Preparation of Oriented β-Form Poly(L-lactic acid) by Solid-State Coextrusion: Effect of Extrusion Variables

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ABSTRACT: A film of melt-crystallized poly(L-lactic acid) (PLLA) consisting of α-form crystals was uniaxially drawn by solid-state coextrusion at 110−170 °C using split billets of different polymers. The effects of extrusion variables, including the extrusion draw ratio (EDR), temperature (T_{ext}), and pressure (P_{ext}), on the crystal transformation from the initial α-form to the oriented β-form crystals were studied. The crystal transformation proceeded rapidly with EDR. It was found that when coextrusion was made at a constant P_{ext} and EDR but at different T_{ext}'s, there was a T_{ext} (130 °C) where the crystal transformation proceeded most efficiently. Furtheremore, when coextrusion was made at a constant T_{ext} and EDR but at different P_{ext}'s, the transformation proceeded more efficiently at a higher P_{ext}. These results show that crystal transformation proceeds with the EDR most efficiently for the coextrusion at a T_{ext} of 130 °C and a higher P_{ext}. As a result of the specific effect for each of the extrusion variables on the crystal transformation and ductility, a highly oriented film consisting of β crystals alone was obtained by coextrusion to the highest EDR of ∼14 achieved at a high T_{ext} of 170 °C, near the T_m, and a high P_{ext} of ∼50 MPa.

Introduction

Poly(L-lactic acid) (PLLA) is a biodegradable and biocompatible polymer with good mechanical properties.[1] Since PLLA undergoes hydrolytic decomposition in the human body to nontoxic lactic acid,[2] this polymer is used for biomedical applications as sutures for microsurgery,[3] bone-fixation devices,[4,5] and drug-delivery systems.[6] The mechanical properties and chemical stability of a crystalline polymer, in general, strongly depend on the morphology and crystal structure.[6−9] Thus, attempts to control these properties of PLLA have been made by introducing anisotropy in the chain alignment within fibers and rods by applying plastic deformation.[2,3,8,9]

PLLA takes two crystal forms[10−16] depending on the conditions for crystallization, spinning, and drawing. The most common polymorph, the α form (pseudo-orthorhombic,[10] pseudo-hexagonal,[11,12] or orthorhombic[13−15]), has a 10_3 helical chain conformation and is obtained by crystallization from solutions or melt. The β form[12,16] (orthorhombic[12] or trigonal[16]) is known to take a 3_1 helical conformation. When an amorphous film was drawn by tensile force slightly above the T_g (55 °C), an oriented film with α crystals was obtained. When a semicrystalline sample with α crystals was drawn, a part of the α crystals was transformed into the oriented β crystals, depending on the draw conditions.[9,12] Eling et al.[10] reported that β crystals were generated upon tensile drawing at a high temperature to a higher DR, whereas the drawing at a low temperature and/or a low draw ratio produced α crystals. Thus, the drawn products of PLLA commonly consist of α crystals or a mixture of α and β crystals. Leenslag et al.[17] and Hoogsteen et al.[13] prepared high-strength fibers that consisted of pure β-form crystals by hot drawing of solution-spun PLLA fibers of high molecular weights ($M_v = (5.6−9) \times 10^5$) at 200−204 °C, 20−25 °C above the static T_m of an α crystal, to a draw ratio of 14−20. They found that the formation of β crystals depended on the sample molecular weight and molecular weight distribution in addition to the drawing temperature and draw ratio. In a previous paper,[18] we reported on the preparation of highly oriented rods consisting of only β crystals by solid-state extrusion of a PLLA billet consisting of α crystals at 170 °C, ∼10 °C below the static T_m (∼180 °C) . Despite these reports, the conditions for the formation of β crystals have not been well clarified yet.

