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Extraction of Hydrogen-Atom Positions in Polyethylene Crystal Lattice from Wide-Angle Neutron Diffraction Data Collected by a Two-Dimensional Imaging Plate System: Comparison with the X-ray and Electron Diffraction Results

Kohji Tashiro,*,† Ichiro Tanaka,‡ Takashi Oohara,‡,§ Nobuo Niimura,‡,‖ Satoru Fujiwara,‡ and Toshiya Kamae†

Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan, Advanced Science Research Center, Japan Atomic Energy Institute, Tokai-mura, Ibaraki 319-1195, Japan, Institute of Materials Structure Science, High Energy Accelerator Research Organization, Oho 1-1, Tsukuba, Ibaraki 305-0801, Japan, and Department of Technology, Ibaraki University, Hitachi, Ibaraki 316-8511, Japan

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ABSTRACT: Two-dimensional wide-angle neutron diffraction patterns have been measured successfully for uniaxially oriented fully deuterated and fully hydrogeneous polyethylene samples by using an imaging plate system (BIX-3) installed at the Japan Atomic Energy Research Institute. The detailed data analysis allowed us to extract the positions of hydrogen atoms in the crystal lattice accurately. The results were compared quantitatively with those obtained from the X-ray and electron diffraction experiments as well as the computer simulation result.

Introduction

To discuss the quantitative relationship between structural and physical properties of a crystalline polymer in the limiting state we need detailed and accurate information about the atomic positions in the crystal lattice. In particular, the positions of hydrogen atoms are quite important because most of the significant intermolecular interactions are hydrogen−hydrogen interactions between the neighboring chains, which may determine the magnitude and anisotropy of such physical properties as elastic constants.[1] One of the best methods to evaluate the atomic positions as accurately as possible is to perform X-ray structure analysis for a highly oriented and highly crystalline polymer sample. Unfortunately, however, different from the single crystals of low-molecular-weight compounds, seimcrystalline polymer samples exhibit, in general, the wide-angle X-ray diffraction (WAXD) data of a small number of broad reflections except for the case of such a large single crystal as polydiacetylene[2,3] and poly(*cis*,*cis*-diethyl muconate).[4,5] One key point to overcome this problem is to collect as many reflections as possible with exact intensity values. Regarding this point, it may be valuable to briefly review the various works analyzing the crystal structure of orthorhombic polyethylene (PE) as a typical case of the above-mentioned problem, since this polymer has the simplest chemical formula and possesses the structure of high space group symmetry.

Since the first report by Bunn, crystal structure analysis of PE has been tried by the various researchers.[6−21] First, we will discuss work on X-ray structure analysis. Swan[8] measured the temperature dependence of the unit cell dimensions for the unoriented PE samples, clarifying that the linear thermal expansion coefficient along the *a* axis is larger than that of the *b* axis in the temperature range from −196 to 130 °C. As one of the important crystal structure parameters of PE, the setting angle of the planar-zigzag chain is used, which is defined as the angle between the skeletal zigzag plane and the $b-c$ plane. Using the 28 *hk*0 reflections measured for the PE single crystal, Kawaguchi et al.[13] carried out structure analysis by trial-and-error under the constraining condition of fixed bond lengths and angles and reported that the setting angle is almost constant (ca. 45°) below 0 °C but changes slightly above 0 °C. Kavesh and Schultz[11] reported that the setting angle (ϕ) becomes larger as the temperature increases from room temperature ($\phi = 45°$ at 20 °C and $\phi = 50°$ at 100 °C). Their crystal structure analysis was based on only nine X-ray Bragg reflections collected for the unoriented sample, where five structural parameters (scale factor, fractional coordinates, and anisotropic temperature factors of the carbon atom) were varied to minimize the difference between the calculated and observed reflectional intensities. Iohara et al.[12] reported the temperature dependence of the mean-squared displacement parameters of the carbon atoms and the setting angle in the temperature range from −160 to 120 °C based on the X-ray reflection data. In their analysis they refined seven parameters including the scale factor, fractional coordinates, and anisotropic displacement parameters(U_{aa}, U_{bb}, U_{cc}, U_{ab}) of the carbon atoms by using the 32 reflections collected by a Geiger-Müller counter. By utilizing a one-dimensional position-sensitive proportional counter, Chatani et al.[14,15] collected the X-ray diffraction data at room temperature for the various types of PE samples, including both the unoriented and oriented samples, and reported that the setting angle becomes larger for the sample with larger lattice strain. Busing[18] measured the X-ray diffraction profiles of ultradrawn PE fibers from the equatorial line to the forth layer line using a Mo Kα line as an incident

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* To whom correspondence should be addressed.
† Osaka University.
‡ Japan Atomic Energy Institute.
§ High Energy Accelerator Research Organization.
‖ Ibaraki University.

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beam and analyzed the crystal structure on the basis of the Rietveld method so that all the observed layer line profiles could be reproduced as well as possible. His result seems a little curious from a stereochemical point of view: CC bond length = 1.509 Å and CCC bond angle = 115.4°. He ascribed these values to the effect of thermal motion. By introducing the two-dimensional imaging plate detector system, Tashiro et al. measured the fiber diagram of uniaxially oriented PE sample up to the second layer line using a Mo Kα beam,[19] and they evaluated the integrated intensities of 68 reflections after the separation of overlapped reflections by homemade software for the analysis of digitized reflection data. They found the carbon-atom positions by applying the direct method for the so-called phase problem,[20] and they also revealed the positions of hydrogen atoms by calculating the so-called $F_o - F_c$ Fourier map, where F_o and F_c were the observed and calculated structure factors for the carbon atoms. However, they could not refine the hydrogen-atom positions in the least-squares refinement stage and reset them to the theoretically derived standard positions. At almost the same time, Dorset[21] applied the direct method to analyze the crystal structure of PE by using X-ray diffraction data reported by Kawaguchi et al.[13] In this analysis the CC bond length was 1.59 Å, and the CCC bond angle was 106°, a little different from the standard values. Tashiro et al.[22] measured the X-ray fiber diagrams of ultradrawn PE sample as well as the normally drawn sample at various temperatures. They analyzed the temperature dependence of various parameters such as the unit cell constants, setting angle, and anisotropic thermal parameters by using ca. 50−60 reflections on average. Consistent with the reports by Kawaguchi et al.,[13] Kavesh and Schultz,[11] and Iohara et al.,[12] the slopes of these structure parameters were found to change around ca. 10 °C. In addition, the thermal behavior was found to be different between the normally oriented sample and the ultradrawn sample. Unfortunately in these analyses, however, they could not refine the hydrogen-atom positions even for diffraction data collected at −100 °C, at which the atomic thermal motions should be suppressed to some extent. However, this is not limited to the case of PE sample. Even for the single crystals of low-molecular-weight compounds giving 5000−6000 reflections in all, there are many examples in which the hydrogen-atom positions cannot be determined accurately.

