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MOLECULAR ALIGNMENT OF NEUTRAL AND p-DOPED HEAD-TO-TAIL TYPE POLY(3-HEXYLTHIOPHENE-2,5-DIYL) AND *n*-ALKANES ON THE SURFACE OF SUBSTRATES

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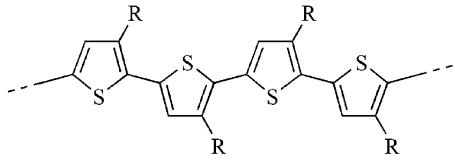
Neutral and p-doped head-to-tail poly(3-hexylthiophene-2,5-diyl), HT-P3HexTh, as well as n*-alkane (e.g., triacontane and nonacosane) are aligned with the alkyl chain oriented toward the surface of substrates such as platinum plate and silicon plate. XRD data support the alignment.*

Keywords: molecular alignment; poly(3-hexylthiophene-2,5-diyl); *n*-alkane

INTRODUCTION

The perpendicular [1–3a] and parallel [3,4] alignment of π-conjugated polymers on the surface of substrates such as carbon sheets and glass plates has been a subject of recent interest. We now report molecular alignment of neutral and p-doped head-to-tail type poly(3-hexylthiophene-2,5-diyl) [5–7], HT-P3HexTh, prepared via an organometallic route.



HT-P3HexTh (R = hexyl) proportion of the HT unit: 98.5%. Number average molecular weight (Mn) = 24000.

In order to reveal the inclination of the alkyl chain for ordering on the surface of substrates, we have also investigated molecular alignment of the following *n*-alkanes on the surface of substrates.

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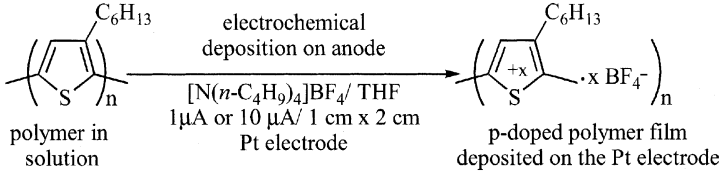
$CH_3(CH_2)_nCH_3$ $n = 28$ (triacontane)
27 (nonacosane)
22 (tetracosane)

Recently, it was reported that a thin film of HT-P3HexTh showed superconductivity when the film was placed in a field-effect-transistor (FET) geometry and doped electrically [8,9]. For the superconductivity, importance of molecule alignment of HT-P3HexTh [10, 11] was proposed [8,9].

RESULTS AND DISCUSSION

Curve (a) in Figure 1 shows the XRD pattern of an as-cast film of HT-P3HexTh (proportion of the HT unit = 98.5%, as evaluated from ^{1}H NMR data [5–7]) on a Pt plate. The XRD pattern was measured with a RINT2100 Ultima+/PC X-ray diffractometer. The film was cast from a $CHCl_3$ solution of HT-P3HexTh ($6.7\,gdm^{-3}$), and $CHCl_3$ was removed by natural evaporation. As shown in Figure 1, the curve (a) shows 3 peaks at 16.2 Å/n ($n = 1$–3). The distance d_1 of 16.2 Å has been assigned to a distance between polythiophene chains separated by the hexyl groups [5–7, 11]. The as-cast film of HT-P3HexTh does not show a d_2 peak assigned to a face-to-face packing distance between polythiophene planes (cf. Figure 2) [5–7, 11], although this d_2 peak is clearly observed after the film is peeled from the surface and crushed (cf. curve (b) in Figure 1). These results indicate that HT-P3HexTh molecules are aligned with the hexyl groups oriented toward the surface of the Pt substrate, as depicted in Figure 2. As-cast films of HT-P3HexTh on glass, gold, crystalline Al_2O_3, and Teflon substrates give XRD patterns (e.g., curve (c) in Figure 1 for the glass substrate) similar to that of the as-cast film of HT-P3HexTh on the Pt plate, revealing that the molecular alignment of HT-P3HexTh also takes place on the substrates. Similar alignment of HT-P3HexTh molecules on glass and SiO_2/Si substrates has previously been reported [6, 10, 11], and the present results indicate such molecular alignment can take place on various kinds of substrates.

