
Technical Note

ADVANCED X-RAY DIFFRACTOMETER AND APPLICATION TO PETROCHEMICAL PRODUCTS

—Measurement of Polymer Compounds by X-ray Diffractometry—

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1. Introduction

X-ray diffractometry (referred to as XRD) is the most suitable technique to investigate into the atomic arrangement in matter. It has a long history. As early as in 1915, W. L. Bragg conducted the world's first crystal structure analysis. The X-ray wavelength used by XRD and the atomic size are at about the same level. Accordingly a regularly spaced row of atoms causes constructive and destructive interference among the scattered X-ray waves from atoms giving rise to what can be observed as diffracted rays.

It is observed in such scattering or diffraction that the Bragg reflection from exceedingly large intraplanar spacings as with polymer crystals, and also the scattering caused by thin films of certain types which periodically constitutes artificial lattices, normally take place in an angular range from 0° to about 5° in terms of 2θ . The occurrence of scattered rays in this region is called small angle scattering (long-periodicity scattering). With the conventional X-ray diffractometer (focusing optical system), the direct beam is limited by a single piece of divergent slit so that the measurable start angle remains 1° or so at best (when using a $1/6^\circ$ slit). On the other hand, if a small angle scattering goniometer equipped with a 3-slit system, etc. for the divergent slit (to limit the direct beam as much as possible) is used, measurement can be made at angles from 0.1° (from 0.01° with the Kratky optics). However, the narrower the direct beam with the divergent slit, the smaller the irradiation area. As a result, the scattering intensity will substantially

decrease, thus prolonging the measurement time. In order to compensate for it and shorten the measurement time, the recent trend is toward the use of more sophisticated detectors such as the PSPC (position sensitive proportional counter) and the IP (imaging plate using a photostimulable luminous body) to replace the conventional SC (scintillation counter).

Introduced here is the outcome of measurement of PET (polyethylene terephthalate) film with the small angle scattering goniometer. Different detectors, SC, PSPC and IP, were used for the experiment. And described also is a new advanced diffractometer.

2. Measurement

2.1 Measurement System

Rotating anode X-ray diffractometer:	D/max-1500
Small angle scattering goniometer:	2203E5
SC:	5738E1
PSPC:	PSPC-10
IP:	IP system

The D/max-1500 system is equipped with a rotating anode X-ray tube which can yield about 10 times higher intensities than with a sealed-off X-ray tube. Also, a 32-bit work station is employed for system control and measurement data processing to enable rapid and concurrent execution. Fig. 1 show the external view of the system.

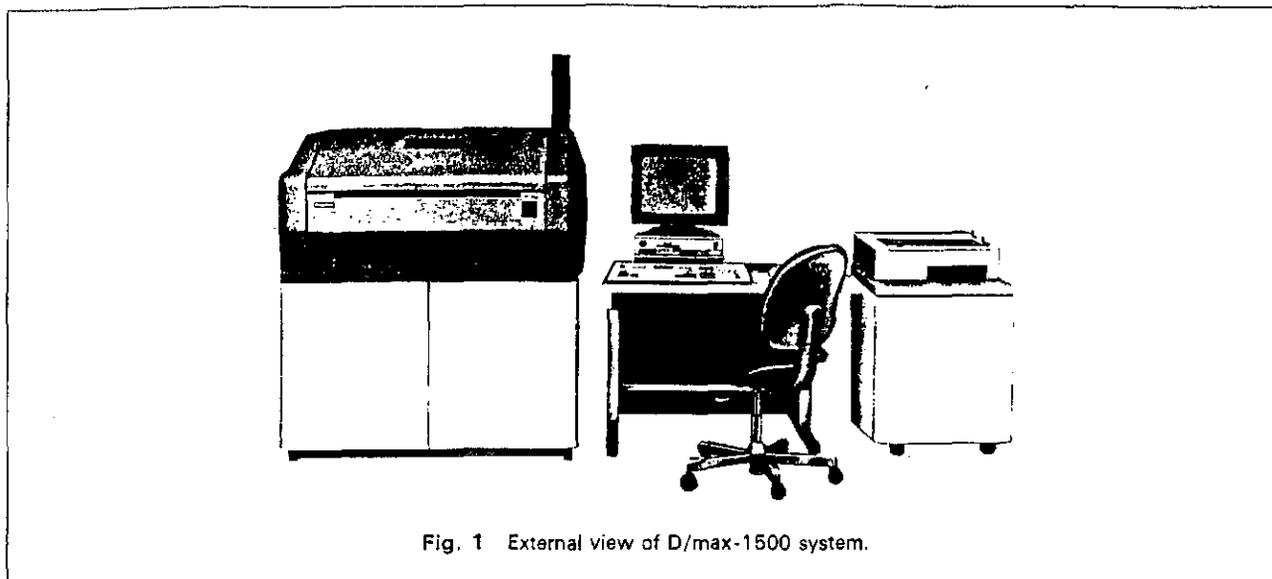


Fig. 1 External view of D/max-1500 system.

