Neutron Structure Analysis of Polyethylene-d_4

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ABSTRACT: The neutron structure analysis of polyethylene-d_4 was carried out for the data (equator) measured at 10, 100, 200, and 300 K by using the rigid body least-squares method, where the translational and librational displacements of the molecular chain were estimated by using the rigid body temperature factor reported by Pawley. The lattice parameters, *a* and *b*, were also estimated by the least-squares method. The φ-value, the azimuthal angle of the molecular plane with respect to the *b*-axis, was estimated as 45° within the accuracy of the standard deviation 1°, independent of temperature. From the translational and librational displacements at 10 K, the static disorder of polyethylene was concluded to be mainly of the translational displacements.

Introduction

The crystal structure of polyethylene was reported by Bunn in 1939.[1] Since then, much work has been done on polyethylene. During this work, the accurate crystal structure and the accurate angle φ (the azimuthal angle of the molecular plane with respect to the *b*-axis) were required. By X-ray diffraction measurements, it is very difficult to determine accurately the crystal structure of polyethylene because of the small radius of the carbon atom and the small scattering length of the hydrogen atom. Neutron diffraction has the advantage that the hydrogen atom contributes to the diffraction intensity stronger than X-ray diffraction.[2−4] Furthermore, the scattering lengths in the neutron diffraction do not depend on the Bragg angle θ. The reflections with large θ values can be observed, and the intensities can be measured accurately. Accordingly, it is possible to determine the accurate crystal structure. On the other hand, the librational motion of the polymer having the long chain structure is an interesting problem. In the previous paper,[5] the librational motion of poly(oxymethylene) was estimated. In the case of polyethylene, the librational motion can be estimated by using neutron diffraction because of the large contribution to the diffraction intensity of the hydrogen atoms having the large radius.

In the present study, the neutron structure analysis of polyethylene-d_4, in which deuterium (scattering length: 6.67) has a scattering length larger than that of hydrogen (scattering length: −3.74), is carried out on the basis of the rigid body postulate. And the rigid body temperature factor of the molecule is estimated and discussed.

Experimental Section

The commercially supplied sample of polyethylene-d_4 (M_w = 91 000, M_n = 37 000), linear high-density polyethylene, was used. The film was made by a hot-press and stretched in boiling water. The films were stacked, and the sample with size 15 × 10 × 20 mm^3 was prepared. The orientation and crystallinity of the sample were examined by X-ray diffraction.

Neutron diffraction experiments were carried out by TAS-2 and HRPD spectrometers equipped on JRR-3M installed at the Japan Atomic Energy Research Institute (JAERI). Intensity distributions on the equator were measured at 10, 100, 200, and 300 K by using λ = 1.823 Å. The ranges of measurements by TAS-2 and HRPD were $2\theta < 100°$ and $2\theta < 150°$, respectively. As the intensity data, the integrated reflection intensities of $2\theta < 100°$ measured by TAS-2 and of $100° < 2\theta < 150°$ measured by HRPD were adopted. Here, the smoothing of the intensity distributions measured by HRPD are made according to the previous work.[2] The numbers of the observed reflections were 17, 17, 17, and 18 for 10, 100, 200, and 300 K, respectively. In Figure 1, the intensity distribution of the equator measured by TAS-2 at 10 K is shown.

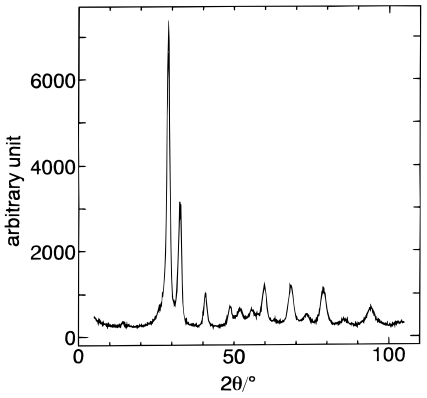

Figure 1. Intensity distribution on the equator of polyethylene-d_4 measured by TAS-2 at 10 K.

Table 1. Unit Cell Dimensions *a* and *b*

	10 K	100 K	200 K	300 K
a/Å	7.120 (0.006)	7.162 (0.004)	7.258 (0.004)	7.417 (0.006)
b/Å	4.842 (0.005)	4.863 (0.004)	4.898 (0.003)	4.939 (0.005)

[a] The standard deviations are shown in parentheses.

