茨城県 IBARAKI Prefectural Government **MLF Experimental Report**	提出日(Date of Report) January 22, 2020
課題番号(Project No.) 2018PX0003 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) 2018PX0003 (2019.3.17 – 2019.3.21)

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)

(1) Our purpose is to increase the number of users of polymer companies for the i-BX experiments. For this purpose, we have been performing a series of experiments and data analyses for the clarification of the relationship between structure and physical properties of soft materials including synthetic polymers.
(2) In the fiscal years of 2018 A, 2018B and 2019A, we have been challenged to analyze the following several themes.
(i) Crystal structure analysis of *atactic* poly(vinyl alcohol) (PVA)
(ii) Crystal structure analysis of iodine complex of PVA
(iii) Quantitative evaluation of the bonded electron density distribution in polydiacetylene giant single crystal (FDAC) by combining the quantitative structure analyses of the synchrotron X-ray diffraction data and the i-BIX neutron diffraction data
(iv) The trace of the structural change and heterogeneous stress distribution in rubber materials subjected to a tensile force

2. 試料及び実験方法

Sample(s), chemical compositions and experimental procedure

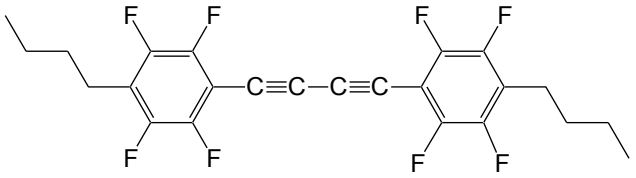
2.1 Samples

(i) Uniaxially-oriented fully-deuterated *atactic* poly(vinyl alcohol) $[\text{-}CD_2CD(OD)]_n\text{-}$
(ii) Iodine complex of PVA prepared by immersion of the sample (i) into $KI\text{-}I_2$ aqueous solution
(iii) Polydiacetylene giant single crystal of FDAC prepared by the solid-state photoinduced

polymerization of FDAC monomer single crystal

(iv) deuterated *cis*-1,4-polyisoprene prepared from deuterated isoprene monomers

FDAC



2.2 Experimental procedure

(i) The PVA sample was set onto a gononiometer head of i-BIX system, and the equatorial line profile was measured.

(ii) The sample of PVA-iodine complex was set onto a gononiometer head of i-BIX system, and the equatorial line profile was measured.

(iii) A FDAC single crystal was set on a goniometer head and the diffraction patterns were measured by changing the orientation angles of the crystal. The diffraction data of 56 sets were obtained in total with each exposure time of 2 hrs.

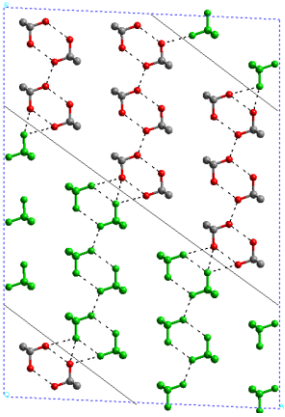
(iv) The stretcher equipment, which was developed in the i-BIX system, was used for stretching deuterated polyisoprene sample. Cooled nitrogen gas was blown to the sample for the low-temperature experiment (-50^{o}C) to make the diffraction pattern clearer.

3. 実験結果及び考察（実験がうまくいかなかった場合、その理由を記述してください。）

Experimental results and discussion. If you failed to conduct experiment as planned, please describe reasons.

(i) Crystal Structure Analysis of *atactic* Poly(vinyl Alcohol) Based on Synchrotron X-ray and Neutron Diffraction Data

The several crystal structure models had been proposed for PVA based on the X-ray structure analysis. But, a final establishment has not yet been made unfortunately. In the present study, it was found to be difficult to reproduce the observed neutron diffraction data reasonably using these structure candidates. A new model has been proposed here by introducing a new concept of structural disorder to satisfy both of the observed X-ray and neutron diffraction data consistently, as shown in Figure.



(ii) Crystal Structure Analysis of PVA-Iodine Complex Based on Synchrotron X-ray and Neutron Diffraction Data

Several years ago we proposed the crystal structure of PVA-iodine complex by analyzing the X-ray diffraction data analysis. However, the newly-measured neutron diffraction data could not be reproduced at all using this model. The reason comes from the difference in the scattering power of the individual atoms in the X-ray and neutron diffractions. The iodine ions play an overwhelmingly large role in the X-ray diffraction, while deuterated PVA chains give the remarkably large contribution to the neutron scattering compared with those of iodine and potassium atoms. By analyzing these two different data consistently, a new structure model has been derived by introducing the structural disorder similar to the above-mentioned PVA case.

(iii) Accurate Crystal Structure Analysis and Quantitative Evaluation of Bonded Electron Density Distribution of FDAC on the Basis of Synchrotron X-ray and Neutron Diffraction Data

The crystal structure analyses based on these two types of data have been almost completed. At present the quantitative estimation of the bonded electron density distribution is being made. In our previous paper, we published the bonded electron density distribution of polydiacetylene single crystal with carbazolyl groups as side chains (PDCHD) [*Macromolecules*, **51** , 3911–3922 (2018)] which was the first success for polymer substances. The result was introduced in the MLF annual report as well as in the periodical letter Shiki of Ibaraki prefecture.

(iv) Investigation of Structural Evolution in the Stretching Process of Rubber

The synthesized *cis*-polyisoprene films were set to the stretcher and the neutron diffraction patterns were tried to collect under tension. However, unfortunately, the clear crystalline diffraction patterns could not be obtained. The reason might come from the too thin thickness of the sample as well as the low population of the cross linkages in the polyisoprene sample, which might cause the serious slippage of the chains. Since this type of neutron experiment is challenged by our group only, we want to try this experiment again.

4. 結論 (Cunclusions)

(i) (ii) Crystal structures of *atactic* poly(vinyl alcohol) and its iodine complex have been successfully derived as the most reliable structures since the start of PVA history about 1 century ago. This polymer and its iodine complex are industrially important, and the newly-revealed structures should contribute remarkably to the advance of PVA science and industry.

(iii) The bonded electron density distribution of FDAC is the second success of this theme. Different from the previously-published PDCHD case, the skeletal chain and side groups are electronically totally conjugated in FDAC. The result may be quite useful for the quantitative check of the reasonableness of the quantum chemical calculation results.

(iv) As for the study of rubber under tension, we need to challenge the experiment again by synthesizing larger amount of deuterated polyisoprene with enough high degree of cross linkages to avoid the chain slippage.