Crystallization Behavior of Polybutene-1 in the Anisotropic System Blended with Polypropylene

T. TAKAHASHI, Y. NISHIO, and H. MIZUNO, *Faculty of Engineering, Fukui University, Bunkyo 3-9-1, Fukui 910, Japan*

Synopsis

Development of supermolecular structure in drawn polypropylene (PP)/polybutene-1 (PB-1) blends was studied. PP (matrix)/PB-1 (70/30) blend films were drawn and heat-treated at fixed length or free ends at temperatures above the melting point of PB-1. It was found that a long axis of the PB-1 lamella is aligned perpendicular to the draw direction, and the c-axis of the PB-1 crystal is oriented perpendicular both to the draw direction and the plane of the surface of the blend film. Drawn, then heat-treated PP/PB-1 blend films gave a SAX pattern having a cross type scattering maximum on the meridian. It was confirmed that vertical scattering originates from the PB-1 crystal developed during melt recrystallization. It was proposed that the structural development of PB-1 in drawn PP/PB-1 film can be explained on the basis of transcrystallization of PB-1 in the confined 2-dimensional space in the PP matrix. The kinetics of isothermal crystallization of PB-1 was examined by use of a DSC technique. The result supports the conclusion that the heterogeneous nucleation of PB-1 followed by 2-dimensional crystal growth prevailed in oriented PP/PB-1 blend film.

INTRODUCTION

A number of papers have thus far dealt with the structure and properties of polyblend systems. Among the many, there are some noteworthy reports on the crystalline texture and morphology of dispersed phase developed in "oriented" polymer composites. For example, new crystallite-orientation textures and unusual lamellar arrangements of polyethylene (PE),[1] polypropylene (PP),[2] and polyethylene glycol (PEG)[3] were observed in melt-extruded fibers blended with polystyrene, nylon 11, and nylon 66, respectively. The results were interpreted in terms of a "confined growth model,"[1] or an "epitaxial crystal growth model,"[2,3] based on the assumption of a crystallographic interaction between the constituent polymers.

Similar structural analysis in oriented polymer blends has been made in our preceding works: The crystallization behaviors of PE[4] and ultra-high-molecular weight PE[5] were examined using the drawn films blended with PP as samples. It was found that when the drawn blends were heat treated above the melting point of PE, (020) reflection of PE was observed at azimuthal angles of $\pm 37°$ and a cross-hatch type of lamellar structure was formed in the dispersed PE phase. An "effect of thermal shrinkage stress" on the crystallization behavior during heat treatment was considered. Recently, Gross and Petermann[6] and Kojima and Satake[7] have also observed the cross-hatch structure of PE lamellae in drawn, then heat-treated PP/PE blends. The

CCC 0021-8995/87/082757-12$04.00

former investigators assumed that such a supermolecular structure was produced as a result of epitaxial crystallization of PE on the PP phase having a fiber texture.

It is necessary to elucidate further the decisive factors affecting the structural development of crystalline polymers in the oriented blend systems. In this article, we would like to describe a crystallization behavior of polybutene-1 (PB-1) in a drawn blend with PP and to compare the present result with that reported already on the PP/PE blends.

EXPERIMENTAL

Sample Preparation

Commercially available PP (Scientific Polymer Products Inc., CAT #130, LOT #6) and PB-1 (Scientific Polymer Products Inc., CAT #338, LOT #1) were used in this study. The two polymers weighed at a ratio of 70/30 (PP/PB-1) were dissolved in hot xylene at concentration of 1% and then precipitated from the solution by rapid cooling. The mixture was filtered, washed with methanol, and dried. A PP/PB-1 blend sheet, about 0.3 mm in thickness, was prepared by compressing molding of the mixed powder at 210°C, followed by rapid quenching in ice water. Oriented samples were prepared by uniaxially drawing a strip cut out from the pressed sheet to a draw ratio of 7 at 95°C in water. The drawn films were heated at fixed or free ends at 140°C for 3 min in silicon oil, in order to allow the PB-1 phase alone to be in the molten state. Recrystallization of the PB-1 component was carried out by cooling the drawn blends at 90°C and keeping them at the temperature for 3 h.

Measurements

Wide-angle X-ray diffraction (WAX) patterns were obtained by using a Toshiba XC-40H X-ray generator equipped with a Laue camera. Small-angle X-ray scattering (SAX) patterns were obtained by using a Nihon-Denshi JRK-12A diffractometer with a photographic attachment. In both cases, nickel-filtered CuK_α radiation was utilized as the X-ray source.

