Temperature Slope Crystallization of Polymers (A survey of polymer crystallization by X-ray diffraction . chapter 5)

Chapter 5. Temperature Slope Crystallization of Polymers

5.1. Introduction

The structure of a single crystal can be precisely analyzed by the X-ray diffraction method. When a single crystal of suitable size is technically difficult to prepare, the sample possessing preferred orientation is more advantageous to study structure and property than the un-oriented sample. In the previous chapter, PET samples are mechanically drawn to have molecular orientation. In this chapter, we use the special technique to attend a preferred orientation for several polymers without mechanical orientation.

In 1956, Seto *et al.* devised an apparatus to crystallize a sample in a temperature slope and successfully applied it to the crystallization of organic compound – triglyceride [1]. In the Seto's method, a specimen is enclosed in a glass capillary, and heated in the heater above the melting temperature. Then the specimen is moved slowly in the temperature slope toward the cooler. As a result, the specimen is crystallized in between the heater and the cooler. From this investigation, he obtained well oriented sample. We named this method as "temperature slope crystallization", which is hereinafter abbreviated to "TSC".

Applications of the TSC method on polymer crystallization can be found in the literatures around 1960 [2-6]. A theory of TSC is introduced by Lovinger [7]. Fujiwara improved several parts of this method and applied it to polymers. The first application of TSC was performed by him on polypropylene with well oriented α- and β-crystals observed by WAXS and SAXS [6]. The results of TSC have been published by Fujiwara in the green book titled "A Survey of Temperature Slope Crystallization for the Oriented Crystallization of Polymer Lamellae"[8]. From the circumstances explained in the preface, we record the copy of the green book at the end of this book.

In the melt state of polymers, randomly disordered molecules are transformed to regular crystals and further organized into lamellae. In the isothermal crystallization, lamellar textures are developed from a nucleus. A spherulite is then grown to size of 1~100μm. During the crystallization, the spherical front moves from the nucleus to periphery. Therefore, it is difficult to analyze the ordering mechanism by the isothermal crystallization.

Using the TSC method, it is possible to observe a stationary melt-solid interface in between the heater and cooler. Moving the specimen slowly along the temperature slope, the melt polymer is crystallized perpendicular to the interface. The resultant texture has a preferential orientation corresponding to a huge-sized spherulite ranging several cm. The well oriented specimen can be used for further measurements. The results of structural, mechanical and thermodynamic studies are shown in Chapters 6, 7 and 9. Moreover, using the stationary melt-solid interface, molecular ordering phenomena can be examined by *in-situ* measurements.

Considering the above issues, we have prepared several types of TSC instruments and surveyed on polymeric materials by TSC. Some polymers are difficult to get successful results, mainly due to degradation of the melted polymers suffered at high temperatures for

long time. Using a well oriented sample by TSC, we investigated by simultaneous measurements using WAXS, SAXS and optical microscopic techniques. The results obtained from these investigations were reported in a series of articles [8-23]. In this chapter, we describe the construction of the TSC apparatus. Then we show examples of the oriented polymers by TSC, and finally we discuss the function of TSC by the *in-situ* studies for some specific polymers.

