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Crystal Structure in the Near-Surface Region of Melt-Crystallized Polyethylene Films Investigated by Grazing Incidence X-ray Diffraction

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Crystal structure in the near-surface and bulk regions of melt-crystallized polyethylene (PE) films was investigated on the basis of laboratory-scaled and synchrotron-sourced grazing incidence X-ray diffraction measurements. We found for the first time that the *a* and *b* axial lengths of the orthorhombic unit cell in the in-plane direction of the PE films were shorter in the near-surface region than in the bulk region. This implied that crystal density in the near-surface region would be higher than that in the bulk region. Paracrystalline analysis for the (110) reflection and its higher-order ones revealed that paracrystalline lattice distortion in the in-plane direction was larger in the near-surface region than in the bulk region but crystallite size in the in-plane direction was almost the same between these regions.

Key words: polyethylene, surface crystal structure, in-plane grazing incidence X-ray diffraction measurement, paracrystalline lattice distortion

1. INTRODUCTION

Surface structural and physical properties of polymeric materials have been received a great deal of attention because they play important roles in surface functional properties. In general, molecular aggregation structure of crystalline polymers is influenced by various external conditions such as temperature, pressure and atmosphere during crystallization. Therefore, it is important to clarify the crystal structure, crystallinity and crystal orientation at the surface of crystalline polymers from the molecular level in consideration of various crystallization conditions. A grazing incidence X-ray diffraction (GIXD) measurement using the evanescent X-rays is one of powerful techniques to evaluate crystal structure in the material's surface.[1-7] Saraf et al. reported that chain ordering of solvent-free processed poly(pyromellitic dianhydride-oxydianiline) film was higher in the near-surface region by GIXD.[4] Durell and Wehrum et al. performed GIXD measurements for spin-coated poly(ethylene terephthalate) films during annealing. They reported preferential chain orientation in the near-surface region of the films.[7] However, the intrinsic properties on crystal structure at the surface of polymers have not been clarified yet. We briefly reported on our experimental results concerning crystal structure in the near-surface region of melt-crystallized polyethylene (PE) films.[8] In this study, crystal structure in the near-surface region of melt-crystallized PE films has been investigated in detail on the basis of laboratory-scaled and synchrotron-sourced GIXD measurements.

2. EXPERIMENTAL

2.1 Sample Preparation

A sample used in this study was a high-density polyethylene without additives (HDPE, Hizex1300J, MI = 14, Mitsui Chemicals, Inc.). Films were prepared from a 1.0 wt % *p*-xylene solution of the HDPE onto the crystallographic (110) plane of silicon substrates by the dip-coating method under N_2 atmosphere. At first, a silicon substrate was dipped into the HDPE solution heated at 373 K and then it was pulled out of the solution at a constant rate of ca. 25 mm / sec. The dip-coated films with a thickness of ca. 400 nm were melted on a hot stage at ca. 443 K for 10 min. Afterwards, the films were crystallized isothermally at various crystallization temperatures, T_c, from 373 K to 393 K for 24 h.

2.2 GIXD Measurements

Figure 1a and 1b show schematic geometry of in-plane and out-of-plane GIXD measurements, respectively. At a grazing angle of incident X-rays, α_i, equal to the critical angle, α_c, the X-rays undergo total external reflection on the sample surface and penetrate into a sample as evanescent waves. With a decrease in α_i smaller than the α_c, the penetration depth of evanescent X-rays from the surface decreases from several micrometers to several nanometers. Reflections from crystallographic planes perpendicular and parallel to the sample surface can be detected with a scintillation

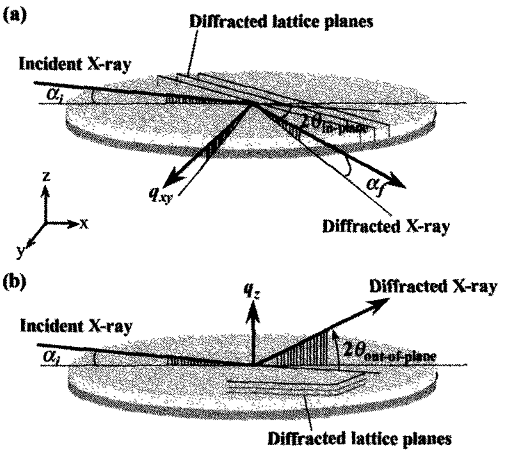

Figure 1 Schematic geometry of in-plane(a) and out-of-plane(b) GIXD measurements

counter scanned in the in-plane and out-of-plane directions, respectively. For the GIXD measurements on the laboratory scale, a graphite-monochromatic Cu-Kα radiation (the wavelength, $\lambda = 0.1542$ nm) was used as the incident beam, which was generated by a RU-300 X-ray generator (Rigaku Ltd., Co.) operated at 50 kV and 250 mA. The α_c of HDPE is ca. 0.15° for $\lambda = 0.1542$ nm. Therefore, crystal structure in the near-surface and bulk regions of the HDPE films was evaluated by GIXD measurements at $\alpha_i = 0.13°$ and 0.20°, respectively. A film on a silicon substrate was placed on a sample stage of a four-axis diffractometer (RINT in-plane goniometer, Rigaku Ltd., Co.). The beam size at incident slits was 2.00 and 0.05 mm in the normal and parallel directions to the ground, respectively. The data collection time was 300 s per step and the angular interval between steps was 0.02°.

