Crystal Structure Analysis of Thiophene Copolymers of Electron Donor-Acceptor Type

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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 CuKα radiation. The diffraction curves were obtained by a powder diffractometer equipped with a scintillation counter in the range of 2θ = 2-50°. 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 2θ = 12° (d_1 = 7.4 Å) and 24° (d_2 = 3.7 Å). 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 (Figure2). The setting angle is probably near to ϕ = 15°. The distinction between ϕ = 0-15° was difficult.

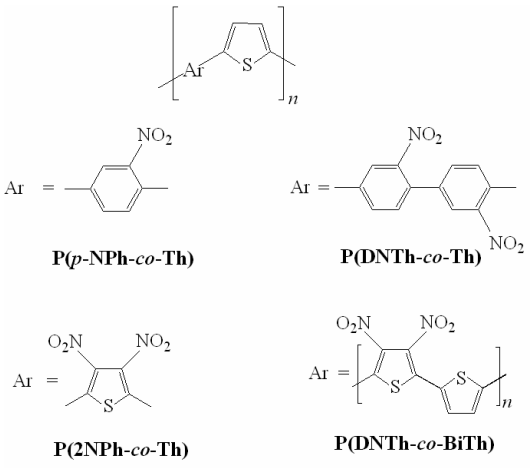
As for the XRD curve of P(DNPh-*co*-Th), the peaks were observed at 2θ = 11.6° (d_1 = 7.6Å) and 24.7° (d_2 = 3.6Å). The sharp peak observed at 2θ = 18° was attributed to the remaining catalyst particles. The structure is similarly disturbed. The simulation suggested the *pgg* type structure (Figure 3).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

As for the XRD curve of P(DNPh-*co*-BiTh), the peaks were observed at 2θ = 11.3° (d_1 = 7.8Å) and 24.7° (d_2 = 3.6Å). The structure is disturbed too. The simulation suggested the *pgg* type structure (Figure 4). The setting angle was in the range of ϕ = 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 *cmm* type. Electron donor-acceptor interactions may play an important role.



Schema 1. Structural formulae of samples.

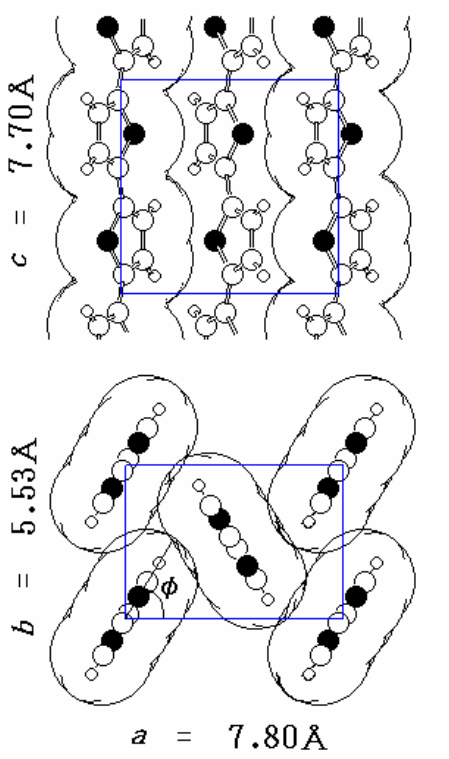


Figure 1. The *pgg* crystal structure of PTh.