In this paper, we report on the effects of extrusion variables, including the extrusion draw ratio (EDR), temperature (T_{ext}), and pressure (P_{ext}), on the crystal transformation from the initial α to the oriented β crystals upon solid-state coextrusion of a PLLA film. A variety of extrusion conditions could be achieved by using appropriate polymers for the split billets in which a PLLA film was sandwiched, and the assembly was coextruded by utilizing the solid-state coextrusion technique developed by Porter et al.[19]

Experimental Section

Drawing. The PLLA used had a viscosity average molecular weight, M_v, of 4.6×10^5. Before compression molding, the sample was dried in vacuo at 100 °C for 24 h. The dried PLLA was molded at 210 °C into a film that was 0.3 mm thick, followed by slowly cooling to room temperature. Thus, a film consisting of α crystals (46% crystallinity) was obtained. Draw was made by solid-state coextrusion.[19]

For solid-state coextrusion, a strip that was 10 mm wide and 70 mm long was placed between two split billet halves of

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high-density polyethylene (HDPE), poly(4-methyl-1-pentene) (P4M1P), or poly(chlorotrifluoroethylene) (PCTFE), depending on the T_{ext} and P_{ext}, and the assembly was coextruded through a conical brass die. Although the ductility of PLLA increased with T_{ext}, the drawn product melted partially after coming out of the extrusion die for the coextrusion at a $T_{\mathrm{ext}} \geq 175$ °C. Therefore, coextrusion was made at a $T_{\mathrm{ext}} \leq 170$ °C. Split billets of P4M1P were commonly used. However, by selecting split billets of appropriate polymers, coextrusion at a constant T_{ext} and EDR but at different P_{ext}'s and coextrusion at a constant P_{ext} and EDR but at different T_{ext}'s could be achieved. The extrusion rate was 1 cm/min independent of the extrusion conditions such as EDR, T_{ext}, and P_{ext}.

Characterization. Wide-angle X-ray diffraction (WAXD) patterns were recorded by a flat-plate camera and by diffractometer scans. WAXD photographs were obtained with Cu Kα radiation generated at 40 kV and 25 mA on a Rigaku Geigerflex RAD-3A and monochromatized with a graphite crystal. WAXD profiles were recorded with Ni-filtered Cu Kα radiation generated at 40 kV and 150 mA on a Rigaku Rotaflex RU-200 rotating anode X-ray generator equipped with a diffractometer and a pulse height discriminator. The (00*l*) profiles on the meridian were measured by a symmetrical transmission mode. Although different unit cells have been proposed for each of the α and β forms, we assume an orthorhombic cell for each of them.[12-14]

Densities were measured by a picnometer method at 30.0 ± 0.1 °C using pure water as a filling liquid to avoid significant absorption of a liquid and the crystallization induced by the absorbed liquid. The crystallinity of a sample consisting of only α or β crystals was calculated assuming a crystal−amorphous two-phase structure. The densities of an amorphous phase (ρ_a), an α crystal [$\rho_c(\alpha)$], and a β crystal [$\rho_c(\beta)$] were assumed to be 1.245 ± 0.001,[18] 1.285,[13] and 1.301 ± 0.001 g/cm^3,[18] respectively.

The crystal transformation from α to β crystals was also followed by infrared (IR) spectroscopy. Polarized spectra were recorded using a JEOL Fourier transform infrared spectrometer (JRS-FT7000W) at a resolution of 1 cm^{-1} and room temperature. An oriented film consisting of α crystals (10_3 helix) exhibits an absorption band at 923 cm^{-1} that is assigned to the CH_3 rocking mode showing the transition moment perpendicular to the chain axis.[20-22] As will be discussed later, a highly oriented β film showed a band at 912 cm^{-1} which was absent in an amorphous sample and an α film. This band was assigned to the CH_3 rocking mode of β crystals (3_1 helix) showing the transition moment perpendicular to the chain axis. Thus, the chain orientation of α and β crystals in an oriented sample could be determined by using the IR dichroic ratio. The crystalline chain orientation function, f_c, was calculated from the dichroic ratio, R, defined as

$$R = A_{\parallel}/A_{\perp} \tag{1}$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbance for electric vectors parallel and perpendicular, respectively, to the fiber axis. R is related to the chain orientation function, f_c, by

$$f_c = {}^1/_2\langle 3\cos^2\theta - 1\rangle = \{(R-1)/(R+2)\}/\{(R_0+2)/(R_0-1)\} \tag{2}$$

where θ is the angle between the molecular axis and the fiber axis and $R_0 = 2\cot^2\alpha$, α being the angle between the transition moment associated with the considered absorption and the molecular axis.[23] For these absorption bands assigned to the CH_3 rocking modes, $\alpha = 90°$ as will be discussed later.