A two-step replication technique was employed for electron microscopic observations. Specimens were placed on a highly viscous solution of cellulose nitrate in isoamyl acetate spread on a glass plate and then detached from the substrate after it dried. The remaining cellulose nitrate film was supplied for preparation of the replica membrane by shadowing with Au/Pd alloy and coating with carbon. A Nihon-Denshi JEM 200B transmission electron microscope was used for the observations.

The kinetics of isothermal crystallization of PB-1 was studied on nonoriented PB-1 and oriented PP/PB-1 films in differential calorimetry. A Perkin-Elmer DSC-4 apparatus was used for the experiment. Samples (ca. 5 and 11 mg for the pure and blend films, respectively) were heated to 135°C and kept at this temperature for 5 min. The heat evolved during the isothermal crystallization was followed as a function of time.

RESULTS

WAX Diffraction

The WAX patterns of an oriented PP/PB-1 sample heat-treated at 140°C at fixed length are shown in Figure 1. These WAX patterns were taken in less than 10 h [Fig. 1(a)] and in a week [Figs. 1(b), 1(c), and 1(d)] after the heat treatment of the sample was finished. Before the treatment, the drawn film
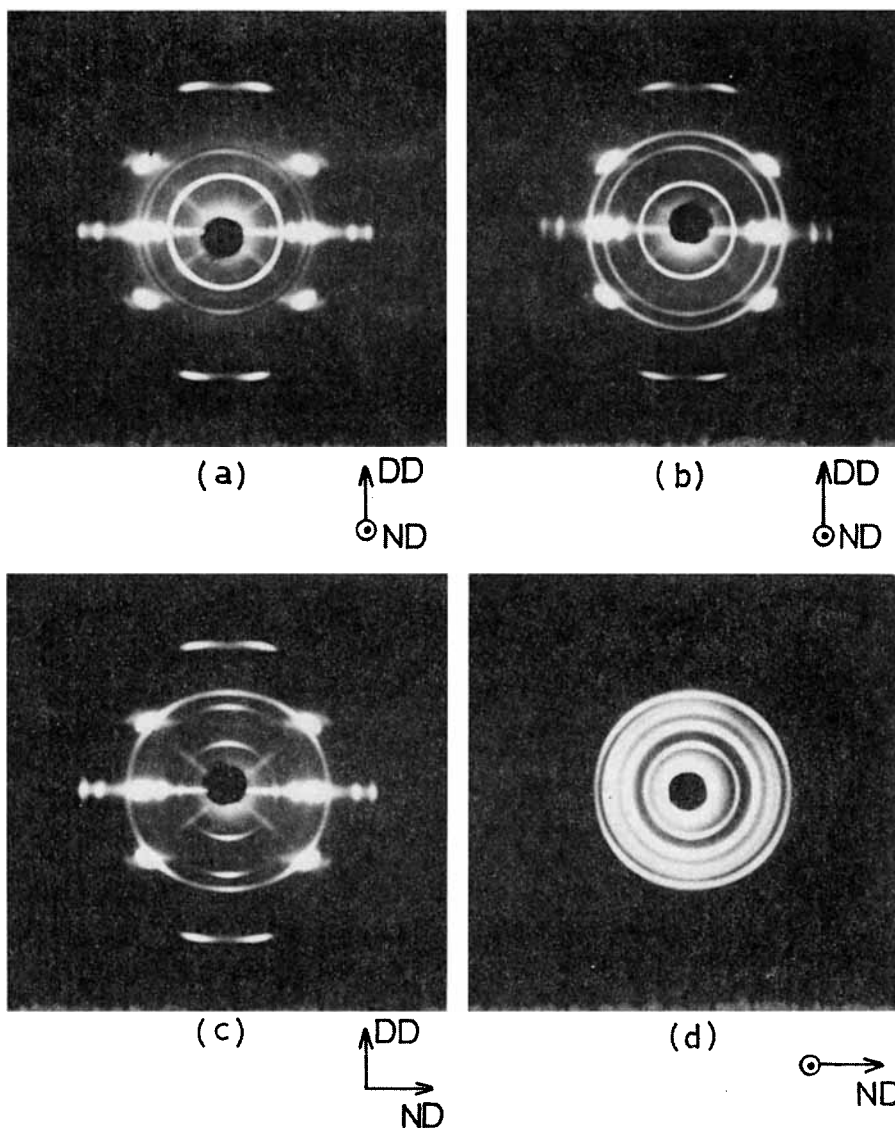

Fig. 1. WAX patterns of a drawn PP/PB-1 blend heat-treated at 140°C for 3 minutes taken (a) within 10 h and (b), (c), (d) in a week after heat treatment. DD and ND indicate, respectively, the axis of drawing and the normal axis of the film specimen.

gave a WAX pattern having the superposition of the fiber textures (*c*-axis orientation texture) of both polymers. However, it is clear from Figure 1 that the crystalline orientation state of PB-1 in this blend remarkably changed during melt recrystallization and even during storage at room temperature, while the fiber texture of the PP component remained unchanged during the heat treatment.