In order to detect the higher-order reflections for precise structural analysis, in-plane GIXD measurements utilizing synchrotron radiation were carried out for the films with a six-axis diffractometer installed at a BL13XU beamline of SPring-8 (Japan Synchrotron Radiation Research Institute, Hyogo, Japan).[9] The monochromatized incident X-rays with the λ of 0.1285 nm and 0.1280 nm were used in this study. The beam size at incident slits was 0.10 and 0.06 mm in the normal and parallel directions to the ground, respectively. The α_c of HDPE is 0.1257° for $\lambda = 0.1285$ nm and 0.1253° for $\lambda = 0.1280$ nm. Therefore, surface-sensitive and bulk-sensitive profiles were obtained by GIXD measurements at 298 K at $\alpha_i = 0.11°$ and 0.20°, respectively. The data collection time was 3 s per step and the angular interval between steps was 0.05°. A sample cell purged with He gas was used to prevent HDPE films from oxidation. Broadening in the width of the profiles caused by angular divergence of the incident X-rays was negligibly small, as evaluated using reflections from silicon crystals. Data correction was performed with respect to the background scattering and the intensity decay of incident X-rays during measurements.

3.RESULTS AND DISCUSSION

Figure 2a and 2b show surface-sensitive and bulk-sensitive in-plane GIXD profiles measured for melt-crystallized HDPE films at $\alpha_i = 0.13°$ and 0.20° at the laboratory, respectively. $2\theta_{\text{in-plane}}$ is the scattering angle in the in-plane direction. No reflections in a higher $2\theta_{\text{in-plane}}$ range could be detected because of their weak intensity. The orthorhombic (110) and (200) reflections and the amorphous scattering were detected in a $2\theta_{\text{in-plane}}$ range from 15.0° to 26.0° for all the HDPE films. The relative intensity of these reflections was independent of the rotational angle of the film around the normal to the film surface. This indicated that the films were crystallographically isotropic in the in-plane direction. The relative intensity of the (110) and (200) reflections in the out-of-plane profile of each film was different from that in the in-plane profile. The (110) reflection was little detected. Therefore, it was found that the films were crystallographically anisotropic in the perpendicular direction to the film surface. This was due to such a thin film where lamellar crystals would grow two-dimensionally. The lattice constants *a* and *b* of orthorhombic unit cell were calculated from the $2\theta_{\text{in-plane}}$ angles of the peaks fitted with a linear combination of

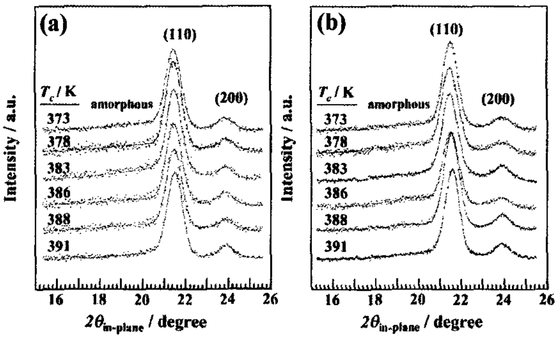

Figure 2 In-plane GIXD profiles measured at $\alpha_i = 0.13°$(a) and $\alpha_i = 0.20°$(b) at the laboratory for the HDPE films crystallized isothermally at various temperature from the melt. The λ of incident X-ray was 0.1542 nm.

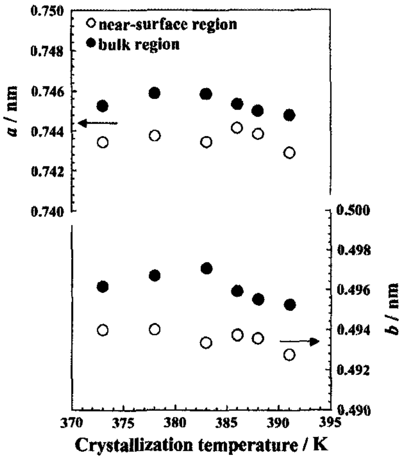

Figure 3 Crystallization temperature dependence the lattice constants *a* and *b* of the orthorhombic unit cell in the near-surface and bulk regions of the HDPE films evaluated by laboratory-scaled in-plane GIXD measurements. O: near-surface region and ●: bulk region.

