茨城県 IBARAKI Prefectural Government **MLF Experimental Report**	提出日(Date of Report) November 16, 2016
課題番号(Project No.) 2015PX0009 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*, Hiroko Yamamoto 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) 2016.5.12 – 5.19

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)

Originally the i-BIX system was developed for the crystal structure analysis of protein single crystals on the basis of the wide-angle neutron diffraction data collected by a time-of-flight method[1,2]. The various characteristic features of this system, such as its wide space around the sample stage, the relatively easy setting of the equipment on the goniometer head part, *etc*. allow us to introduce the various types of experimental tools into the system. In these several years, Professor Katsuhiro Kusaka and his team members of Ibaraki University and our group have been cooperatively developing the experimental tools for the structural study of polymer substances by utilizing the i-BIX system. The purpose is to widen the application field of i-BIX to the industrial people. The first trials for this purpose are to build up a stretching apparatus and a heater cell, both of which should be quite useful for the industrial application of the i-BIX system. This report describes the preliminary experimental results obtained for some polymer materials by utilizing these apparatuses.

Development of a Stretching Apparatus

<Outline>

Figure 1 shows the snapshot of a stretching apparatus which was installed at the center position of the spherical frame of i-BIX system. The sample can be set horizontally or vertically using a pair of metal holders and is stretched to 150 mm at maximum. The range of applicable force is 0 – 200 N. The stretching rate is in the range of 0 – 1 mm/sec. The scattered neutron signals are collected by the detectors arrayed around the sample. In the case of vertical setting of the sample (Figure 1 (d)), the equatorial line diffractions can be collected easily by using the horizontally-set detectors. In the horizontal setting of the stretcher, the sample must be set in a tilted angle from the incident neutron beam in order to measure the 2-dimensional diffraction pattern consisting of the various layer lines (Figure 1 (b)).

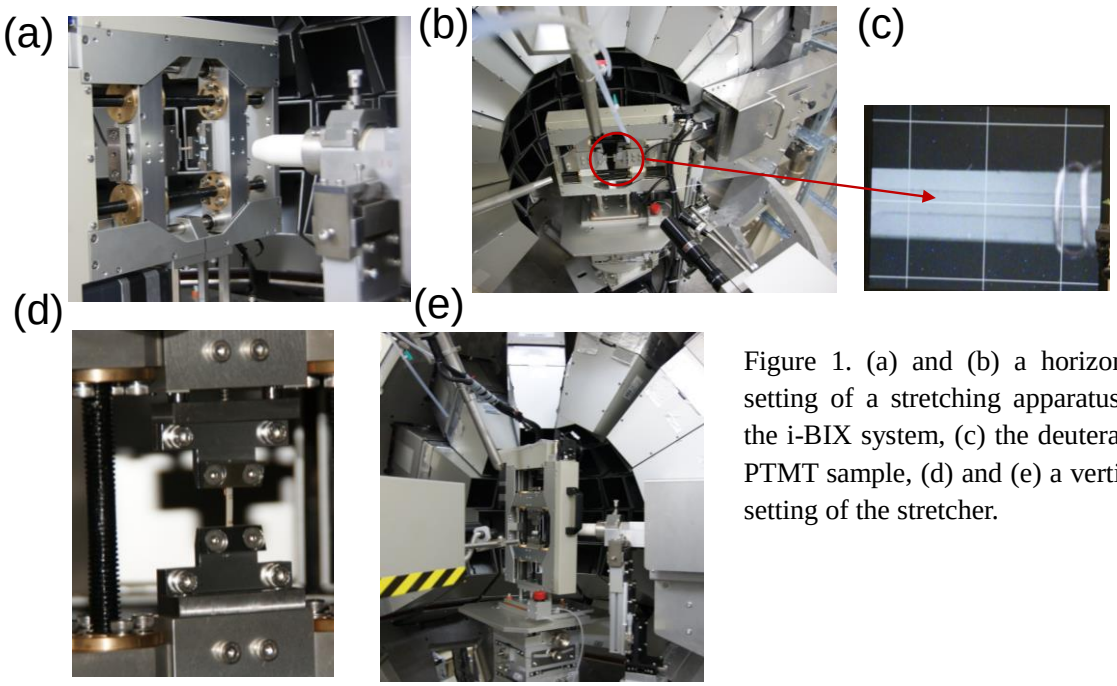

Figure 1. (a) and (b) a horizontal setting of a stretching apparatus in the i-BIX system, (c) the deuterated PTMT sample, (d) and (e) a vertical setting of the stretcher.