In the WAX pattern shown in Figure 1(a), an intense, arc (*d*-spacing = 0.73 nm) having the intensity maximum at an azimuthal angle of 45° is outstanding. This could be indexed as a (200) reflection of the PB-1 crystal of modification II[8,9] with a tetragonal unit cell. A (220) reflection (*d*-spacing = 0.52 nm) of the tetragonal crystal can also be observed as sharp arcs with the intensity maximum located on the meridian in this pattern. It follows that the majority of the PB-1 tetragonal unit cells are aligned with their (110) planes perpendicular to the axis of drawing.

As is already well-known,[10,11] the crystalline modification II of PB-1 is unstable and gradually transforms into a stable rhombohedral (hexagonal) modification I with axes $a = 1.77$ nm and $c = 0.65$ nm. Figures 1(b), 1(c), and 1(d) are the WAX patterns of the blend specimen aged at room temperature for a week to allow the complete transformation of the PB-1 crystals to their stable form I. It was confirmed by the DSC study that the transformation in the present system was completed within at least 5 days at room temperature.
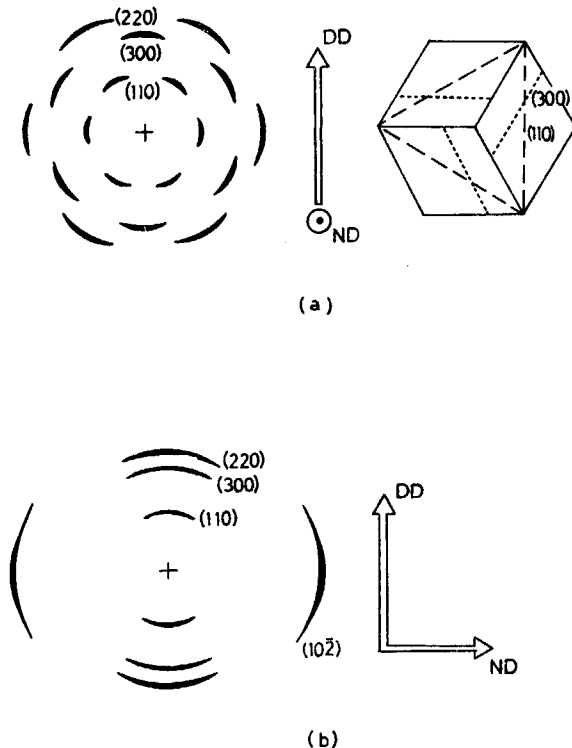

(a)

(b)

Fig. 2.   WAX diagrams of the PB-1 component (modification I), showing the distinct crystalline orientation with respect to the sample coordinate system.

In Figure 1(b) (through-view pattern), (110), (300), and (220) reflections of the PB-1 crystal (modification I) appear as six arcs on each Debye ring. A diagram of the reflections of the PB-1 hexagonal crystal is illustrated in Figure 2(a). In the edge view [Fig. 1(c)] and end view [Fig. 1(d)], however, the ($hk0$) reflections appear with appreciable intensity on the meridian and the (10$\bar{2}$) reflection can be observed near the equator as sharp arcs. The pattern is diagrammatically depicted in Figure 2(b). As can be seen from Figure 2, the c-axis of the PB-1 crystallites are oriented preferentially perpendicular not only to the draw direction but also to the surface of the blend film.

Almost the same result of WAX measurements as described above was obtained for an oriented PP/PB-1 film heat-treated at 140°C under a relaxed condition, except that the degree of orientation of PP was somewhat lower compared with the case using a sample treated at constant length.

SAX Scattering

In order to obtain the information about the supermolecular structure of drawn, then heat-treated PP/PB-1 blends, the SAX measurements were performed. The SAX patterns of an oriented sample aged for 8 days after heating at 140°C are shown in Figure 3; the patterns (a) and (b) were taken at room temperature, and the other pattern (c) was taken under a condition where the sample was reheated up to 140°C and kept at the temperature.

