Thin-film structure of semiconducting end-capped oligothiophenes

N. Yoshimoto\textsuperscript{1}, W. Y. Li\textsuperscript{2}, K. Omote\textsuperscript{3}, J. Ackermann\textsuperscript{4}, C. Videlot-Ackermann\textsuperscript{4}, H. Brisset\textsuperscript{4} and F. Fages\textsuperscript{4}

\textsuperscript{1} Graduate School of Engineering, Iwate University, Ueda Morioka 020-8551, Japan
\textsuperscript{2} JST Innovation Satellite Iwate, Iiokashinden Morioka 020-0852, Japan
\textsuperscript{3} Rigaku Corporation, 3-9-12 Matsubara-cho Akishima, Tokyo 196-8666, Japan
\textsuperscript{4} Laboratoire des Matéraux Moléculaires et des Biomatiériaux, GCOM2 UMR CNRS 6114 Faculté des Sciences de Luminy, Case 901, F-13288, Marseille cedex 09, France

yoshimoto@iwate-u.ac.jp

Abstract. Distyryl-oligothiophenes (DS-nT) is one of the promising semiconducting materials that use for organic thin-film transistors (OTFTs). The in-plane structures of vapor deposited ultrathin films of DS-4T, and its derivatives with different end-cap groups, on SiO\textsubscript{2} substrate were characterized by grazing incidence x-ray diffractometry (GIXD). The morphology and film structure change with the nature of end-cap groups. The increase in volume of end-cap group causes the decrease in crystallinity and increase in frequency in nucleation. These characteristics could affect to the transport properties in OTFTs.

1. Introduction
In recent years, organic thin-film transistors (OTFTs) have attracted great attention, and their performance has continually improved [1,2]. OTFTs have many advantages in terms of a low-cost, low-temperature process, compatibility with flexible substrates, and a large variety of composite materials. In comparison to transistors made from conventional inorganic semiconductors such as amorphous silicon, the stability and uniformity of OTFTs require however improvements. Control of crystal growth of the semiconducting molecules is an effective method to increase device performance, because the physical properties of organic semiconductors show significant anisotropy. Furthermore, a technique for control of crystallinity of the films is required to decrease carrier scattering at grain boundaries. Therefore, investigation and control of crystallinity in thin-film state are demanded to improve device performance of OTFTs.

Distyryl-quaterthiophene (DS-4T), one of the organic semiconductors, has been used in OTFTs as a promising material. Recently, Videlot-Ackerman \textit{et al.} [3, 4] have reported that the OTFTs based on DS-4T show the remarkable stability in air. The high field-effect mobility (up to 0.1 cm/Vs) was unchanged for more than 300 days. However, the details of the film structure as well as crystal structure from single crystal have not been reported. Because the charge carriers move on the interface
between organic semiconductor layer and the dielectric surface in the OTFTs, the structure of initial stage of crystal growth of DS-nT could be important to understand its remarkable transport properties.

In this study, in-plane structures of ultrathin films based of DS-4T and its derivatives (Fig. 1), on SiO₂ substrates were investigated by grazing incidence x-ray diffractometry (GIXD). The effects of film thickness and end-cap group on the in-plane structure were examined.

2. Experimental
DS-4T and end-capped derivatives, DFS-4T and Py-4T were synthesized and sublimated from k-cell-type crucible onto SiO₂ substrates. The details of the synthesis method are described elsewhere [3, 5, 6]. The substrate temperature and deposition rate were 20 °C and 0.01 nm / s, respectively. Film thicknesses and the base pressure were 0.2 to 100 nm and 1 ×10⁻⁴ Pa, respectively. Film thicknesses were monitored by a quartz crystal microbalance during the deposition process, and calibrated by cross-sectional height profiles, area and coverage of islands observed by using atomic force microscopy (AFM) after deposition. Characterization of the films was done by using x-ray diffractometers (Rigaku Co., ATX-G and synchrotron radiation at the BL13XU ATX-GSOR in SPring-8), which were specially designed for characterization of thin films. Both in-plane and out-of-plane diffractions could be measured, because the goniometer has not only conventional θ/2θ axes but also in-plane φ/2θ axes. The used wavelengths of x-ray in the experiments were 0.1542 nm for lab-source and 0.1000 nm in SPring-8.

