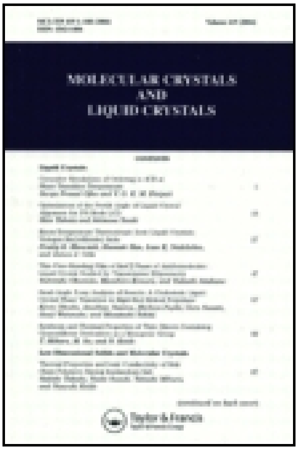

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On the Similarity and Difference of Molecular Structure and Packing Between Organopolysilanes with Symmetric and Asymmetric Side-Chains

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On the Similarity and Difference of Molecular Structure and Packing Between Organopolysilanes with Symmetric and Asymmetric Side-Chains

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Molecular structure and packing of various organopolysilanes with symmetric and asymmetric side-chains have been obtained by comparing the theoretical X-ray diffraction pattern with the experimental pattern. Molecular structure of the organopolysilanes with asymmetric side-chains, such as, poly(methyl propyl silane) and poly(methyl phenyl silane), is mainly determined by the intra-molecular van der Waals interaction between the adjacent side-chains, which is similar to that of the organopolysilanes with symmetric side-chains, such as, poly(di-methyl silane) and poly(di-propyl silane). Packing of the organopolysilanes is determined to occupy closely in space in both cases. However, density of the organopolysilanes with asymmetric side-chains is smaller than that of the organopolysilanes with symmetric side-chains because of the large space between the adjacent side-chains.

Keywords: molecular structure; organopolysilane; packing; poly(di-methyl silane)

1. INTRODUCTION

Recently, many researchers are interested in organic devices, such as, organic light emitting diode [1]. We are able to fabricate large scale light emitting diode using organic material. Up to the present time, many papers concerning carbon-based polymers have been published [2]. Electric conductivity of the carbon-based polymers is high when the polymers have double-bonds. On the other hand, silicon-based

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polymers, that is, organopolysilanes, have single-bonds. However, the σ electrons in the organopolysilanes are extended along the main-chain, so that the electric conductivity becomes large compared with that of the carbon-based polymers without double-bonds [3]. Moreover, the conformation of the silicon backbone changes with a change of temperature. This causes a change of the wavelength of the optical absorption peak [4]. Therefore, organopolysilanes are expected to be used for future optical and electronic devices. We have already reported the light emitting diode and the solid-state dye-sensitized solar cell using the poly(di-methyl silane) thin film which was fabricated by the vacuum evaporation technique [5,6].

Concerning the silicon-based polymers, it is very difficult for us to obtain crystal structure (strictly speaking, molecular structure and packing) of organopolysilanes, because a large single-crystal cannot be obtained. Therefore, we have obtained the molecular structure and packing of various organopolysilanes with symmetric and asymmetric side-chains by comparing the theoretical X-ray diffraction pattern with the experimental pattern [7]. The packing of the silicon-based polymers is also checked on the computer graphic display. Up to the present time, we have clarified the molecular structure and packing of poly(di-methyl silane) [7], poly(di-ethyl silane) [8], poly(di-propyl silane) [8], poly(di-butyl silane) [9], poly(di-pentyl silane) [9], and poly(di-hexyl silane) [10].

In this article, we have clarified the molecular structure and packing of the organopolysilanes with asymmetric side-chains, such as, poly-(methyl ethyl silane), poly(methyl propyl silane), poly(methyl phenyl silane), and poly(butyl pentyl silane). As a result, it is found that the molecular structure of the organopolysilanes with asymmetric side-chains is mainly determined by the intra-molecular van der Waals interaction between the adjacent side-chains, which is similar to that of the organopolysilanes with symmetric side-chains, such as, poly (di-methyl silane), poly(di-ethyl silane), and poly(di-propyl silane). It is found, however, that density of the organopolysilanes with asymmetric side-chains is smaller than that of the organopolysilanes with symmetric side-chains because of the large space between the adjacent side-chains.

2. THEORETICAL CALCULATION

Theoretical calculation was performed using the conventional diffraction theory. First, the unit cell, the conformation of the silicon backbone, and the positions of the atoms of the side-chains were assumed. Then, the structure factor for each Miller index was calculated.