An intense equatorial scattering observed only in the pattern (b) (edge view) occurred due to the surface reflection of parallel-stacked films, and not due to a structural cause. In Figures 3(a) and 3(b), a cross type of scattering maximum is located on the meridian, whereas in Figure 3(c) the vertical component is completely missing. This result indicates that the vertical scattering originates from the supermolecular structure of PB-1 phase developed in the course of melt recrystallization, while the other scattering is attributable to the PP matrix. The appearance of the vertical maximum in the SAX patterns (a) and (b) suggests that some structural entities, probably lamellar crystals of PB-1, are stacked along the draw direction in the dispersed phase, with their long axes perpendicular to the draw direction. In the previous study concerning PP/PE oriented blends, we found a preferential growth of PE lamellae crystals with the longer axes oriented at 30–40° to the draw direction. It is interesting to note that the texture of PB-1 formed in the PP matrix is entirely different from that of PE formed in the same matrix.

Electron Microscopy

The morphological features of the oriented PP/PB-1 blend heat-treated at 140°C was examined by electron microscopy. For comparison, a spherulitic structure formed in a pure PB-1 film was also observed. The replica membranes were used for the observations. The result is shown in Figure 4. Figure 4(a) is an electron micrograph of a part of a PB-1 spherulite. This micrograph reveals that well-developed, lamellar crystals are radially arranged to construct the PB-1 spherulite. In Figure 4(b), as we expected, long structural entities, presumably corresponding to PB-1 lamellae, grow on the surface of the PP phase, with their long axes perpendicular to the draw direction. Smaller arrows show incomplete, 2-dimensional spherulitic structures of PB-1.
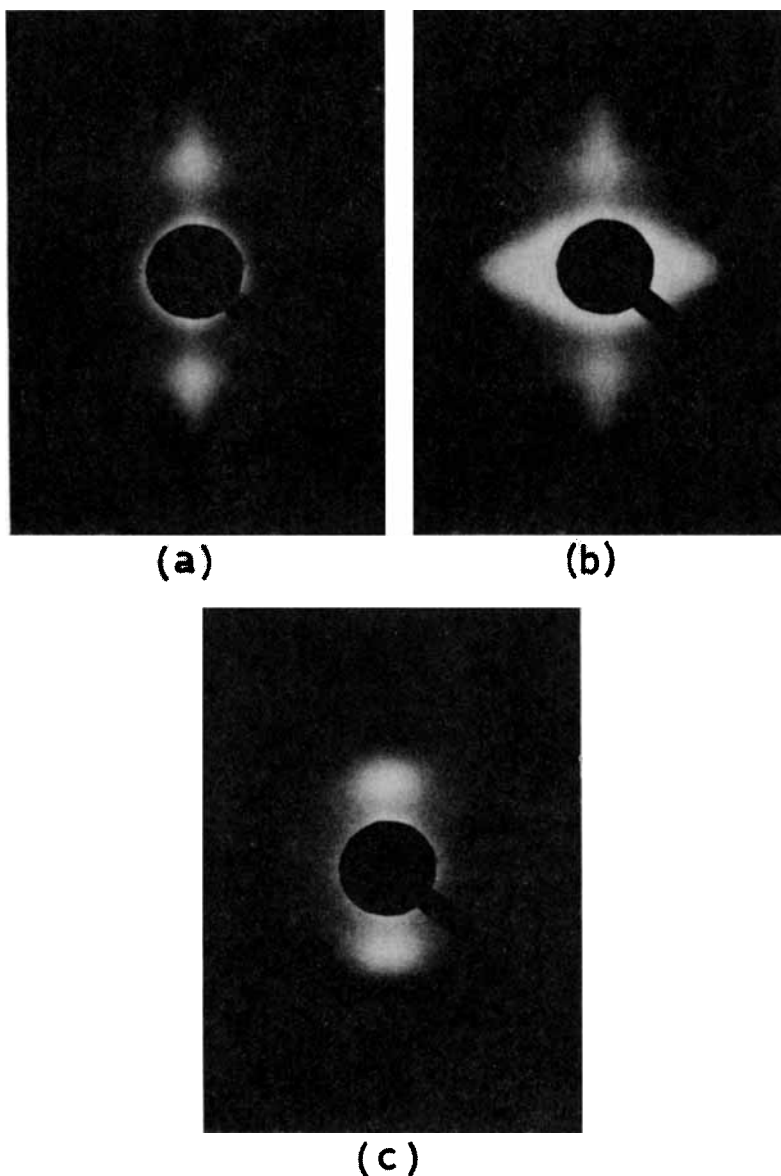
Fig. 3. SAX patterns of a drawn, then heat-treated PP/PB-1 blend, measured at room temperature and 140°C: (a) through view (room temperature); (b) edge view (room temperature); and (c) through view (140°C).
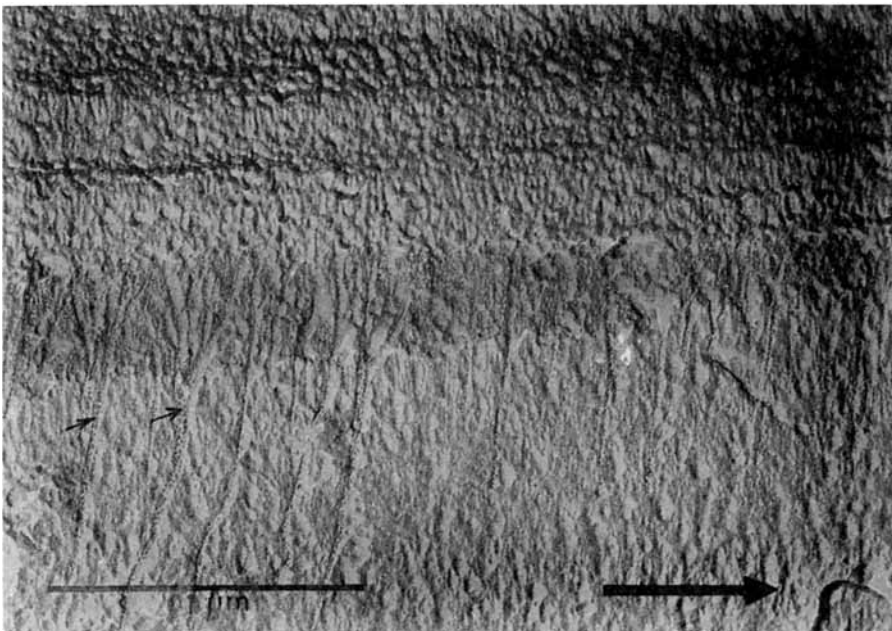
The morphological evidence is not in conflict with the result of the SAX measurement.