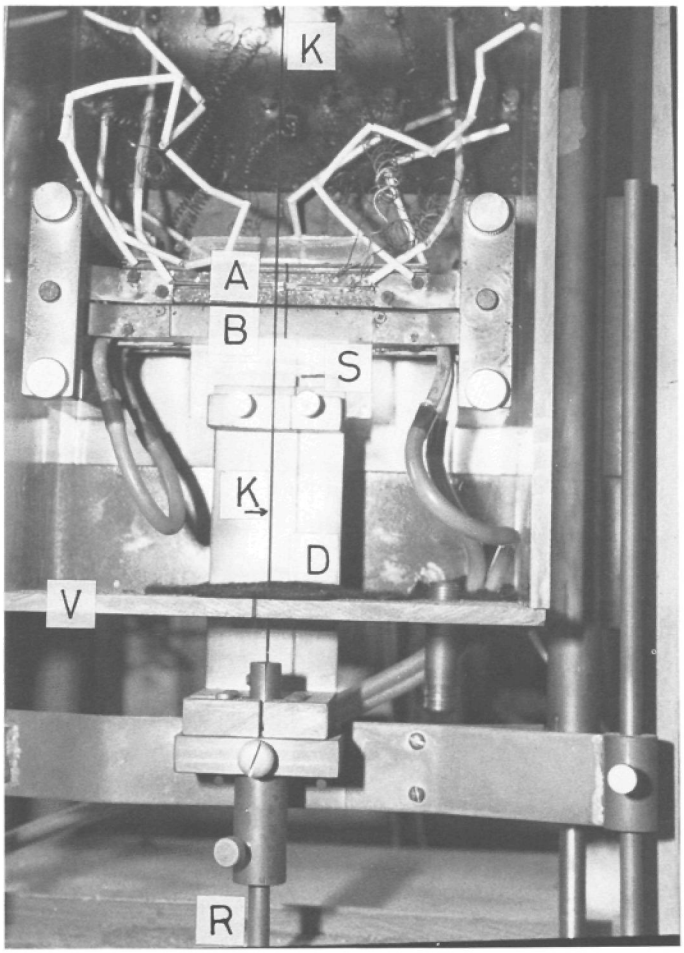

Fig. 5.1 Main parts of TSC apparatus constructed by Fujiwara. A: heater, B: cooler, D: clamping block of sample holder, R: connecting rod to the smoothing device, S: specimen, K: steel belt, V: sample case.[8]

5.2 Construction of TSC Instruments

5.2.1 TSC apparatus for a film specimen by Fujiwara

In order to measure lamellar textures by an optical microscope, a film specimen is prepared by TSC. For a flat sample, Fujiwara originally developed the TSC instrument. The main part of this apparatus is shown in Fig. 5.1, and the side view is schematically shown in Fig. 5.2.

In these figures, the sample cell, S, is connected to a specimen holder, D, which is firmly fixed to a rod R. In the bottom direction, R is connected with a damping device to remove mechanical oscillations. R is moved downward by a steel belt K, whose speed is controlled by a geared motor. A and A' are copper heaters, heated to a constant temperature T_A by a temperature controller beyond the melting point of the specimen. Symmetrical shaped copper coolers, B and B', are kept at 18 °C by circulation of water through them. The gap between A and B (likewise between A' and B') is fixed to 1 mm distance. Polymer samples are sandwiched by thin glass plates. We usually use micro cover glass with 50mm x 40mm in height and width and 0.1-0.2mm in thickness. The polymer sample is once melt and hot pressed between the cover glasses. For film samples thicker than 0.3 mm, we use spacer glasses surrounding the polymer film. The polymer specimen covered by the glass plates is set to D as shown in Fig.5.2. Using soft springs, A and A' (likewise B and B') are pushed to the sample glass for attending good thermal contact. S is moved downward by a constant speed ranging 0.1 - 2.0 mm/hr. The main part of the apparatus is enclosed in a plastic case V to keep from air disturbance, and to suppress oxidation of the specimen by flowing inert gas or nitrogen gas if necessary. The whole apparatus is put on a quake proof floor.

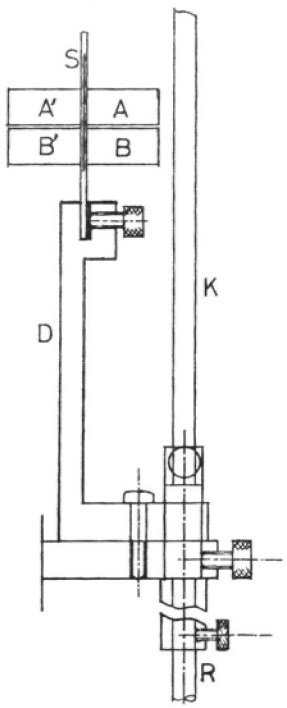

Fig. 5.2 Side view of Fig. 5.1 [8]

5.2.2 Apparatus of TSC devised by Asano

Asano prepared a modified TSC instrument to investigate the ordering phenomena at the melt-solid boundary. For this purpose, he performed simultaneous measurements using TSC with either of the following observations:

