

Evaluation of crystalline polymer materials using a 2D-SAXS/WAXS system

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1. Introduction

In a crystal, atoms or molecules are arranged in a three-dimensional, repetitive pattern, and the properties of the crystal are determined by the chemical composition of the constituent atoms or molecules. The typical image of a crystal is a grain of a single crystal such as salt or alum, but many familiar materials, such as metals, ceramics, and crystalline polymers, are solids composed of microcrystals. These are called polycrystals, in contrast to single crystals. There are cases where the texture and crystallinity of the crystals constituting the material at larger scale are related to properties such as the strength and hardness of crystalline materials composed of a polycrystal.

Evaluation of crystalline polymer materials in powder X-ray diffraction is roughly divided into analysis of the small angle X-ray scattering (SAXS) region, corresponding to a long-period structure of about 1–100 nm, and analysis of the wide angle X-ray scattering (WAXS) region, corresponding to an atom-to-atom interval on the order of 0.1 nm (1 Å) (see Table 1). The fact that evaluation must be done by combining the SAXS and WAXS regions when considering the

structure and properties of crystalline polymer materials is a point of difference from the evaluation of inorganic materials.

Cases have been reported, including in this journal, where measurement in the WAXS region was carried out via scanning with a 2D detector^{(1)–(3)}, but there are no reports of exposure measurement using transmission. This paper presents examples of analyzing polypropylene (PP), polyethylene (PE), and polybutylene terephthalate (PBT) with measurements carried out using the SmartLab fully-automated multi-purpose X-ray diffractometer and the 2D-SAXS/WAXS transmission attachment.

2. Features of 2D-WAXS measurement

In wide angle X-ray scattering (WAXS), it is possible to obtain diffraction lines derived from atom-to-atom intervals on the order of 0.1 nm (1 Å). Other types of analysis can also be done, such as phase identification, quantitative analysis, crystallinity, crystallite size, and degree of orientation. The typical approach with general-purpose equipment is to measure data using the scanning method.

Table 1. Information obtained from powder X-ray diffraction and evaluation content.

	Information obtained from measurement data	Evaluation content
Wide angle	X-ray diffraction peak position, intensity	Crystal identification (qualitative analysis) Crystal structure
	X-ray diffraction peak width	Crystallite size Crystal perfection →Disturbance of molecules in crystal lattice →Disturbance of crystal lattice
	Attenuation of intensity at high-order diffraction angle (high scattering angle)	Size of molecule thermal oscillations
	Relationship between sample placement and direction where X-ray diffraction peak is obtained	Presence of texture, degree of texture (strength of texture), crystal orientation
	Intensity variation in sample tilt direction and in-plane direction (pole figure)	Crystal orientation, strength of texture
	Ratio of integrated intensity of amorphous halo and crystalline peak	Crystallinity
	Intensity distribution of amorphous halo	Radial distribution function (Amorphous structure analysis)
Small angle	Angle where long-period peak is obtained	Period of lamellar structure
	Relationship between sample placement and direction where long-period peak is obtained	Orientation of lamellar structure
	Spread of long-period peak	Disturbance of lamellar structure
	Center scattering width, intensity distribution	Grain diameter, hole diameter, and their size distribution

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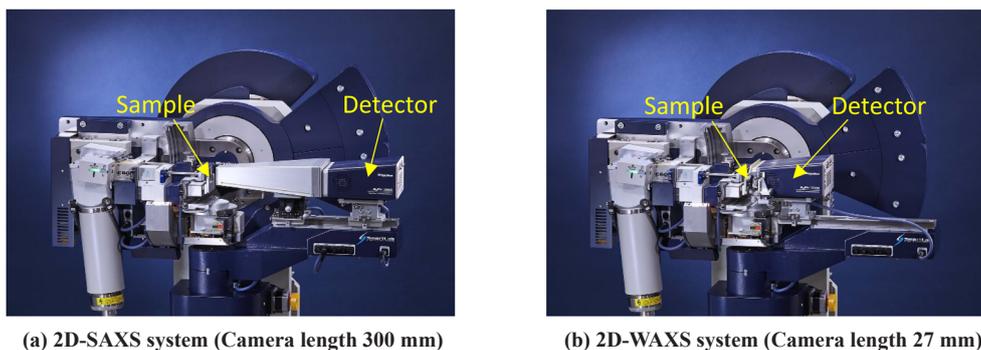


Fig. 1. SmartLab 2D-SAXS/WAXS system.

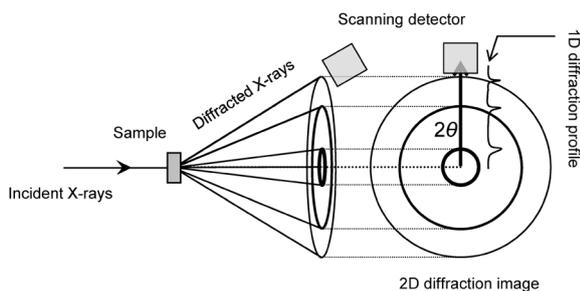


Fig. 2. Diffracted X-rays spreading out from sample, and counting of X-rays.