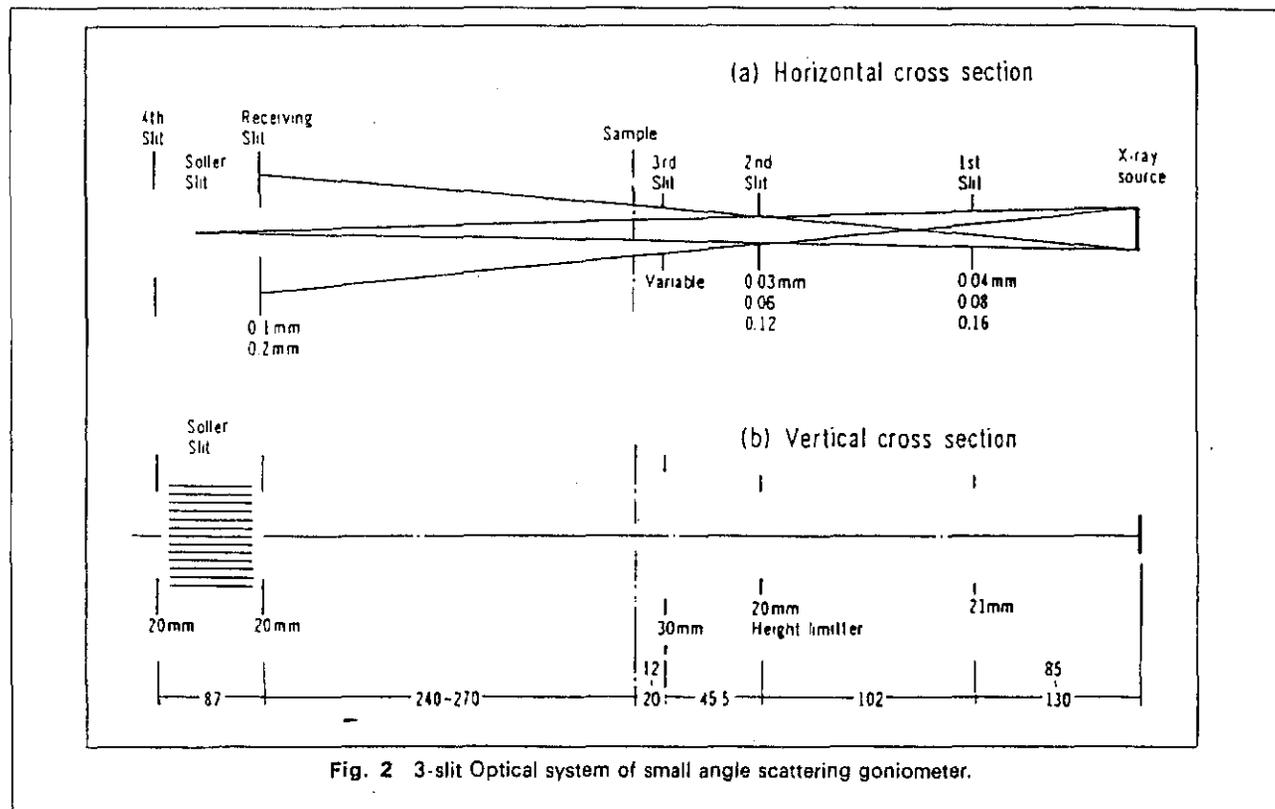


Fig. 2 3-slit Optical system of small angle scattering goniometer.

2.2 Measurement Condition

X-ray tube : Cu
 Tube voltage: 50 kV
 Tube current: 300 mA

The 3-slit optical system was used for the measurement, as shown in Fig. 2.

3. Measurement Result

The respective measurement results are described below.