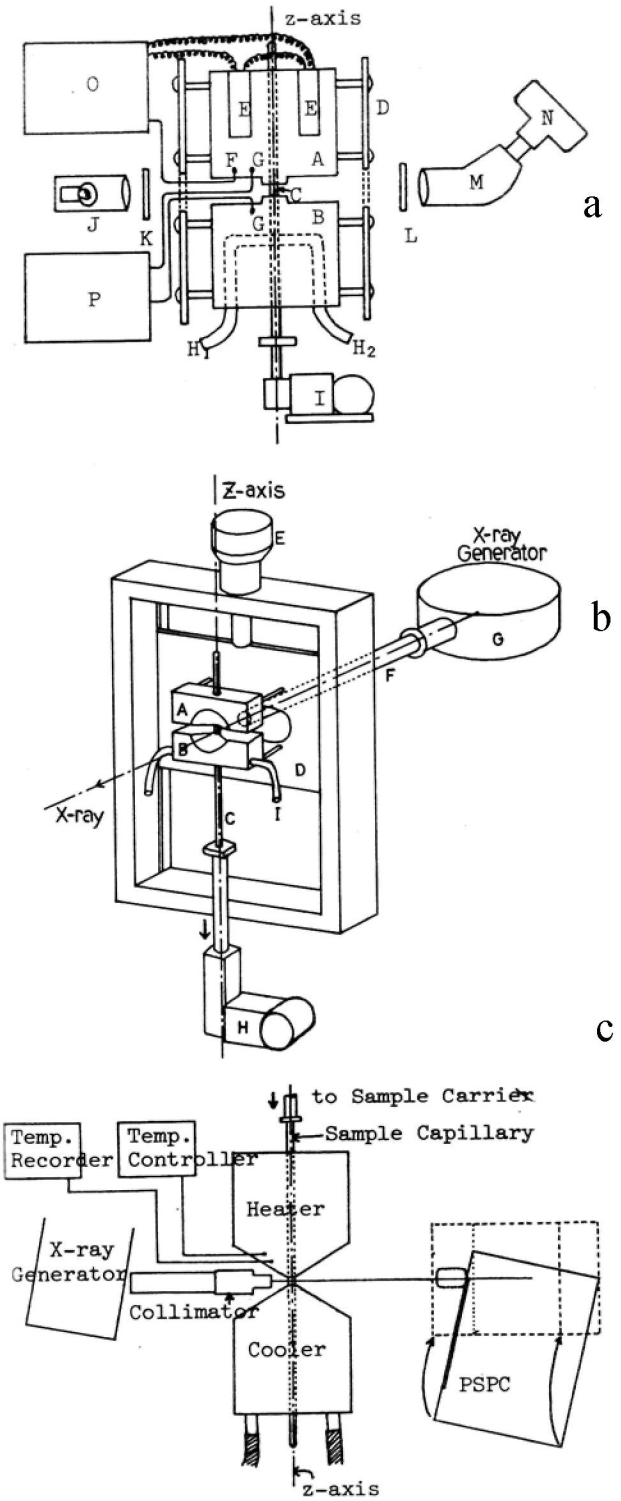

Fig. 5.3 (a) Simultaneous TSC and microscopic observations, (b) simultaneous TSC and X-ray diffraction, and (c) simultaneous measurements for X-ray PSPC or Laser-Raman spectroscopy.

(a) Microscopic observation

Figure 5.3 (a) shows a TSC apparatus for a rod specimen with a 2 mm gap between the heater and the cooler, so as to make it possible to observe the growth interface by polarization microscope. The symbols show; A: heater, B: cooler, C: sample tube, D: holder, E: heater, F: thermistor, G:thermocouple, H_1:water inlet, H_2:water outlet, I : sample carrier, J: light source, K: polarizer, L; analyzer, M: microscope, N: camera, O: temperature regulator, and P: recorder.

The sample capillary has 1-2 mm in diameter with 0.1mm glass thickness. The polymer sample is melted and then inserted into the capillary. The observation of the melt-solid surface is explained in the latter half of this chapter.

(b) X-ray diffraction

Figure 5.3 (b) shows a set up for simultaneous measurements of TSC and X-ray diffraction for a rod specimen. Here, A, B and C are similar to Fig. 5.3(a). The different equipments are; D: sliding plate, E:finely moving micrometer, F: incident X-ray collimator, G: monochromator and I: water flow tube. The gap and other parts of the apparatus are the same as before. In this case, the heater and cooler can be shifted up and down for changing the relative position of the incident X-ray. The central part of the heater and cooler is conically bored so as not to obstruct the diffracted reflections. In order to check the ordering process, it is necessary to use a fine X-ray beam, collimated less than 10 μ, on the crystallizing surface. We measured *in-situ* WAXS and SAXS using high intensity beam at the synchrotron facilities of Photon Factory in Tsukuba or SPring 8 in Harima, Japan.

