茨城県 IBARAKI Prefectural Government **MLF Experimental Report**	提出日(Date of Report) November 5, 2021
課題番号(Project No.) 2019PX2001 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)i (2020.3.7 – 2020.3.10)

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)

(i) Crystal structure analysis of *isotactic* polypropylene-d5 (*it*-PP-d5)

it-PP is one of the most representative multi-purpose polymers and it is becoming more important for the automobile and aircraft industry etc. The structure-property relation of this polymer has been studied for these 70 years, but, unfortunately, the crystal structure itself as the most basically important knowledge has not yet been established enough well. In order to overcome this serious problem, we have challenged to collect more precise data for both the X-ray and neutron diffractions, which may be useful for the analysis from the different points of view. We have already measured the 2-dimensional X-ray diffraction patterns of highly-oriented *it*-PP sample at ambient and low temperatures using a high-energy synchrotron X-ray beam. The 2D-neuron diffraction data were measured by us using a JRR BIX3 system. But those data are still insufficient for the quantitative analysis. We have challenged here to measure the 2-dimensional wide-angle neutron diffraction data of the fully-deuterated *it*-PP samples using a powerful TOF method.

(ii) Crystal structure analysis of *syndiotactic* polystyrene-organic solvent complexes

syndiotactic Polystyrene (*st*-PS) forms the crystalline complexes with various kinds of organic solvent. The spatial relation between *st*-PS chains and organic solvents in the unit cell is important for the study of formation mechanism of these complexes as well as for the clarification of polymer-solvent interactions. We have measured the neutron diffraction data of *st*-PS-solvent complexes to clarify the concrete geometrical relation of *st*-PS and solvent molecules through the quantitative analyses of neutron data combined with the X-ray data.

2. 試料及び実験方法

2.1 Samples

(i) Uniaxially-oriented fully-deuterated *isotactic* polypropylene -[$CD_2CD(CD_3)$]$_n$-

(i-1) The sample (i) annealed at 143ºC under tension (crystal form α1)
(i-2) The sample (i) annealed at 153ºC under tension (crystal form α2)

(ii) Uniaxially-oriented fully-deuterated *syndiotactic* polystyrene -[$CD_2CD(C_6D_5)$]$_n$-

(ii-1) The complex of (ii) with the deuterated chloroform ($CDCl_3$)
(ii-2) The complex of (ii) with the deuterated benzene (C_6D_6)

(iii) Uniaxially-oriented fully-deuterated polyethylene -[CD_2CD_2]$_n$-

2.2 Experimental procedure

(i) These samples were set on a gononiometer head of i-BIX instrument, in which the samples were oriented so that all the layer line data were obtained finally.
(ii) The measurements were performed at room temperature and 100K.
(iii) The thus obtained 2D WAND data were converted to those of the reciprocal lattice coordinate system.

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.

3. Results and Discussion

(i) 2D-WAND patterns of HDPE-d_4 measured at 300K and 100K

In order to check the experimental system at low temperature, the diffraction data were collected for the oriented polyethylene sample. The 2-dimensional wide-angle neuron diffraction data collected by the TOF experiments were converted to the 2-dimensional patterns of the reciprocal lattice coordinate system. Figure 1 shows the 2d-WAND patterns obtained for HDPE-d4 samples at 300K and 100K. In our previous experiment performed in JRR3 using a BIX3 system, the 2D WAND patterns were obtained at these two different temperatures as shown in Figure 2, where the diffraction data were observed up to the 1st layer line. In contrast, the TOF experiments allowed us to collect the diffraction peaks from the equatorial line up to the 4th layer lines. The diffraction peaks at low temperature became sharper and could be detected up to the higher diffraction angle region compared with those at room temperature. The 1-dimensional data of individual layer lines were extracted from these 2D data and compared with the profiles calculated for the orthorhombic polyethylene crystal structure, giving a good agreement between them.

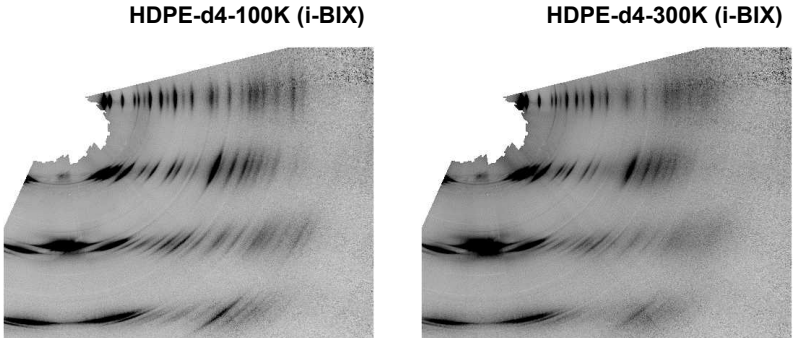

Figure 1. 2D WAND patterns of HDPE-d_4 sample measured at 100K and 300K using an iBIX system