After that, we can obtain the theoretical X-ray diffraction pattern. The theoretical X-ray diffraction pattern obtained was compared with the experimental X-ray diffraction pattern. The packing of the polymers was also checked on the computer graphic display.

3. RESULTS AND DISCUSSION

Figure 1 shows the experimental and theoretical X-ray difraction patterns of poly(di-methyl silane). The position of the diffraction peak is determined by the lattice parameters of the unit cell, and the strength of the diffraction peak is determined by the positions of the atoms in the unit cell. Because the first-order structure of the poly(di-methyl silane) molecule is confirmed, it is concluded that the theoretical X-ray diffraction pattern is in good agreement with the experimental pattern.

The theoretical X-ray diffraction pattern shown in Figure 1(b) was calculated using the model shown in Figure 2. In Figure 2, ***a***, ***b***, and ***c*** denote the primitive translation vectors of the sub-cell. The direction of the vector ***c*** is the same as the direction of the main-chain. The large

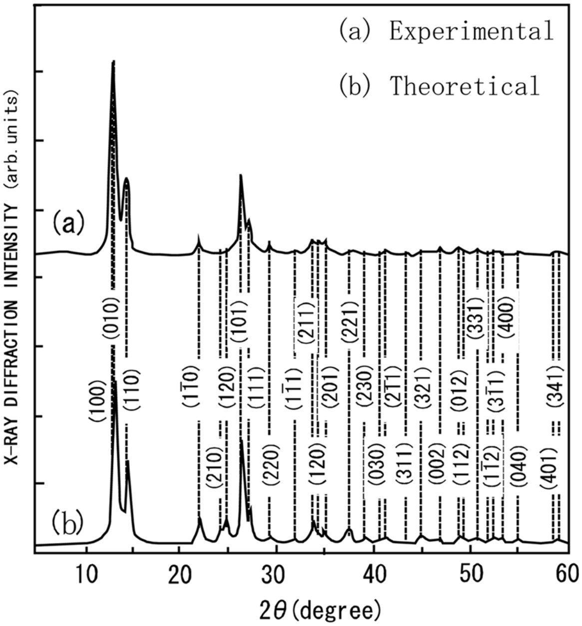

FIGURE 1 Experimental (a) and theoretical (b) X-ray diffraction patterns of poly(di-methyl silane).

circles indicate methyl groups. The conformation of the silicon backbone is *all-trans*. As shown in Figure 2, the molecules are closely packed in space. The most important point is that the van der Waals diameter of the methyl group is about 0.4 nm, which is almost the same as the magnitude of the vector ***c***. This causes well-defined *all-trans* conformation. Therefore, it is concluded that the molecular structure of poly(di-methyl silane) is mainly determined by the intra-molecular van der Waals interaction between the adjacent methyl groups.

Figure 3 shows the obtained molecular structure and packing of poly(di-propyl silane). Similar to Figure 2, ***a***, ***b***, and ***c*** denote the primitive translation vectors of the sub-cell. The conformation of the silicon backbone is *all-trans*, which is the same as that of poly(di-methyl silane). The important point is that the two propyl side-chains are asymmetrically stretched due to the intra-molecular steric hindrance.

Figure 4 shows the side-chains of poly(di-propyl silane). The envelope shows the van der Waals radius of the methyl CH_3 and methylene CH_2 groups. As shown in Figure 4, the van der Waals diameter of the methyl and methylene groups is about 0.4 nm, which is the same as that of the period along the ***c*** axis. Therefore, each methyl and methylene group is attached to the adjacent methyl and methylene groups bonded to the second nearest neighbor silicon atoms by van der Waals force. This causes the well-defined *all-trans* conformation as well as well packing of poly(di-propyl silane) molecules. These circumstances are the same as those of poly(di-ethyl silane) [8], poly(di-hexyl silane) [10], and poly(di-octyl silane) [11].