(c) X-ray PSPC measurement/Laser-Raman spectroscopy

Figure 5.3 (c) illustrates a top view for simultaneous measurements of TSC with X-ray PSPC or Laser Raman spectroscopy. By rotation of the PSPC, it is possible to observe both equatorial and meridional profiles. For counting the intensity from 2θ = 5 to 30°, PSPC is inclined by 15° from the normal position. This apparatus was basically designed to commonly use TSC with X-ray PSPC or Laser-Raman spectroscopy. By spatial restriction, the moving direction of the specimen is set horizontally. A polarization microscope is adjusted to select the irradiating portion of X-ray or Laser light on the specimen.

5.3 Features of the Specimens Prepared by the TSC Method

Characteristic features of some samples, which were obtained by TSC, will be presented here. Figs. 5.4 (a) and (b) show the WAXS patterns (left side) and micrographs (right side) of oriented poly(ethylene oxide) and polybutene-I, respectively. In the micrograph of poly(ethylene oxide), the fibrils are well oriented along the growth direction (parallel to the temperature slope). In the optical picture of polybutene-I, the spherulitic nucleus appears in the lower-left side. Normally in the isothermal crystallization, a spherulite develops around the nucleus. However in TSC, the crystallization proceeds on the flat boundary perpendicular to the temperature slope. Then the spherulitic fibrils soon develop along the growth direction.

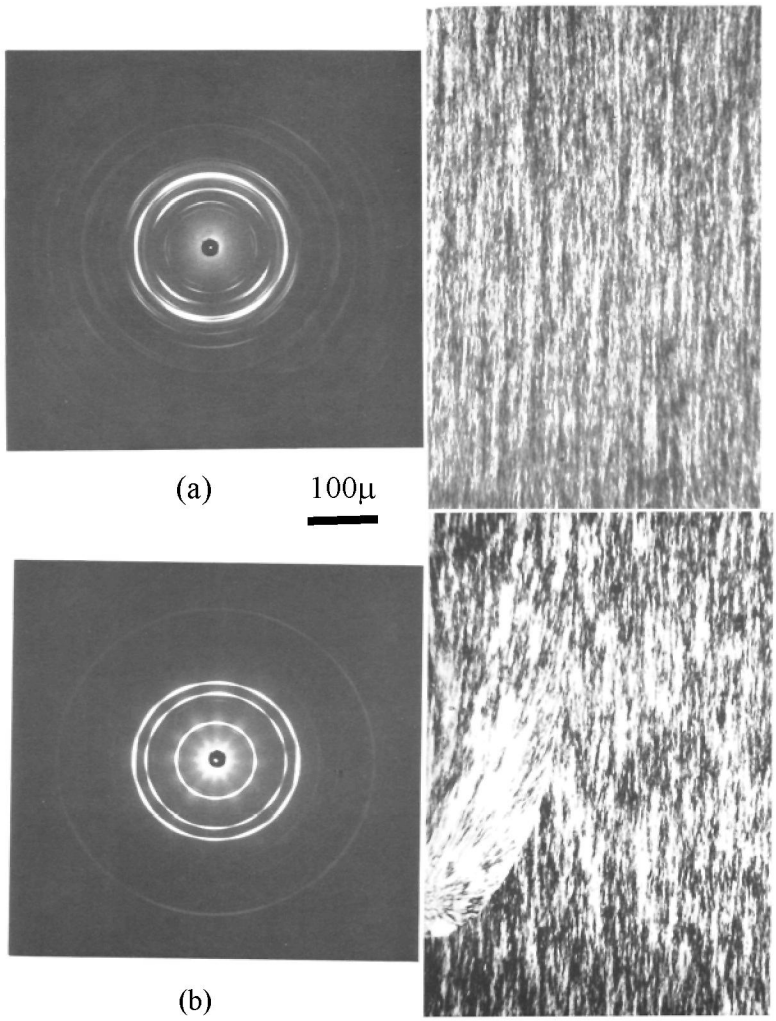

Fig. 5.4 WAXS and optical patterns of (a) Poly(ethylene oxide), and (b) Polybutene-I. The growth direction is vertical. In the WAXS patterns, a sharp crystalline orientation is indicated. The optical micrograph shows well oriented fibril structures. The scale bar indicates the magnitude of the micrographs [8].

Figure 5.5 indicates the micrographs of the oriented polypropylene prepared by TSC. The temperature of the heater and cooler was 200°C and 20°C, respectively. The growth rate was controlled by the geared motor at 0.5 mm/hr. As a result of the TSC method, the textures reveal good orientation along the growth direction shown by the arrow.