Figure 2 shows a schematic diagram of diffracted X-rays spreading out from the sample, and of X-ray counting. When the sample is irradiated with X-rays, the scattered X-rays and diffracted X-rays spread out as though tracing a cone shape with the sample at the vertex, and the X-ray intensity is counted via detector scanning or 2D imaging. 0D measurement is one method of counting diffraction intensity by scanning. In 0D measurement, intensity is counted so as to cut out part of the ring-shaped diffraction image corresponding to the base of the cone (known as Debye rings), and thus the information obtained in a single measurement is limited. In 2D measurement, on the other hand, the entire circumference of the Debye rings obtained for multiple diffraction angles via the transmission method is acquired at once. From the 2D diffraction image obtained in this way, it is possible to visually understand the molecules contained in the sample and their long-period texture. By analyzing the diffraction angles and widths obtained from the 2D image, it is possible to determine the direction and degree of orientation. In addition, since there is no scanning by the detector, the measurement time is short compared to 0D measurement. Figure 3 shows a 2D diffraction image of zeolite obtained with a 2D-WAXS measurement. When the longitudinal direction of the HyPix-3000 2D detector is placed horizontally, with a camera length of 27 mm it is possible to obtain a 2D diffraction image for $2\theta=6.5\text{--}55^\circ$ in the horizontal direction and $2\theta=6.5\text{--}35^\circ$ in the vertical direction at once.

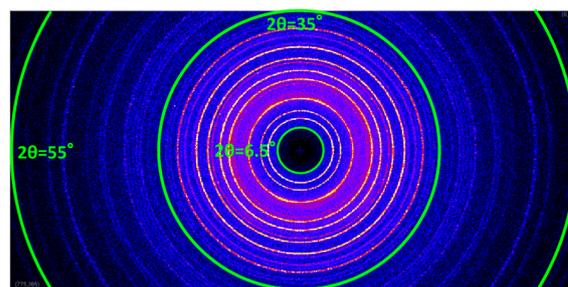


Fig. 3. 2D diffraction image for zeolite powder. Measurable angles: $2\theta=6.5\text{--}55^\circ$ (horizontal direction), $2\theta=6.5\text{--}35^\circ$ (vertical direction).

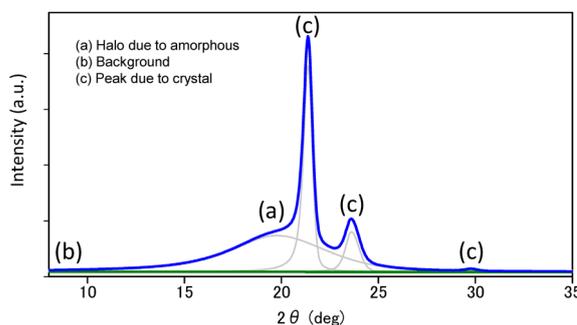


Fig. 4. Example of multiple peak separation of PE profile.

3. Crystallinity analysis in the WAXS region

In crystallinity analysis, the crystalline percentage is calculated for a material made up of crystalline and amorphous parts. The intensity of coherent scattering of X-rays is constant regardless of whether the substance is amorphous or crystalline. Crystallinity X_c is calculated by separating the multiple peaks into scattering due to the crystalline part (normally sharp peaks) and scattering due to the amorphous part (a broad halo), as shown in Fig. 4, and substituting each integrated intensity into the following equation⁽⁴⁾. In 0D measurement, the diffraction angle vs. X-ray intensity (2θ - I) profile is obtained through 2θ or $2\theta/\theta$ scanning.

$$X_c = \frac{I_c}{I_c + I_a} \times 100 \quad (1)$$

X_c : Crystallinity (%)