Another useful method to detect hydrogen atoms is the electron diffraction (ED) technique. As pointed out already,[23] the electron scattering factor of the hydrogen atom remains almost constant in a wide scattering angle range, in contrast to the relatively rapid decrease of the electron (and X-ray) scattering factor of the carbon atom, making it preferable to detect the hydrogen atoms than in the X-ray diffraction case. For solution-grown single crystals of PE and *n*-alkanes, Dorset[23,24] and Ogawa et al.[25] analyzed the crystal structure on the basis of ED data. Only a brief review is made here because the details about the thorough structure analysis of these samples were described well in Dorset's excellent textbook.[23] In a relatively early period of ED analysis of *n*-paraffin crystals, Vainshtein and Pinsker reported the "reasonable" structure parameters of CC 1.52 Å, CH 1.17 Å, CCC 110°, and HCH 105° by utilizing about 90 reflections in all.[26] Afterward many analyses were tried for *n*-paraffin single crystals, but the structure parameters were more or less curious from a stereochemical point of view. Careful and thorough structure analysis of ED data was reported by Dorset for both *n*-paraffin[27] and PE[24,28] single crystals: the HCH angle was 98° for n-$C_{36}H_{72}$ (total number of reflections = 42) and the CC = 1.52 Å and CCC = 114.3° for PE crystal (51 unique reflections). They tried to refine the hydrogen-atom positions also, but the hydrogen positions had to be reset to the idealized positions after least-squares procedures. Ogawa et al.[25] applied the imaging plate detector for collecting ED data for PE single crystal and found the hydrogen atoms by calculating the $F_o - F_c$ map, but even the geometry of the carbon skeleton was still unreasonable: CC = 1.51 Å and CCC = 115°. In this way, despite many efforts in data collection and structure analysis, ED data cannot give highly reasonable structure parameters for PE crystal. As pointed out by Dorset,[23] this may originate from the multiple scattering effect occurring in the single-crystal sample: an electron beam reflected on a lattice plane is diffracted again by some other lattice plane. The relative intensity of the observed reflections is modified more or less due to this scattering effect, resulting in the curious structure parameters. Dorset indicated several methods valuable for escape from this burdensome problem: increase in accelerating voltage, decrease of sample thickness, analysis based on dynamical scattering theory, etc.[23]

How can we obtain accurate hydrogen-atom positions in the crystal lattice of a semicrystalline polymer, in particular those in the orthorhombic PE? One idea is to utilize a fully deuterated sample and measure the wide-angle neutron diffraction (WAND) data since the heavy hydrogen atom gives appreciably large coherent scattering power, different from the strong incoherent background from light hydrogen atom, and this coherent cross section is comparable to that of the carbon atom. We know many successful cases for low-molecular-weight compounds.[29] For polymer materials, however, most of the measurements were made for deuterated but unoriented samples[30,31] or only the equatorial reflections of oriented samples with or without deuteration.[32−35] As for PE, Avitabile et al. collected the WAXD data for deuterated samples at 4 and 90 K.[36] Their analysis gave a CC bond length of 1.574 Å and CCC bond angle of 108°, although the reasons are not clear at present. Takahashi[32] measured 17 equatorial (*hk*0) reflections of a fully deuterated PE sample and analyzed the temperature dependence of the crystal structure (in Table 4 of his paper the 27 *hk*0 reflections are listed but some are overlapped to give an apparent one observed reflection). Unfortunately, however, a rigid-rod body was assumed for the PE chain and the molecular parameters were fixed in the structure refinement. In other words, the best use of the merits of neutron scattering from the deuterated species or the power to extract the hydrogen-atom positions was not made. In addition, it is necessary to collect not only the equatorial *hk*0 reflections but also the layer line reflections in order to determine the hydrogen-atom positions as accurately as possible. Langan et al. reported the two-dimensional neutron diffraction pattern of deuterated cellulose fibers and successfully extracted the hydrogen atoms in the hydrogen bonds between the neighboring cellulose chains.[37] In their experiment they collected the reflections with a four-circle single-crystal diffractometer equipped with a position-sensitive detector. For polymer materials, however, it might be better to take the two-dimensional diffraction pattern, from which the shape and relative intensity of the broad and overlapped reflections can be evaluated accurately, as exemplified for the structure analysis by using the X-ray imaging plate detector mentioned above. One decade ago Niimura et al. developed a neutron imaging plate (NIP) system[38,39] and succeeded to extract the hydrogen-atom positions in the crystal lattices of proteins.[40] The imaging plate detector gave them the highly resolved two-dimensional diffraction data at a highly quantitative level. We utilized this NIP system to obtain the fiber diffraction pattern of uniaxially oriented and fully deuterated PE samples as a first trial. As a result we succeeded in finding the hydrogen-atom positions clearly and refined the crystal structure of orthorhombic PE with reasonable molecular geometry in a more accurate manner than that reported in the previous paper.[19,22]

In the present paper we will describe the details of the structure analysis of the PE crystal on the basis of two-dimensional WAND patterns taken for the uniaxially oriented fully deuterated PE sample as well as for the uniaxially oriented normal (or hydrogeneous) PE sample. At the same time we compare the thus obtained results with those by the X-ray diffraction data, as reported before,[19,22] and also with the results obtained from the ED data collected for a solution-grown single crystal. We believe this first trial will make some contribution to the development of the structure analysis of polymer crystals with more accurate information about the atomic positions including hydrogen atoms, which should be absolutely necessary for quantitative discussion of the structure−property relationship.

Experimental Section

Samples. Fully deuterated high-density PE ($-(CD_2CD_2)-$, HDPE-d_4) was purchased from Merck Chemical Inc. Hydrogeneous (or normal) high-density PE ($-(CH_2CH_2)-$, HDPE-h_4) was supplied by Exxon Co. Ltd. These samples were melted and quenched into an ice−water bath. Rectangular strips were cut and stretched by ca. 7 times the original length on a hot plate, followed by heat treatment at 120 °C for a few hours under tension. These samples were cut into several pieces of rods. These oriented rods were bundled together in parallel to prepare thick samples for the neutron diffraction measurements. A single crystal of HDPE-h_4 (Marlex 50) for electron diffraction measurement was grown from *p*-xylene solution (concentration 0.01 wt %) at 80 °C for 2 days. Other samples used for electron diffraction measurement were prepared by an epitaxial method on a benzoic acid crystal surface (for the measurement of the *0kl* reflections) and also by melt-crystallization of a thin film on a KBr crystal with the beforehand-rubbed surface (for the measurement of the 2*k*1 and 3*k*1 reflections).[28,41−43] In the former case, the chain axis was parallel to the surface of the benzoic acid crystal, while the chains were tiled by 45° in the latter case. It is said that inorganic substrates such as KBr often need to be outgassed in vacuo after cleavage before they can serve as such substrates, but this procedure was not done in the present experiment.[23]

Measurements. *(1) Wide-Angle Neutron Diffraction.* A BIX-3 system (high-resolution neutron diffractometer dedicated to biological macromolecules) built in the JRR-3M reactor hall of the Japan Atomic Energy Research Institute was used for measurement of two-dimensional WAND patterns of the uniaxially oriented PE samples.[39,40] A schematic illustration of the BIX-3 cylindrical camera is shown in Figure 1. The sample was set vertically on a goniometer head, which was set on top of a cylindrical camera 40 cm in diameter. An imaging plate containing Gd_2O_3, Ba_2BF, and Eu^{2+} was initially positioned around the sample. The monochromatized neutron beam with a wavelength of 1.51 Å was incident on the sample through a slit 3 mm in diameter. The imaging plate was defended from γ-rays by covering with a lead plate and also from neutron scatterings coming from outer sources by covering with a B_4C plate. After a predetermined exposure time, the imaging plate was moved continuously to the lower part of the camera, during which the reflection data were read by irradiating a He−Ne laser beam. For one PE sample, two WAND diagrams with 6 and 12 h exposure time were taken in order to collect as many reflections of strong to weak intensities as possible.