Results and Discussion

Unit Cell Dimensions. The accurate unit cell dimensions, *a* and *b*, were estimated by the least-squares method, where only the independent reflections were used. *a* and *b*, are given in Table 1 along with the standard deviations, and the temperature dependences of the unit cell dimensions are shown in Figure 2. The values above 100 K correspond well to the values reported by Swan.[6] The values at 10 and 100 K correspond well to the values at 4 and 90 K reported by Avitabile et al.,[3] respectively. The temperature dependence of *a* is larger than that of *b*.

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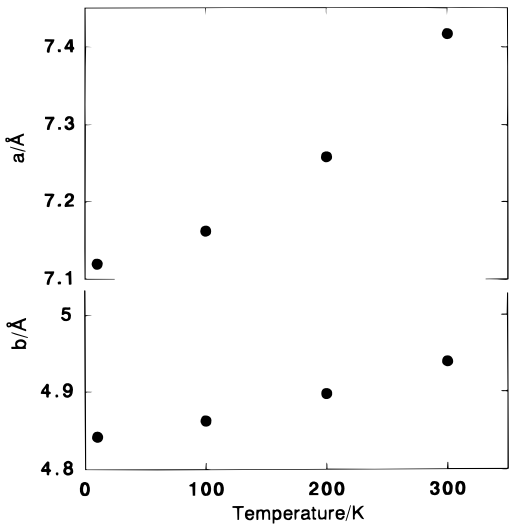

Figure 2. Temperature dependences of the cell dimensions *a* and *b*.

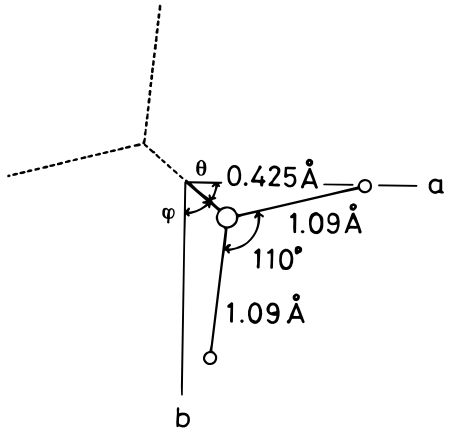

Figure 3. Molecular framework of polyethylene-d_4 on the *c*-projection.

Rigid Body Least-Squares Refinements. The rigid body least-squares method was first reported by Scheringer,[7] in which well-defined groups of atoms within the structure are treated as rigid bodies. Thereafter, Pawley[8] reported the rigid body temperature factor as follows:

$$\mathrm{T} = \exp\{-\mathbf{h}\cdot\mathbf{A}^{-1}\cdot(\mathbf{T} + \mathbf{V}_i\cdot\boldsymbol{\omega}\cdot\tilde{\mathbf{V}}_i)\cdot\tilde{\mathbf{A}}^{-1}\cdot\tilde{\mathbf{h}}\}$$

$$\mathbf{V}_i = \begin{bmatrix} 0 & -(Z_i - \zeta) & (Y_i - \eta) \\ -(Z_i - \zeta) & 0 & -(X_i - \xi) \\ (Y_i - \eta) & -(X_i - \xi) & 0 \end{bmatrix}$$

where **h** is the reflection indices, **A** is the transformation matrix from the fractional coordinates $\mathbf{x}_i$ to the orthogonal coordinates $\mathbf{X}_i$, **T** is the mean-square translational tensor, $\boldsymbol{\omega}$ is the mean-square rotational tensor, and (ξ, η, ζ) is the position of the center of gravity of the molecule.

Polyethylene assumes the planar zigzag conformation. On the projection through the fiber axis, the molecule assumes the structure shown in Figure 3. The molecular orientation in the unit cell can be defined by the angle θ, i.e., the complement of the angle φ. In the mean-square translational tensor **T**, the elements, T_{11}, T_{22}, and T_{12}, are significant, and in the mean-square rotational tensor $\boldsymbol{\omega}$, ω_{33} is significant. Actually, the

Table 2. Variable Parameters Finally Obtained by the Rigid Body Least-Squares Refinements

	10 K	100 K	200 K	300 K
θ/deg	44.93 (0.83)	45.22 (0.81)	45.65 (0.95)	45.09 (1.29)
T_{aa}/Å^2	1.31 (0.40)	1.78 (0.38)	2.16 (0.42)	2.49 (0.42)
T_{ab}/Å^2	0.85 (0.42)	1.13 (0.37)	1.10 (0.45)	0.66 (0.53)
T_{bb}/Å^2	1.61 (0.45)	1.91 (0.41)	2.41 (0.48)	2.43 (0.47)
ω_{33}/rad^2	0.30 (0.37)	0.48 (0.35)	0.63 (0.39)	1.04 (0.44)
R/%	11.7	10.1	10.9	13.3

[a] The standard deviations are shown in parentheses.

