Combinatory Usage of X-ray and Neutron Diffraction Techniques for the Refined Structure Analysis of Polymer Crystals: from Hydrogen Atoms to Bonded Electron Density Distribution

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Abstract. In order to predict the physical property of polymers, we need to know the atomic coordinates including hydrogen atoms as accurately as possible. However, polymer samples give us limited number of broad X-ray reflections in general. In order to improve this problem, we have made many efforts to collect the X-ray diffraction data as accurate as possible. In this paper, we report the structure analysis including the extraction of hydrogen/deuterium atomic positions for the oriented polyoxymethylene by the combination of X-ray diffraction method with neutron diffraction method. In such a cases of polydiacetylene giant single crystal the bonded electron density distribution was evaluated along the skeletal chain by the so-called X-N method based on the wide-angle X-ray diffraction data and the wide-angle neutron diffraction data.

1. Introduction
In order to predict the ultimate physical properties of polymer crystals, we need to know the molecular interactions and atomic coordinates including hydrogen atoms which play an important role in giving the anisotropy in the physical property [1]. However, general polymers give us only small number of broad X-ray reflections, making it difficult to analyze the crystal structure with high reliability. We have made many efforts to increase the reliability as listed below.
(1) Utilization of an X-ray beam with short wavelength to increase the total number of observable reflections [2].
(2) Development of a software to separate the overlapped reflections and evaluate the integrated intensity of separated reflections accurately [2].
(3) Utilization of energy calculation technique to extract energetically acceptable structure models, which can be used as the initial model for the structure analysis [3].

(4) Extraction and refinements of hydrogen atomic positions utilizing electron diffraction and wide-angle neutron diffraction (WAND) methods [4].

(5) Utilization of giant single crystals of polymers [5].

In an ideal case many reflections can be collected from a giant single crystal of polymer, and it becomes possible to clarify the bonded electron density distribution on the basis of reasonable combination of X-ray and neutron data (X-N method). In the present paper, we report the results of structure refinement made for polyoxymethylene (POM) and polydiacetylene on the basis of diffraction peaks obtained as many as possible.

2. Experimental Section

Normal POM samples used in the experiment were prepared by γ-ray induced solid-state polymerization reaction of tetraoxane single crystals. The deuterated trioxane crystal gave the deuterated POM, -(CD₂-O)n-, after the γ-ray polymerization reaction. The giant single crystals of polydiacetylene with bulky side groups, poly [1.6-di(N-carbazoyl)-2,4-hexadiyne] (PDCHD), were synthesized from a single crystals of the corresponding diacetylene monomer by irradiating γ-ray beam.

The X-ray diffraction data were collected using Rigaku Rapid-II diffractometer with Mo-Kα beam. In parallel, the high-energy synchrotron X-ray diffraction measurement was performed in the beam line 04B2 of SPring-8, Japan. The WAND measurements of hydrogenated and deuterated POM samples and normal PDCHD crystal were performed using an imaging plate system BIX-3 [6] installed in JRR-3 of Japan Atomic Energy Agency (Tokai-mura).

3. Results and Discussion

3.1. Structure Refinement of POM

The crystal structure of POM had been reported by many researchers [7 - 13]. Several chain models containing some conformational distortions were proposed. But, more detailed structure including the hydrogen atomic positions was not yet reported satisfactorily. The X-ray fiber diagram of POM taken

![Figure 1](image1.png)

**Figure 1.** WAXD data of POM sample measured with synchrotron X-ray beam at BL04B2 of SPring-8.

![Figure 2](image2.png)

**Figure 2.** WAND data of (a) hydrogenated and (b) deuterated POM samples measured at room temperature. The vertical direction is parallel to the fiber axis.
at -150 °C using a synchrotron X-ray source of 0.328 Å wavelength is shown in Figure 1. From this pattern, 700 reflections were collected, in which the unique reflections were 202. The unit cell parameters were $a = b = 4.464 (4)$ Å, $c \text{ (fiber axis)} = 17.389 (2)$ Å and $\gamma = 120^\circ$ at room temperature, and $a = b = 4.373 (4)$ Å, $c \text{ (fiber axis)} = 17.274 (2)$ Å and $\gamma = 120^\circ$ at -150 °C. The space group is $P3_2\overline{2}$. Based on thus-collected large number of reflections, the initial structure model and the hydrogen atomic positions were extracted successfully by a direct method and also by the differential Fourier synthesis. The refinement was made for all the coordinates of carbon, oxygen and hydrogen atoms by taking the anisotropic (carbon and oxygen atoms) and isotropic thermal parameters (hydrogen atoms) into consideration. The final reliability factors were 6.9 % at -150°C and 8.8 % at room temperature.

The 2-dimensional WAND patterns taken for hydrogenated and deuterated POM samples are shown in Figure 2. The total number of unique neutron reflections were 28 and 72 reflections, respectively. The structure refined by the X-ray analysis was transferred to the WAND analysis. The final reliability factors were 13.9 % for hydrogenated POM and 22.4 % for deuterated POM. The hydrogen atomic positions were extracted successfully as the negative and positive peaks in the 3-dimensional Fourier maps as shown in Figure 3. More accurate analysis of synchrotron X-ray diffraction data of POM gave us more ore less different structure model from the above-mentioned (9/5) helical model, in which the (29/16) helices are packed in the cell. The reliability factor calculated for this model (8.6 %) is almost the same as that calculated for the (9/5) helices. But, the existence of a series of 00l reflections, which can not be predicted for the (9/5) helical model, was confirmed on the Weissenberg photograph and supports the (29/16) helical structure with 55.7 Å period.

### 3.2. Bonded Electron Density Distribution of PDCHD

Figure 4 shows the molecular chain conformation analyzed using WAXD data. The main chain of planar-zigzag form consists of an alternation of single, double and triple bonds. An X-ray beam is scattered by the electron clouds around the atomic nuclei and the WAXD analysis gives us the information on electron density distribution. The neutron beam is scattered by the nuclei, and the nuclear density distribution information is obtained. By utilizing both of these two kinds of diffraction data, we may find the bonded electron density distribution (X-N method) [14]. Figure 5 shows the thus-obtained bonded electron density distribution map along the main chain of PDCHD. The electron density around the triple bonds shows the highest density compared with those around the single and double bonds. But, the electron densities of single bonds and double bonds are almost the same height as known from Figure 5, suggesting a development of some degree of electronically conjugated system along the skeletal chain. In order to confirm the result, the electron density distribution of PDCHD chain was calculated on the basis of a density functional theory (DMol3, Material Studio Version 4.2 (acelrys)). The calculated bonded electron density distribution is consistent qualitatively at least with the experimental result.
4. Conclusions

In the present paper, we have reviewed the structure analysis results of two types of polymer crystals, POM and PDCHD on the basis of organized combination of X-ray and neutron diffraction techniques. The increased total number of observed reflections has allowed us to obtain the hydrogen atomic positions for POM and the bonded electron density distribution for PDCHD. But, these two examples are lucky cases with great amount of observed reflections. The general synthetic polymers give only limited number of reflections and are still at the stage in difficulty of the refined structure analysis. We need to apply the ideas listed in the introductory section to the general cases.

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