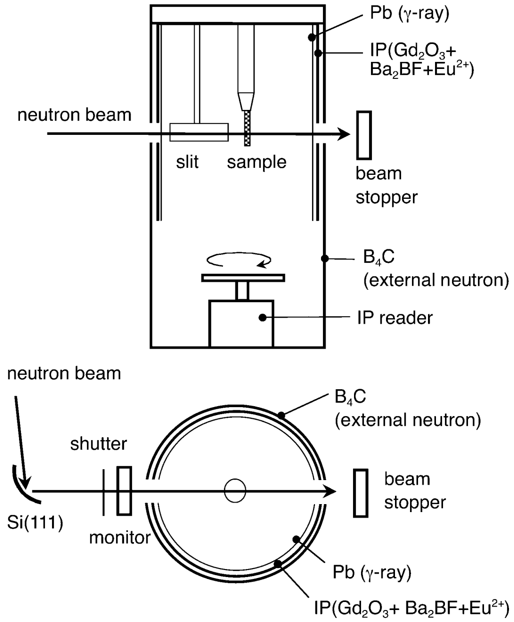


Figure 1. Schematic illustration of BIX-3 system.

(2) Electron Diffraction Measurement. Single crystals were set onto a carbon-coated collodion mesh from the solution and put into a transmission electron microscope, JEOL-JEM 1010. The wavelength of the electron beam was 0.0037 Å (100 kV). The diffracted image was taken by an imaging plate detector and read by a JEOL DL2000 IP reader. The samples were tilted in the range from −30° to 30° to collect as many reflections as possible. To reduce sample damage by an incident electron beam, the electron beam intensity was reduced as much as possible with the combination of a highly sensitive imaging plate detector.[44]

(3) X-ray Diffraction Measurement. Details have been described in previous papers.[19,22] The incident X-ray beam was a graphite-monochromatized Mo Kα line (wavelength 0.711 Å). The sample used for the measurement was a ultradrawn PE sample.

Data Analysis. The two-dimensional diffraction pattern was analyzed by software developed in-house.[19,22] The position and integrated intensity of a reflection were evaluated after separating an overlap of neighboring reflections. The integrated intensity was corrected for the Lorentz factor for neutron diffraction data. No correction was made for the absorption effect. The structure factors were evaluated by taking multiplicity into account. For ED data, the structure factor was evaluated as a square root of the integrated intensity with the multiplicity taken into account.[23] Quantitative analysis of X-ray diffraction data has been described in previous papers.[19,22]

The thus collected structure factor data were used for calculation of the density map (or electrostatic potential map for ED), where the phase angles of the reflections were estimated from the already reported crystal structure information for orthorhombic PE.[19] Refinement of the atomic positions extracted from the density map was performed so that the calculated structure factors became as close to the observed ones as possible. As described in a previous paper,[19] in some cases, several reciprocal points with almost the same lattice spacings contribute to the same reflection [e.g., a pair of (4, 1,

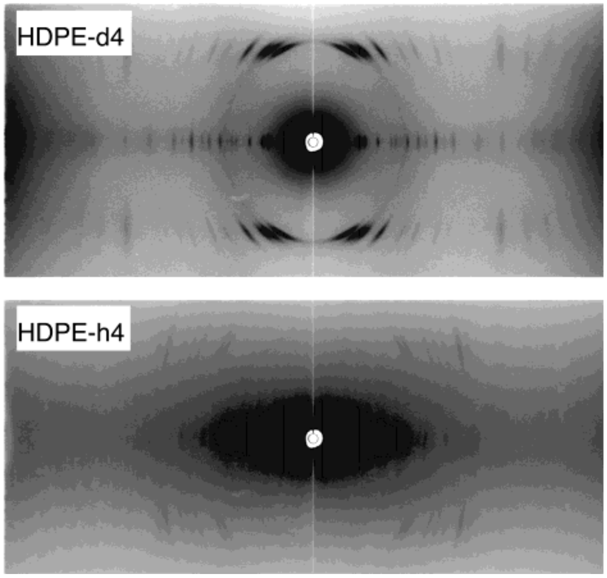


Figure 2. WAND diagrams taken for uniaxially oriented polyethylene samples: (top) HDPE-d_4 and (bottom) HDPE-h_4. The chain axis is parallel to the vertical direction.

0) and (3, 2, 0)]. These reflections were separated by assuming the observed intensity (I_{obsd}) is a summation of these reflection intensities (I_i): $I_{\text{obsd}} = \Sigma_i I_\text{i}$ and $I_\text{i} = w_i I_{\text{obsd}}$ where $w_i = m_i|F_{\text{calc},i}|^2/\Sigma_i\, m_i|F_{\text{calc},i}|^2$ with the multiplicity m for the calculated structure factor $F_{\text{calc},i}$. At first the weight w_i was calculated on the basis of the structure revealed by only unique (nonoverlapped) reflections. After one cycle of refinement, the new w_i was estimated by using $F_{\text{calc},i}$ for the slightly changed structure. This process was repeated until w_i (and the reliability factor R, defined later, and geometrical parameters) remained unchanged.

Results and Discussion

WAND Patterns of HDPE-d_4 and HDPE-h_4 Samples. Figure 2 shows the WAND diagrams taken for the uniaxially oriented HDPE-d_4 and HDPE-h_4 samples. HDPE-d_4 gave a clear and intense diffraction pattern with relatively low background. In the case of the HDPE-h_4 sample, in contrast, the background is quite strong, making observation of coherent scatterings difficult. It is noticed immediately that the relative intensities are very different between these two patterns and different also from the WAXD pattern. When the diffraction diagrams of Figure 2 were investigated in detail, the peak heights were found to be different, though slightly, at the corresponding positions in the right and left quadrants. This may come from the inherent characters of the BIX-3 system. However, the integrated intensity of the corresponding reflection was found to be essentially the same between the right and left quadrants. The structure factors were evaluated from these integrated intensities after separation of overlapped reflections into components. Then the neutron density map $\rho(x, y, z)$ was calculated on the basis of the following equation

$$\rho(x, y, z) = \Sigma_h\, \Sigma_k\, \Sigma_l\, F(hkl) \exp[-2\pi i(hx + ky + lz)]$$

where (x, y, z) is the fractional coordinate and $F(hkl)$ is a structure factor for the hkl reflection

$$F(hkl) = |F(hkl)| \exp[i\alpha(hkl)] = \Sigma x\, \Sigma y\, \Sigma z\, f(hkl) \exp[2\pi i(hx + ky + lz)]$$

Table 1. Atomic Fractional Coordinates and Temperature Factors of HDPE-d_4 Obtained from WAND Data Analysis

atom	x/a	y/b	z/c	$B_{\text{iso}}/\text{A}^2$
C	0.460 ± 0.012	0.560 ± 0.018	0.25	4.700 ± 0.000
D_1	0.490 ± 0.023	0.780 ± 0.038	0.25	6.818 ± 5.368
D_2	0.312 ± 0.023	0.539 ± 0.041	0.25	6.322 ± 4.805