Polypropylene is known to have different crystalline phases; α- and β-crystal forms. Normally the α-phase develops in the initial stage of TSC (Fig.5.5a), because the nucleation rate is far low in the β-phase. As the linear growth rate exceeds in the β-phase than the α-phase, the β-phase texture develops preferentially from the occasional β-nucleation, excluding the α-phase, and soon occupies entire available space of the sample plate (Fig.5.5b). In the thinner texture shown in Fig.5.5c, the polarization micrograph of the β-phase texture reveals clear stripes corresponding to the lamellar twisting. The twisting structure is analyzed in the Chapter 7 (pp 99).

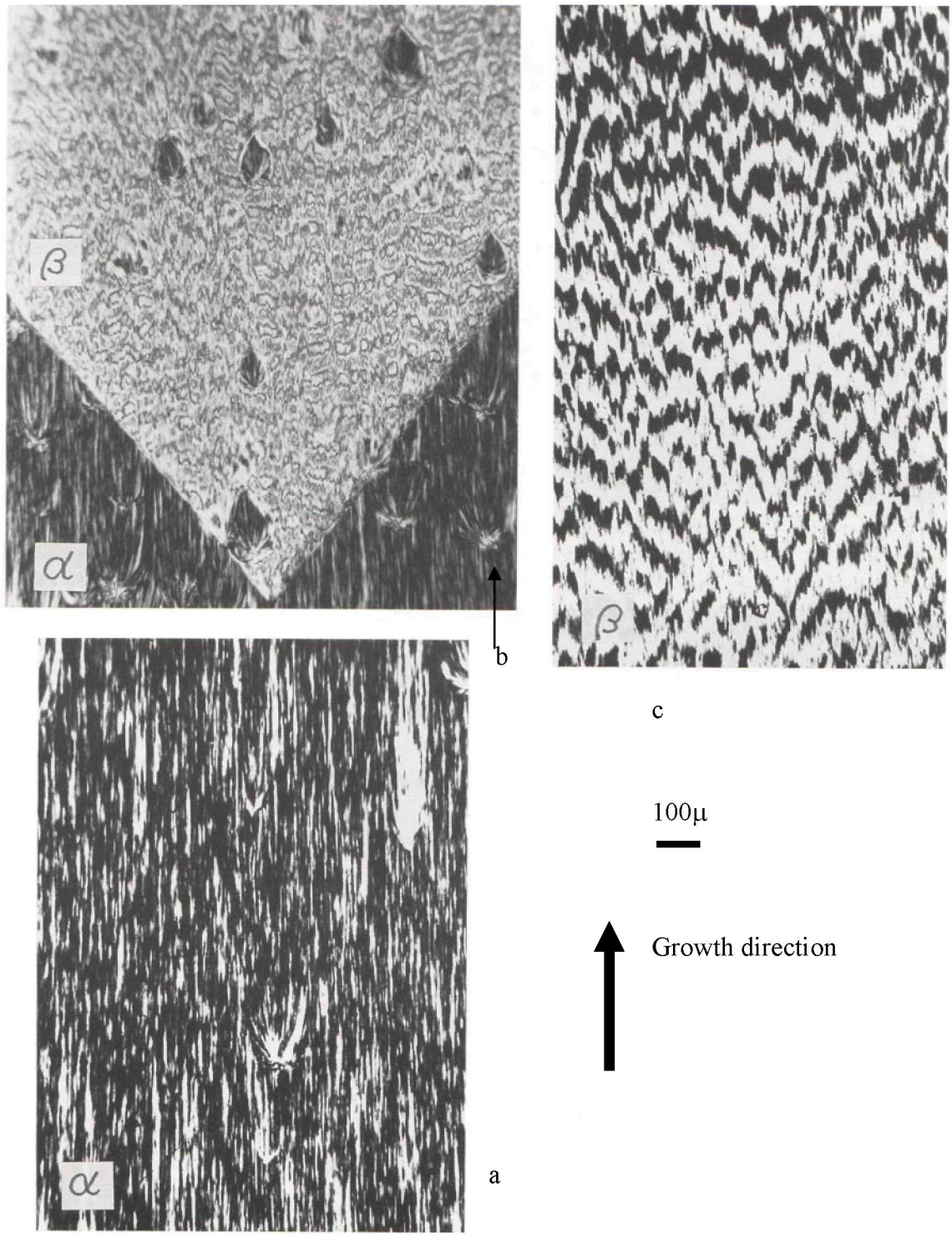

Fig. 5.5 (a) Micrographs of oriented PP (α-phase), (b) Sporadic nucleation of β-phase in the α-phase matrix and (c) thinner part of the β-phase [8].

