

NOTE

Synchronous and separate homo-crystallization of an enantiomeric oligomeric poly(L-3-hydroxybutanoic acid)/poly(D-3-hydroxybutanoic acid) blend

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INTRODUCTION

The crystallization of enantiomeric blends of L- and D-configured polymers or (S)- and (R)-configured polymers is of great interest to macromolecular scientists and engineers.^{1,2} Some hydroxyalkanoic acid-based enantiomeric polyester blends such as poly(lactide) (that is, poly(lactic acid) (PLA))^{1,2} and its substituted polymers such as poly(2-hydroxybutanoic acid) [P(2HB)]³ and poly(2-hydroxy-3-methylbutanoic acid) [P(2H3MB)]⁴ are known to form stereocomplex or racemic crystallites (Figure 1). Other hydroxyalkanoic acid-based optically active polyesters that can form stereocomplex crystallites include the following L- and D-polyesters: poly(2-hydroxymethyl-2-methylbutanoic acid) [P(2HM2MB)] or poly(α -methyl- α -ethyl- β -propiolactone),⁵ poly(3-hydroxy-4,4-dichlorohexanoic acid) [P(3H44DCH)],⁶ and poly(3-hydroxy-4,4-dichloropentanoic acid) [P(3H44DCP)].⁶

However, in the case of bulk crystallization of equimolar poly(L-lactic acid) (PLLA)/poly(D-lactide) (that is, poly(D-lactic acid) (PDLA)) blends from a melt, exclusive stereocomplexation is limited to PLLA and PDLA pairs, either of which has a molecular weight below $1 \times 10^4 \text{ g mol}^{-1}$, whereas solely homo-crystallites are formed when both PLLA and PDLA have molecular weights higher than $1 \times 10^5 \text{ g mol}^{-1}$.^{1,7} By contrast, racemic isotactic poly(3-hydroxybutanoic acid) [P(3HB)],⁸ poly(3-hydroxypentanoic acid)⁹ and poly(propylene sulfide)¹⁰ synthesized from racemic monomer mixtures are crystallizable and form homo-crystallites, not stereocomplex crystallites. In the reported case of P(3HB),⁸ the racemic isotactic P(3HB) synthesized from a racemic mixture of DL- β -ethyl- β -propiolactone should be a stereoblock P(3HB) copolymer or a racemic blend of poly(L-3-hydroxybutanoic acid) [P(L-3HB)] and poly(D-3-hydroxybutanoic acid) [P(D-3HB)]. However, the probability of the latter is very low owing to the difficulty of performing completely separate polymerizations of the L- and D-monomers. Therefore, to the best of our knowledge, the crystallization behavior of a well-defined enantiomeric equimolar P(L-3HB)/P(D-3HB) blend from separately synthesized P(L-3HB) and P(D-3HB) has not been reported to date.

P(D-3HB) and its copolymers are well-known bio-based polyesters, and numerous studies have been performed on their biosynthesis, structure, crystallization, physical properties, biodegradation and applications.^{2,11–13} The specific feature of their crystallization is isomorphism in the copolymers of D-3-hydroxybutanoic acid (or D-3-hydroxybutyric acid) and D-3-hydroxypentanoic acid (or D-3-hydroxyvaleric acid).^{2,11} Blends of P(3HB) with another polymer have been intensively studied to investigate crystallization behavior and to improve and tune mechanical properties and biodegradability.^{11,12}

In the present study, we synthesized oligomeric P(L-3HB) and P(D-3HB) separately from L- and D-3-hydroxybutanoic acids, respectively, and investigated the crystallization behavior of neat P(L-3HB), P(D-3HB), and their well-defined enantiomeric equimolar blend using wide-angle X-ray diffractometry (WAXD), differential scanning calorimetry (DSC) and polarized optical microscopy.

EXPERIMENTAL METHODS

Materials

The synthesis of P(L-3HB) and P(D-3HB) and sample preparation are shown in the Supplementary Information. Natural, high-molecular-weight poly(D-3-hydroxybutanoic acid) [HMW P(D-3HB)] was purchased from Sigma-Aldrich (Tokyo, Japan) and used as received. The molecular characteristics of the synthesized and as-received polymers are summarized in Table 1.

Physical measurements and observation

The weight- and number-average molecular weights (M_w and M_n , respectively) were evaluated in chloroform by a Tosoh (Tokyo, Japan) GPC system (refractive index monitor: RI-8020) with two TSK Gel columns (GMHXL) using polystyrene standards. The ¹H NMR spectra were obtained using a Bruker Biospin (Yokohama, Japan) AVANCE III 400 Spectrometer. The melting temperature and enthalpy (T_m and ΔH_m , respectively) of the crystallized samples were determined with a Shimadzu (Kyoto, Japan) DSC-50 differential scanning calorimeter under a nitrogen gas flow. The samples (~3 mg) were heated from 0 to 200 °C at a rate of 10 °C min⁻¹. The crystallinity (X_c) of the samples was estimated using WAXD. WAXD measurements were