The unit cell parameters were a = 7.43 Å, b = 4.93 Å, c (fiber axis) = 2.545 Å, and the space group was $Pnam$. In this calculation the phase angle $\alpha(hkl)$ of each structure factor was estimated through calculation of the structure factors for the carbon atoms, the positions of which were already known by X-ray structure analysis.[19] The neutron density maps are shown in Figure 3, where some region of the unit cell is magnified for clarity. In the case of HDPE-d_4, the positions of heavy hydrogen atoms were detected relatively clearly in addition to the carbon-atom position. The light hydrogen atoms are detected also for HDPE-h_4, where the density is a negative value since the coherent neutron scattering factor of light hydrogen atom is negative. (In Figure 3 the peaks are indicated by dark gray corresponding to the negative density height.) The $F_\text{o} - F_\text{c}$ maps were calculated by subtracting the contribution of carbon atoms (F_c) from the observed structure factors (F_o). The $F_\text{o} - F_\text{c}$ maps are shown on the right side of Figure 3. The hydrogen atom peaks are seen quite clearly in the case of both HDPE-d_4 and HDPE-h_4. However, the geometrical parameters estimated from these positions were not very reasonable. For example, C−D bond distances were too long, 1.33 and 1.28 Å, compared with the standard value (about 1.1 Å).

Structure refinement was made by least-squares method so that the agreement between the observed and calculated structure factors was best. Since the total number of observed reflections was only 29 (for HDPE-d_4 sample) including accidentally overlapped reflections (refer to the Experimental Section), the variable parameters in the least-squares calculation were reduced to the x, y, z coordinates and the isotropic temperature factors (B_{iso}) for carbon and hydrogen atoms in addition to the scale factor. The results are summarized as follows.

(1) HDPE-d_4. The reliability factor (R) was 13.5% for 29 reflections, where R is defined as 100% × $\Sigma_i\, (|F_{\text{obsd}}|_i - |F_{\text{calcd}}|_i)/\Sigma_i |F_{\text{obsd}}|_i$ (F_{obsd} and F_{calcd} are the observed and calculated structure factors, respectively). The fractional coordinates and the temperature factors are listed in Table 1. Comparison between the observed and calculated structure factors is made in Table 2. The molecular parameters are C−C = 1.530 ± 0.023 Å, C−D_1 = 1.099 ± 0.045 Å, C−D_2 = 1.105 ± 0.045 Å, C−C−C = 112.6° ± 2.1°, and D_1–C−D_2 = 107.3° ± 5.7°. The crystal structure is shown in Figure 4. The setting angle of the planar-zigzag chain plane measured from the b axis is 42.4° ± 3.3°, almost coincident with the value 44.0° ± 0.9° estimated by X-ray analysis.[19,22] Since the samples used in the neutron and X-ray diffraction experiments are different, the setting angle might be different, strictly speaking, between the two cases due to the difference in the internal residual strain, the crystallite size, etc.[14−17,22] However, as pointed out by Hu and Dorset,[28] it might not be significant to compare the setting angles evaluated by the various methods if the experimental errors are not very small. To discuss it in more detail we need to lower the estimation error of atomic positions as much as possible by increasing the total number of the observed reflections in the neutron experiment.

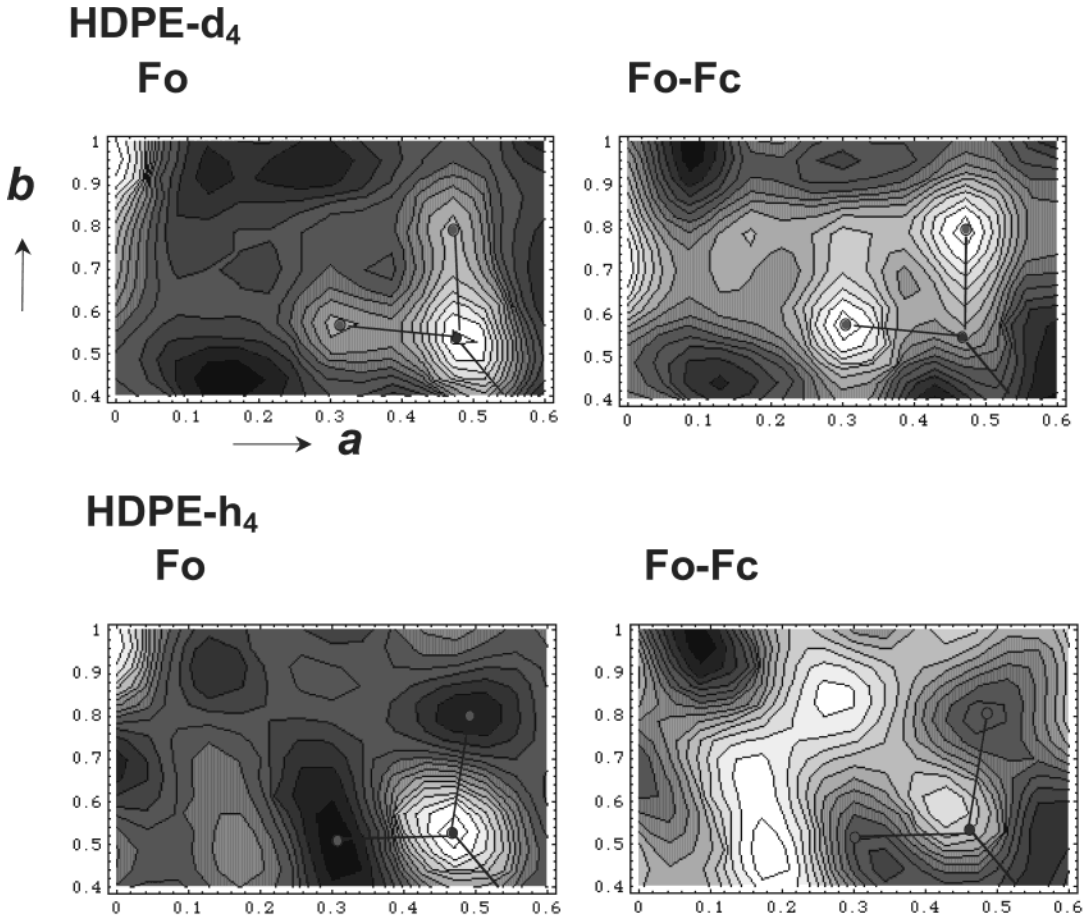


Figure 3. Fourier neutron density maps obtained from the WAND data taken for uniaxially oriented polyethylene samples: (top) HDPE-d_4 and (bottom) HDPE-h_4.