Kinetics of Crystallization

The kinetics of isothermal crystallization of PB-1 was examined by use of a DSC technique. For determination of the characteristic parameters of poly-
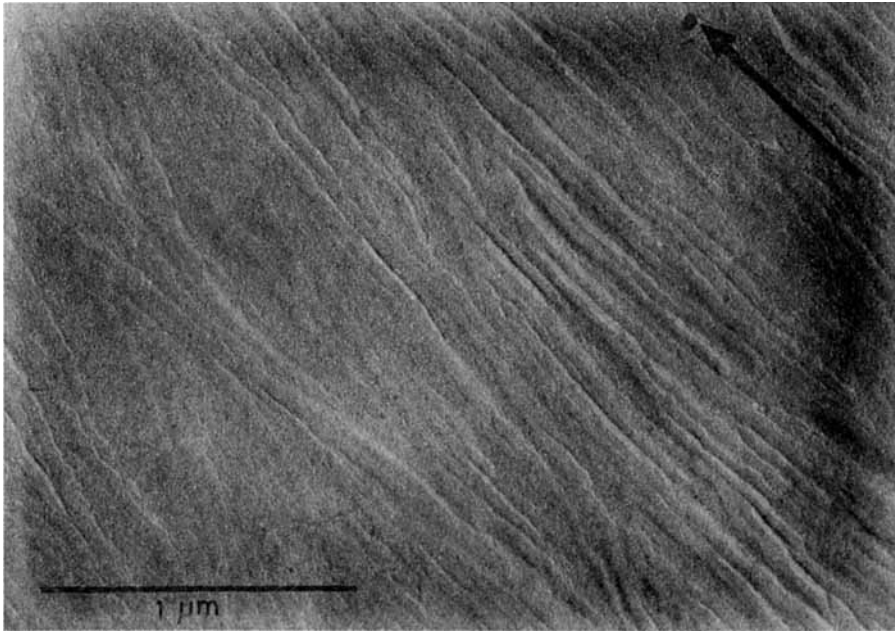
(a)

(b)

Fig. 4.   Electron micrograph of the surface replica of (a) a pure PB-1 film and (b) an oriented PP/PB-1 film heat-treated at 140°C. An arrow indicates the draw direction.
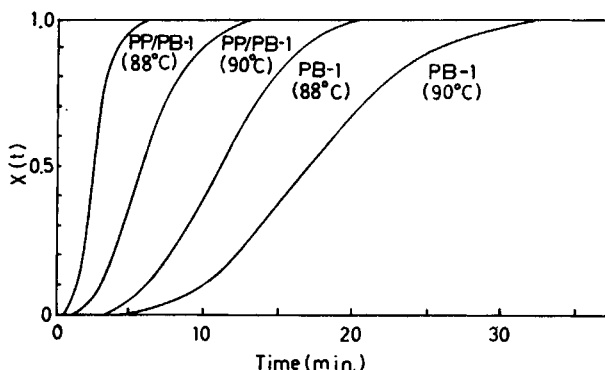
Fig. 5. Transformed fraction $X(t)$ vs. time (t) in isothermal crystallization of nonoriented PB-1 and oriented PP/PB-1 blend.

mer nucleation and crystal growth. It was convenient to use a well-known Avrami's basic theory.