Table 3. Fractional Coordinates Finally Obtained

	x	*y*
	(a) 10 K	
C	0.042	0.062
D	0.193	0.023
D	0.016	0.284
	(b) 100 K	
C	0.042	0.062
D	0.192	0.024
D	0.015	0.283
	(c) 200 K	
C	0.041	0.062
D	0.189	0.026
D	0.013	0.282
	(d) 300 K	
C	0.040	0.061
D	0.185	0.023
D	0.015	0.278

constrained least-squares method[9] was used for the rigid body least-squares refinements by fixing the bond lengths and bond angles (Figure 3), where the rigid body temperature factor[8] was taken into consideration. Consequently, the variable parameters to be refined are the scale factor, the angle θ, the elements of the mean-square translational tensor, T_{aa}, T_{bb}, and T_{ab}, and the element of the mean-square rotational tensor ω_{33}. By the refinements, the *R* factors reduced to 11.7%, 10.1%, 10.9%, and 13.3% for the intensity data at 10, 100, 200, and 300 K, respectively. The parameters finally obtained are given in Table 2. The fractional coordinates are given in Table 3. In Table 4, the comparison between observed and calculated structure factors is given. The temperature dependence of the angle θ is given in Figure 4. The angle θ, the complement of the angle φ, is estimated as 45°, independent of temperature, within the accuracy of the standard deviation 1° (Table 2). This value of 45° corresponds well to the value reported by Stamm et al.[5]

Temperature Parameters. The elements in the mean-square translational tensor and the mean-square rotational tensor are related to the mean-square displacements by the following equations:

$$T_{ij} = 2\pi^2\langle u_{ij}^2\rangle$$

$$\omega_{33} = 2\pi^2\langle\omega^2\rangle$$

The temperature dependences of mean-square translational and librational displacements are shown in Figures 5 and 6, respectively. In Figure 5, the *aa* and *bb* elements of the translational displacement tensor are almost the same. This shows that the translational displacements on the *c*-projection are approximately represented by a circle, i.e., isotropic. The mean-square translational displacement at 10 K is about half that at 300 K (Figure 5), while the mean-square librational

Table 4. Comparison between the Observed and Calculated Structure Factors

(a) 10 K			(b) 100 K			(c) 200 K			(d) 300 K		
index	$\sqrt{I_o}$	$\sqrt{I_c}$	index	$\sqrt{I_o}$	$\sqrt{I_c}$	index	$\sqrt{I_o}$	$\sqrt{I_c}$	index	$\sqrt{I_o}$	$\sqrt{I_c}$
110	38.03	35.60	110	36.27	35.34	110	35.37	34.86	110	37.17	35.59
200	24.13	25.05	200	23.62	23.95	200	23.59	23.64	200	22.50	22.95
210	14.15	14.56	210	12.88	13.57	210	12.27	12.77	210	11.20	12.54
020	13.10	13.50	020	11.43	11.72	020	9.54	9.91	020	7.54	8.33
120	14.75	10.96	120	13.17	10.45	120	12.13	9.69	120	8.95	8.17
310	13.86	9.17	310	11.60	7.48	310	10.48	6.93	310	11.30	6.55
220	20.44	21.57	220	17.56	17.92	220	15.32	14.84	220	13.25	12.93
400	21.99	24.47	400	18.30	19.84	400	14.02	16.71	400	11.00	12.65
320 410	11.76	13.89	320 410	10.47	11.35	320 410	7.86	8.64	320 410	7.32	7.80
130	23.16	25.63	130	19.72	22.28	130	15.63	17.75	130	12.91	15.79
230	8.93	11.81	230	8.74	11.14	230	5.89	9.21	230	4.94	6.78
510	20.44	22.37	510	16.81	18.50	510	13.79	15.03	510	10.16	11.96
520 040 600 430 140	26.29	23.63	520 040 600 430 140	22.69	19.43	520 040 600 430 140	17.00	14.08	520 040 600 430 140	4.36 13.05	5.12 10.61
610 240	18.29	15.22	610 240	14.11	11.92	610 240	9.95	8.75	610 240	5.63	4.38
340 620 530	24.60	22.61	340 620 530	19.85	18.81	340 620 530	13.49	12.35	340 620 530	9.82	7.44
710 440	15.55	13.36	440 710	12.01	10.54	440 710	6.65	6.05	630 150	5.91	4.94
150 630	13.99	16.31	150 630	11.34	13.15	150 630	7.03	8.15	720 250 540	3.63	3.47