HT-P3HexTh can be electrochemically deposited on various metal electrodes [13], similar to electron-donating compounds such as tetrathiafulvalene and its derivatives.



(1)

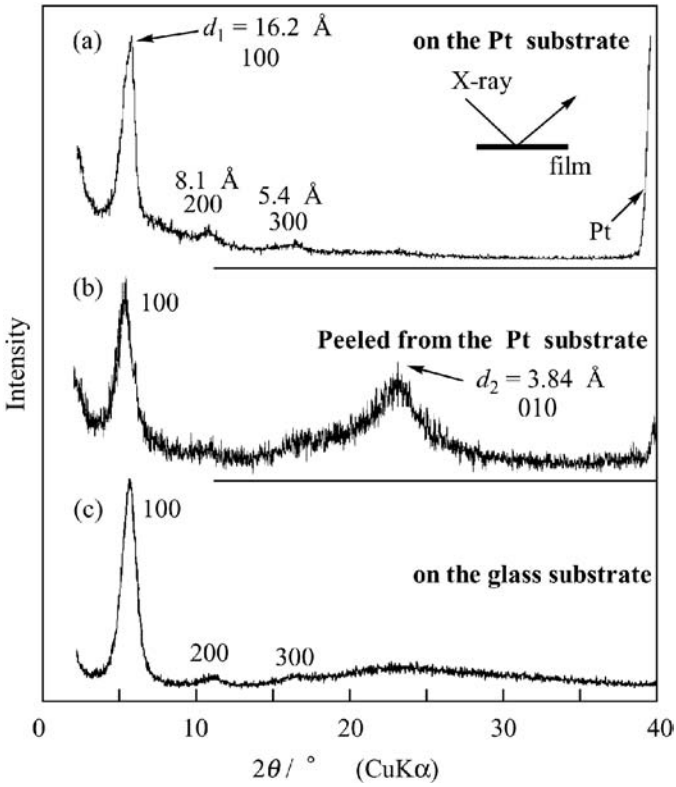


FIGURE 1 (a) XRD pattern of an as-cast film of HT-P3HexTh on a Pt plate. After the film is peeled from the Pt plate and crushed, it exhibits curve (b) which shows a 010 diffraction peak at $d_2 = 3.84$ Å. (c) XRD pattern of an as-cast film of HT-P3HexTh on a glass substrate. For curves (a) and (c), X-ray was irradiated from the out-of-plane direction as depicted in Figure 1(a). The XRD pattern was measured with a symmetrical-reflection technique.

The electrochemically deposited film of HT-P3HexTh is in a p-doped (or oxidized) state. Curves (a) and (b) in Figure 3 exhibit XRD patterns of the as-grown, electrochemically deposited films of HT-P3HexTh. XRD patterns of two samples obtained at different current densities are exhibited.

The complete absence of the 010 (or d_2) peak in the curves (a) and (b) in Figure 3 indicates that the electrochemically deposited p-doped HT-P3HexTh molecules are also aligned in a manner similar to that depicted in Figure 2. A somewhat longer d_1 value of the p-doped HT-P3HexTh than that of nondoped HT-P3HexTh may be due to the incorporation of the BF_4^- dopant. When the electrochemically deposited film is peeled from the Pt

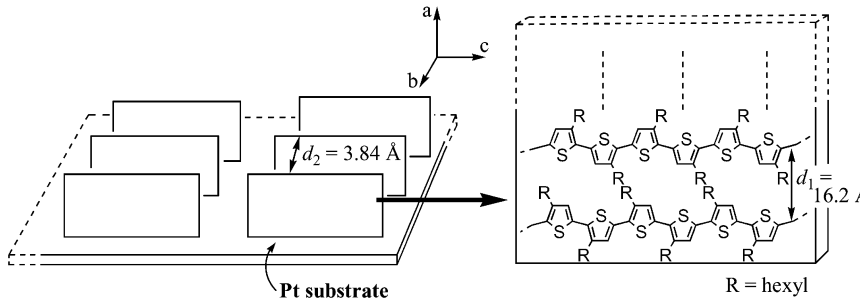


FIGURE 2 Alignment of HT-P3HexTh molecules on the surface of the substrate.

electrode and crushed, it exhibits a curve (c) which shows a 010 (or d_2) diffraction peak.

