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Author(s)	茂村, 雄也
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Crystal Structure Analysis of Thiophene Copolymers of Electron Donor-Acceptor Type

Yuya Shigemura
*School of Materials Science,
Japan Advanced Institute of Science and Technology*
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Introduction

The molecular chain of polythiophene (PTh) takes all-*trans* planar conformation, and they are packed in the *pgg* manner (Figure 1). The setting angle (ϕ) between the molecular side and the *ac* plane is about 60° , namely, the packing is not of face-to-face stacking type. Positional disorders exist along the chain axis.

In this study, the crystal structure of copolymers that consist of electron-donating thiophene and the electron-accepting arylene group with nitro groups, P(*p*-NPh-*co*-Th), P(2NPh-*co*-Th), P(DNTh-*co*-Th), and P(DNTh-*co*-BiTh) (schema 1), were analyzed by X-ray diffraction technique.

Experimental

The samples were offered from Prof. Yamamoto (Chemical Resource Laboratory, Tokyo Institute of Technology). X-ray measurements were carried out with CuK α radiation. The diffraction curves were obtained by a powder diffractometer equipped with a scintillation counter in the range of $2\theta = 2\text{--}50^\circ$. Analysis was performed with linked-atom Rietveld method with standard bond lengths and bond angles.

Results and Discussion

As for the XRD curve of P(*p*-NPh-*co*-Th), the peaks were observed at $2\theta = 12^\circ$ ($d_1 = 7.4 \text{ \AA}$) and 24° ($d_2 = 3.7 \text{ \AA}$). Positional disorder along the chain axis was suggested by this feature. The structure to reproduce such an XRD curve was only the *pgg* type structure (Figure 2). The setting angle is probably near to $\phi = 15^\circ$. The distinction between $\phi = 0$ - 15° was difficult.

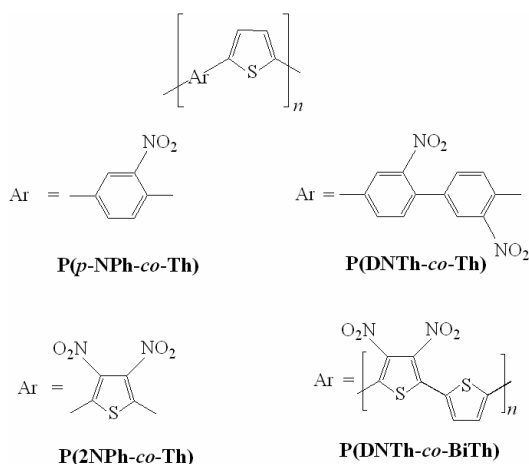
As for the XRD curve of P(DNPh-*co*-Th), the peaks were observed at $2\theta = 11.6^\circ$ ($d_1 = 7.6 \text{ \AA}$) and 24.7° ($d_2 = 3.6 \text{ \AA}$). The sharp peak observed at $2\theta = 18^\circ$ was attributed to the remaining catalyst particles. The structure is similarly disturbed. The simulation suggested the *pgg* type structure (Figure 3). The setting angle was in the range of $\phi = 0$ - 15° .

As for the XRD curve of P(DNPh-*co*-BiTh), the peaks were observed at $2\theta = 11.3^\circ$ ($d_1 = 7.8 \text{ \AA}$) and 24.7° ($d_2 = 3.6 \text{ \AA}$). The structure is disturbed too. The simulation suggested the *pgg* type structure (Figure 4). The setting angle was in the range of $\phi = 0$ - 10° .

Because P(2NPh-*co*-Th) was amorphous, it was not able to evaluate the structure.

Conclusion

P(*p*-NPh-*co*-Th), P(DNPh-*co*-Th), and P(DNPh-*co*-BiTh) took disordered structure of the *pgg* type. The setting angles were much smaller than that in PTh. Basically the packing is close to the *cm* type. Electron donor-acceptor interactions may play an important role.



Scheme 1. Structural formulae of samples.

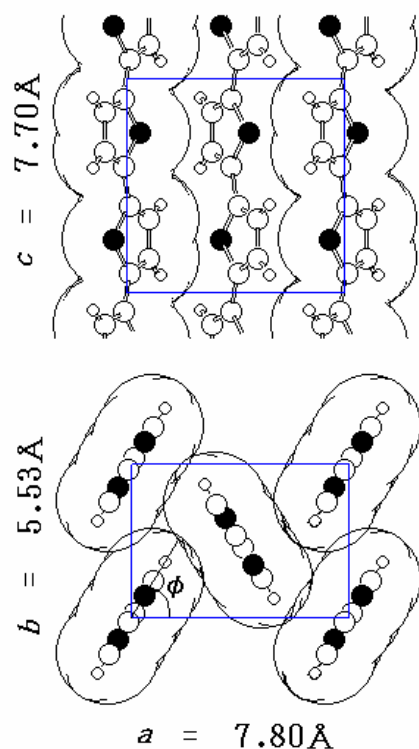


Figure 1. The pgg crystal structure of PTh.

