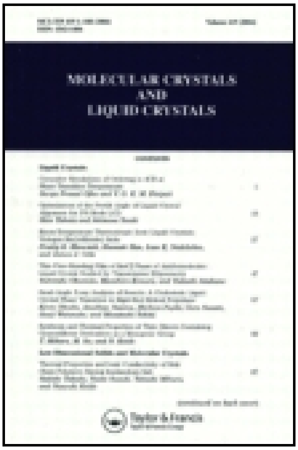

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Solution Growth and Structures of Semiconducting Distyryl-Oligothiophene

M. Ito [a], W. Y. Li [b], N. Yoshimoto [a], H. Muraoka [a], S. Ogawa [a], H. Fujishiro [a], Y. Asabe [c], J. Ackermann [d], C. Videlot - Ackermann [d], H. Brisset [d] & F. Fages [d]

[a] Graduate School of Engineering, Iwate University, Ueda Morioka, Japan

[b] JST Innovation Satellite Iwate, Iiokashinden Morioka, Japan

[c] Alps Co., Onahama Iwaki, Japan

[d] Laboratoire des Matériaux Moléculaires et des Biomatériaux, GCOM2 UMR CNRS 6114 Faculté des Sciences de Luminy, Marseille cedex, France

Version of record first published: 22 Sep 2010

To cite this article: M. Ito, W. Y. Li, N. Yoshimoto, H. Muraoka, S. Ogawa, H. Fujishiro, Y. Asabe, J. Ackermann, C. Videlot - Ackermann, H. Brisset & F. Fages (2008): Solution Growth and Structures of Semiconducting Distyryl-Oligothiophene, Molecular Crystals and Liquid Crystals, 491:1, 264-269

To link to this article: http://dx.doi.org/10.1080/15421400802330895

Mol. Cryst. Liq. Cryst., Vol. 491, pp. 264–269, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802330895

Solution Growth and Structures of Semiconducting Distyryl-Oligothiophene

M. Ito[1], W. Y. Li[2], N. Yoshimoto[1], H. Muraoka[1], S. Ogawa[1], H. Fujishiro[1], Y. Asabe[3], J. Ackermann[4], C. Videlot – Ackermann[4], H. Brisset[4], and F. Fages[4]
[1]Graduate School of Engineering, Iwate University, Ueda Morioka, Japan
[2]JST Innovation Satellite Iwate, Iiokashinden Morioka, Japan
[3]Alps Co., Onahama Iwaki, Japan
[4]Laboratoire des Matériaux Moléculaires et des Biomatériaux, GCOM2 UMR CNRS 6114 Faculté des Sciences de Luminy, Marseille cedex, France

Large single crystals of 5,5′-distyryl-2,2′-bithiophene (DS-2T) were grown from tetrahydrofurane (THF) solution, and the crystal structure was analyzed by x-ray diffractometry. In-situ observation of crystal growth in solution was performed, and a unique change in the crystal habit depending on growth conditions is found. The change in crystal habit from a truncated parallelogram shape to a slender hexagonal shape with re-entrant angles at the both side can be explained as the consequence of kinetic roughing and Berg effect.

Keywords: organic semiconductor; solution growth; structural analysis

1. INTRODUCTION

Recently, organic thin-film transistors (OTFTs) have attracted great attention, because of their advantages in terms of a low-cost, low-temperature process, compatibility with flexible substrates, and a large variety of composite materials. In order to realize these advantages in practical OTFTs, the fabrication system should be based on solution process. Therefore, studies on crystal growth of organic

This work was financially supported in part by Japan Science and Technology Agency.

Address correspondence to N. Yoshimoto, Graduate School of Frontier Materials and Functional Engineering, Iwate University, Ueda Morioka 020-8551, Japan. E-mail: yoshimoto@iwate-u.ac.jp

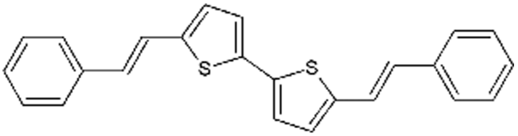

FIGURE 1 Molecular structure of DS-2T.

semiconductors from solution phase are demanded to improve the technique in fabrication of OTFTs.