Result and Discussion

Effect of Extrusion Draw Ratio. Wide-Angle X-ray Diffraction. Figure 1 shows WAXD photographs for an EDR series prepared at an optimum T_{ext} of 170 °C where the highest EDR was achieved. These photographs were recorded for the sheath portions of the coextrudates. Although the WAXD meridional scans showed that the crystal transformation from the initial α to oriented β crystals proceeded slightly more rapidly at the sheath than at the core regions, as was found in the solid-state extrusion of a PLLA billet,[18] the difference was minor and could not be detected in their photographs. The initial film (EDR = 1) consisted of Debye−Scherrer rings from randomly oriented α crystals. Upon extrusion to an EDR of 3, the intensity of the strongest $(200)_\alpha$ and $(110)_\alpha$ composite reflection of α crystals became slightly stronger on the equator, showing that the initial α crystals were partially deformed and that the chains showed slightly preferential orientation along the extrusion direction. Upon further extrusion, the chain orientation and the relative amount of β crystals increased rapidly with the EDR. At the highest EDR of ~14, all of the reflections were basically spotty with no arc, showing a highly oriented β structure. A more quantitative evaluation of the crystal transformation will be discussed below on the basis of the WAXD meridional profiles and IR absorption bands characteristic for the α and β forms (Figure 3).

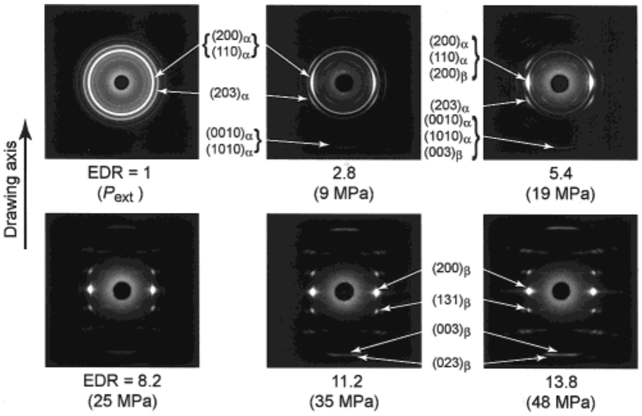

Figure 1. WAXD photographs for an EDR series of PLLA prepared at a $T_{\mathrm{ext}} = 170$ °C using split billets of P4M1P. The patterns were recorded with the incident beam perpendicular to the coextruded films. The extrusion pressure, P_{ext}, increased with EDR as shown below the EDR for each sample.

Infrared Spectroscopy. The crystal transformation and the chain orientation upon the coextrusion draw were also characterized by polarized IR spectroscopy. Cohn et al.[20] reported an absorption band at 921 cm^{-1} characteristic of α crystals. Subsequently, Lee et al.[21] found that this band exhibits perpendicular dichroism in oriented α films prepared by tensile drawing of an amorphous film at low temperatures (55−95 °C). Recently, Kang et al.[22] assigned this band associated with the transition moment perpendicular to the chain axis to the CH_3 rocking mode combined with a minor contribution from the C−COO and O−CH stretching modes of α crystals.

Figure 2 shows polarized infrared spectra measured with the incident beam polarized parallel (solid lines) and perpendicular (dotted lines) to the draw direction for an EDR series consisting of oriented α crystals, a mixture of oriented α and β crystals, and oriented β crystals. The spectra for an amorphous film and an oriented α sample were also included. The band at 923 cm^{-1} was found in all the samples containing α crystals as characterized by WAXD. It was found in Figure 2 that a highly oriented film with an EDR of 13.8 consisting of β crystals alone exhibited a new band at