I_c : Scattering intensity due to crystalline part of material

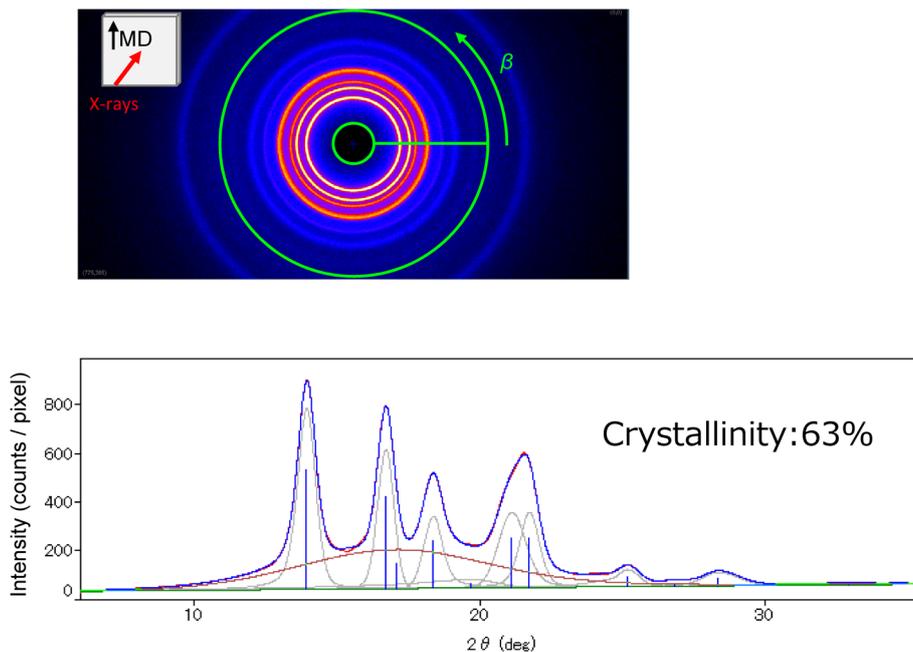


Fig. 5. Example of 2D diffraction image and crystallinity analysis of press molded PP.

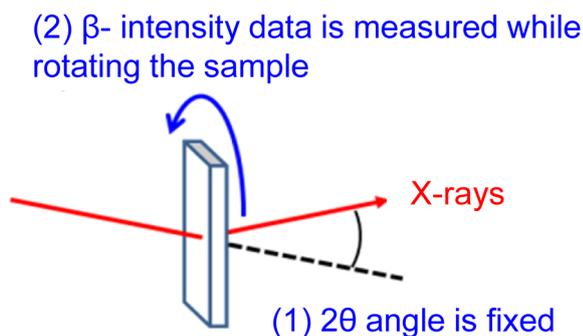


Fig. 6. Schematic diagram of measuring degree of orientation via 0D measurement.

I_a : Scattering intensity due to amorphous part of material

Figure 5 shows an example of a 2D diffraction image of press molded PP and analysis of its crystallinity.

Air scattering was measured under the same conditions as the sample and, taking transmittance into account, the β full-circumference part shown inside the red lines in the figure was converted to a $2\theta-I$ profile. In the $2\theta-I$ profile, scattering due to the crystalline part and scattering due to the amorphous part were obtained, and crystallinity was calculated through analysis using the peak separation method. By using the β full-circumference part of the diffraction image for 2θ conversion, an effect was obtained equivalent to 0D measurement while rotating the sample.

4. Analysis of orientation in the WAXS region

Analysis of polymer chains involves steps such as investigating the direction of orientation, and converting the degree of orientation to a numerical value. Figure 6 shows a schematic diagram of degree of orientation

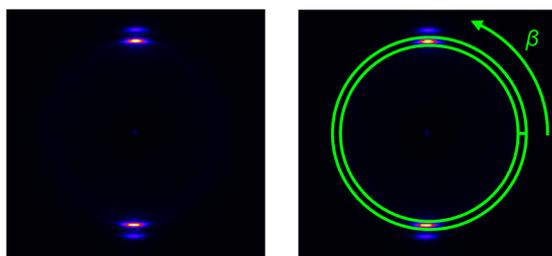
measurement via 0D measurement. In 0D measurement, the 2θ angle is fixed at the diffraction angle of a specific lattice plane and the diffraction intensity is measured while rotating the sample through 360° . This rotation angle vs. diffracted X-ray intensity ($\beta-I$) profile is used for the calculation of degree of orientation. Figure 7(a) shows a 2D diffraction image for PE fiber. When a 2D diffraction image is used for the analysis, the diffraction image of a specific crystal plane is converted to a $\beta-I$ profile. For PE110 in Fig. 7(a), the profile in Fig. 7(b) was obtained by converting the range indicated in green to a $\beta-I$ profile. The peak width of the $\beta-I$ profile reflects the degree of orientation, A , which is calculated from the following equation⁽⁵⁾. The degree of orientation of this PE fiber was 95%. The narrower the peak width, the higher the degree of texture.

$$A = \frac{360 - \sum w_i}{360} \times 100 \tag{2}$$

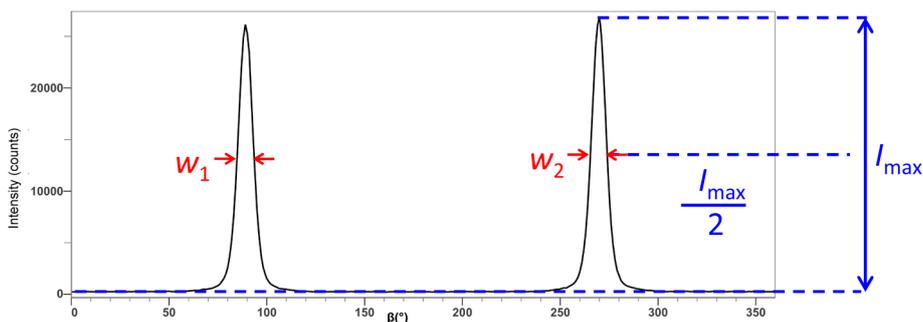
A : Degree of texture (%)

w_i : Full width at half maximum of peak, obtained as a result of intensity measurement