5,5′-distyryl-2,2′-bithiophene (DS-2T), one of the semiconducting distyryl-oligothiophenes, is known as a promising material for use in OTFTs because of its marvelous stability in air [1]. Figure 1 shows the molecular structure of DS-2T. Recently, Videlot-Ackerman *et al.* [1,2] have reported that the OTFTs based on distyryl-oligothiophenes show the remarkable stability against air-oxidation. The high field-effect mobility (up to 0.1 cm/Vs) was unchanged for more than 100 days. Although the thin-film structures for the two polymorphs have been investigated [3], the crystal structures of the single crystals have not been reported.

In this study, large single crystals of DS-2T were successfully grown from tetrahydrofurane (THF) solution, and the crystal structure was analyzed by x-ray diffractometry. Furthermore, in-situ observation of crystal growth in solution was performed.

2. EXPERIMENTAL

DS-2T was synthesized according to a procedure described elsewhere [2]. Large single crystals were grown from TFT solution by cooling the saturated solution from 40°C to 20°C in 10 days. Using the obtained single crystals, crystal structure was analyzed by using x-ray diffractometer (Rigaku RAXIS RAPID) with imaging plate area detector and graphite monochromated Mo-Kα radiation.

In-situ observation of crystal growth of DS-2T was preformed under a polarizing microscope (Olympus CKX31). The DS-2T/THF solution was sealed in a grass-made crystal growth cell whose temperature was controlled by thermostated water surrounding the cell. A seed crystal was put in the solution, and the behaviors of growth and dissolution depending on temperature were observed.

3. RESULTS AND DISCUSSION

Figure 2 shows the morphology of DS-2T single crystal grown from THF solution. Most of the grown single crystals show a unique

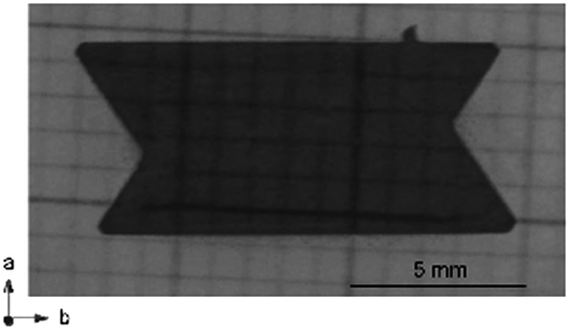

FIGURE 2 Morphology of a grown single crystal of DS-2Tfrom THF solution. The size is $12 \times 5 \times 1\,\mathrm{mm}^3$.

hexagonal shape with re-entrant angles at the both side. Generally, the crystals having re-entrant angle in the crystal habit are twin-crystals. However, in the case of DS-2T, x-ray diffraction experiments demonstrate that it is not a twin-crystal. Therefore, the unique crystal habit is not the equilibrium-form but a growth-form which is consequence of some kinetic factors during crystal growth.

Figure 3 and Table 1 show the crystal structure and unit cell parameters of DS-2T, respectively. This structure was solved by analyzing x-ray diffraction data using direct method [4]. The crystal structure of DS-2T exhibits close cofacial packing in either of molecular fragments, arene- and thiophene-groups, in the *ab*-plane, and the lamellas stack along with c-axis direction. The molecular structure is almost flat, and no torsion can be observed between the molecular fragments. By comparison the structure of the thiophene subunit with that of octithiophene [5], the difference in packing density can be discussed. Figure 4 shows the sub-cell structures of thiophene subunit of DS-2T and octithiophene (8T). As the area S of *ab*-plane of DS-2T is slightly smaller than that of octithiophene, it can be estimated that the packing density of thiophene subunit of DS-2T is larger than octithiophene. Projections from *a*-axis direction reveal the difference in the in-plane structures. In the case of octithiophene, molecules incline to only *a*-axis direction. In contrast, two inclination directions alternately occur with mirror symmetry to *b*-axis direction as well as *a*-axis direction in DS-2T crystal as shown in Figure 4.