Table 2. WAND Structure Factors of HDPE-d_4 Sample

hkl	*F*(obsd)	*F*(calcd)
110	99.8	106.3
200	82.6	80.7
210	−34.8	−42.6
020	37.1	43.0
120	−35.0	−44.1
310	−17.8	−16.4
220	−37.4	−45.7
400	69.4	68.5
410	−20.0	−25.0
130	65.3	64.6
510	55.1	45.9
140	−42.7	−32.5
600	42.0	34.4
610	-41.2	-40.6
520	−35.4	-28.5
040	25.5	21.6
430	−23.6	−18.7
140	−39.8	−32.5
610	−30.4	−32.6
240	7.0	4.6
011	113.0	83.9
111	79.4	78.2
201	72.4	66.9
211	74.6	75.1
121	36.0	41.7
221	40.0	46.6
411	35.8	48.4
131	26.8	29.3
141	52.9	61.4

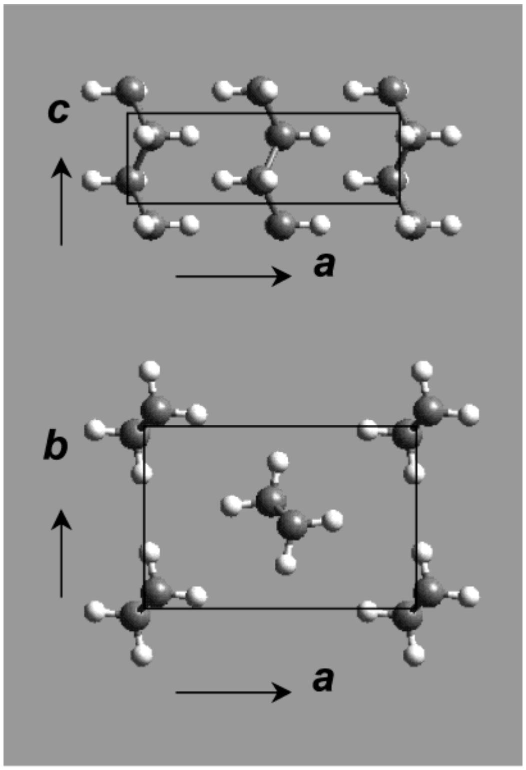


Figure 4. Crystal structure of orthorhombic polyethylene.

(2) HDPE-h_4. The R factor was 19.1% for 17 reflections. Atomic fractional coordinates and temperature factors are given in Table 3. Structure factors are listed in Table 4. The molecular geometry is C−C = 1.527 ± 0.089 Å, C−H_1 = 1.107 ± 0.201 Å, C−H_2 = 1.103 ± 0.319 Å, C−C−C = 112.9° ± 8.1°, and H_1−C−H_2 = 107.2° ± 32.9°. The setting angle is 45.4° ± 11.8°. Since the total number of observed reflections is smaller and the incoherent background is higher for HDPE-h_4 than

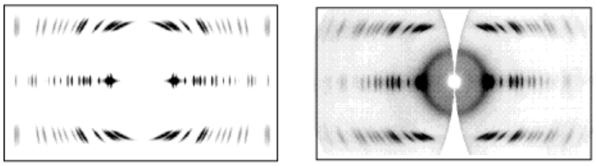
Table 3. Atomic Fractional Coordinates and Temperature Factors of HDPE-h_4 Obtained from WAND Data Analysis

atom	x/a	y/b	z/c	B_{iso}/A^2
C	0.460 ± 0.012	0.560 ± 0.018	0.25	4.700 (fix)
H_1	0.490 ± 0.023	0.780 ± 0.038	0.25	6.818 ± 5.368
H_2	0.312 ± 0.023	0.539 ± 0.041	0.25	6.322 ± 4.805

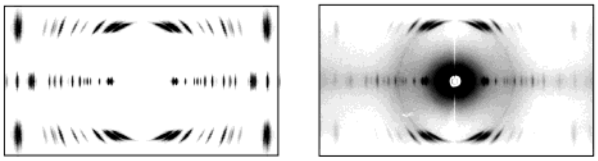
Table 4. WAND Structure Factors of HDPE-h_4 Sample

hkl	*F*(obsd)	*F*(calcd)
110	69.5	79.6
200	68.2	50.4
020	67.3	46.0
310	107.5	102.9
220	96.2	113.7
320	−38.0	−43.2
410	−20.2	−22.9
230	−32.5	−17.0
420	43.8	48.1
011	−37.5	−15.0
111	−32.2	−18.2
211	−19.4	−4.7
121	52.4	54.0
311	59.0	59.0
401	74.1	53.9
321	49.7	51.7
421	58.3	56.9

(a) WAXD



(b) WAND (d4)



(c) WAND (h4)

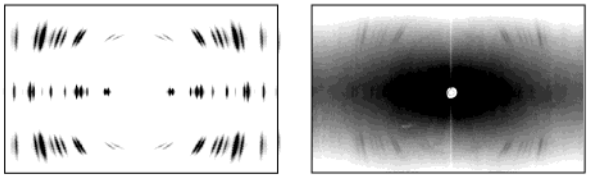


Figure 5. Comparison of (a) the X-ray diffraction pattern and (b and c) the neutron diffraction patterns of uniaxially oriented high-density polyethylene between the calculated (left) and observed patterns. The fully deuterated sample is used for b and the hydrogeneous sample for c. The WAXD pattern was observed with a flat imaging plate and transferred to the cylindrical coordinate system.[19] The WAND patterns were taken with a cylindrical camera.

HDPE-d_4, the accuracy of the molecular geometry is lower in the case of HDPE-h_4.

The two-dimensional neutron diffraction patterns are calculated with Cerius^2 (version 4.6, Accelrys Inc.) by using the thus obtained atomic coordinates and are compared with the actually observed patterns as shown in Figure 5b and 5c for HDPE-d_4 and HDPE-h_4, respectively. The calculation condition was as follows: crystallite size $a = b = c = 200$ Å, lattice strain $a = b = c = 0.1\%$, and degree of chain orientation 3°. In Figure 5a the calculated and observed X-ray diffraction diagrams are also shown for reference. The simulated patterns are in good agreement with the observed ones for all three cases.

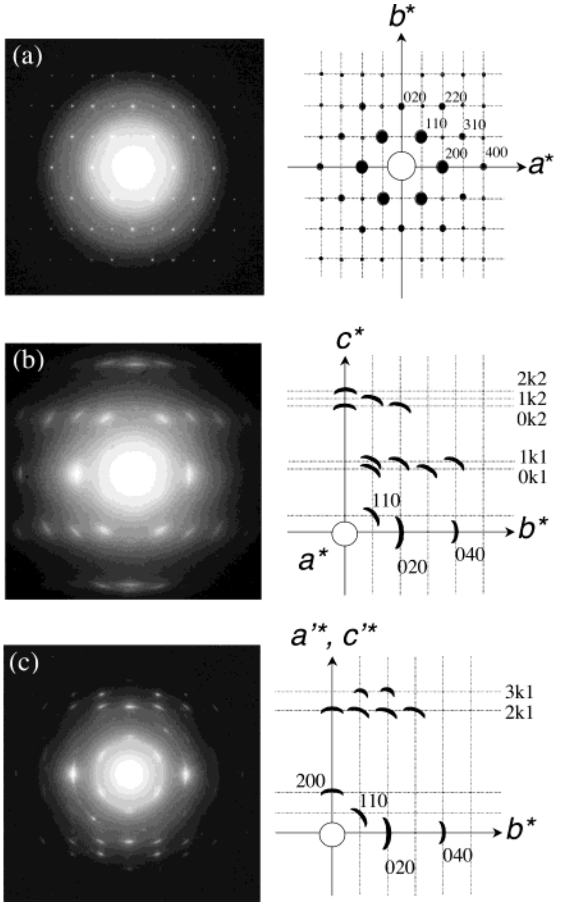


Figure 6. Electron diffraction patterns taken for polyethylene crystals: (a) *hk*0 reflections for a solution-grown single crystal, (b) *hk*1 and *hk*2 reflections for a sample epitaxially grown on a benzoic single-crystal substrate, and (c) 2*k*1 and 3*k*1 reflections for a sample which was melt-cooled on a KBr single-crystal substrate.