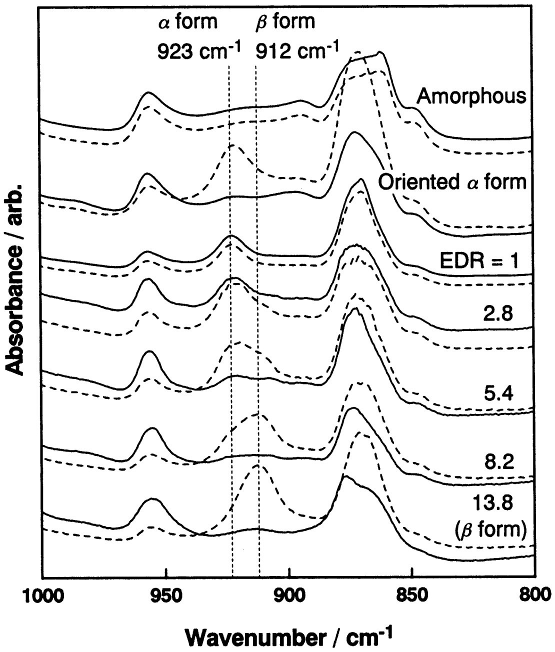

Figure 2. Polarized infrared spectra in the 800−1000 cm^{-1} region for an EDR series prepared at a T_{ext} = 170 °C and measured with the incident beam polarized both parallel (—) and perpendicular (- - -) to the draw direction. Spectra of an amorphous film and an oriented α-form sample are also included. Note the appearance of the bands at 923 and 912 cm^{-1} characteristic of α and β crystals, respectively.

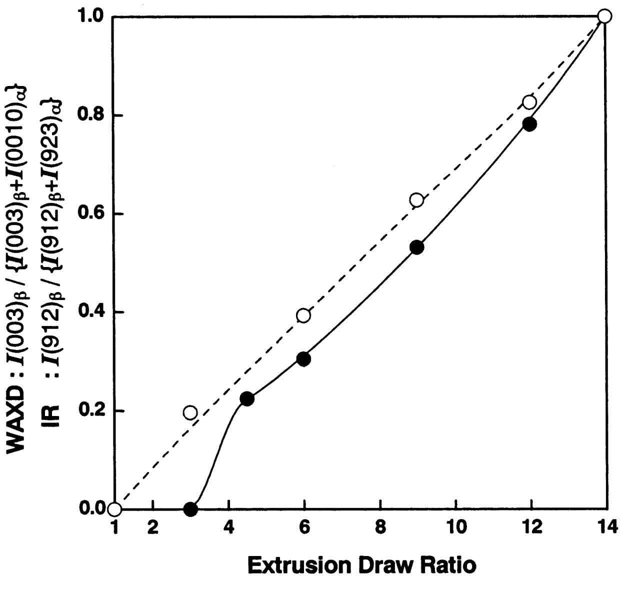

Figure 3. Formation of β-form crystals as a function of EDR as evaluated from the WAXD intensity ratio of $I(003)_\beta/[I(003)_\beta + I(0010)_\alpha]$ (●) and IR intensity ratio of $I(912)_\beta/[I(912)_\beta + I(923)_\alpha]$ (○).

912 cm^{-1}, which was absent in the spectra of a sample consisting of α crystals alone and an amorphous film. This band characteristic of β crystals appeared at a slightly lower frequency of the α band at 923 cm^{-1} and showed a number of similarities to the α band in shape, intensity, and dichroism. Moreover, the intensity ratios of the 923 and 912 cm^{-1} bands agreed fairly well with the relative amounts of α and β crystals estimated from the WAXD profiles as will be discussed below (Figure 3). These facts suggest that the band at 912 cm^{-1} found in the β sample is assigned to the CH_3 rocking mode for β crystals.

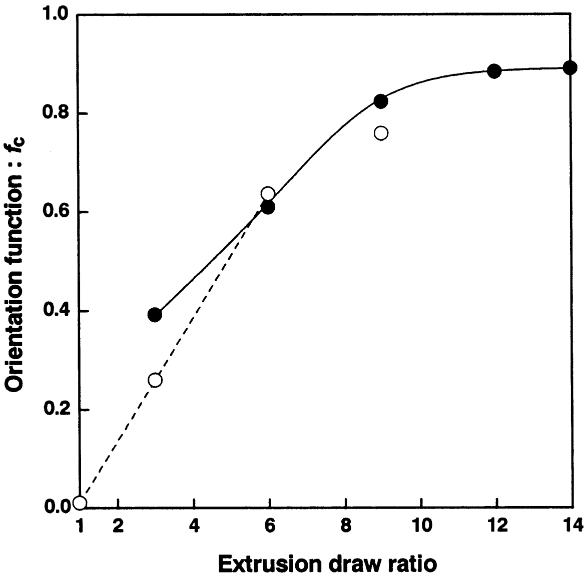

Figure 4. Crystalline chain orientation functions $f_c(\alpha)$ (○) and $f_c(\beta)$ (●) for α and β crystals, respectively, as a function of the EDR, calculated from the IR dichroism shown in Figure 2.

