattern was calculated for the model structure indicated in figure 4. The result thus obtained was similar to that for  $[\text{Si}(\text{C}_2\text{H}_5)_2]_n$  i.e., the peaks indexed by  $(hk0)$  were explained by the model, whereas those indexed by  $(hkl)$ ,  $l \neq 0$ , were not. Therefore, the effect of the phase shift of the nearest-neighbour chain along the  $c$  axis was also taken into account. The pattern was calculated 12 times by varying the value of the phase shift, as has been done for  $[\text{Si}(\text{C}_2\text{H}_5)_2]_n$ . Figure 3(b) shows the 12 superimposed x-ray diffraction patterns of the  $[\text{Si}(\text{C}_3\text{H}_7)_2]_n$  crystal. The result is in good agreement with figure 3(a). The reason for the phase shifts mentioned above is not clear. However, they may be explained by a small rotation of the  $n$ -alkyl substituents.

Figure 5(a)–(c) shows the conformations of the side chains of  $[\text{Si}(\text{C}_2\text{H}_5)_2]_n$ ,  $[\text{Si}(\text{C}_3\text{H}_7)_2]_n$ , and  $[\text{Si}(\text{C}_6\text{H}_{13})_2]_n$  (Furukawa *et al* 1993a) crystals, respectively. In all

the cases, two of the four C–Si–C–C groups have a *cis*-like conformation due to the intramolecular steric hindrance. In the case of *n*-alkyl groups, however, a *cis*-like C–C–C–C conformation is not plausible, because of the steric interaction in the same chain. The present *cis*-like conformation is possible, because the Si–C bond length is larger than that of the C–C bond. This result is very important, because the conformation of the C–Si–C–C group determines the overall structure of the molecule, and hence determines the overall packing of the chains. Other poly(*di-n*-alkyl silane)s having an all-*trans* Si backbone may have similar *cis*-like C–Si–C–C groups.

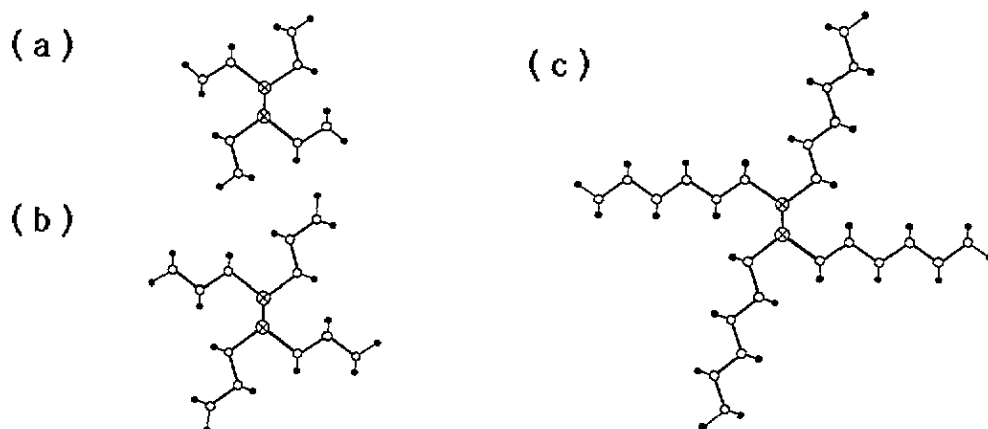


Figure 5. Configurations of *n*-alkyl substituents of  $[\text{Si}(\text{C}_2\text{H}_5)_2]_n$  (a),  $[\text{Si}(\text{C}_3\text{H}_7)_2]_n$  (b), and  $[\text{Si}(\text{C}_6\text{H}_{13})_2]_n$  (c). The notations are the same as those of figures 2 and 4.

In conclusion, the packings of the  $[\text{Si}(\text{C}_2\text{H}_5)_2]_n$  and  $[\text{Si}(\text{C}_3\text{H}_7)_2]_n$  crystals have been investigated by comparing the experimental x-ray diffraction pattern reported previously with the present theoretical pattern. The Si backbone conformation of both crystals is all *trans*, whereas the side-chain conformation is asymmetric due to the intramolecular steric hindrance. The latter circumstance is the same as that of the  $[\text{Si}(\text{C}_6\text{H}_{13})_2]_n$  crystal, so the side chains of other poly(*di-n*-alkyl silane) crystals may have similar conformations. In these crystals, the molecules are closely packed in space. The unit cell for the  $[\text{Si}(\text{C}_2\text{H}_5)_2]_n$  crystal reported by Lovinger *et al* is not acceptable, because the polymer chains cannot be closely packed in it. Moreover, it is found that there exist a variety of phase shifts of the nearest-neighbour chains along the *c* axis in these crystals.

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