As an example where orientation has been analyzed, the following considers CPP (Cast Polypropylene) and OPP (Oriented Polypropylene), which are used as packaging materials. Figure 8 shows 2D diffraction images of the film part and side seal part of commercial OPP and CPP bags. The side seal parts are placed in the vertical directions of the diagram. In the 2D diffraction image for CPP, intensity in the circumferential direction is uniform for both the film part (Fig. 8(a)) and the seal part (Fig. 8(b)), but with OPP an intensity distribution is evident, and the PP molecules have orientation. In the side seal part of OPP (Fig. 8(c)), orientation is stronger than for the film part (Fig. 8(d)), and there is a change to



(a) 2D diffraction image of PE fiber



(b) β -I profile of PE110

Fig. 7. Method of analyzing degree of orientation based β -I profile.

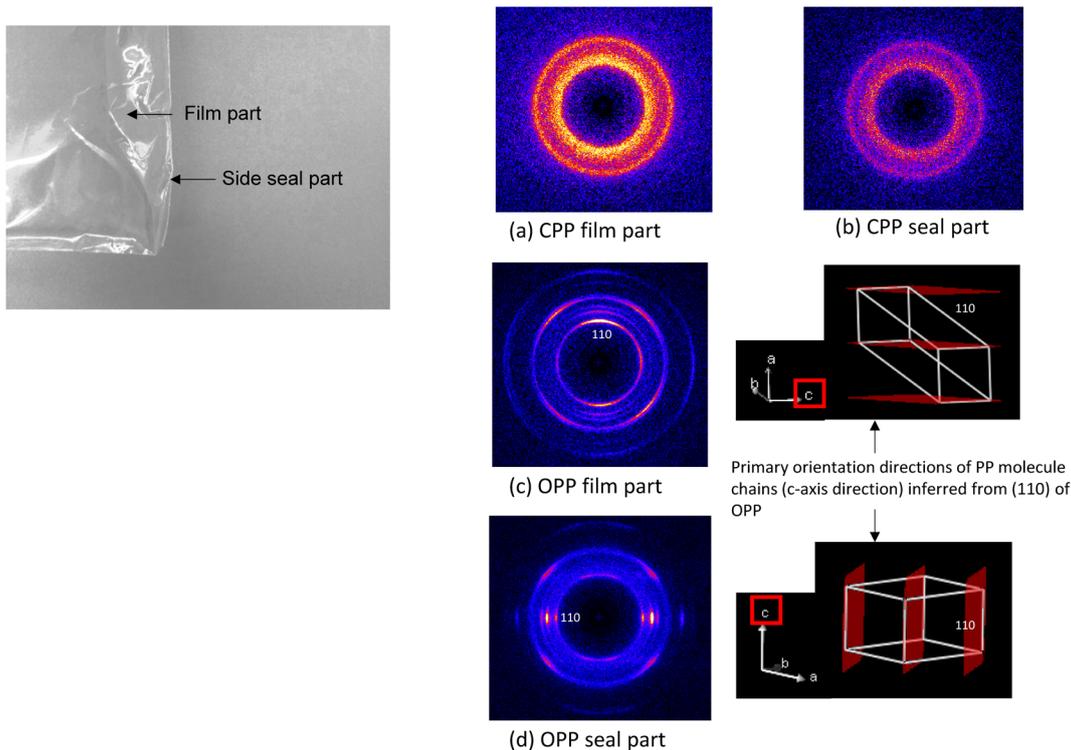


Fig. 8. 2D diffraction image and degree of orientation of OPP and CPP.

an orientation state similar to uniaxially stretched, where the PP molecule axes are almost parallel with the side seal part. OPP bags are also used for packaging leafy vegetables such as spinach. It is likely that this OPP bag is designed to be easy to tear to remove the contents by

aligning the molecular chains along the side seal part.