In order to investigate the tendency for the alkyl chain to be ordered on the surface of substrates, we have investigated alignment of *n*-alkanes on the surface of substrates. Curve (a) in Figure 4 shows an XRD pattern of powdery triacontane. This XRD pattern agrees with reported data [14]. Triacontane reportedly forms a monoclinic crystal with the dimensions of $a = 5.581$ Å, $b = 7.445$ Å, c (the direction of the alkyl chain) $= 40.71$ Å, and $\beta = 118.95°$ as depicted in the inset in Figure 4(a).

Curves (b), (c), and (d) in Figure 4 show XRD patterns of triacontane film (0.1 μm) obtained by casting from a $CHCl_3$ solution (8.5 gdm^{-3}) on a Si zero background sample plate, Pt plate, and glass plate, respectively. Strong remaining 00n diffraction peaks at $d = 35.6$ Å/n [14] (n = 1–15) in the XRD pattern film and considerable weakening of other peaks, especially weakening of the 110 peak, indicate that the long *n*-alkane (triacontane) itself has a strong tendency to be aligned essentially perpendicular to or with the angle of $\beta = 118.95°$ toward the surface of the substrate.

Nonacosane and tetracosane form somewhat different types of crystals—orthorhombic and triclinic crystals, respectively [14]. However, both the long *n*-alkane molecules are also aligned in the cast film, similar to the case of triacontane. For example, strong remaining $00n$ (n $= 2, 4, 6, \ldots$) diffraction peaks in the XRD curve (e) in Figure 4 support the view that nonacosane molecules are also aligned with the alkane chain directed toward the surface of the substrate. The cast film of tetracosane gives strong peaks at $d = 30.3$ Å/n [14] (n $= 1, 2, 3, \ldots$), which also agrees with a similar alignment.

As described above, alkanes themselves have nature to be aligned on the surface of the substrate, and the molecular alignment of HT-P3HexTh on the surface of the substrates seems based on the inclination of the hexyl chain to be aligned toward the surface of the substrate. The side hexyl