<The First Case Study>

As the first application of this stretching apparatus, the structural change of deuterated poly(tetramethylene terephthalate) (PTMT) sample [-($OCH_2CD_2CD_2CH_2$-O-CO-C_6H_4-CO)$_n$-] was investigated. The sample was already drawn and annealed at 150°C for 3 hrs for increasing the degree of crystallinity.

The motivation of this experiment was in such a situation of this polymer. The PTMT has the 2 types of crystalline modifications, α and β forms[3], which have the crystal structures illustrated in Figure 2[4-7]. The application of tensile force to the oriented sample causes the reversible phase transition between the α and β forms. The conformation of the methylene

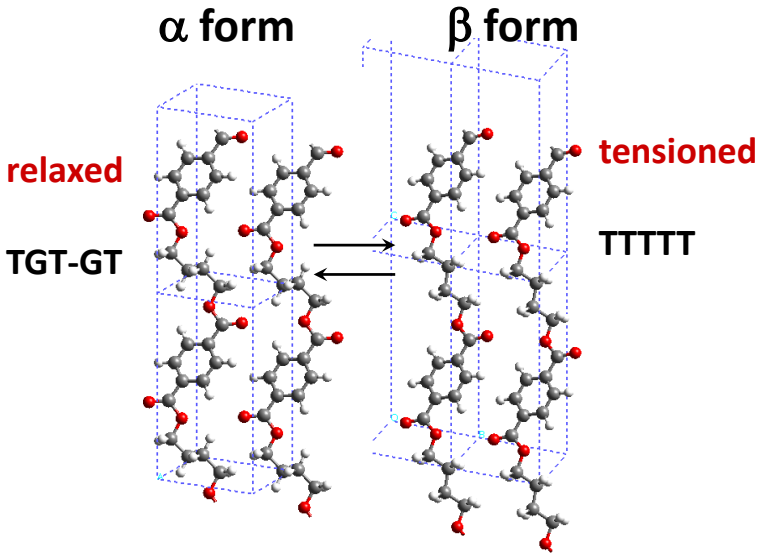

Figure 2. Crystal structures of PTMT α and β forms.

segmental parts was already analyzed by the X-ray structure analysis. The α form has the TGTG*T conformation and the β form the TTTTT conformation, where T, G and G* denote the internal rotation angles of trans, gauche and minus gauche, respectively. In our previous papers we studied the phase transition behavior from the various hierarchical points of view by performing the simultaneous measurement of 2-dimensional wide-angle and small-angle X-ray scatterings and transmission FTIR spectra in the stretching and relaxing processes[8]. Even at this stage, however, one problem remains unsettled about the methylene segmental parts. The analysis of the solid state NMR spectra of these two crystal forms casted a question onto the methylene conformations of these crystal forms[9-12]. One serious problem of the X-ray structure analysis was in such a point that the total number of the observed diffraction spots was not enough for the reliable derivation of the methylene conformation. The measurement of wide-angle neutron diffraction may give us some indication about this point, because the deuterated methylene segments can enhance the coherent neutron diffraction intensity to emphasize the structural feature of this part.