Figure 9 shows a PE bag with zipper, a 2D diffraction image obtained through mapping measurement, and a β -I profile for PE200. This bag has the problem that it tears parallel to the zipper at a location 5 mm from the

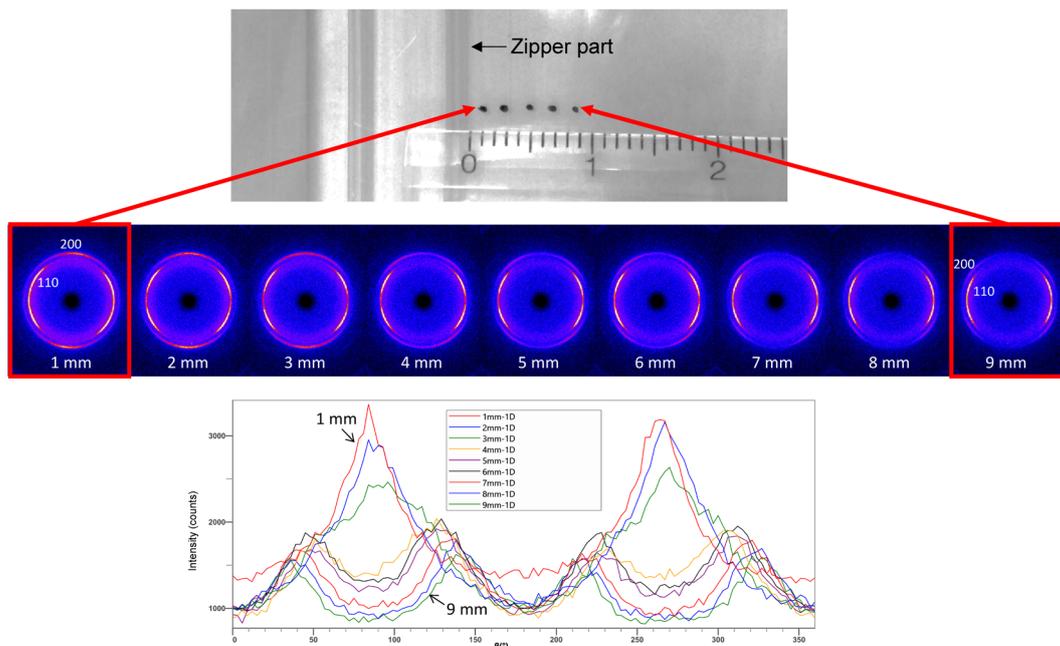


Fig. 9. 2D diffraction image of PE bag with zipper, obtained through mapping measurement, and β -I profile of PE200.

zipper part. As shown in the photo, the length direction of the zipper was placed in the vertical direction of the diagram, and automatic mapping measurement of the part 1–9 mm from the edge of the zipper was carried out at an interval of 1 mm. The 2D diffraction images originate in the 110 plane and 200 plane from the low-angle side, and both are planes parallel to the PE molecular chains. For the parts at 4–9 mm, it is evident that the diffraction images for the 2 planes gather in the horizontal direction of images, and the PE molecule chains have orientation nearly parallel to the zipper. It is conjectured that perhaps bags with zippers tear along the molecular chains as a result.

5. Features of 2D-SAXS

With the small angle X-ray scattering (SAXS) method, it is possible to analyze long periods and particle/hole diameters of roughly 1–100 nm. Just as for the WAXS region, there are both 0D measurements (0D-SAXS) and 2D measurements (2D-SAXS) in the SAXS region. To ensure understanding of the difference between the two measurement methods, the authors would like to first explain “line extraction” and “point extraction” of X-rays.

X-rays are produced when electrons generated from a long, thin filament strike a target material such as copper or cobalt. Extracting X-rays parallel to the longitudinal direction of this long, thin focal point is called line extraction, and extracting X-rays in the direction parallel to the shorter transverse direction is called point extraction. Figure 10 illustrates X-ray line extraction and point extraction. Line extraction of X-rays is used in general-purpose powder X-ray diffractometers for tasks such as qualitative and quantitative analysis.

Figure 11 shows schematic diagrams of the optical systems of 0D-SAXS and 2D-SAXS. In 0D-SAXS,

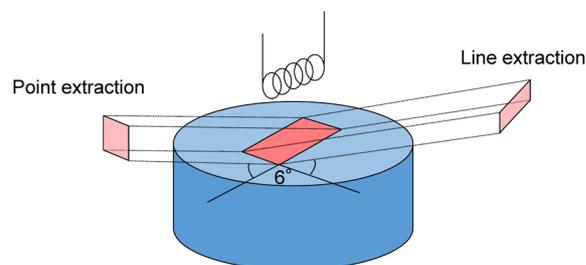


Fig. 10. X-ray “line extraction” and “point extraction.”

a line-shaped X-ray is combined with scanning using a detector. In general, it is possible to make the beam thinner at the sample position than point extraction, and thus angular resolution and low-angle resolution are high. On the other hand, the radii of the Debye rings where diffraction lines are drawn are small on the low-angle side, where 0D-SAXS information is obtained, and therefore the result is greatly affected by line-shaped X-rays, and peaks are not obtained at the correct angles reflecting the structure. This is called “smearing.” Figure 12 illustrates smearing when using line-shaped X-rays. With 0D-SAXS, analysis is performed while correcting distortion via software-based slit correction⁽⁴⁾. The 2D-SAXS method combines point-shaped X-rays obtained through point extraction and imaging using a 2D detector. From a 2D diffraction image obtained with 2D-SAXS, it is possible to visually understand the molecules contained in the sample and the orientation status of the long period. By analyzing the angle and width where the 2D diffraction image was obtained, it is possible to obtain the direction of orientation and the associated degree of orientation. In the past, it was typical for 2D-SAXS to be performed with special-purpose equipment for point extraction of X-rays, but