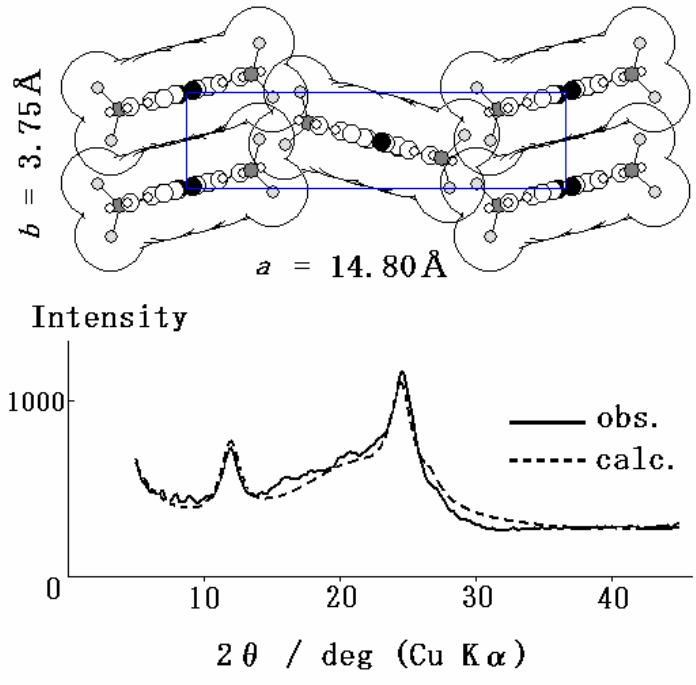


Figure 2. A *pgg* packing model of P(*p*-NPh-*co*-Th) ($\phi = 15°$), and the XRD profiles.

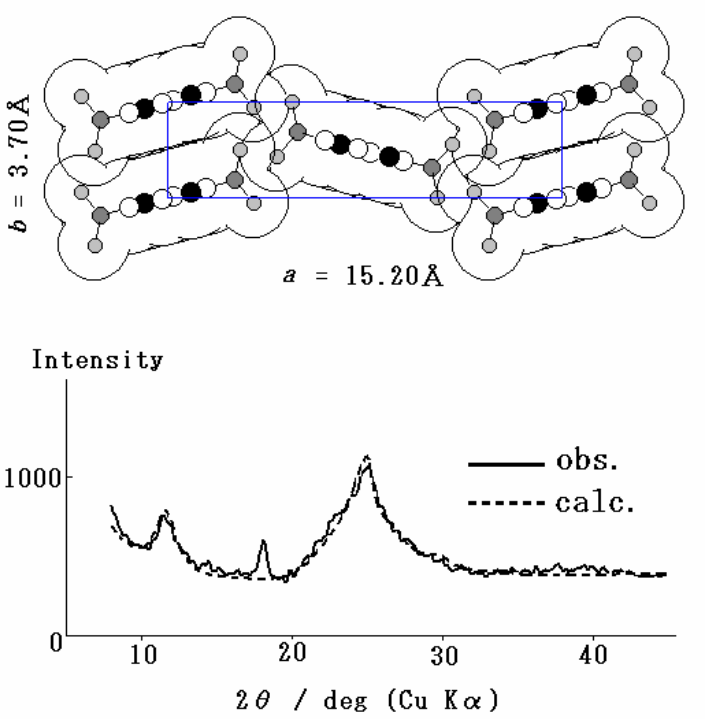


Figure 3. A *pgg* packing model of P(DNPh-*co*-Th) ($\phi = 15°$), and the XRD profiles.

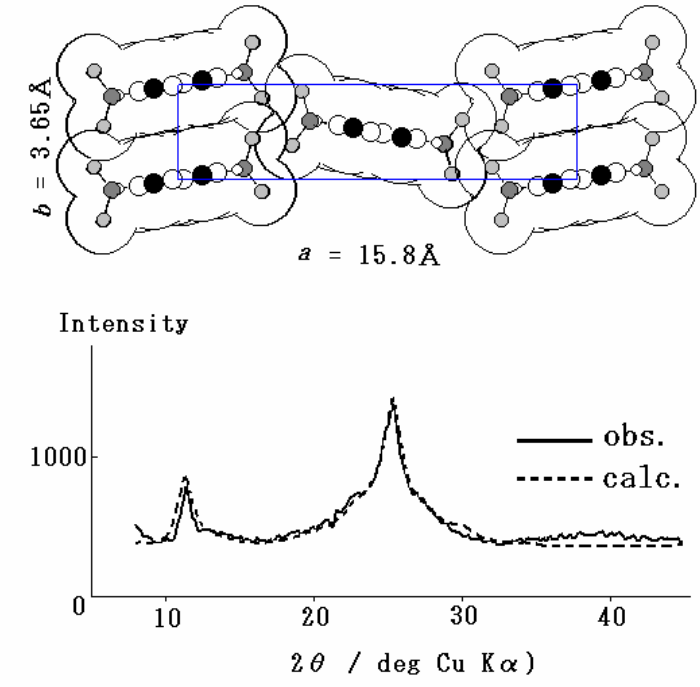


Figure 4. A *pgg* packing model of P(DNTh-*co*-BiTh) ($\phi = 10°$), and the XRD profiles.