Fig. 3: Measurement was made with the conventional wide angle focusing optical system. A 0.5° divergent slit was used so that the direct beam was reduced to approximately 2° . The outcome was a sharp diffraction profile in both the longitudinal and transverse directions of the sample showing

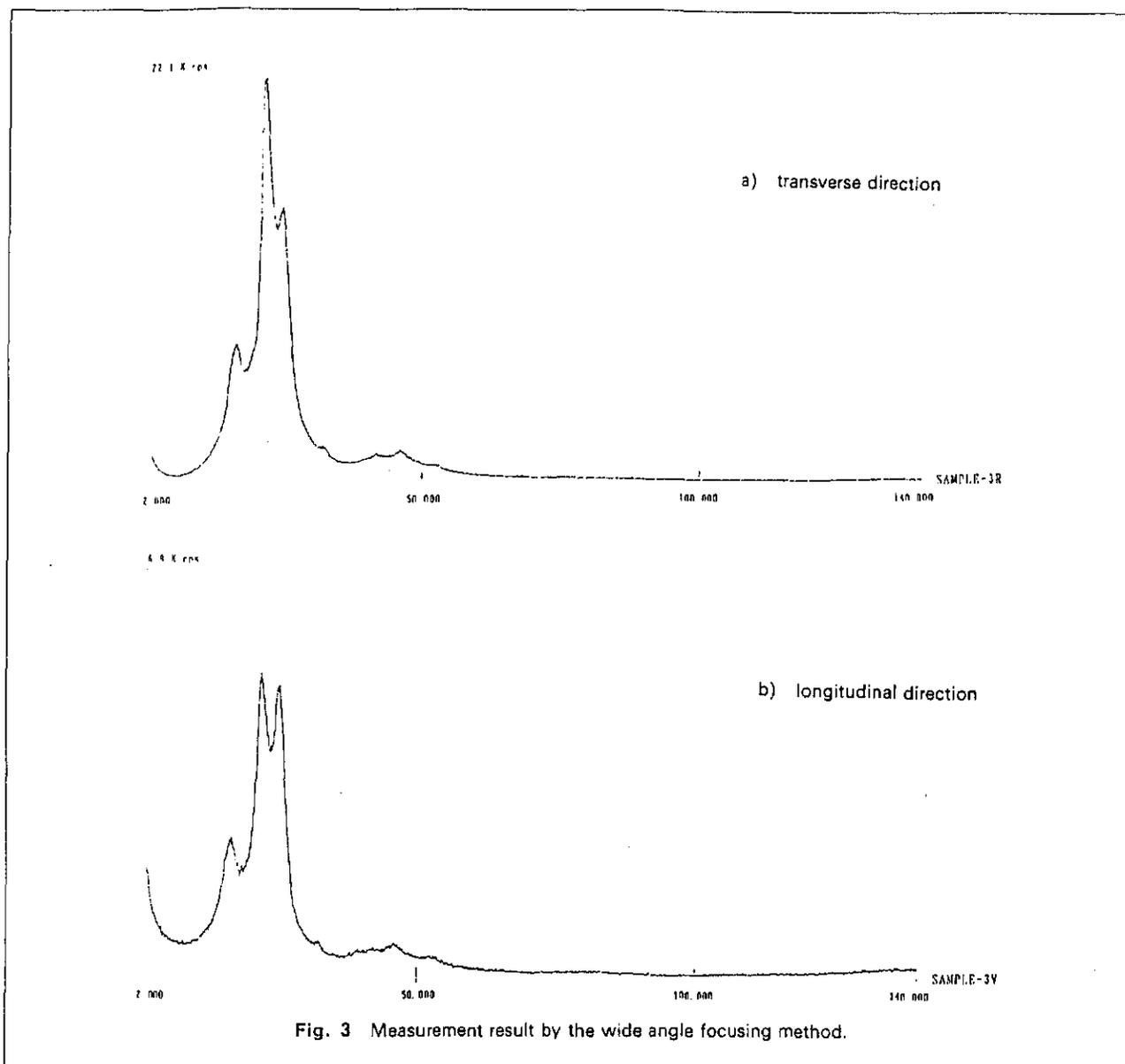


Fig. 3 Measurement result by the wide angle focusing method.

the existence of a crystal. A large difference in the relative intensity suggests the directionality of the PET crystal with respect to the intraplane (termed the preferred orientation in XRD).

Fig. 4: Measurement was made with the small angle scattering goniometer using the SC. The direct beam was reduced to 0.1° . A long-periodicity peak of about 9 nm of the PET film was observed at around 0.8° of the measurement profile in the traverse direction. However, because of the presence of the preferred orientation in the plane, as with the result in Figure 3, no observation could be made in the longitudinal direction except for the central scattering (a phenomenon such that if the density of matter is uneven when the X-rays pass through it, the direct beam will be broadened to

that extent).