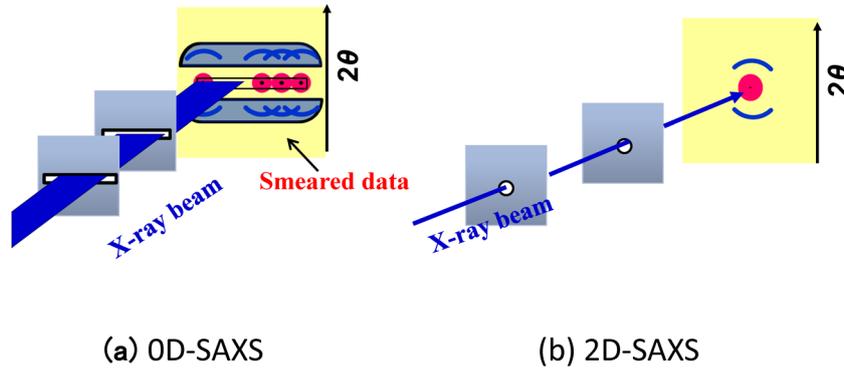


Fig. 11. Schematic diagram of optical systems of 0D-SAXS and 2D-SAXS.

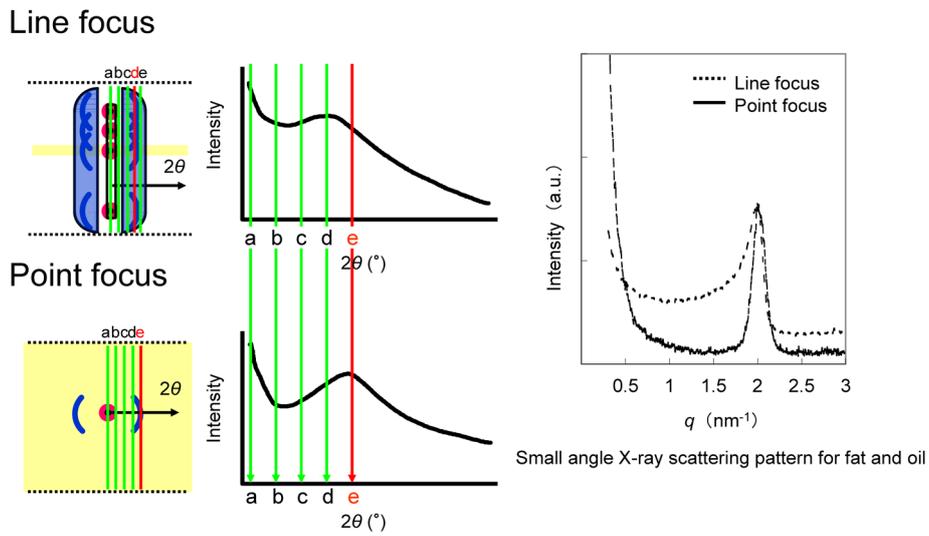


Fig. 12. Smearing in 0D-SAXS.