The neutron diffraction measurement was performed with the time-of-flight mode. The collection time of about 16430 photons in total was about 100 min. The sample was a bundle of highly-drawn rods and the total thickness was about 2.3 mm in diameter [Figure 1 (c)]. The sample was set to the stretcher and fixed to the predetermined length during the measurement. In other words the measurement was performed under the constant strain condition, during which some stress relaxation occurred. The equilibrated stress value was used as an averaged stress. The strains were 0, 7, 12 and 18%. The thus-collected equatorial-line diffraction data were transformed to the 1-dimensional profiles. Figure 3 shows the strain dependence of the 1-dimensional diffraction profile measured along the equatorial line. The increase of strain induced the change of profile clearly. At present the

incident neutron beam was relatively weak and so the diffracted signals were not enough strong for the detailed quantitative analysis of the 2-dimensional data. This should be a future work. The point to emphasize here is that the stretching apparatus was successfully installed on the i-BIX system. This apparatus has opened a chance of studying the polymer materials subjected to the external stress in this i-BIX system.

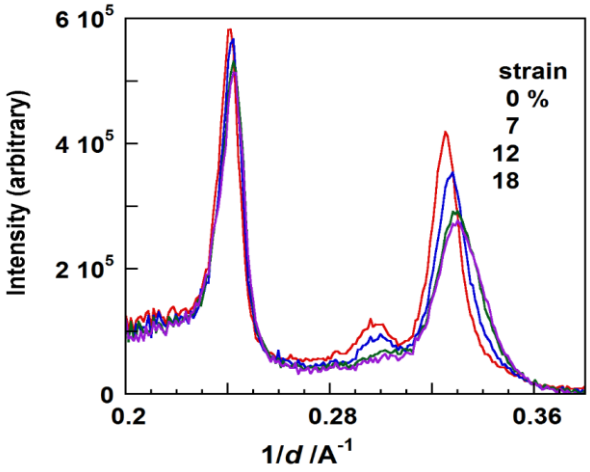

Figure 3. Strain dependence of wide-angle neutron diffraction profiles of PTMT sample measured during the mechanical stretching

Development of a Heating Apparatus

<Outline>

A heating apparatus was produced as shown in Figure 4. A pair of cartridge heaters were set at the center, and the sample wrapped with aluminum foil was sandwiched between them. The thermocouple was set to the sample position. The temperature was increased at a stepwise mode or in a continuous mode under the PDI control. The temperature range is from 20°C to 300°C. In the present experiment, the neutron diffraction measurement was performed during the continuous heating process.

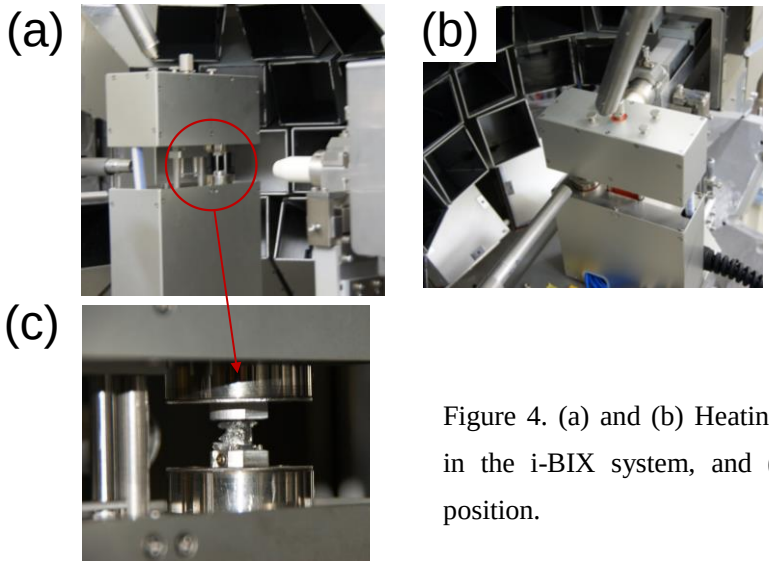

Figure 4. (a) and (b) Heating apparatus set in the i-BIX system, and (c) the sample position.