The crystallization isotherms obtained at 88 and 90°C for nonoriented PB-1 and oriented PP/PB-1 sample are shown in Figure 5, where the weight fraction $X(t)$ of PB-1 crystallized from the melt is plotted against time t. The transformed fraction $X(t)$ was determined using the relation $X(t) = Q(t)/Q(\infty)$; $Q(\infty)$ is the total heat generated from the sample at the end of crystallization, being proportional to the overall area of exotherm, and $Q(t)$ is the heat generated up to time t.

The crystallization kinetics of PB-1 followed the Avrami equation up to high degree of transformation. If $\ln\{-\ln[1 - X(t)]\}$ is plotted against $\ln t$, Avrami exponent n can be determined as the slope of the curve by a linear regression. The Avrami exponents obtained for both samples at each crystallization temperature (T_c) are listed in Table I, where the induction period $t(i)$ and the half time $t(1/2)$ are also summarized. Although the Avrami's theory contains much simplification, the Avrami exponent can be used as a convenient parameter to characterize the crystallization behavior of polymers.

TABLE I
Values of Avrami Exponent (n), Induction Time $t(i)$, and Half Crystallization
Time $t(1/2)$ obtained for Nonoriented PB-1 and an Oriented PP/PB-1
Blend Sample in Isothermal DSC Measurement

Sample	Crystallization temp (°C)	Avrami exponent	Induction time (min)	Half cryst. time (min)
Nonoriented	85	3.4	1.2	6.8
PB-1	88	3.4	3.0	12.0
	90	3.3	3.0	17.0
Oriented	85	2.6	—	1.8
PP/PB-1	88	2.5	0.8	2.7
blend	90	2.3	0.8	6.0
	92	2.2	2.6	11.0

DISCUSSION

Development of PB-1 Texture in Oriented PP Matrix

On the basis of the result shown above, the development of PB-1 texture in a drawn PP matrix is discussed below. A schematic representation for understanding the distinct crystalline texture of PB-1 found in the present system is illustrated in Figure 6. Here, incomplete, 2-dimensional spherulitic structures are shown. A long axis of the PB-1 lamella is aligned perpendicular to the draw direction, and the c-axis of the PB-1 crystal is oriented perpendicular both to the draw direction and the plane of the surface of the blend film. The orientation state of the tetragonal unit cell of the unstable modification II is also shown in this figure together with that of hexagonal one of the modification I. It should be noted that the (110) plane of the PB-1 tetragonal crystal is oriented preferentially perpendicular to the draw direction immediately after the melt recrystallization.

Up to date some workers found interesting new crystalline textures in some oriented polymer blend systems. The structural development in nylon 11/PP,[2] nylon 66/PEG,[3] and PP/PE[6] systems were interpreted on the basis of epitaxy. Confined growth in the restricted space and thermal shrinking effect were also proposed for polystyrene/PE system[1] and PP/PE system,[5] respectively.

In the present case, the structural development can be explained on the basis of transcrystallization of PB-1 in the PP matrix. The result of kinetics of isothermal crystallization of PB-1 suggests that heterogeneous nucleation of PB-1 occurs on the surface of PP domain, as schematically shown in Figure 6 (left). Since PB-1 crystal tends to grow fast in one direction, long lamellae grow with their long axes perpendicular to the draw direction. Electron micrographs and SAX patterns of PP/PB-1 blend (Figures 3, 4) support the
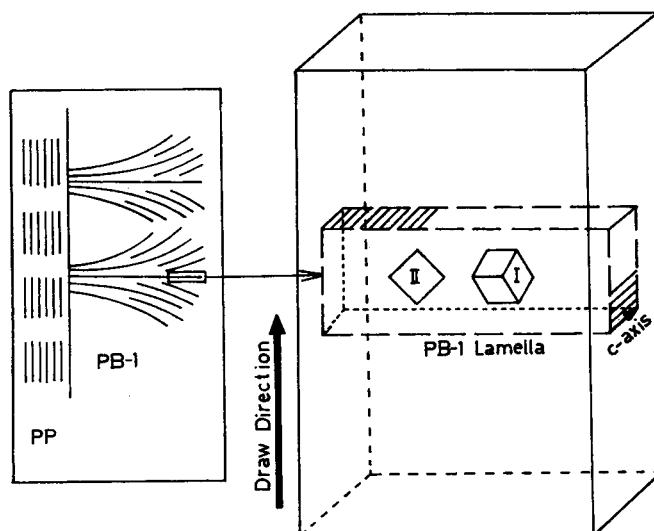

Fig. 6.   Schematic representation of the lamellar arrangement and unit cell orientation of PB-1 developed in an oriented blend with PP.

above suggestion. It is possible to conclude from the results of WAX and electron microscopy that PB-1 crystal grows fast in ⟨110⟩ direction of the unit cell of modification II to form a long lamella.