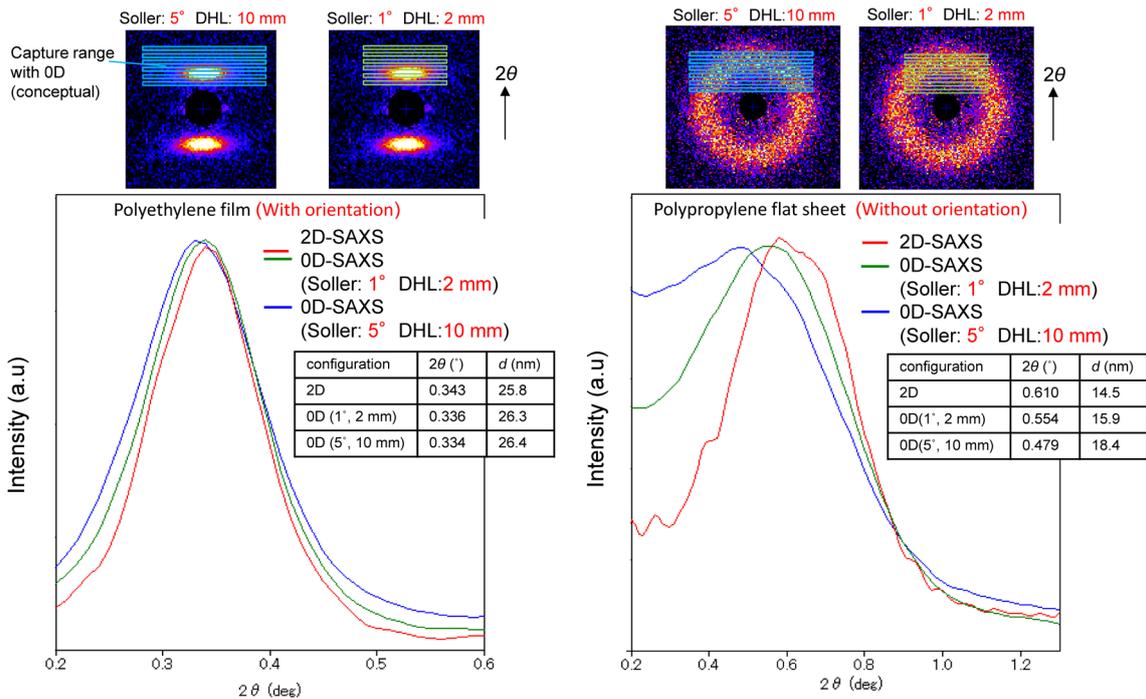


Fig. 13. 1D profile comparison of 0D-SAXS and 2D-SAXS employing a line radiation source.

with the 2D-SAXS/WAXS attachment, it is possible to convert line-shaped X-rays into point form using a double pinhole optical system, and this has made it easy to do 2D-SAXS measurement.

Figure 13 shows an example of 0D-SAXS and 2D-SAXS measurement of PE film and PP sheet using line-shaped X-rays. With 0D-SAXS, comparative data was also measured with divergence of line-shaped X-rays in the longitudinal direction suppressed using a Soller slit and longitudinal restriction. For PE film with a texture in its long-period structure, an almost correct d value was obtained even with 0D-SAXS, but for PP film with no orientation in its long-period structure, the

peak was shifted to a lower angle, and the d value was estimated larger. The 2D-SAXS value was approached by suppressing divergence in the longitudinal direction of 0D-SAXS, and thus it is evident that 0D-SAXS is affected by smearing.

6. Evaluation of long-period structure using SAXS

In the angular range of a few degrees or less in terms of 2θ , called the small angle region, an X-ray diffraction peak is observed, deriving from the electron density difference between the crystalline part and amorphous part in a crystalline polymer. The sizes of the crystalline

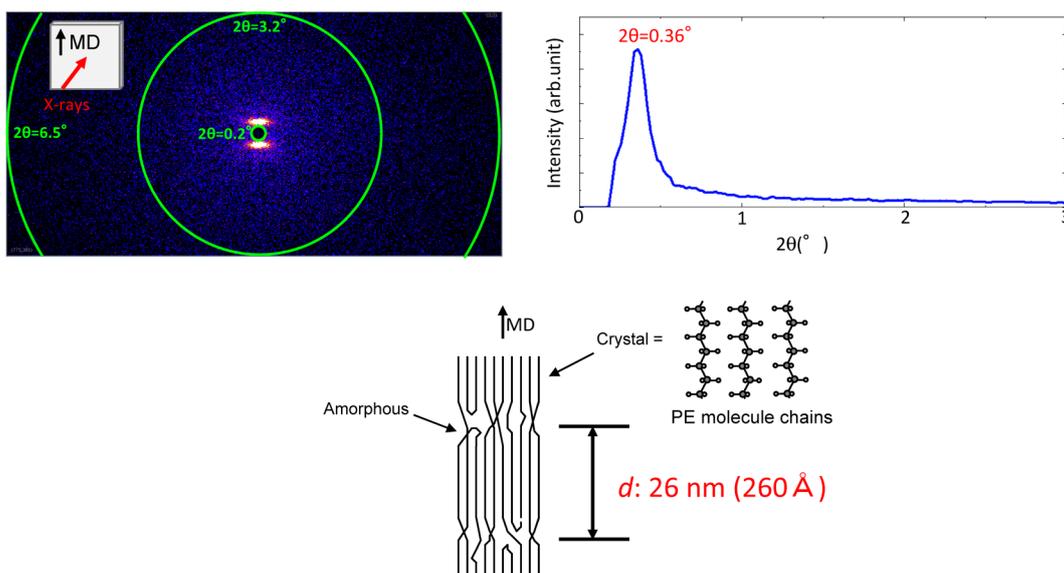


Fig. 14. 2D-WAXS measurement results for highly-stretched PP film.
Measurable angles: $2\theta=0.2-3.2^\circ$ (vertical direction), $2\theta=0.2-6.5^\circ$ (horizontal direction)

- (a) WAXS 2D diffraction image for PBT fiber.
- (b) $2\theta-I$ profile and crystal plane identification results.
- (c) Arrangement of various crystal planes in PBT unit lattice.
- (d) SAXS 2D diffraction image for PBT fiber.