<The First Case Study>

The fully-deuterated high-density polyethylene [DHDPE, -$(CD_2CD_2)_n$-] sample was used for the first trial sample. The sample was heated continuously at 1°C/min rate. The neutron exposure time was 10 min. Therefore, one diffraction image was an average in the temperature span of 10°C. Figure 5 shows the snapshots of the wide-angle neutron diffraction pattern, which was converted from the data collected in a time-of-flight mode at the various temperatures. The 1-dimensional diffraction profiles were calculated from these patterns as shown in Figure 6. The relatively sharp diffraction peaks changed their intensities and positions during the heating process, and became broad after being melted at high temperature[13]. These data can tell us definitely the successful application of this heating cell in the study of any substances including polymer materials in the heating and cooling processes using the i-BIX system.

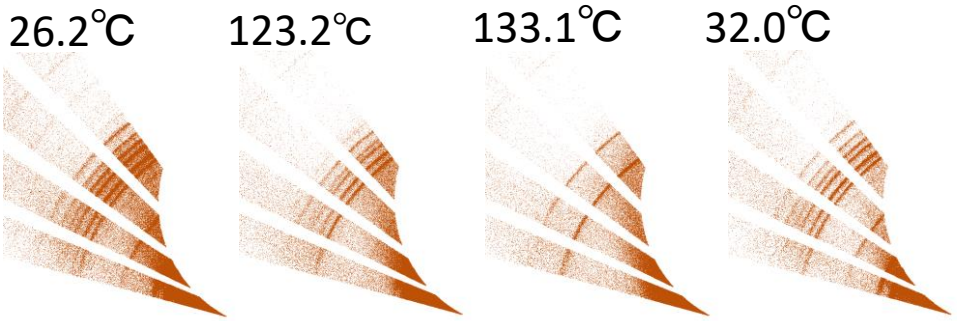

Figure 5. The 2-dimensional neutron diffraction patterns measured in the heating and cooling processes of deuterated high-density polyethylene sample.

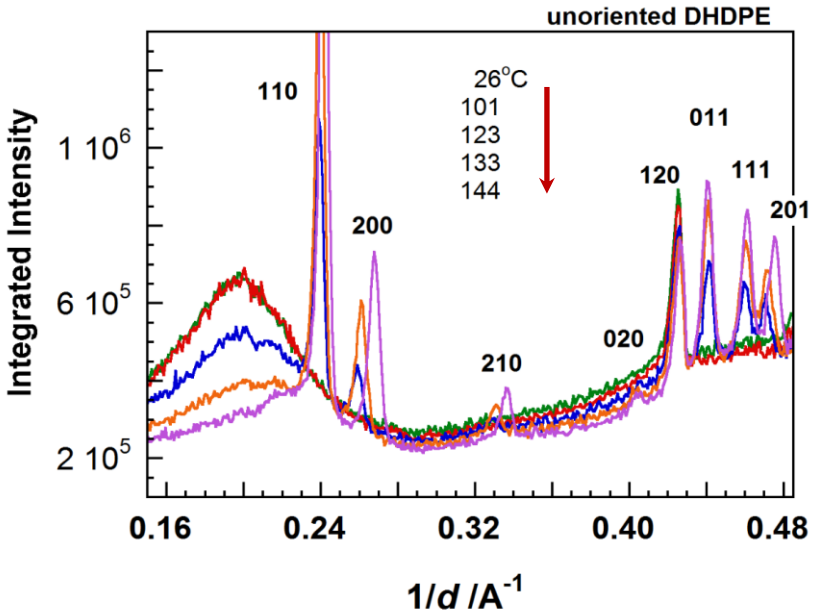

Figure 6. Temperature dependence of wide-angle neutron diffraction profile measured for deuterated high-density polyethylene.

4. 結論(Conclusion) 、参考文献(References)

In the present study we have performed the first preliminary measurement of wide-angle neutron diffraction data in the course of uniaxial stretching or in the heating and cooling process of the polymer materials by developing the stretching and heating devices installed in the i-BIX system. The purpose was to develop the present i-BIX system to the more widely-applicable equipment, which can make it possible to study more general and practical substances in addition to the protein single crystals. The experimental data collected in this study were only preliminary, but they have confirmed the usefulness of these apparatuses for the structural study using the neutron diffraction data collected by the i-BIX system.

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