Lorenzian and Gaussian functions to the (110) and (200) reflections. Figure 3 shows crystallization temperature dependence of the lattice constants *a* and *b* in the near-surface and bulk regions of the HDPE films. It was revealed that the *a* and *b* axial lengths in the near-surface region were shorter than those in the bulk region. Relative crystallite size estimated from the half-width of the peaks using Scherrer's equation was larger in the near-surface region in a T_c range lower than 386 K. However, this tendency reversed at T_c = 391 K. It is well known that the half-width of reflections reflects the degree of crystal lattice distortion as well as crystallite size. Therefore, these structural factors were independently evaluated on the basis of paracrystalline analysis for the higher-order reflections as explained in the latter section.

In order to investigate the detail of crystal structure in the near-surface region of melt-crystallized HDPE films, in-plane GIXD measurements were carried out for the films by utilizing synchrotron radiation as the X-ray source. Figure 4a and 4b show surface-sensitive and bulk-sensitive synchrotron-sourced in-plane GIXD profiles measured at α_i = 0.11° and 0.20° for the HDPE films, respectively. The scattering vector parallel to the sample surface, $q_{\text{in-plane}}$, was defined as $q_{\text{in-plane}} = 4\pi(\sin\theta_{\text{in-plane}}) / \lambda$. The higher-order reflections which could not be detected by the laboratory-scaled measurements were clearly observed as shown in Figure 4. Overlapping peaks were separated by the least squares fitting with Lorenzian and Gaussian functions. Each peak was assigned to the reflection from the orthorhombic crystal as shown by the solid line in Figure 4. Figure 5 shows the crystallization temperature dependence of the lattice constants *a*, *b* and *c* of the orthorhombic unit cell in the near-surface and bulk regions of the HDPE films. The lattice constants were determined using the $2\theta_{\text{in-plane}}$ angles of all the reflections. The *a* and *b* axial lengths were shorter in the near-surface region than in the bulk region, which was the same tendency as the axial lengths evaluated at the laboratory. On the other hand, the *c* axis was almost the same length in both the regions. Therefore, these results indicated that the dimension of crystal lattice in the near-surface region was smaller than that in the bulk region. In other words, the crystal density would be higher in the near-surface region.

The distortion of crystal lattice in the in-plane direction was estimated on the basis of the paracrystalline theory proposed by Hosemann.[10-12] In the paracrystalline lattice model, the lattice vectors of adjacent unit cells vary in magnitude and direction due to large displacement of lattice points from their ideal positions, which results in a loss of the long-range crystallographic order. Assuming that the coordination statistics distribution function for the paracrystalline lattice model is in the form of Gaussian distribution, paracrystalline lattice factor $Z(s)$ of the h-th order reflection is defined as

$$Z(s) = Z(h) = [1-\exp(-4\pi^2 g^2 h^2)] / [(1-\exp(-2\pi^2 g^2 h^2))^2 + (4\sin^2 2\pi h)\exp(-2\pi^2 g^2 h^2)] \qquad (1)$$

where s is the reciprocal lattice vector and g is the standard deviation of the Gaussian distribution divided by the average lattice vector, $\tilde{a}$. Thus, the g is a parameter to evaluate the degree of paracrystalline

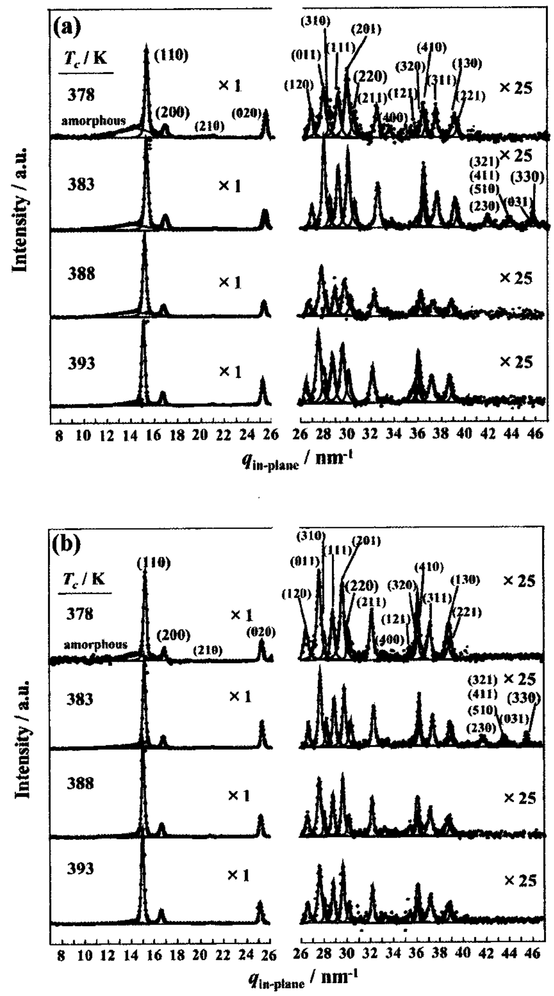

Figure 4 Synchrotron-sourced in-plane GIXD profiles measured at α_i = 0.11°(a) and α_i = 0.20°(b) for the HDPE films crystallized isothermally at various temperature from the melt. The λ of incident X-ray was 0.1285 nm and 0.1280 nm.