Structure Analysis by Electron Diffraction Data. Figure 6a shows the ED pattern taken for a PE single crystal with the electron beam incident along the normal to the crystal surface, from which the integrated intensities of the *hk*0 reflections were evaluated. Figure 6b shows the ED pattern for a PE crystal epitaxially grown on a benzoic acid crystal surface, from which a series of 0*kl*, 1*kl*, and 2*kl* reflections were observed. In Figure 6c is shown the ED pattern for a PE sample which was melt-cooled on a KBr substrate with the surface rubbed beforehand. In this case, the 2*kl* and 3*kl* reflections were detected. There were 45 reflections used for structure analysis. The unit cell parameters were $a = 7.46$ Å, $b = 4.98$ Å, and c (fiber axis) $= 2.55$ Å. By calculating the electrostatic potential map, the carbon and hydrogen atom positions were determined as shown in Figure 7. The structure was refined by least-squares method, where the (x, y) coordinates and isotropic temperature factors of both the carbon and hydrogen atoms were varied. (We did not introduce constraining conditions to fix the hydrogen-atom positions to fit the idealized geometry because we wanted to check the convergence of atomic positions after refinement.) The *R* factor was 17.6% for 45 reflections. The $F_o - F_c$ map was calculated by using the thus refined carbon-atom positions, as also

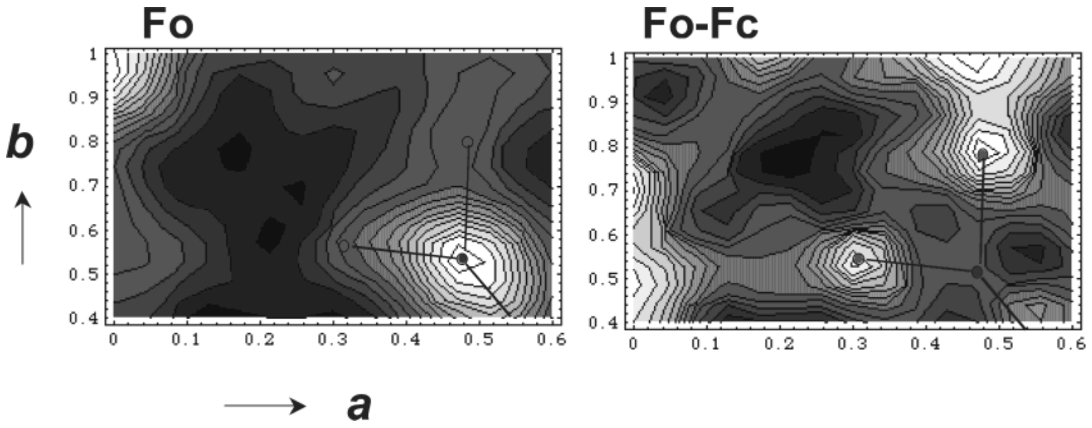


Figure 7. Electrostatic potential maps calculated for electron diffraction data taken for polyethylene single crystal.

Table 5. Atomic Fractional Coordinates and Temperature Factors of Polyethylene Crystal Obtained from Electron Diffraction Data Analysis

atom	x/a	y/b	z/c	B_{iso}/A^2
C	0.463 ± 0.002	0.559 ± 0.003	0.25	7.120 ± 0.679
H_1	0.491 ± 0.017	0.837 ± 0.022	0.25	15.14 ± 4.378
H_2	0.297 ± 0.014	0.530 ± 0.021	0.25	12.445 ± 3.849

Table 6. Structure Factors of Electron Diffraction for Polyethylene Single Crystal

hkl	F(obsd)	F(calcd)
002	−2.62	−4.08
011	5.05	10.01
020	8.17	9.19
031	2.89	5.68
040	0.94	0.28
110	16.63	26.74
120	−2.44	−4.36
130	2.49	4.21
140	−1.08	−1.39
141	1.17	4.51
150	−0.98	−0.86
200	14.40	17.93
201	4.96	9.31
210	−3.37	−5.63
211	3.91	8.64
220	4.61	5.22
221	2.19	5.10
230	−1.96	−3.86
231	1.80	5.01
241	0.53	0.08
250	−0.73	−0.82
310	5.23	7.88
311	3.54	7.95
320	−2.60	−4.98
330	1.27	1.47
331	0.87	1.35
340	−1.34	−2.09
341	0.93	2.23
400	3.80	5.83
410	−2.00	−3.60
420	1.65	1.93
430	−1.61	−3.12
441	−0.30	−0.13
450	−0.79	0.84
510	1.36	2.45
520	−1.60	−3.19
530	1.08	0.65
540	−0.87	−1.58
600	1.04	0.71
610	−1.12	−1.80
630	−1.01	−1.82
650	−0.59	−0.54
720	−0.83	−1.33
810	−0.61	−0.53
820	−0.66	−0.41

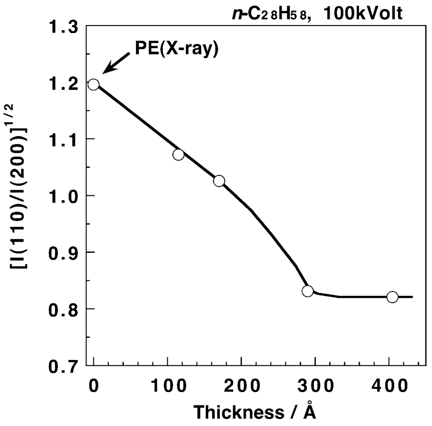


Figure 8. Variation of intensity ratio between the 110 and 200 reflections measured in the electron diffraction experiments for n-$C_{28}H_{58}$ single crystals with different thickness. The value at thickness 0 comes from the X-ray diffraction data as a kinematical limit in an approximation.

shown in Figure 7. The hydrogen-atom positions are detected clearly, as already pointed out by Ogawa et al.[25] Fractional coordinates and isotropic temperature factors of C and H atoms are listed in Table 5. Structure factors are given in Table 6. The molecular geometry is C−C = 1.506 ± 0.015 Å, $C-H_1$ = 1.404 ± 0.109 Å, $C-H_2$ = 1.247 ± 0.103 Å, C−C−C = 115.3° ± 1.4°, and H_1-C-H_2 = 105.2° ± 12.6°, and the setting angle of the zigzag chain is 44.0° ± 2.0°. For reference, the parameters analyzed by Dorset are C−C = 1.52 Å, C−C−C = 114.3°, and $B_{iso}(C) = 5.2$ Å^2 and the setting angle = 47°, where the hydrogen-atom positions were reset to the idealized positions after refinement cycles.[23−25] Similarly, the parameters reported by Ogawa et al.[25] are C−C = 1.51 Å and C−C−C = 115° and the setting angle = 46°.