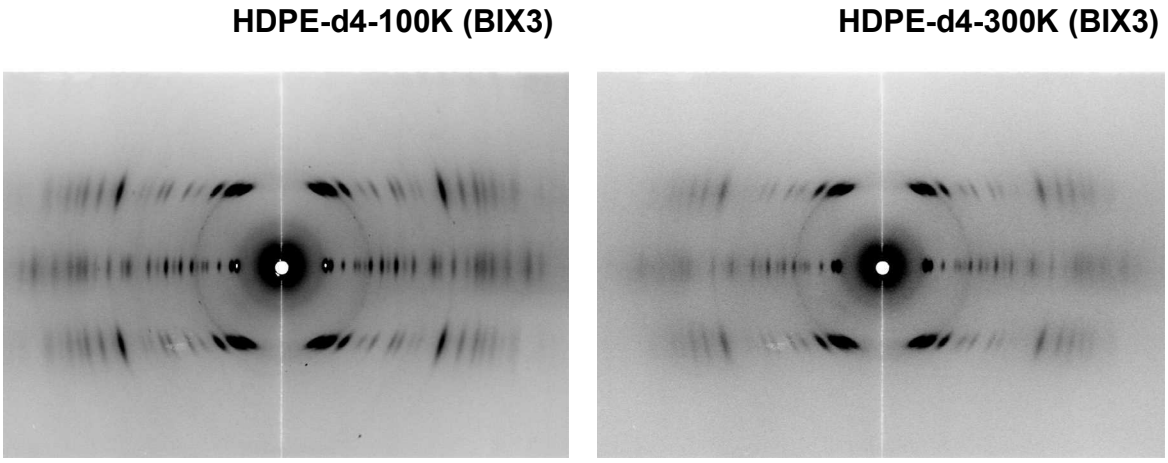

Figure 2. 2D WAND patterns of HDPE-d_4 sample measured at 100K and 300K using a BIX3 system of JRR3.

(ii) 2D-WAND patterns of *it*-PP-d5 measured at 300K and 100K

Figure 3 shows the 2D-WAND patterns obtained at 100K for the uniaxially-oriented *it*-PP-d5 samples annealed at the two different temperatures. The heat treatment at a lower temperature (143°C) results in the formation of crystal modification α1. On the other hand, the crystal form α2 is obtained by the 153°C annealing, which gives relatively sharper diffraction peaks up to the higher diffraction angle region, although the difference is not very clear. The crystal structures of the α1 and α2 forms were already reported in the literature. However, the agreement of the observed and calculated diffraction peak intensities is not very satisfactory. The quantitative analysis of both of the X-ray and neutron diffraction data should allow us to establish the crystal structures of these crystalline forms of it-PP confirmatively. The analysis is now being performed.

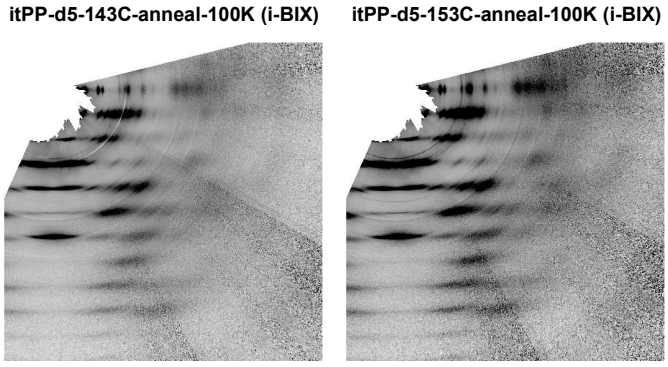

Figure 3. 2D WAND patterns measured at 100K for the *it*-PP-d5 samples annealed at 143K and 153K using an iBIX system.

(iii) 2D-WAND patterns of *st*-PS-d8-solvent complexes

The 2D-WAND patterns were collected for the uniaxially-oriented *st*-PS-solvent complex samples. The solvents chosen there were deuterated benzene and deuterated chloroform ($CDCl_3$). As an example Figure 4 compares the X-ray and neutron diffraction patterns obtained for the complex of chloroform. Although the equatorial line profile is difficult to detect in the iBIX data, the relative intensity of the several representative peaks is appreciably different between the X-ray and neutron data. These data are now being analyzed in a quantitative way.

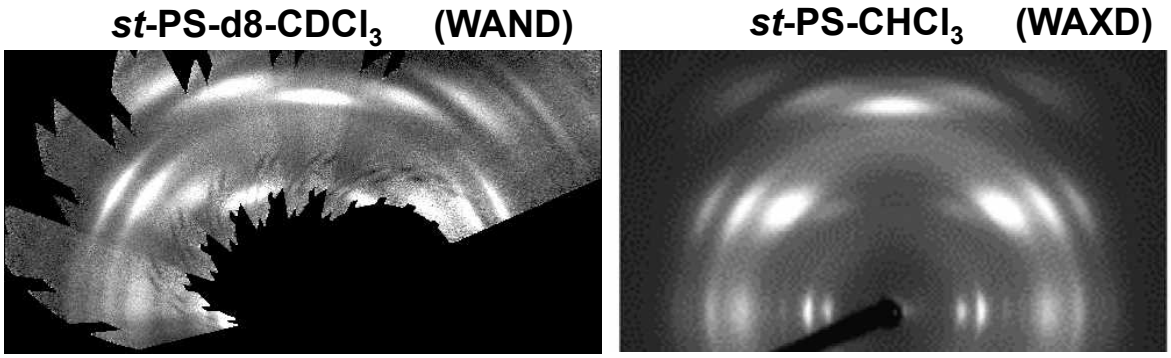

Figure 4. 2D-WAND and WAXD data of *st*-PS-chloroform complex