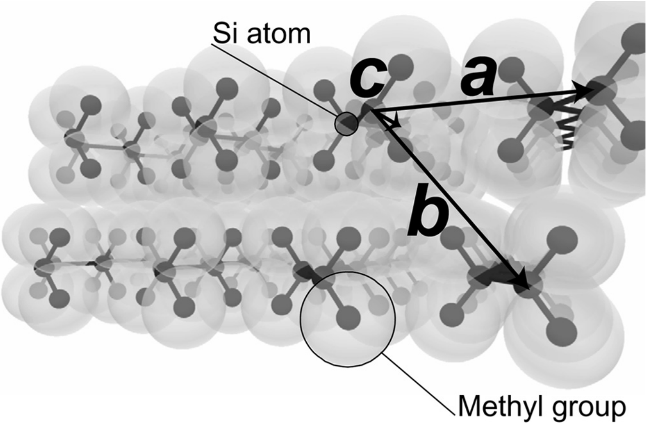

FIGURE 2 Molecular structure and packing of poly(di-methyl silane).

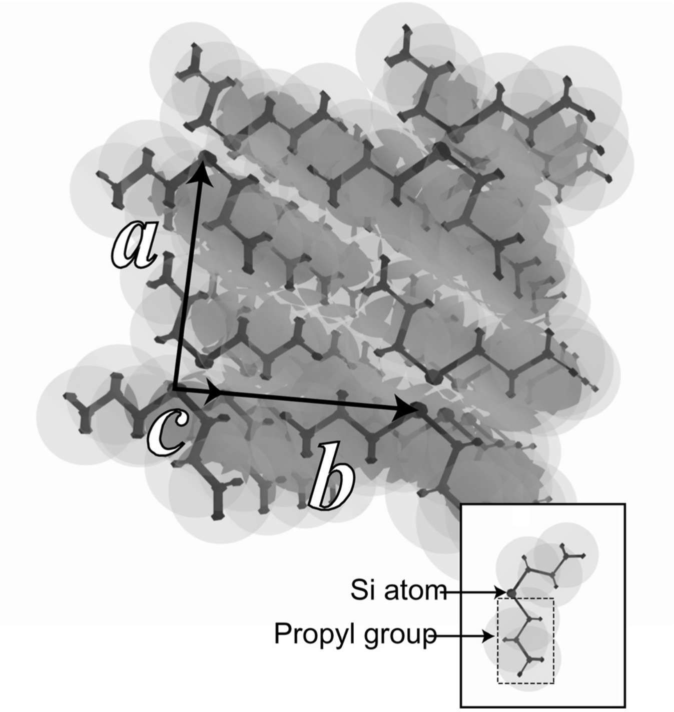

FIGURE 3 Molecular structure and packing of poly(di-propyl silane).

Figure 5 shows the molecular structure and packing of poly(methyl propyl silane), which has an asymmetric side-chain. In Figure 5, ***a***, ***b***, and ***c*** denote the primitive translation vectors of the sub-cell. The conformation of the silicon backbone is *all-trans*. Strictly speaking, we cannot use the word “crystal”, because the arrangement of the side-chains of poly(methyl propyl silane) is considered to be atactic. Therefore, we should use the word “molecular structure and packing” for organopolysilanes with asymmetric side-chains. In the case of poly(methyl propyl silane), intra-molecular steric hindrance does not occur, because one of the two side-chains is methyl group. So the conformation of the carbon backbone in the propyl side-chains becomes *all-trans*, as shown in Figure 5. Each methyl and propyl group is attached to the adjacent methyl or propyl side-chains bonded to the second nearest neighbor silicon atoms by van der Waals force, which is similar to that of the organopolysilanes with symmetric side-chains. Figure 5 was obtained by superimposing the two arrangement of the side-chains in poly(methyl propyl silane) [12–14]. Because the

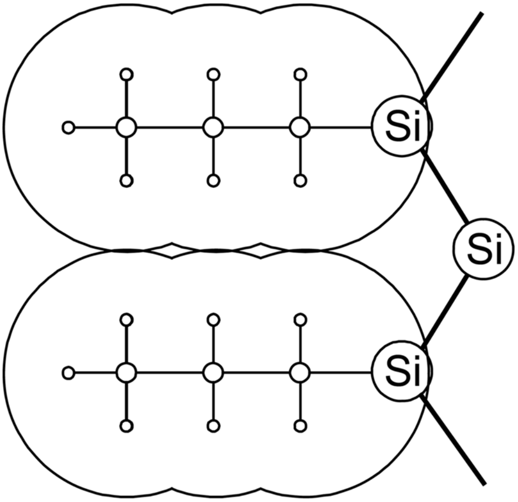

FIGURE 4 Side-chains of poly(di-propyl silane).

arrangement of the side-chains is atactic, the density of the poly(methyl propyl silane) is a little bit smaller than that of the poly(di-propyl silane) crystal (see Figure 3).