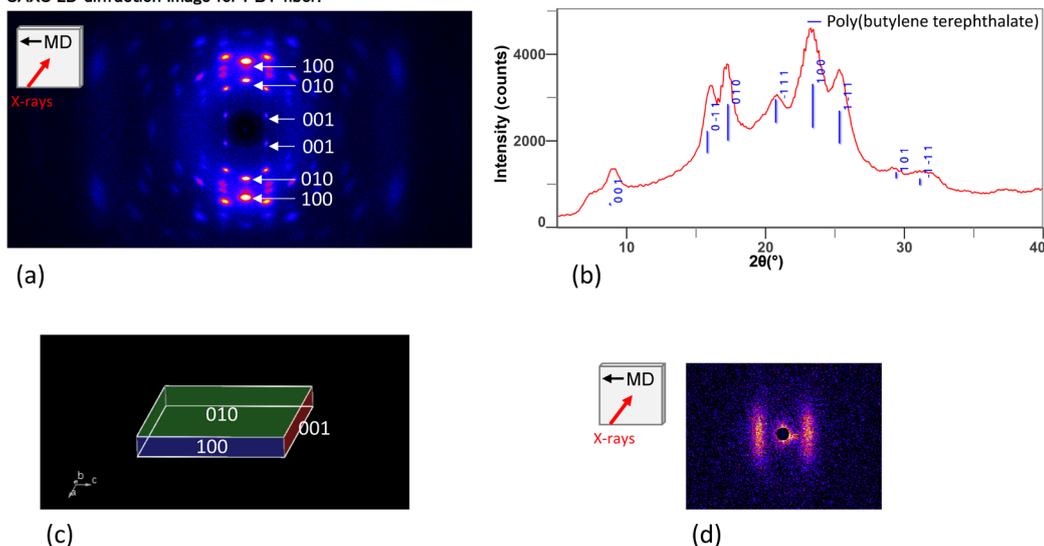


Fig. 15. 2D-SAXS/WAXS measurement results for PBT.
(a) WAXS 2D diffraction image for PBT fiber. (b) $2\theta-I$ profile and crystal plane identification results.
(c) Arrangement of various crystal planes in PBT unit lattice. (d) SAXS 2D diffraction image for PBT fiber.

and amorphous parts of the crystalline polymer range from a few nanometers to a few tens of nanometers, and if they are lined up in a regular way, then the Bragg diffraction condition is satisfied as in the case of lattice planes in a crystal. Therefore, if the d value is calculated using the Bragg equation from the peak observed in the small angle region, while taking into account the irradiation direction of X-rays with respect to the sample, then it is possible to determine the period and orientation of the crystalline and amorphous parts.

Figure 14 shows the results of 2D-SAXS measurement of highly-stretched PP film. In 2D-SAXS measurement, it is possible to obtain a 2D diffraction image for $2\theta=0.2\text{--}6.5^\circ$ in the horizontal direction and $2\theta=0.2\text{--}3.2^\circ$ in the vertical direction at once when the longitudinal direction of the detector is placed horizontal. Here, the range with $2\theta=0\text{--}3^\circ$ was converted to a 2θ vs. intensity profile. In the 2D diffraction image, a peak was observed at $2\theta=0.36^\circ$ with a d value = approx. 26 nm in the machine direction (MD) direction only, and thus for the period of the lamellar structure. It is evident that at about 26 nm the lamellar structure is layered along the MD direction.

7. Example of analysis using both 2D-SAXS/WAXS

Finally, this section presents an example of analysis combining both 2D-SAXS and 2D-WAXS. Figure 15 shows the results of 2D-SAXS/WAXS measurement of PBT fiber. The crystal planes that contributed to the diffraction were identified through crystal phase identification from the diffraction angles obtained with 2D-WAXS. Diffraction images of (100) and (010) are obtained in the direction orthogonal to the MD-axis (vertical direction of the 2D diffraction image), and

thus it is evident that the c-axis is in a state with fiber orientation parallel to MD. From the diffraction angle where the peak is obtained with 2D-SAXS, on the other hand, it is evident that the long-period interval is approximately 11 nm. Due to the fact that a diffraction image is obtained only in the MD direction, it is thought that the lamellae are layered in the MD direction. By combining 2D-SAXS and 2D-WAXS analysis results in this way, it is possible to simultaneously grasp the texture state of molecular chains on the 0.1 nm (1 Å) order, and the orientation state in the crystal region and amorphous region at the 10 nm order, and it is concluded that the material has a lamellar structure.

8. Conclusion

In 2D diffractometry employing exposure, there is no need for scanning, and thus it is possible to acquire a diffraction image for a wide 2θ and β range in a short time. It is also possible to visually understand polymer chains and the long-period orientation status from the 2D diffraction image. This paper has explained the differences between scanning type measurement and transmission/exposure measurement, and analyzed crystallinity, orientation, and long-period structure based on 2D diffraction images of crystalline polymers.

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