Figure 5 shows time-lapse photographs of DS-2T single crystals during solution growth. With decreasing temperature of solution, crystal grew with time. At first, the seed crystal becomes a truncated parallelogram shape surrounding by (100) (110) and (001) faces under

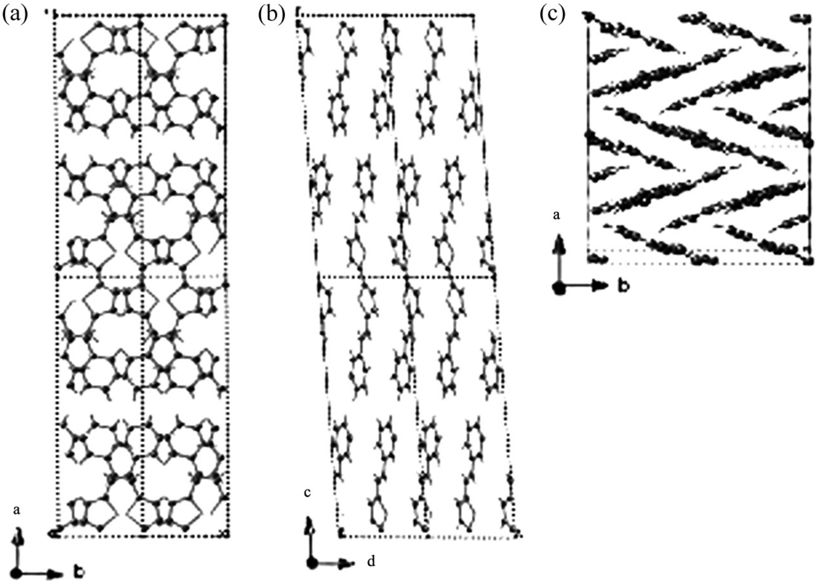

FIGURE 3 Crystal structure of DS-2T. (a) *a*-axis projection, (b) *b*-axis projection, and (c) *c*-axis projection.

low supersaturation conditions as shown in Figures 5(a) and (b). This crystal habit should be near to the equilibrium form. With decreasing temperature from Figures 5(b) to (d), changes in the crystal habit occur with roughing of (110) faces, and re-entrant angles appear on the (110) faces as shown in Figure 5(e). Finally, (110) faces become smooth and unique crystal habit showing a slender hexagonal shape with re-entrant angles completes (Fig. 5 (f)). The cause of occurrence of the unique crystal habit is understood to be due to the Berg effect, that is, the growing speed of the edge of (110) faces is much faster than that at the center owing to the concentration gradient in the solution. Figure 6 shows a schematic illustration of the change in the crystal

TABLE 1 Unit Cell Parameters of DS-2T Crystal

a (nm)	0.7739(8)
b (nm)	0.5602(6)
c (nm)	2.0945(18)
β (°)	94.39(8)
V (nm^3)	0.9054(15)
Space group	$P2_1/a$ (monoclinic)
Z	2

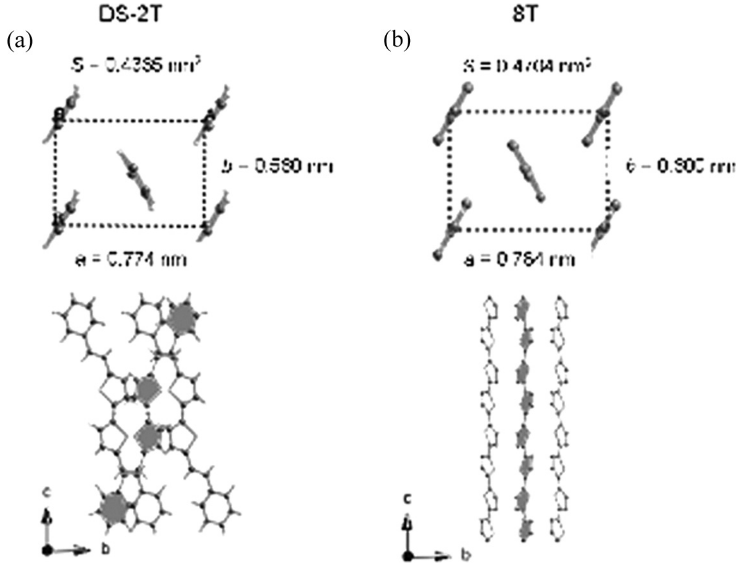

FIGURE 4 Subcell structure of thiophene subunit of (a) DS-2T and (b) octithiophene (8T).