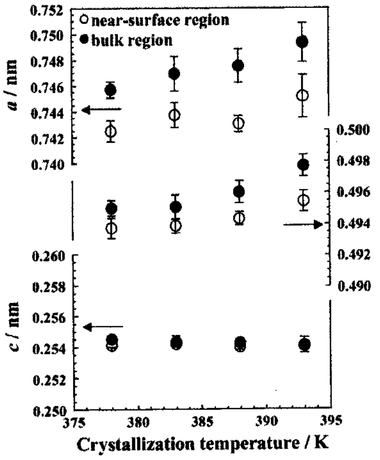

Figure 5 Crystallization temperature dependence the lattice constants *a*, *b* and *c* of the orthorhombic unit cell in the near-surface and bulk regions of the HDPE films evaluated by synchrotron-sourced in-plane GIXD measurements. ○: near-surface region and ●: bulk region.

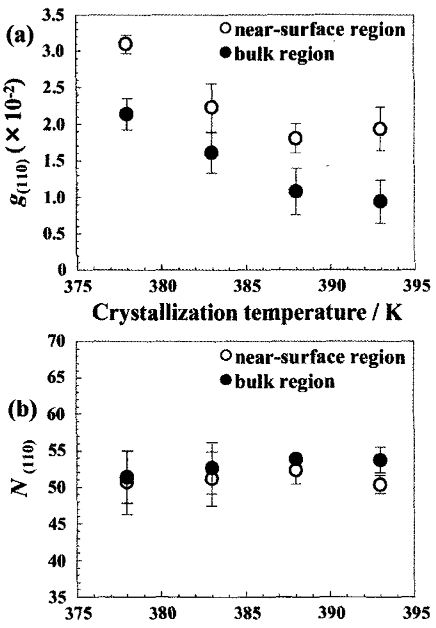

Figure 6 Crystallization temperature dependence the $g_{(110)}$(a) and $N_{(110)}$(b) in the near-surface and bulk regions of the HDPE films. ○: near-surface region and ●: bulk region

lattice disordering. The integral width of Gaussian peaks fitted to reflections, $\delta\beta$, is expressed by

$$(\delta\beta)^2 = (1 / \tilde{a}^2)[(1 / N^2) + \pi^4 g^4 h^4] \quad (2)$$

Here, h is the scattering order and N is the number of scattering units. For the (110) and its higher-order reflections, the $g_{(110)}$ and $N_{(110)}$ were calculated using the equation 2. Figure 6a and 6b show the crystallization temperature dependence of the $g_{(110)}$ and $N_{(110)}$ in the near-surface and bulk regions of the HDPE films, respectively. It was revealed that the $g_{(110)}$ in the near-surface region was larger than that in the bulk region in a T_c range from 378 K to 393 K. This indicated that the paracrystalline lattice distortion of the orthorhombic unit cell would be larger in the near-surface region than in the bulk region. On the other hand, the $N_{(110)}$ was almost the same magnitude between the near-surface and bulk regions. That is to say, crystallite size in the in-plane direction would be uniform in the films. These results implied that PE chains in the near-surface region were packed closer with large crystallographic disordering in comparison with ones in the bulk region. It was considered that chain packing structure specific for the surface would relate to surface free energy of the film, residual stress of the film induced by quenching from the melt, and thermal fluctuation at the surface during crystallization.

4. CONCLUSION

Crystal structure in the near-surface and bulk regions of melt-crystallized HDPE films was investigated by GIXD measurements at the laboratory and SPring-8. We experimentally and quantitatively found for the first time the difference in molecular aggregation structure between the near-surface and bulk regions of solid-state PE. From laboratory-scaled and synchrotron-sourced in-plane GIXD data, it was clarified that the dimension of orthorhombic crystal lattice in the in-plane direction was smaller in the near-surface region than in the bulk region. Moreover, paracrystalline analysis for the higher-order reflections indicated that paracrystalline lattice distortion in the in-plane direction was larger in the near-surface region than in the bulk region but crystallite size was almost the same between these regions. It was considered that these results would reflect intrinsic structural property at the solid-state free surface of crystalline polymers.

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