The molecular parameters deduced from the ED data commonly are not very reasonable to these three independent analyses, although the total number of observed reflections was not very small. As Dorset discussed in detail[23] and as explained in the Introduction, this may come from the so-called multiple scattering effect in the single crystal: the electron beams diffracted on a set of crystal planes are reflected again on another different set of crystal planes and the scattering intensity is modified more or less from the kinematical limitation value. For example, Figure 8 shows variation of the intensity ratio of the 110 and 200 reflections taken for a series of n-$C_{28}H_{58}$ single crystals with different thickness, where the thickness was estimated by a shadowing method. As seen here, the intensity ratio between the 110 and 200 reflections changes remarkably depending on the sample thickness: the thick sample gave an intensity ratio almost opposite to that predicted for the kinematical limitation (the X-ray value in Figure 8). A similar situation was

Table 7. Comparison of Molecular Parameters of Polyethylene between WAND, WAXD, and ED

method	C−C[a]	C−C−C	C−H[d]	H−C−H	B_{iso}(C)	B_{iso}(H)	φ
WAND[b]	1.530(23)[c]	112.6(21)	1.102(45)	107.3(57)	4.19(83)	8.70(118)	42.4 (33)
WAXD	1.537 (8)	111.7 (7)	1.100(fix)	108.1(fix)	4.73(80)	7.97(fix)	43.0 (1)
ED	1.506(10)	115.3(19)	1.323(10)	105.2(16)	7.12(68)	13.8(41)	44.0 (1)

[a] Units: [C−C, C−H] Å, [C−C−C, H−C−H, *f*] degree, [B_{iso}] Å^2. [b] WAND: for deuterated polyethylene sample. [c] The parentheses indicate the standard deviation. For example, 1.538 (38) means 1.538 ± 0.038 Å. [d] The averaged value between C−H_1 and C−H_2.

already pointed out by Dorset.[23] Figure 8 suggests using as thin of a single crystal as possible to escape from the multiple scattering effect. In other words, even when an appreciably large number of accurately observed reflections is utilized in the structure analysis, the result might be different depending on the sample thickness of the single crystal used in the ED experiment as long as the analysis is made on the basis of the kinematical theory. Therefore, it is difficult as a general tendency to obtain stereochemically reasonable geometrical parameters when we use PE single crystals of relatively large thickness, which are grown under normal conditions.

Comparison of Structural Data among WAND, WAXD, and ED. Table 7 shows the structural parameters of orthorhombic PE crystal, which were obtained by the different kinds of diffraction data: WAND (for deuterated sample), WAXD, and ED. Analysis of WAXD and WAND data gave almost the same values for the structure parameters, although the standard deviations indicated in parentheses are larger for WAND than WAXD because of smaller number of the observed reflections in the former case. However, as for the hydrogen-atom positions, the large number of observed reflections does not necessarily give a chemically reasonable geometry, although the standard error may be smaller. In fact, despite the large number of observed reflections compared with the total number of variables, structure analysis based on WAXD data could not give us the reasonably converged hydrogen-atom positions, which had to be fixed to the theoretical positions determined by the conditions of C−H = 1.1 Å and H−C−H = 108.1°.[19,22] This situation was not limited to the present orthorhombic PE case. In the WAXD analysis, in general, the position of hydrogen atoms is quite difficult to determine even for the single crystals of low-molecular-weight compounds giving 5000−6000 reflections. In the WAND analysis, on the other hand, the positions of hydrogen atoms were extracted clearly and reasonable molecular parameters were obtained even when the hydrogen-atom positions were varied in the least-squares refinement. The ED data also gave the hydrogen-atom positions, as seen in the $F_o - F_c$ map of Figure 7, but the refined molecular parameters were not reasonable to a greater or less extent, although the total number of observed reflections was much larger than the WAND data. Of course, we should not misunderstand that the ED method is not useful for determination of hydrogen-atom positions. As pointed out in many times in this paper, the most serious problem in ED analysis is how to escape from the multiple scattering effect which modifies the relative intensity of reflections from the values expected for kinematical theory (see Figure 8). Since the observed reflections are many in number and sharp in their shape, ED analysis may give us quite reasonable structure information when various considerations are made properly: to use the dynamical scattering theory, to increase the accelerating voltage, to decrease the sample thickness, etc., all of which are mainly for reducing the multiple scattering effect.[23]

In the present paper the authors wish to emphasize the usefulness of WAND data for the extraction of hydrogen-atom positions in polymer crystals, which had not been discussed in a quantitative manner. However, we must not say, of course, that only the WAND technique is powerful for structure analysis of polymer crystal. As seen above, the standard deviations of the geometrical parameters are not very small compared with those by WAXD and ED. WAXD is the most convenient technique to collect large numbers of reflections, which can be used for kinematical structure analysis. However, unfortunately, the polymer sample gives the data of small number of broad reflections except for some special cases of large single crystals.[2−5] In this regard, ED is great for collecting many sharp reflections from a single crystal, but the multiple scattering effect gives us various problems in the convenient structure analysis. Therefore, the best way to obtain accurate and reasonable structure information for all constituent atoms in the polymer crystal lattice may be an organized combination of these three types of techniques, WAXD, ED, and WAND. (As another method to evaluate the C−H (C−D) distance and HCH bond angle, one of the reviews suggested performing neutron-based pair distribution analysis of very high scattering angle data. At sufficiently high momentum transfer the major residual contribution to the oscillatory portions of the scattering function would be dominated by the H···H, C···C, and C···H (C···D) pair correlations. Therefore, one could achieve a good measure of the C−H (C−D) pair distances if the C−C distance is well known.)

The thus-collected information about the three-dimensional coordinates of all the atoms included in the crystal lattice is useful for various purposes. One typical example is given here. We often want to predict the crystal structure of a polymer by performing a potential-energy calculation. Good choice of potential function parameters is quite important in such a calculation. As discussed in a previous paper,[45] we modified the potential function parameters proposed for PE crystal by Karasawa et al.[46] so that the crystal structure parameters and vibrational data[36] measured at 4 K were reproduced satisfactorily. Using this potential function set we performed the molecular dynamics calculation of PE crystal at 300 K.[45] The structure parameters, which were averaged over a long calculation time range, were estimated as follows: a = 7.26 Å, b = 4.83 Å, c (fiber axis) = 2.53 Å, setting angle of the zigzag chain = 43.7°, isotropic temperature factors $B_{iso}(C) = 3.4$ Å^2 and $B_{iso}(H) = 5.1$ Å^2, molecular geometry C−C = 1.50 Å, C−H = 1.04 Å, C−C−C = 115.4°, H−C−H = 106.1°, and C−C−C−C = 180.0°. Compared with the observed data shown in Table 7, the molecular dynamics calculations are not bad as a whole but the potential function parameters need to be modified further to satisfactorily reproduce the data observed at room temperature or the temperature dependence of the structure parameters. In this way, the refined structure information shown in Table 7 is important and useful for the various problems in the discussion of the structure and physical properties of PE crystal.