habit of DS-2T, and the relationship between the crystal axes and crystal habit is also shown in this figure. At the beginning of crystal growth, the crystal habit close to the equilibrium form that should be surrounding by two (100) and four (110) faces, because these are the specular surfaces having higher surface densities. The equilibrium

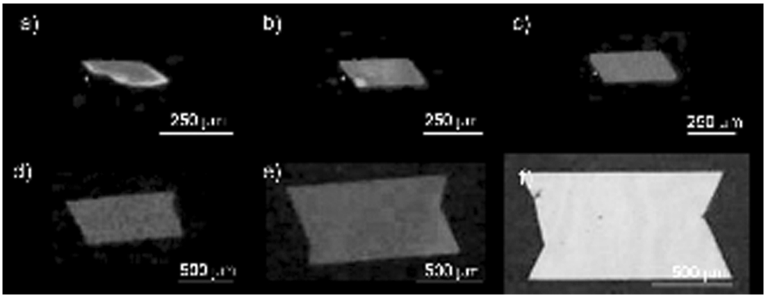

FIGURE 5 In-situ observation of crystal growth of DS-2T in THF solution. The temperature of the solution decreased with time; (a) 40.8°C, 0 min., (b) 34.7°C, 14 min., (c) 31.9°C, 21 min., (d) 29.4°C, 30 min., (e) 23.4°C, 46 min. and (f) 21.6°C, 51 min.

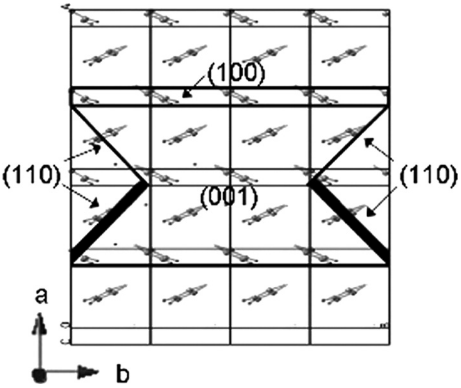

FIGURE 6 Schematic illustration of crystal habits of equilibrium form and growth form.

form must not have any re-entrant angles on the surface because of requirement of minimization in surface energy. With the progress of crystal growth, kinetic roughing occurs on (110) faces, and the source of steps concentrate at the edge of (110) face owing to the Berg effect. Finally, a unique growth form with re-entrant angles appears at high supersaturation.

In summary, large-size single crystals of DS-2T were successfully grown from THF solution, and the crystal structure was solved by x-ray diffractometry. A change in the crystal habit of the single crystal depending on growth conditions was found. The change in crystal habit could be explained as the consequence of kinetic roughing and Berg effect.

REFERENCES

[1] Videlot-Ackermann, C., Ackermann, J., Kawamura, K., Yoshimoto, N., Brisset, H., Raynal, P., El Kassmi, A., & Fages, F. (2006). *Organic Electronics*, *7*, 465.

[2] Videlot-Ackermann, C., Ackermann, J., Brisset, H., Kawamura, K., Yoshimoto, N., Raynal, P., El Kassmi, A., & Fages, F. (2005). *J. Am. Chem. Soc.*, *127*, 16346.

[3] Yoshimoto, N., Aosawa, K., Tanisawa, T., Omote, K., Ackermann, J., Videlot – Ackermann, C., Brisset, H., & Fages, F. (2007). *Cryst. Res. Tech.*, *42*, 1228.

[4] Altomare, A., Burla, M., Camalli, M., Giacovazzo, G., Guagliardi, A., Moliterni, A., Polidori, G., & Spagna, R. (1999). *J. Appl. Cryst.*, *32*, 115.

[5] Fichou, D., Bachet, B., Demanze, F., Billy, I., Horowitz G., & Garnier, F. (1996). *Adv. Mater.*, *8*, 500.