According to the experimental results, the orientation of PB-1 lamellae are perpendicular to the draw direction and besides the majority of them are arranged parallel to the surface of the film specimen, as shown in Figure 6. The reason for the latter arrangement of PB-1 lamellae still remains unclear. In order to interpret the singularity, we cannot but assume that the shape of PB-1 domains dispersed in the drawn PP matrix were not rotationally symmetric around each longitudinal axis parallel to the draw direction, i.e., the dimension in the direction of thickness of the film was much smaller than that in the direction of the width. If it had not been for such anisotropy in the domain shape, the development of PB-1 lamellar crystals had proceeded in the perpendicular direction as well as in the parallel one to the film surface, but with restriction of the orientation of (110) planes perpendicular to the draw direction. Accordingly, it seems reasonable to believe that the arrangement of PB-1 long lamellae parallel to the film surface is attributable to the crystal growth confined to an approximately 2-dimensional space in the PP matrix.

As described above, some workers interpreted the structural development as a consequence of epitaxy due to the crystallographic interaction at the interface between two constituent polymers. If epitaxy plays a decisive role in formation of the distinct texture observed here, an appreciable interaction must exist between the fold surface of PB-1 crystal and a ($hk0$) plane of the substrate with the fiber texture.

However, such an interaction between the chain-fold surface and the substrate can rarely be found. For example, Holland and Lindenmayer[12] observed that dislocation networks were formed in the plane between two platelets of folded-chain PE single crystals, due to the crystallographic interaction at the interface. Also one of the authors reported previously that single crystals of poly(ethylene oxide) grew epitaxially on a (001) plane of KBr with their fold surface parallel to the (001) plane, when the polymer was crystallized from a dilute solution on the cleavage surface of KBr.[13] Taking into account a general proposition that amorphous defects exist on the fold surface of melt-grown polymer crystals in contrast with solution-grown single crystals, it is difficult to expect that molten PB-1 crystallizes epitaxially on the surface of the PP matrix in such a manner as discussed above.

In conclusion, it is the authors' view that the structural development of PB-1 in the oriented PP/PB-1 blend film can be attributed to the transcrystallization of PB-1 in the 2-dimensionally confined space in PP matrix.

Kinetics of Isothermal Crystallization of PB-1

Figure 5 shows that the rate of crystallization of PB-1 in the oriented blend is much faster than that in the nonoriented homopolymer sample and that the period of induction of the crystallization is also shorter in the former system. It is suggested that heterogeneous nucleation of PB-1 on the surface of the PP matrix brought about such a reduction in the induction period. In fact, as shown below, transcrystallinity phenomena was observed in optical microscopy when an experiment of melt crystallization of PB-1 was carried out in the presence of PP fibers.

100μm   (a)
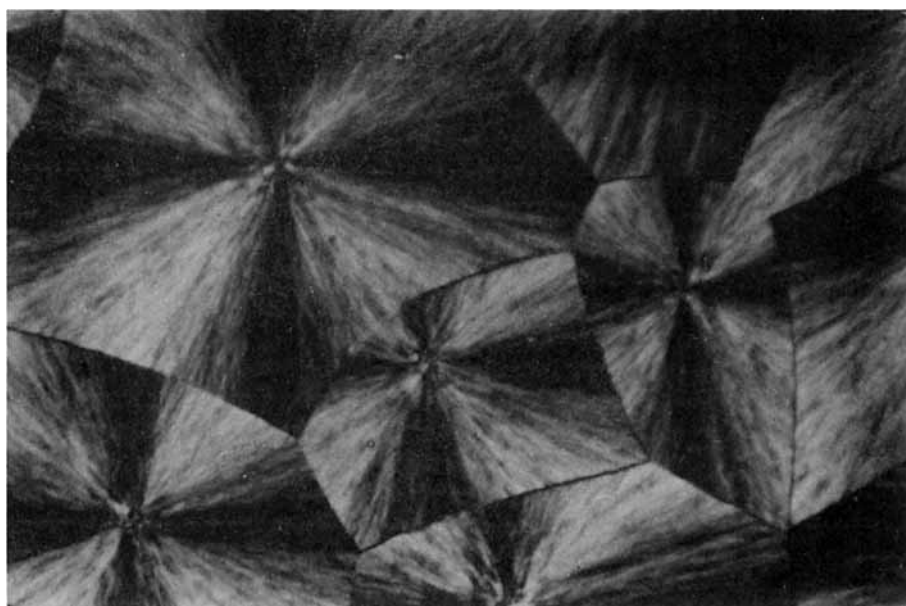
100μm   (b)