Fig. 5: Measurement was made in the transverse direction with the small angle scattering goniometer. The PSPC used had an effective length of 10 cm. In the case of this optical system the simultaneously measurable range is $\pm 10^\circ$. The measurement was conducted with the PSPC center set at 0° . A split is seen at the center of the measurement profile. It was caused by the use of a direct beam stopper to protect the detector. Also, diffraction lines are observed on the positive and negative sides centering on 0° . The measurement time was 1000 seconds. Compared with the results in Fig. 4 where measurement was made with the SC using the same optical system, the measurement time was 1/10 while the obtained intensity was 7

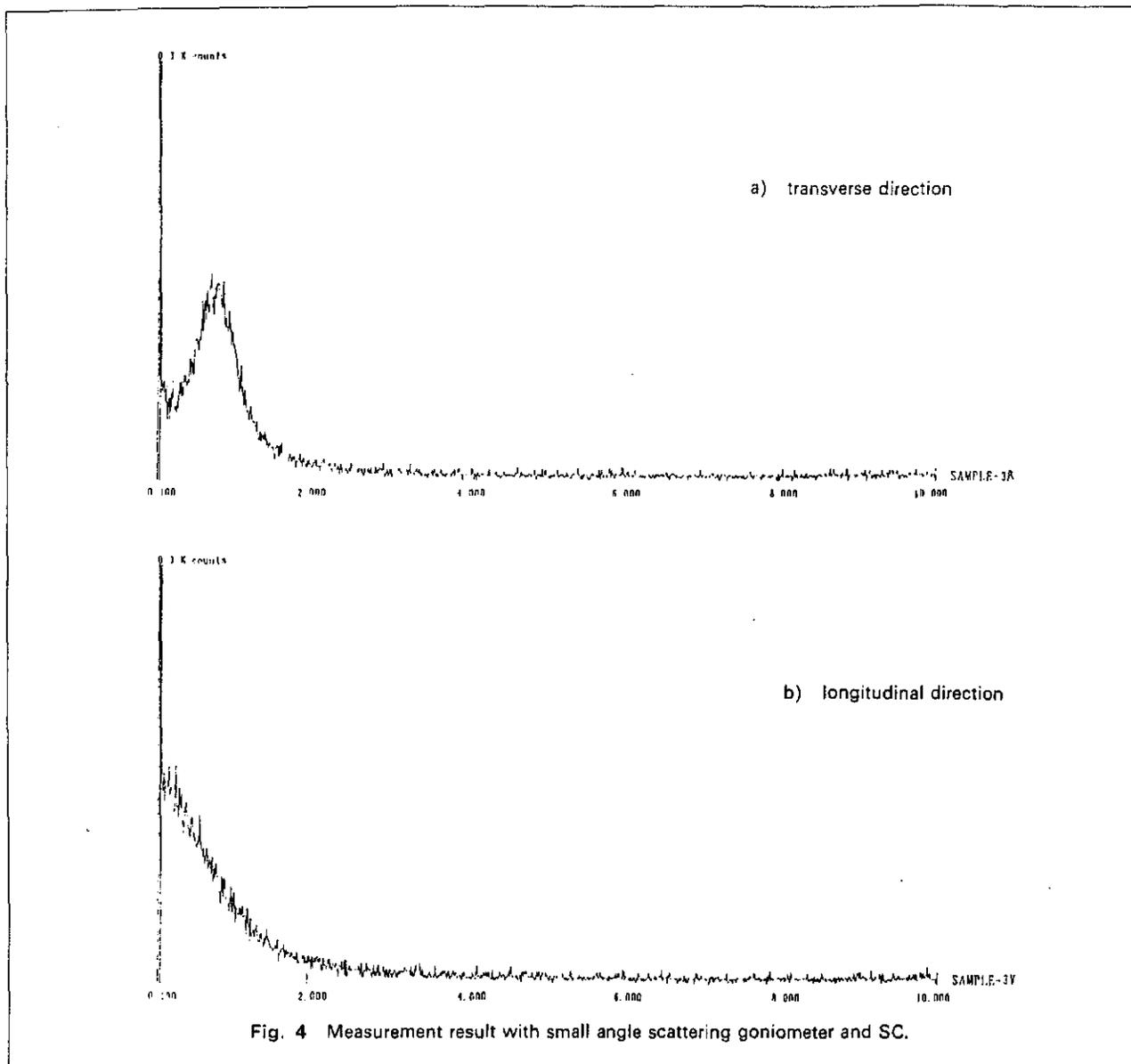


Fig. 4 Measurement result with small angle scattering goniometer and SC.

times higher.