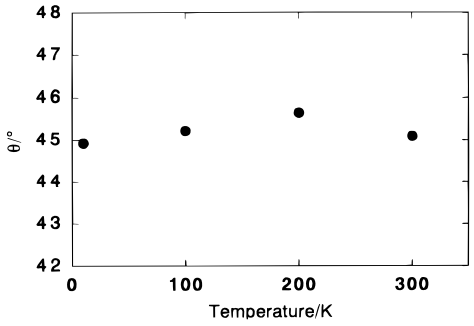

Figure 4. Temperature dependence of the angle θ, the azimuthal angle of the molecule with respect to the *a*-axis.

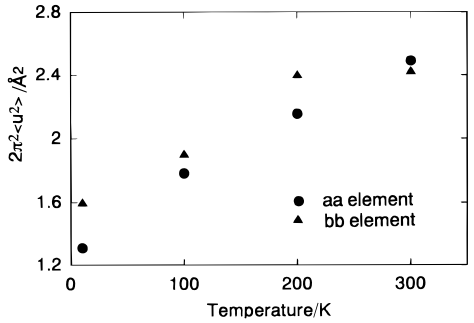

Figure 5. Temperature dependences of the translational displacements estimated by the rigid body temperature factor.

displacement at 10 K is about one-fourth that at 300 K (Figure 6). This suggests that the static disorder of polyethylene is mainly of the translational displacements. The root-mean-square amplitude $\langle\omega^2\rangle^{1/2}$ was estimated as 13.2° at 300 K, which corresponds well to the values of the carbon (15.8°) and oxygen (13.8°) atoms of poly(oxymethylene).[3] This may suggest that the librational motion of polymers having long chain structure is generally large. Cruickshank reported that the mean-square translational and librational motion can

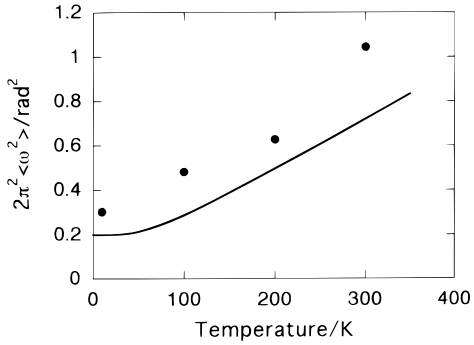

Figure 6. Temperature dependence of the librational displacement estimated by the rigid body temperature factor. The curve shows the calculated values.

be calculated by the Debye temperature and lattice vibrations.[10] The Debye temperature of polyethylene-d_4 is not known, but the optically active lattice vibrations are calculated by Tasumi and Shimanouchi.[11] The frequencies of two modes of librational motions, A_g and B_{3g}, are reported to be 134 and 109 cm^{-1}, respectively. The mean-square librational motion was estimated by the following equation:[10]

$$2\pi^2\langle\omega^2\rangle = \frac{h}{2I}\left\{\frac{1}{2\nu_1}\coth\left(\frac{h\nu_1}{2kT}\right) + \frac{1}{2\nu_2}\coth\left(\frac{h\nu_2}{2kT}\right)\right\}$$

where h is the Planck constant, I is the moment of inertia, ν_1 and ν_2 are the frequencies of the librational motions. The calculated curve is shown in Figure 6. The difference between the observed and calculated values shows the static disorder. The observed and calculated values are almost parallel. This suggests that the static librational disorder is independent of the temperature.

The difference between usual (protonated) polymer and deuterated polymer was discussed.[12,13] The crystal structure of polyethylene-d_4 is considered to be es-

sentially the same as that of the usual polyethylene, although the temperature factors are somewhat different from the usual polyethylene.

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