Fig. 7. Polarized optical micrograph of PB-1 crystal grown at 90°C from the melt (a) on a glass plate and (b) in contact with PP fibers.

The faster crystallization kinetics of PB-1 in the oriented blend with PP may be attributed to an effect of thermal shrinking stress on the dispersed domains during the melt recrystallizatin of PB-1; that is , it seems reasonable to assume that compressive deformation of the PB-1 domain causes a kind of oriented crystallization to accelerate the crystal growth of PB-1 component.

Table I indicates that the value of n observed for the oriented PP/PB-1 are lower than those observed for the nonoriented PB-1 pure sample. The lowering in the exponent for blend sample is possibly attributable to the heterogeneous nucleation of PB-1 on the surface of the oriented PP matrix. The values ranging from 2.2 to 2.5 suggest that the 2-dimensional crystal growth of PB-1 prevalently proceeded in the confined space in preference to the three-dimensional growth. We found previously that polycaprolactone crystallized epitaxially on the surface of a drawn polyethylene film.[14] In the case, the Avrami exponent was evaluated as about unity in the isothermal DSC experiment, indicating that the 1-dimensional crystals (fibrillar lamellae) of polycaprolactone anchored to polyethylene crystals grew perpendicular to the substrate surface.[15] It is reasonably deduced that the present crystallization behavior of PB-1 in the oriented PP matrix, which is characterized as the heterogeneous nucleation followed by the 2-dimensional crystal growth is essentially different from such an epitaxial crystallization.

To rationalize the above consideration based on the DSC study, the melt crystallization of PB-1 in the presence of oriented PP fibers was examined on a hot stage in a polarized microscope. Figure 7 shows a polarized optical micrograph of the PB-1 crystal growth at 90°C from the molten state in contact with PP fibers. Here transcrystallization of PB-1 is clearly evident; apparently the surface of the oriented PP fibers has nucleating efficiency for PB-1. This result strongly supports the conclusion that the heterogeneous nucleation of PB-1 followed by the 2-dimensional crystal growth prevailed in the oriented PP/PB-1 blend.

References

1. Z. Mencik, H. K. Plammer, and H. Van Oene, *J. Polym. Sci.*, A-2, 10, 507 (1972).
2. K. K. Seth and C. J. E. Kempster, *J. Polym. Sci., Polym. Symp.*, 58, 297 (1977).
3. R. E. Fornes, P. L. Grady, S. P. Hersh, G. R. Bhat, and N. Morosoff, *J. Polym. Sci., Polym. Phys. Ed.*, 14, 559 (1976).
4. Y. Nishio, T. Yamane, and T. Takahashi, *J. Macromol. Sci.-Phys.*, B23, 17 (1984).
5. T. Takahashi, Y. Nishio, and K. Maruoka, *Bull. Res. Inst. Mater. Sci. Eng. (Fac. Eng. Fukui Univ.)*, 22, 15 (1984).
6. B. Gross and J. Petermann, *J. Mater. Sci.*, 19, 105 (1984).
7. M. Kojima and H. Satake, *J. Polym. Sci., Polym. Phys. Ed.*, 22, 285 (1984).
8. A. Turner Jones, *J. Polym. Sci.*, B1, 45 (1963).
9. V. Petraccone, B. Pirozzi, A. Frasci, and P. Corradini, *Eur. Polym. J.*, 12, 323 (1976).
10. G. Natta, P. Corradini, and I. W. Bassi, *Nuovo Cimento Suppl.*, 15, 52 (1960).
11. J. Boor, Jr. and J. C. Michell, *J. Polym. Sci.*, A1, 59 (1963).
12. V. F. Holland and P. H. Lindenmayer, *J. Appl. Phys.*, 36, 3065 (1965).
13. K. Kobayashi and T. Takahashi, *Kagaku*, 34, 325 (1964).
14. T. Takahashi, M. Inamura, and I. Tsujimoto, *J. Polym. Sci.*, B8, 651 (1970).
15. T. Takahashi, N. Odani, and S. Nagase, *Kobunshi-Ronbunshu*, 32, 173 (1975).