Fig. 6: Measurement was made with the small angle scattering goniometer using the IP. Since the IP permits two-dimensional measurement, measurement can be performed without considering the preferred orientation in the plane. Hence there is no need of changing the sample direction in measurement. Fig. 6 (a) shows the result of directly reading the IP. It is known from this diffraction pattern that the diffracted rays concentrated on the axis of abscissa due to the preferred orientation in the plane. Also, (b) shows the result of readout of (a) by scanning. Compared with Fig. 4 where measurement was made with the SC using the same optical system, the measurement time was 1/100 while the obtained intensity was 10 times

higher. Besides, it is not necessary to change the measurement direction.

4. Study

As verified in the above, the use of the PSPC or IP can drastically reduce the measurement time. In particular, it has now become practical to carry out such measurements where the direct beam has to be extremely narrowed because of the periodicity or where the intraplanar lattice spacings are notably broad. These are the sorts of measurements that up to now were regarded as impossible.

5. Concluding Remarks

Generally, the evaluation of polymer compounds is often conducted by the following two methods.

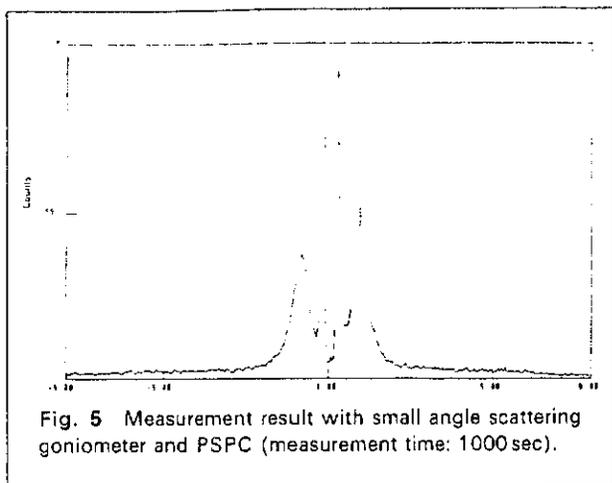


Fig. 5 Measurement result with small angle scattering goniometer and PSC (measurement time: 1000 sec).

One of the methods is to measure the crystallinity of a polymer compound in question. Needless to say, there exist differences in terms of the chemical and physical properties between crystalline samples and amorphous ones.

The other method is to measure the direction and extent of the preferred orientation of crystalline components in the sample. For instance, in the case of the PET crystal cited in this report, the preferred orientation was verified to a large extent not only by the result of wide angle measurement (of a local area of small periodicity) but also by the result of small angle measurement (of a whole area of large periodicity). It is accordingly presumed that such findings have close connections with, for instance, the tensile and bending strengths of the PET film and also its discoloring and transparency.

In XRD, fairly in-depth discussions have hitherto been made about inorganic substances, which are less in number and stable in form than organic

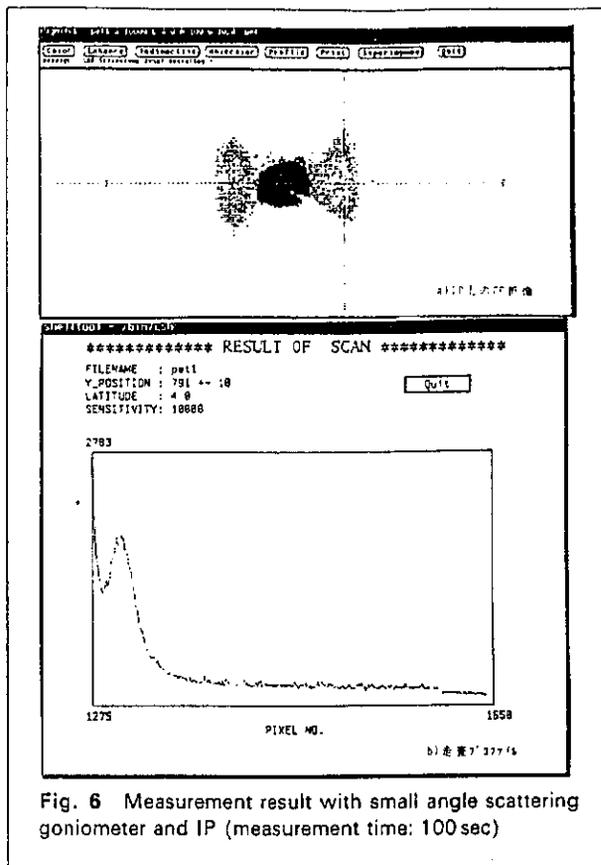


Fig. 6 Measurement result with small angle scattering goniometer and IP (measurement time: 100 sec)

substances. But in the field of organic substances where numerous forms exist, a thorough study has not been made. Since XRD is the one and only means of analysis at the crystal level, we anticipate further progress of the evaluation techniques for organic compounds by making the most of the characteristics of XRD.