On the basis of these assignments of the IR bands at 923 and 912 cm^{-1} and assuming that both bands have the same absorption coefficient, the relative amount of β crystals to the sum of α and β crystals can be calculated by $I(912)_\beta/[I(912)_\beta + I(923)_\alpha]$, where the $I(912)_\beta$ and $I(923)_\alpha$ are the intensities of the 912 and 923 cm^{-1} bands, respectively, measured after the correction for IR dichroism.[24] The WAXD meridional scans showed that the intensity of the $(003)_\beta$ reflection progressively increased with the EDR at the expense of the $(0010)_\alpha$ reflection intensity. Since the degree of chain orientation was comparable for α and β crystals within a given sample as will be shown later (Figure 4), the relative amount of β crystals was also evaluated from the WAXD by $I(003)_\beta/[I(003)_\beta + I(0010)_\alpha]$, assuming that the scattering powers of the $(0010)_\alpha$ and $(003)_\beta$ planes were not so much different because the chain conformation (3_1 and 10_3 helix) as well as the chain packing of both crystal forms are similar to each other. Here, the $I(003)_\beta$ and $I(0010)_\alpha$ were the intensities of the $(003)_\beta$ and $(0010)_\alpha$ reflections, respectively. To calculate these values, the observed IR spectra and WAXD profiles were resolved into the appropriate peaks by assuming a symmetrical function consisting of Gaussian and Cauchy profiles for each of the peaks.

Figure 3 shows the relative amounts of β crystals as a function of the EDR, estimated from the WAXD and IR data for an EDR series prepared at 170 °C. The values for the relative amount of β crystals agree fairly well for the two methods and increased nearly linearly with the EDR, except at a low EDR of 2.8. However, the WAXD $(003)_\beta$ reflection around $2\theta = 30°$ was not distinguished at lower EDR's ≤ 2.8 probably due in part to the overlapping with other reflections. Another possible reason for the difference in WAXD and IR evaluations at a low EDR may be that the IR band of 912 cm^{-1} is active to the 3_1 helix independent of the sequence lengths, whereas only long sequences of the 3_1 helix contribute to the X-ray $(003)_\beta$ reflection and shorter ones do not contribute to the intensity of this reflection. Thus, infrared spectroscopy was more sensitive to detect a small amount of β crystals within a sample. It is noted that both WAXD and IR spectroscopy showed that oriented β crystals grew at the expense of α crystals. Furthermore, the crystallinity (χ_c) of an extrudate (EDR = 13.8) consisting of only β crystals was comparable to that of the starting film consisting of α crystals (χ_c = 51% vs 46%). These observations suggest that most of the oriented β crystals were generated from α crystals through the crystal transformation.

The quantitative evaluation of the crystalline chain orientation was difficult for the WAXD technique because the azimuthal intensity distribution for the $(0010)_\alpha$ and $(003)_\beta$ reflections was not possible to determine due to overlapping with other reflections such as the $(023)_\beta$ and $(1010)_\alpha$ reflections (see Figure 1). In addition, the equatorial $(hk0)_\alpha$ and $(hk0)_\beta$ reflections were also overlapped, and again their azimuthal intensity distribution could not be determined.