Figure 6 shows the experimental and theoretical X-ray diffraction patterns of poly(methyl phenyl silane). Figure 6(a) shows the X-ray diffraction pattern of poly(methyl phenyl silane) powder. As shown in Figure 6(a), there is a large diffraction peak near 10°. Concerning the thin film, there were no diffraction peaks for the films fabricated from the poly(methyl phenyl silane) solution. Figures 6(b)–(e) show

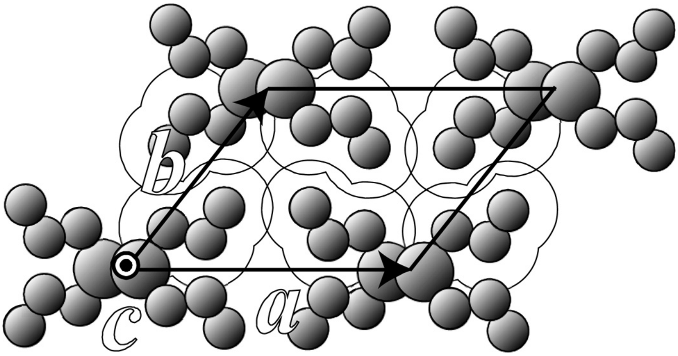

FIGURE 5 Molecular structure and packing of poly(methyl propyl silane).

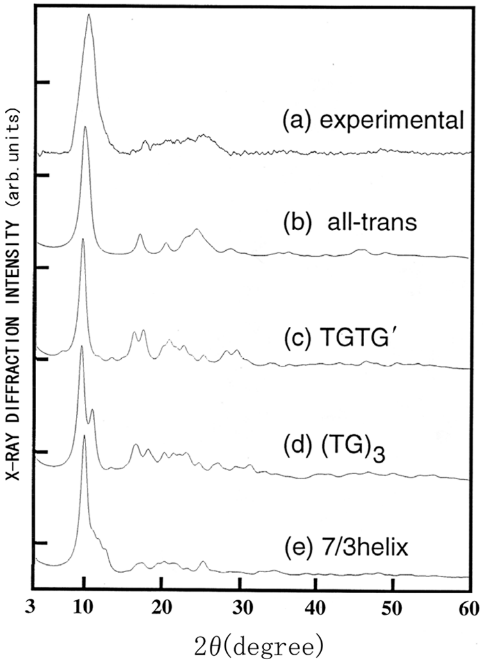

FIGURE 6 Experimental and theoretical X-ray diffraction patterns of poly(methyl phenyl silane).

the theoretical X-ray diffraction patterns calculated with silicon backbone conformations of *all-trans*, *trans-gauche-trans-gauche'*, *trans-gauche-trans-gauche-trans-gauche*, and *7/3 helix*, respectively. These theoretical X-ray diffraction patterns are not in good agreement with the experimental pattern shown in Figure 6(a). However, these theoretical patterns are not so different from the experimental pattern. The most plausible silicon backbone conformation of poly(methyl phenyl silane) is *helix*, because one of the two side-chains is phenyl group. A large diffraction peak in Figure 6(a) indicates that the distances of the three lattice planes parallel to the ***c*** axis deduced from the adjacent three polymer chains are same, suggesting the hexagonal columnar structure.

Figure 7 shows the side-chains of poly(methyl phenyl silane). When the plane of the phenyl group is perpendicular to the ***c*** axis, steric hindrance occurs between the methyl and the phenyl groups. Therefore, the phenyl group should be inclined from the plane perpendicular to the ***c*** axis, suggesting a helical conformation.

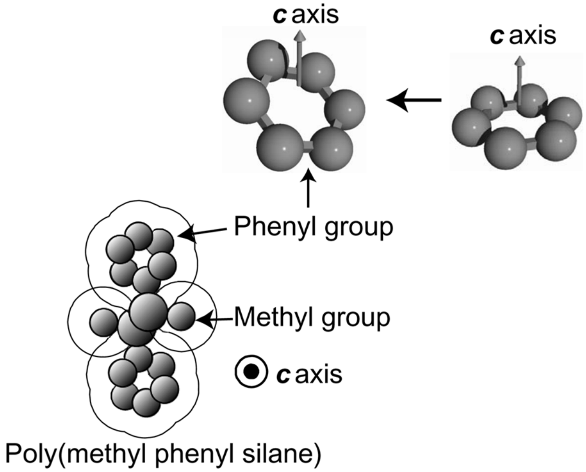

FIGURE 7 Side-chains of poly(methyl phenyl silane).