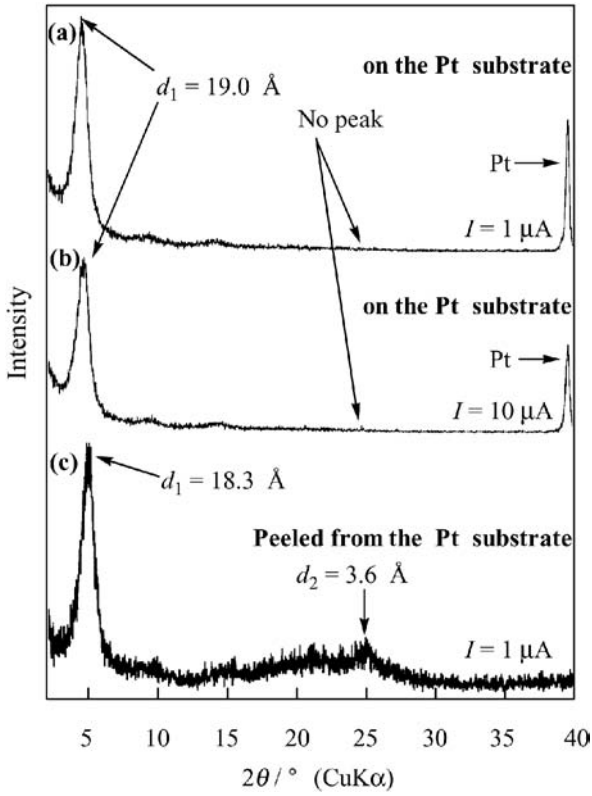


FIGURE 3 Curves (a) and (b): XRD pattern of as-grown, electrochemically deposited film of p-doped HT-P3HexTh. The electrochemical deposition was carried out at a galvanostatic mode on a Pt plate (1 cm × 2 cm) immersed in a THF solution containing HT-P3HexTh (saturated: about 2 gdm^{-3} [7]) and $[N(n\text{-}C_4H_9)_4]BF_4$ (3.29 gdm^{-3}) at room temperature; (a) at 1 μA for 5 h; (b) at 10 μA for 3 h. The former and latter films had thickness of 4 μm and 3 μm, respectively, as measured with a Dektak^3 ST Surface Profiler. XPS analysis of S and B indicates that the sample for the XRD curve (a) is formulated as $(C_{10}H_{14}S{\cdot}0.008\ BF_4)_n$. When the film used for the measurement of XRD curve (a) is peeled from the Pt plate and crushed, it exhibits curve (c), which shows a 010 diffraction peak. For (a) and (b), X-ray was irradiated as described in the caption of Figure 1.

chains in HT-P3HexTh are considered to take a well-packed structure [5–7]; consequently, the local molecular packing mode of the hexyl side chain is considered to be similar to the packing mode of *n*-alkane.