Therefore, the crystalline chain orientation functions $f_c(\alpha)$ and $f_c(\beta)$ for α and β crystals, respectively, were reevaluated from the dichroic ratios of the polarized IR spectra and are shown in Figure 4 as a function of the EDR for an EDR series prepared at a T_{ext} = 170 °C. At a low EDR of 2.8, the $f_c(\beta)$ showed a slightly higher value than that of $f_c(\alpha)$, showing that the chain orientation of β crystals is slightly higher than that of α crystals. It is interesting to note that, at yet higher EDR's, the chain orientations of both crystal forms were comparable, approaching $f_c(\beta) = 0.90$ at higher EDR's ≥ 12 where the crystal transformation was almost completed. The relatively low $f_c(\beta)$ value of 0.90 even at the highest EDR of ~14 is likely related to the existence of significant crystal disorder in β crystals as suggested by the significant broadening of the strong $(200)_\beta$ reflection and the existence of streak on the layer lines as seen on the WAXD patterns in Figure 1. These observations suggest that the randomly oriented α crystals in an initial film were partially deformed and oriented along the extrusion direction and that the crystal transformation then proceeded steadily with the EDR.

Effects of Extrusion Temperature, T_{ext}. As discussed, α crystals transformed to oriented β crystals steadily with increasing EDR in solid-state coextrusion. Thus, a highly oriented film consisting of β crystals alone was obtained by solid-state coextrusion at a T_{ext} of 170 °C, ~7 °C below the static T_m of β crystals, to the highest achieved EDR of ~14. A similar effect of deformation ratio on the crystal transformation has also been observed in tensile drawing. Indeed, oriented fibers consisting of only β crystals were obtained by the tensile drawing of solution-spun fibers of high molecular weight PLLA at 200−204 °C, ~25 °C above the static T_m of β crystals, to draw ratios of 14−20.[13,17] Drawing at lower temperatures produced a mixture of α and β crystals. Furthermore, it was found that all the pure β containing fibers were prepared under drawing conditions leading to inhomogeneous drawing.[13] Although solid-state coextrusion was not achieved at such high T_{ext}'s due to melting, an oriented film consisting of β crystals alone was obtained at a T_{ext} of 170 °C. These facts suggest that the effect of drawing temperature on the crystal transformation is different between the two techniques.

To clarify the effect of T_{ext} on the crystal transformation, extrudates having a constant EDR of 6 were prepared at a constant P_{ext} of ~40 MPa but at different T_{ext}'s of 110−170 °C by coextrusion using split billets of appropriate polymers. The WAXD meridional profiles for these extrudates are shown in Figure 5. The sample prepared at a T_{ext} = 170 °C showed a strong $(0010)_\alpha$ reflection in addition to a weaker $(003)_\beta$ reflection. The intensity of $(0010)_\alpha$ reflection significantly decreased, and that of the $(003)_\beta$ increased markedly in the sample prepared at a T_{ext} = 130 °C. However, at a yet lower T_{ext} of 110 °C, the $(003)_\beta$ reflection appeared as a shoulder at a lower angle of the strong $(0010)_\alpha$ reflection, indicating that only a small portion of α crystals transformed to β crystals. In consistency with these WAXDs, the relative amounts of β crystals estimated from the IR spectra were 45, 92, and 47% for the coextrusion at T_{ext}'s of 110, 130, and 170 °C, respectively. These WAXD and IR results show that there is a T_{ext} of 130 °C where the efficiency of the crystal transformation is the highest.

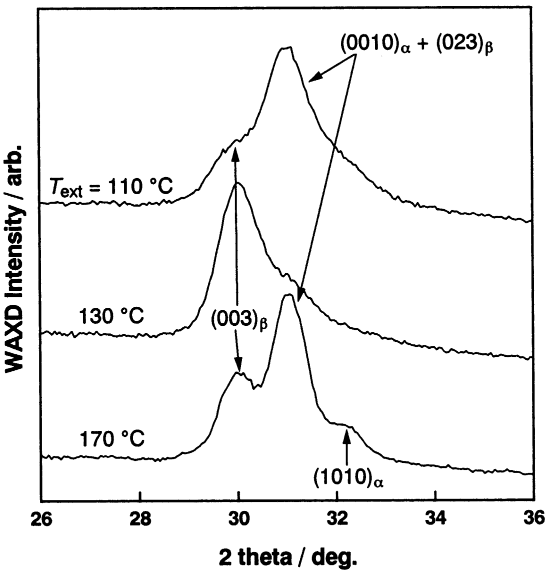

Figure 5. WAXD meridional profiles showing the effect of the extrusion temperature, T_{ext}, on the α to β crystal transformation. The coextrudates with an EDR of 6 were prepared at a constant P_{ext} of 40 MPa but at different T_{ext}'s of 110−170 °C.