We have also studied the molecular structure and packing of poly(methyl ethyl silane) and poly(butyl pentyl silane). As a result, it is found that the silicon backbone conformations of poly(methyl ethyl silane) and poly(butyl pentyl silane) are *all-trans* and *7/3 helix*, respectively. In both cases, the silicon backbone conformation is mostly determined by the intra-molecular van der Waals interaction between the adjacent side-chains, which is the same as those of the organopolysilanes stated before. Density of poly(methyl ethyl silane) and poly(butyl pentyl silane) is smaller than that of poly(di-methyl silane), poly(di-ethyl silane), poly(di-butyl silane), and poly(di-pentyl silane), because there is large space between the adjacent side-chains in the case of the organopolysilanes with asymmetric side-chains.

4. SUMMARY AND CONCLUSION

Molecular structure and packing of various organopolysilanes with symmetric side-chains, such as, poly(di-methyl silane) and poly(di-propyl silane), and asymmetric side-chaines, such as, poly(methyl propyl silane) and poly(methyl phenyl silane), have been obtained by comparing the theoretical X-ray diffraction pattern with the experimental pattern. Molecular structure of the organopolysilanes with asymmetric side-chains is mainly determined by the intra-molecular van der Waals interaction between the adjacent side-chains, which is similar to that of the organopolysilanes with symmetric side-chains. Packing of the organopolysilanes is determined to occupy closely in space in both cases. However, density of the organopolysilanes with asymmetric side-chains is smaller than that of the organopolysilanes with symmetric side-chains, because the side-chains of the asymmetric organopolysilanes are atactic, so that there exists large space between the adjacent side-chains.

REFERENCES

[1] Baldo, M. A., Lamansky, S., Burrows, P. E., Thompson, M. E., & Forrest, S. R. (1999). *Appl. Phys. Lett.*, *75*, 4.

[2] West, R. (1988). *American Chemical Society Symposium Series 360, Inorganic and Organometallic Polymers*, American Chemical Society, Washington, DC.

[3] Tachibana, H., Matsumoto, M., Tokura, Y., Morimoto, Y., Yamaguchi, A., Koshihara, S., Miller, R. D., & Abe, S. (1993). *Phys. Rev. B*, *47*, 4363.

[4] West, R. (1986). *J. Organometallic Chemistry*, *300*, 327.

[5] Furukawa, S. (1998). *Thin Solid Films*, *331*, 222.

[6] Furukawa, S., Ohta, H., Takamoto, T., Hayashida, Y., Wada, K., & Yasuda, T. (2005). *IEEE 2005 International Symposium on Electrical Insulating Materials*, P2-36, Kitakyushu, 5–9 June.

[7] Furukawa, S. & Takeuchi, K. (1993). *Solid State Commun.*, *87*, 931.

[8] Furukawa, S., Takeuchi, K., Mizoguchi, M., Shimana, M., & Tamura, M. (1993). *J. Phys.: Condensed Matter*, *5*, L461.

[9] Furukawa, S., Takeuchi, K., & Shimana, M. (1994). *J. Phys.: Condensed Matter*, *6*, 11007.

[10] Takeuchi, K. & Furukawa, S. (1993). *J. Phys.: Condensed Matter*, *5*, L601.

[11] Kanai, T., Ishibashi, H., Hayashi, Y., Oka, K., Dohmaru, T., Ogawa, T., Furukawa, S., & West, R. (2001). *J. Polymer Science: Part B: Polymer Phys.*, *39*, 1085.

[12] Furukawa, S. & Koga, T. (1997). *J. Phys.: Condensed Matter*, *9*, L99.

[13] Furukawa, S. (2000). *J. Organometallic Chemistry*, *611*, 36.

[14] Furukawa, S. & Ohta, H. (2005). *Jpn. J. Appl. Phys.*, *44*, 495.