茨城県 IBARAKI Prefectural Government **MLF Experimental Report**	提出日(Date of Report) March 25, 2019
課題番号(Project No.) 2017PX0016 実験課題名(Title of experiment) **Clarification of Structure-Property Relationship in the Crystalline Phase Transitions of Polymers on the Basis of Wide-Angle Neutron Diffraction Measurement as a Trial to Build-up a New Utilization System of i-BIX** 実験責任者名(Name of principal investigator) Kohji Tashiro 所属(Affiliation) Toyota Technological Institute	装置責任者(Name of responsible person) Katsuhiro Kusaka (Ibaraki University) 装置名(Name of Instrument : BL No.) i-BIX 実施日(Date of Experiment) 2018.3.18 – 2018.3.20

実験目的、試料、実験方法、利用の結果得られた主なデータ、考察、及び結論を記述して下さい。
実験結果などの内容をわかりやすくするため、適宜図表添付して下さい。
Please report experimental aim, samples, experimental method, results, discussion and conclusions. Please add figures and tables for better explanation.

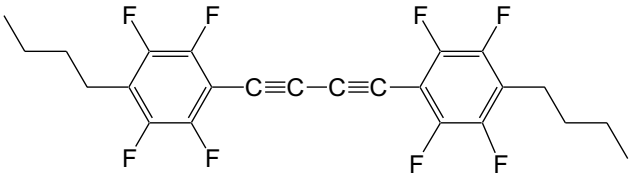
1. 実験目的(Objectives of experiment)

In order to extend the application area of the i-BIX system, which was originally developed for the crystal structure analysis of protein single crystals on the basis of the wide-angle neutron diffraction (WAND) data collected by a time-of-flight method, we have been challenging to modify this system from the various points of view. So far we introduced such experimental tools as the heating cell and the stretching device for the polymer materials. In parallel, we have measured the various kinds of polymers to confirm the usefulness of the i-BIX system for the crystal structure analysis of these substances. In the present report, the experimental results of the several polymer substances are described briefly.

2. 実験、3. 結果と考察 Experimental procedure, Results and Discussion

(1) Evaluation of Aspherical Electron Density Distribution in Polydiacetylene

As already published in the journal *Macromolecules* of the American Chemical Society [1], we succeeded to evaluate the bonded electron density distribution of polydiacetylene (PDCHD) with the carbazoryl groups as the side chains for the first time for the synthetic polymers on the basis of the organized combination of the X-ray and neutron structure analysis information (X-N method). In this polymer case, however, the electron conjugation of the skeletal polymer chain is isolated from the electron conjugation of the bulk side groups due to the interruption by the methylene (CH_2) unit. This is one of the reasons why PDCHD cannot give the high electron conductivity but stay in the level



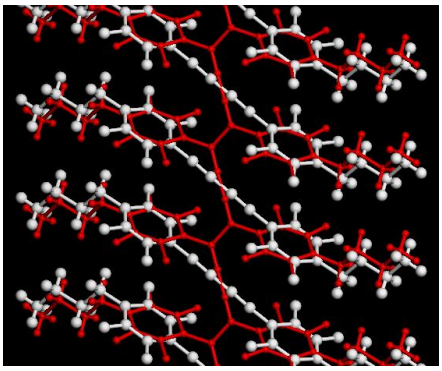


Figure 1. Crystal structures of FDAC monomer (white) and polyFDAC (red) analyzed using the X-ray diffraction data.

of semiconductor. In order to develop a polydiactylene with higher electron conductivity, we synthesized a polydiacetylene substance (FDAC) of the totally electronically-conjugated system over both of the skeletal and side chains with the chemical formula shown above.

The single crystal of FDAC monomer was grown from the solution and subjected to an irradiation of X-ray beam for 72 hours at room temperature to get the polyFDAC single crystal. The crystal structure of polyFDAC itself was already analyzed using the X-ray diffraction data, but we need to collect the neutron diffraction data additionally. The large single crystal was set on a goniometer head of i-BIX system and the TOF (time-of-flight) WAND data were collected by changing the orientation direction of the sample axis. The crystal structure has been deduced successfully as shown in Figure 1. However, because of the relatively low quality of the single crystal used in the experiment, the accuracy of the thus-analyzed structure was not very high compared with that of the X-ray results, making it difficult to perform the X-N calculation necessary for the extraction of the deformed electron density distribution. We are now trying to prepare the single crystal of higher quality, which is necessary for the structure analysis with higher accuracy.

(2) PVA-Iodine Complex

Starch is well known to form a complex with iodine ions. Similarly, poly(vinyl alcohol) (PVA) also forms the iodine complex, which is industrially used as an optical polarizer, indispensable for the computer display screen, sunglass etc. In order to improve the quality of the polarizer furthermore, the structure of PVA-iodine complex must be clarified in detail. In a series of papers [2-5], we have studied the crystal structure of PVA-iodine complex on the basis of the X-ray structure analysis mainly. Figure 2 shows the thus-analyzed crystal structure of the complex. PVA chains are combined with the iodine ions through the mechanism of charge transfer from iodine ions to OH groups. Unfortunately, however, the exact positions of PVA chain segments in the unit cell have not yet been established enough well for the theoretical prediction of the optical polarizability. This is because of the overwhelmingly large X-ray scattering power of iodine (I) ions compared with those of PVA chains and potassium (K) ions. The wide-angle neutron diffraction is more useful for the purpose to determine the positions of PVA because of the comparable scattering power between C, O and I atoms.