Effect of Extrusion Pressure, P_{ext}. To determine the effect of P_{ext} on the crystal transformation, coextrusion was made at a constant EDR of 9 and T_{ext} of 170 °C but at different P_{ext}'s of 25 and 42 MPa by using split billets of appropriate polymers. Figure 6 shows the WAXD meridional scans for these samples. The relative intensity of the $(003)_\beta$ reflection to that of the $(0010)_\alpha$ reflection for the sample prepared at a higher P_{ext} of 42 MPa was significantly stronger than that for the one prepared at a lower P_{ext} of 25 MPa. These observations show that the crystal transformation proceeded more efficiently at a higher P_{ext} for the coextrusion at a P_{ext} of 170 °C.

As discussed above, each of the EDR, T_{ext}, and P_{ext} has a specific effect on the efficiency of the crystal transformation. However, as a consequence of these different effects of the extrusion variables, an oriented sample consisting of only β crystals was obtained at a higher T_{ext} around 170 °C and a higher P_{ext} of ~50 MPa because the highest EDR was achieved at this T_{ext}, slightly below the T_m.

Conclusion

The effects of extrusion variables including EDR, T_{ext}, and P_{ext} on the crystal transformation from α to oriented β crystals have been studied for the solid-state coextrusion of a melt-crystallized PLLA film consisting of α

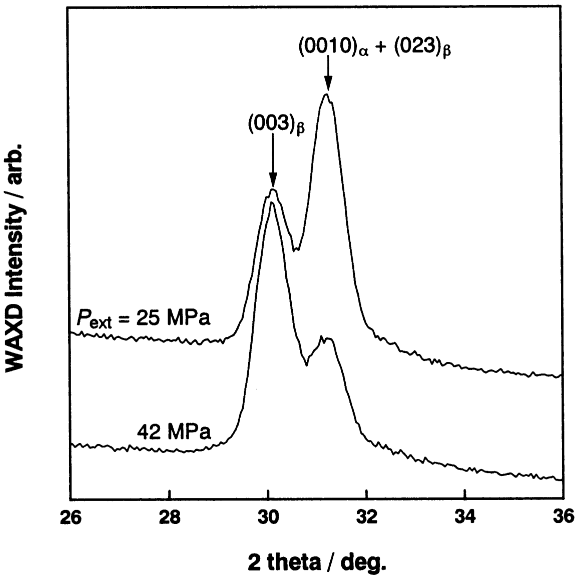

Figure 6. WAXD meridional profiles showing the effect of the extrusion pressure, P_{ext}, on the α to β crystal transformation. The coextrudates with an EDR of 9 were prepared at a constant T_{ext} of 170 °C but at different P_{ext}'s of 25 and 42. MPa.

crystals. The structure of coextrusion-drawn products was characterized by WAXD, IR spectroscopy, and DSC.

The changes with the EDR in the relative intensities of the $(0010)_\alpha$ and $(003)_\beta$ WAXD reflections as well as these of the IR bands at 912 and 923 cm^{-1} showed that the crystal transformation proceeded rapidly with increasing the EDR. It was found that the efficiency of the crystal transformation was higher at a higher P_{ext} than at a lower P_{ext} for the coextrusion at the same T_{ext} and EDR. Furthermore, at a given P_{ext} and EDR, there was a T_{ext} where the crystal transformation proceeded most effectively. This T_{ext} was 130 °C, ~47 °C lower than the T_{m} of β crystals. However, as a result of these characteristic effects of T_{ext}, P_{ext}, and EDR, a highly oriented film consisting of only β crystals was obtained at a higher T_{ext} of 170 °C, near the T_{m}, and a high P_{ext} of ~50 MPa because the highest EDR of ~14 was achieved at this T_{ext}.

Polarized IR spectra of a β film exhibited a new absorption at 912 cm^{-1} that was assigned to the CH_3 rocking mode of a β crystal. This β band and the α band at 923 cm^{-1} due to the CH_3 rocking mode of α crystals showed strong dichroism perpendicular to the chain axis. By using these IR bands, the crystalline chain orientation function f_{c} was calculated for each of α and β crystals within a drawn sample as a function of EDR.

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