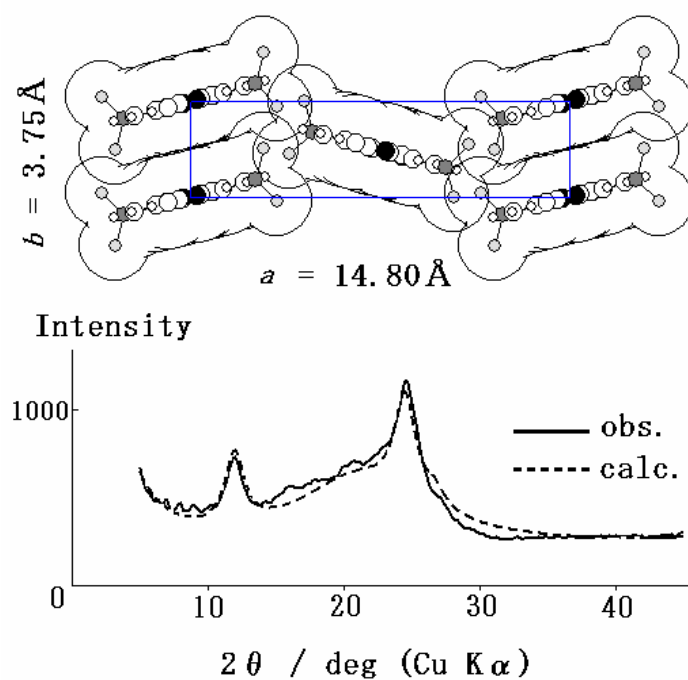


Figure 2. A pgg packing model of $P(p\text{-NPh-co-Th})$ ($\phi = 15^\circ$), and the XRD profiles.

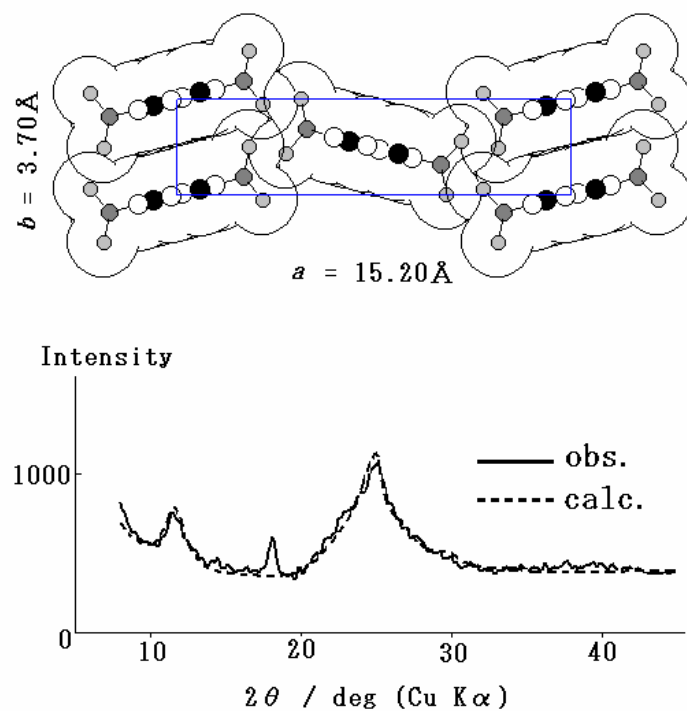


Figure 3. A *pgg* packing model of P(DNPh-*co*-Th) ($\phi = 15^\circ$), and the XRD profiles.

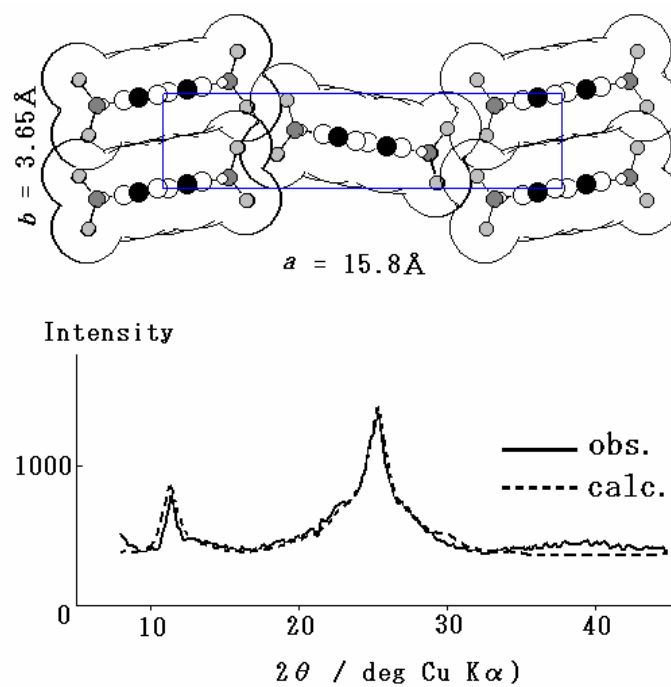


Figure 4. A *pgg* packing model of P(DNTh-*co*-BiTh) ($\phi = 10^\circ$), and the XRD profiles.