Conclusions

In the present paper we analyzed the WAND data taken for the uniaxially oriented deuterated and hydrogeneous PE samples by utilizing the BIX-3 system equipped with an imaging plate detector. When the thus-analyzed structure information is compared with those obtained by WAXD and ED analyses, the structure data by the WAND method seems to be accurate concerning the positions of hydrogen atoms as well as carbon atoms, although the standard deviations are not low enough due to the small number of observed reflections. By changing the wavelength of the incident neutron beam from 1.51 Å to a shorter one, for example, the number of observable reflections should be increased, making the standard deviations much lower. It must be noted here that our previous WAXD data collected by an imaging plate system was not bad or rather excellent in such a meaning that even the hydrogen-atom positions could be extracted.[19,22] Unfortunately, however, the final refinement of the hydrogen-atom positions could not be made successfully. A similar situation is seen also for the ED data. Because of the multiple scattering effect in the single crystal, the intensity data are more or less modified, resulting in the unreasonable stereochemical structure despite the successful collection of so many of sharp reflections. The WAND data collected for hydrogenous PE sample (HDPE-h_4) gave us the positions of hydrogen atoms, though the peak heights were negative. In regard we might use a nondeuterated (or hydrogeneous) polymer sample for the structure analysis to determine hydrogen atom positions in the crystal lattice. However, as shown in the previous section, the background originating from the incoherent scattering makes evaluation of the coherent reflections quite difficult (see Figure 5). In addition, the total number of observable reflections should be reduced appreciably, as actually exemplified in the present paper. Although a fully deuterated polymer sample is difficult to prepare, the usefulness of this sample is clear as discussed here. We are now being challenged to the analysis of the crystal structures of various kinds of deuterated semicrystalline polymer samples on the basis of WAND experiments with the two-dimensional NIP system.

References and Notes

(1) Tashiro, K. *Prog. Polym. Sci.* **1993**, *18*, 377.
(2) Enkelmann, V. *Adv. Polym. Sci.* **1984**, *63*, 91.
(3) Tashiro, K.; Nishimura, H.; Kobayashi, M. *Macromolecules* **1996**, *29*, 8188.
(4) Matsumoto, A.; Yokoi, K.; Aoki, S.; Tashiro, K.; Kamae, T.; Kobayashi, M. *Macromolecules* **1998**, *31*, 2129.
(5) Tashiro, K.; Zadorin, A. N.; Saragai, S.; Kamae, T.; Matsumoto, A.; Yokoi, K.; Aoki, A. *Macromolecules* **1999**, *32*, 7946.
(6) Bunn, C. W. *Trans. Faraday Soc.* **1939**, *35*, 482.
(7) Kilian, H. G. *Kolloid-Z. Z. Polym.* **1962**, *185*, 13.
(8) Swan, P. R. *J. Polym. Sci.* **1962**, *56*, 403.
(9) Kasai, N.; Kakudo, M. *Rep. Prog. Polym. Phys. Jpn.* **1968**, *11*, 145.
(10) Aoki, Y.; Chiba, A.; Kaneko, M. *J. Phys. Soc. Jpn.* **1969**, *27*, 1579.
(11) Kavesh, S.; Schultz, J. M. *J. Polym. Sci., Part A-2* **1970**, *8*, 243.
(12) Iohara, K.; Imada, K.; Takayanagi, M. *Polym. J.* **1972**, *3*, 357.
(13) Kawaguchi, A.; Ohara, M.; Kobayashi, K. *J. Macromol. Sci., Phys.* **1979**, *B16*, 193.
(14) Chatani, Y.; Ueda, Y.; Tadokoro, H. *Rep. Prog. Polym. Phys. Jpn.* **1977**, *20*, 179.
(15) Tadokoro, H. *Fiber Diffraction Methods;* French, A. D., Gardner, K. H., Eds.; ACS Symposium Series 141; American Chemical Society: Washington, D.C., 1980; p. 43.
(16) Phillips, P. J.; Tseng, H. T. *Polymer* **1985**, *26*, 650.
(17) Schauer, K.; Wilke, W. *Polym. Bull.* **1995**, *34*, 477.
(18) Busing, W. R. *Macromolecules* **1990**, *23*, 4608.
(19) Tashiro, K.; Asanaga, H.; Ishino, K.; Tazaki, R.; Kobayashi, M. *J. Polym. Sci.: Part B: Polym. Phys.* **1997**, *35*, 1667.
(20) For example, see: Giacovazzo, C. *Direct Methods in Crystallography*; Academic Press: New York, xxxx.
(21) Dorset, D. L. *Polymer* **1997**, *38*, 247.
(22) Tashiro, K.; Ishino, K.; Ohta, T. *Polymer* **1999**, *40*, 3469.
(23) Dorset, D. L. *Structural Electron Crystallography*; Plenum Press: New York, 1995.
(24) Dorset, D. L. *Macromolecules* **1991**, *14*, 1175.
(25) Ogawa, T.; Moriguchi, S.; Isoda, S.; Kobayashi, T. *Polymer* **1994**, *35*, 1132.
(26) Vainshtein, B. K.; Pinsker, Z. G. *Dokl. Akad. Nauk SSSR* **1950**, *72*, 53.
(27) Drset, D. L. *Acta Crystallogr.* **1976**, *A32*, 207.
(28) Hu, H.; Dorset, D. L. *Acta Crystallogr.* **1989**, *B45*, 283.
(29) Wilson, C. C. *Single-Crystal Neutron Diffraction from Molecular Materials*; World Scientific: New York, 2000.
(30) Stamm, M.; Fischer, E. W.; Dettenmaier, M.; Convert, P. *Faraday Discuss.* **1979**, *68*, 263.
(31) Johnson, J. A.; Saboungi, M.-L.; Price, D. L.; Ansell, S.; Russell, T. P.; Halley, J. W.; Nielsen, B. *J. Chem. Phys.* **1998**, *109*, 7005.
(32) Takahashi, Y. *Macromolecules* **1998**, *31*, 3868.
(33) Takahashi, Y. *Macromolecules* **1999**, *32*, 4010.
(34) Takahashi, Y. *Macromolecules* **2001**, *34*, 2012.
(35) Takahashi, Y. *Macromolecules* **2002**, *35*, 3942.
(36) Avitabile, G.; Napolitano, R.; Pirozzi, B.; Rouse, K. D.; Thomas, M. W.; Willis, B. T. M. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 351.
(37) Langan, P.; Nishiyama, Y.; Chanzy, H. *J. Am. Chem. Soc.* **1999**, *121*, 9940.
(38) Niimura, N.; Karasawa, Y.; Tanaka, I.; Miyahara, J.; Akahashi, K.; Saito, H.; Koizumi, S.; Hidaka, M. *Nucl. Instrum. Methods* **1994**, *A349*, 521.
(39) Tanaka, I.; Kurihara, K.; Chatake, T.; Niimura, N. *J. Appl. Crystallogr.* **2002**, *35*, 34.
(40) Niimura, N.; Chatake, T.; Ostermann, A.; Kurihara, K.; Tanaka, I. *Z. Kristallogr.* **2003**, *218*, 96.
(41) Wittmann, J. C.; Lotz, B. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1837.
(42) Wittmann, J. C.; Hodge, A. M.; Lotz, B. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 2495.
(43) Wittmann, J. C.; Lotz, B. In *Electron Crystallography of Organic Molecules*; Fryer, J. R., Dorset, D. L., Eds.; Kluwer Academic Publishers: The Netherlands, 1990; p 241.
(44) Tashiro, K.; Kamae, T.; Asanaga, H.; Oikawa, T. *Macromolecules* **2004**, *37*, 826.
(45) Tashiro, K. *Comp. Theor. Polym. Sci.* **2001**, *11*, 357.
(46) Karasawa, N.; Dasgupta, S.; Goddard, W. A., III. *J. Phys. Chem.* **1991**, *95*, 2260.

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