In the preliminary experiment of neutron diffraction experiment, we used the normal PVA sample -[-$CH_2CH(OH)]_n$-, resulting in the appearance of too strong incoherent background to get the highly-qualified diffraction peaks. We need necessarily to prepare the deuterated species for the PVA chain to avoid such an overwhelmingly large incoherent scattering from the light H atoms. We synthesized the deuterated PVA-d_3 -[-$CD_2CD(OH)]_n$- and prepared the corresponding iodine complex. The actual sample used for the neutron diffraction measurement was a uniaxially-oriented PVA-d_3, which was immersed for a long time in the KI-I_2 3M aqueous solution. The wide-angle neutron diffraction (WAND) TOF measurement was performed at J-PARC beamline 03 by using an i-BIX system.

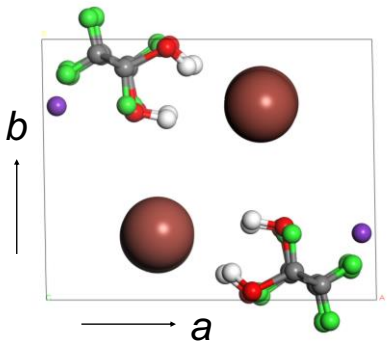


Figure 2. Crystal structure of PVA-iodine complex [2], which has been refined by analyzing both X-ray and neutron diffraction data.

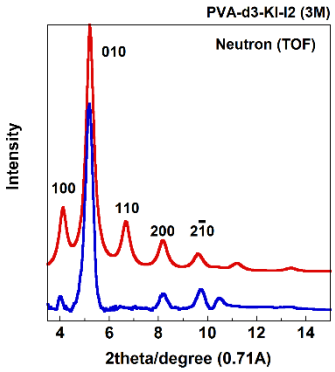


Figure 3. Comparison between the observed (blue) and calculated (red) neutron diffraction profile of PVA-iodine complex.

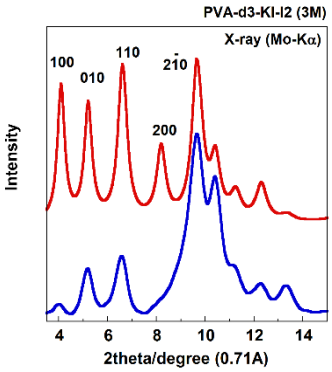


Figure 4. Comparison between the observed (blue) and calculated (red) X-ray diffraction profile of PVA-iodine complex.

In Figures 3 and 4 the thus-collected equatorial line profiles are compared with those calculated by modifying the crystal structure model shown in Figure 2. The X-ray diffraction was found to be quite sensitive to the position of iodine atomic positions, while the neutron diffraction was sensitive to only the PVA-d_3 chain positions. By using both of these data, the unique positions of I_3 ions (large balls in Figure 2) and PVA-d_3 chains in the unit cell were successfully determined. We are now refining the structure furthermore by the least-squares method.

4. 結論(Conclusion) 、参考文献(References)

(1) The crystal structure of the totally-conjugated polydiacetylene compound FDAC was analyzed by combining the X-ray and Neutron diffraction data to obtain the bonded electron density distribution, which spreads widely over both of the skeletal chain and the aromatic side groups. This information is quite important for the discussion of the physical property of this polymer from the electron level.
(2) The crystal structure of PVA-iodine complex was refined uniquely by analyzing both the X-ray and neutron diffraction data collected for the deuterated PVA-iodine complex sample. In the structural analysis, the mutually-different characteristic sensitivities of the various atomic species to the X-ray

and neutron diffraction data (the iodine atoms sensitive to the X-ray diffraction and the deuterated PVA molecules to the neutron diffraction) were utilized effectively, resulting in the successful determination of the atomic positions in the unit cell without ambiguity.

In this way, the organized combination of X-ray and neutron diffraction data is quite useful for the exact analysis of the crystal structure and the electron density information.

Acknowledgements

The authors wish to thank Professor Katsuhiro Kusaka of Ibaraki University for the performance of the cooperative research in the development of the experimental apparatuses as well as for their supports of the neutron diffraction measurements. They also thank Professor Takaaki Hosoya of Ibaraki University for the data analysis of polyFDAC.

References

(1) Kohji Tashiro, Katsuhiro Kusaka, Takaaki Hosoya, Takashi Ohhara, Makoto Hanesaka, Yoshinori Yoshizawa, Hiroko Yamamoto, Nobuo Niimura, Ichiro Tanaka, Kazuo Kurihara, Ryota Kuroki, and Taro Tamada, "Structure Analysis and Derivation of Deformed Electron Density Distribution of Polydiacetylene Giant Single Crystal by the Combination of X-ray and Neutron Diffraction Data", *Macromolecules*, **51**, 3911 (2018).

(2) Kohji Tashiro, Hideyuki Kitai, Siti Munirah Saharin, Akira Shimazu, Takahiko Itou, "Quantitative Crystal Structure Analysis of Poly(vinyl Alcohol)-Iodine Complexes on the Basis of 2D X-ray Diffraction, Raman Spectra, and Computer Simulation Techniques", *Macromolecules*, **48**, 2138 (2015).

(3) Siti Munirah Saharin, Tomohiko Takahama, Shota Nonogaki, Koki Saito, Kohji Tashiro, "Effect of OH Segmental Length on the Iodine Complex Formation of Ethylene-Vinyl Alcohol Random Copolymers", *Macromolecules*, **48**, 8867 (2015).

(4) Siti Munirah Saharin, Tomohiko Takahama, Shota Nonogaki, Koki Saito, Kohji Tashiro,
"The effect of counter cation species on the formation of various crystal forms and their phase transition behavior of poly(vinyl alcohol)-iodine complex", *Polymer*, **89**, 81 (2016).

(5) Takahama, Tomohiko, Saharin, Siti Munirah, Tashiro, Kohji, "Details of the intermolecular interactions in poly(vinyl alcohol)-iodine complexes as studied by quantum chemical calculations", *Polymer*, **99**, 566 (2016).