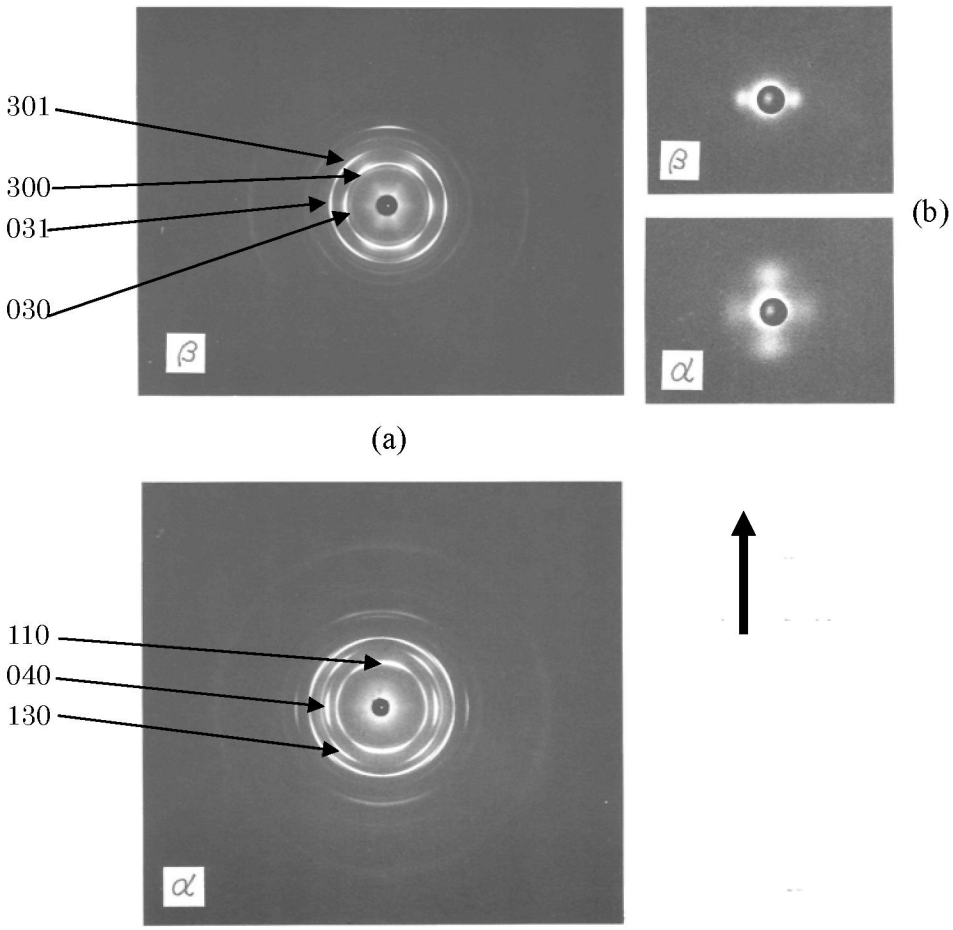

Fig. 5.6 (a) WAXS and (b) SAXS patterns of PP prepared by TSC, β-phase: uniaxial orientation of hexagonal lattice, α-phase: double orientation of monoclinic lattice. The thick arrow indicates the growth direction [8].

WAXS results of the oriented α- and β-phase are assigned in Fig.5.6a. In the α-phase texture, the reciprocal a* direction is parallel to the growth direction. The monoclinic crystal is known to produce double orientation where the branched crystal develops perpendicular to the main crystal. The branching or epitaxial growth of the α-phase crystal is discussed in the end of this chapter. In the hexagonal β-phase crystal, the a-axis is parallel to the growth direction.

In the SAXS patterns, shown in Fig 5.6b, the α-phase lamellae are developed both parallel (main texture) and perpendicular (branched texture) to the growth direction with a lamellar period of 200 Å. Two kinds of lamellae reveal the 4-point pattern. The molecular c-axis of the main lamellae is parallel to the growth interface, whereas perpendicular in the branched lamellae. The SAXS pattern of the β-phase shows the 2-point appeared on the equator, indicating the lamellar normal perpendicular to the growth direction. In the β-phase lamellae the molecular c-axis is parallel to the growing plane.