![Molecular structures of end-capped oligothiophenes DS-4T, DFS-4T and Py-4T.](image)

3. Results and discussion
Figure 2 shows AFM images of deposited films DS-4T, DFS-4T and Py-4T. The size and the number density of islands changed with the kind of end-cap group. The number density of islands increases with increasing volume of end-cap group. This is due to the frequency of nucleation on the substrate depends on surface energy of clusters which is decreased with the packing density of molecules in the crystals. The decrease in the number density of nuclei causes the increase in grain size in thicker films.

Figure 3 shows the x-ray diffraction patterns in conventional θ/2θ mode of DS-4T, DFS-4T and Py-4T deposited on SiO₂ substrates. The thickness of the films was 100 nm. The peaks observed in Fig. 3 were tentatively indexed as (001) and higher orders. This means that the ab- planes of the grains orient parallel to the substrate surfaces. The obtained d₀₀₁ spacings of DS-4T, DFS-4T and Py-4T were respectively 2.802, 3.220 and 3.110 nm, which are comparable to the molecular length.
FIGURE 2. AFM images of ultra thin films DS-4T, DFS-4T and Py-4T. The average thickness was 1 nm and the islands were composed by monolayers.

FIGURE 3. X-ray diffraction patterns in conventional $\theta/2\theta$ mode of DS-4T, DFS-4T and Py-4T films.

Figure 4 shows the thickness dependence of in-plane GIXD patterns of thin films of DS-4T, DFS-4T and Py-4T. By comparison with reported crystal structure of oligothiophene and pentacene, the peaks observed in Fig. 4 can be indexed as shown in the figures [7, 8]. Depending on thickness, slight peak shifts are observed in 020 of DS-4T and 110 of DFS-4T. The peak shift of 020 of DS-4T is due to occurrence of another polymorph with increasing thickness. Such thickness-dependent polymorphic behavior is similar to that observed in pentacene and DS-2T [8,9]. As to the slight peak shift observed in 110 of DFS-4T, it could be due to changes in the molecular packing between ultra-thin films and thicker one.

From the XRD data of DS-4T, the area of $ab$-plane and the unit cell volume are obtained as 0.438 nm$^2$ and 1.223 nm$^3$, respectively. As for DFS-4T, the area of $ab$-plane and the unit cell volume are 0.458 nm$^2$ and 1.476 nm$^3$, respectively. FWHM of in-plane GIXD peaks of Py-4T (Fig. 4 c) are larger than that of DS-4T and DFS-4T. From these facts it is clarified that the volume of end-cap group
causes decrease in crystallinity in this series of compound. This could be due to decrease in molecular interaction by the steric hindrance. Because smaller molecular interaction makes smaller surface energy of nuclei during crystal growth process, the difference in number density of the island shown in Fig.2 can be attributed to the difference in the molecular packing.

This difference could be related to the transport properties in OTFTs. Since π-orbital in the molecules extend to ab-axis direction, the difference in the area of ab-plane should be essential to the transport properties between derivatives. The area of ab-plane of DS-4T has smaller value than that of DFS-4T. Therefore, introducing end-cap groups with increasing volume into oligothiophene molecules seems to bring the decrease in grain size and in conductivities in each grain.

FIGURE 4. Thickness dependence of in-plane GIXD patterns of deposited DS-4T, DFS-4T and Py-4T films on SiO₂.

In summary, this study introduces in-plane structure of vapor deposited thin films of DS-4T and its derivatives on SiO₂ substrate. The in-plane GIXD pattern was obtained from ultrathin-films of 0.2 nm thick to of 100 nm thick. The position of peaks does not depend on film thickness except for 020 of DS-4T and 110 of DFS-4T. By comparing the lattice constants between the derivatives, difference in morphology could be explained. Namely, the increase in volume of end-cap group causes the decrease in crystallinity and increase in frequency in nucleation. This could be attributed to the contribution of surface energies during nucleation process.

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