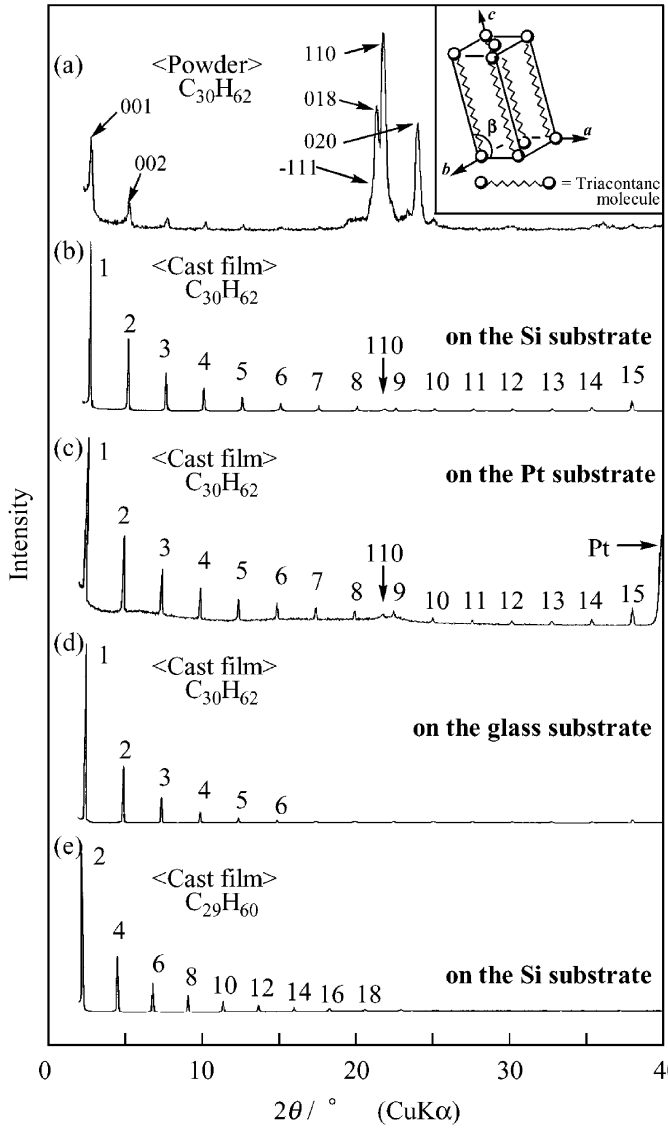


FIGURE 4 XRD patterns of (a) a powder of triacontane, (b) cast film of triacontane on a Si plate, (c) cast film of triacontane on a Pt plate, and (d) cast film of triacontane on a glass plate. The −111 diffraction peak of triacontane [14] appears as a shoulder peak in the curve (a). The numbers 1 through 15 in curves (b), (c), and (d) refer to the corresponding 00n peaks. Curve (e) exhibits the XRD pattern of cast film of nonacosane on a Pt plate. For curves (b)–(e), X-ray was irradiated from the out-of-plane direction, and the XRD pattern was measured with a symmetrical-reflection technique. Thickness of the films of n-alkanes = 0.10 μm.

REFERENCES

[1] Yamamoto, T., Kanbara, T., & Mori, C. (1990). *Synth. Met.*, *38*, 399–402.

[2] Yamamoto, T., Morita, A., Miyazaki, Y., Maruyama, T., Wakayama, H., Zhou, Z.-H., Nakamura, Y., Sasaki, S., & Kubota, K. (1992). *Macromolecules*, *25*, 1214–1223.

[3] (a) Yamamoto, T., Maruyama, T., Zhou, Z.-H., Ito, T., Fukuda, T., Yoneda, Y., Begum, F., Ikeda, T., Sasaki, S., Takezoe, H., Fukuda, A., & Kubota, K. (1994). *J. Am. Chem. Soc.*, *116*, 4832–4845.
(b) Fukuda, T., Yamamoto, T., Kurihara, T., & Ooba, N. (1993). *Synth. Met.*, *60*, 259–264.

[4] Cai, C., Bösch, M. M., Tao, Y., Müller, B., Gan, Z., Kündig, A., Bosshard, C., Liakatas, I., Jäger, M., & Günter, P. (1998). *J. Am. Chem. Soc.*, *120*, 8563–8564.

[5] Chen, T., Wu, X., & Rieke, R. D. *J. Am. Chem. Soc.*, *117*, 233–244.

[6] McCullough, R. D., Tristam-Nagle, S., Williams, S. P., Lowe, R. D., & Jayaraman, M. (1993). *J. Am. Chem. Soc.*, *115*, 4910–4911.

[7] Yamamoto, T., Komarudin, D., Arai, M., Lee, B.-L., Suganuma, H., Asakawa, N., Inoue, Y., Kubota, K., Sasaki, S., Fukuda, T., & Matsuda, H. (1998). *J. Am. Chem. Soc.*, *120*, 2047–2058.

[8] Jérome, D., & Bechgaard, K. (2001). *Nature*, *410*, 162–163.

[9] Schön, J. H., Dodabalapur, A., Bao, Z., Kloc, Ch., Schenker, O., & Batlogg, B. (2001). *Nature*, *410*, 189–192.

[10] Sirringhaus, H., Brown, P. J., Friend, R. H., Nielsen, M. M., Bechgaard, K., Langeveld-Boss, B. M. W., Spiering, J. H., Janssen, R. A. J., Meijer, E. W., Herwig, P., & de Leeuw, D. M. (1999). *Nature*, *401*, 685–688.

[11] Yamamoto, T., Kokubo, H., & Morikita, T. (2001). *J. Polym. Sci.: Part B: Polym. Phys., 39,* 1713–1718.

[12] Tashiro, K., Ono, K., Minagawa, Y., Kobayashi, M., Kawai, T., & Yoshino, K. (1991). *J. Polym. Sci.: Part B: Polym. Phys.*, *29*, 1223–1233.

[13] Yamamoto, T., & Kokubo, H. (1999). *Chem. Lett.*, 1295–1296.

[14] Heyding, R. D., Russell, K. E., & Varty, T. L. (1990). *Powder Diffr., 5*, 93–100. The *d* values for 001 peaks of triacontane and tetracosane are 35.6 Å and 30.6 Å, respectively, which, in an experimental error, agree with the data observed in the present experiments.