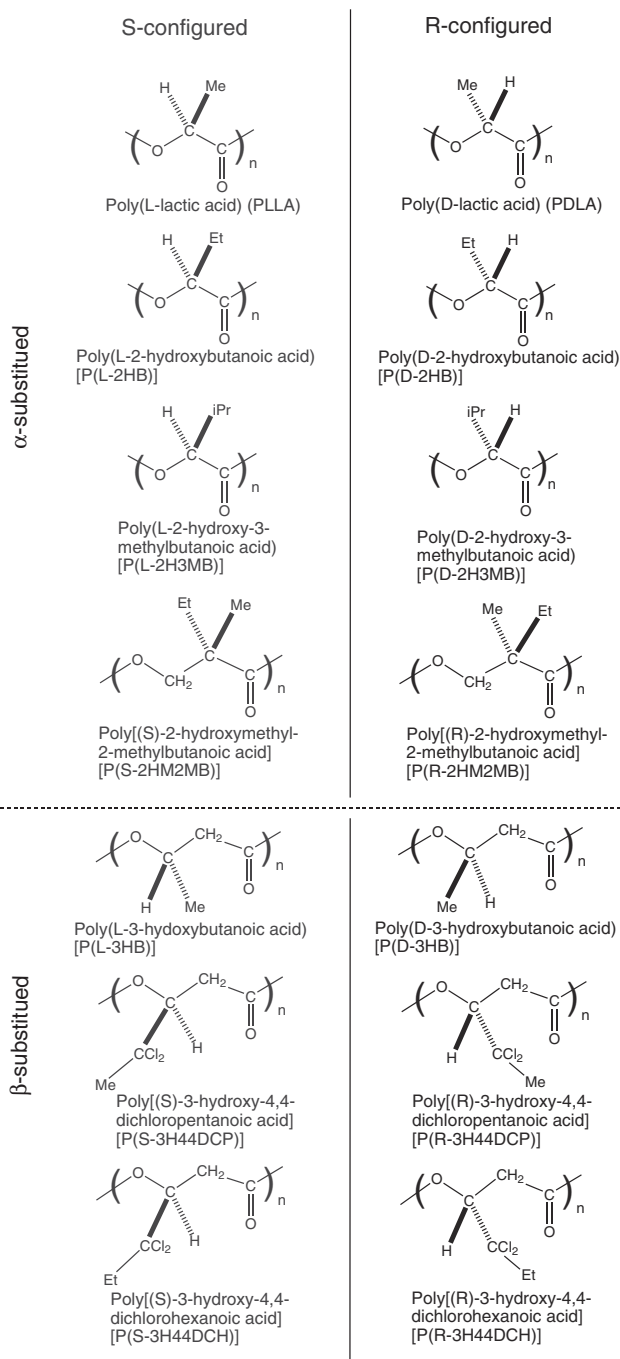


Figure 1 Molecular structures of hydroxycarboxylic acid-based enantiomeric polyesters reported to form stereocomplex crystallites and of enantiomeric P(3HB)s. A full color version of this figure is available at *Polymer Journal* online.

performed at 25 °C using a Rigaku (Tokyo, Japan) RINT-2500 equipped with a Cu-K α source ($\lambda = 0.15418$ nm). Spherulite growth behavior was observed with an Olympus (Tokyo, Japan) polarized optical microscope (BX50) equipped with a heating-cooling stage and temperature controller (LK-600PM, Linkam Scientific Instruments, Surrey, UK) under a constant nitrogen gas flow. The solution-crystallized samples were first heated from room temperature to 160 °C at 100 °C min⁻¹, held at the same temperature for 3 min to erase thermal history, cooled to an arbitrary T_c (60–80 °C) at 100 °C min⁻¹ and then held at T_c at which spherulite growth was observed.

RESULTS AND DISCUSSION

Wide-angle X-ray diffraction

To investigate crystallization behavior, crystalline species, and X_c , WAXD measurements were carried out (Figures 2a and b). The diffraction profile of HMW P(D-3HB) in the present study was very similar to the profile previously reported for P(D-3HB).¹⁴ The intense crystalline diffraction peaks observed at 2θ values of 13.5, 17.0, 21.6, 22.7, 25.6° and so on for HMW P(D-3HB) were in agreement with reported peaks.¹⁴ The diffraction profiles of neat P(L-3HB), P(D-3HB) and their blend in the present study were very similar to the profiles of HMW P(D-3HB) and P(D-3HB) reported in the literature¹⁴ but were different from the profile of D-3HB reported in the present study. This result further confirmed the synthesis of P(L-3HB) and P(D-3HB) and indicates that the homo-crystallites of P(L-3HB) and P(D-3HB), with no stereocomplex crystallites, were formed separately in the solution-crystallized blend. The latter result was consistent with the result for racemic isotactic P(3HB).⁸ Similar to the solution-crystallized samples, the melt-crystallized blend had a diffraction profile very similar to the profiles of melt-crystallized P(L-3HB) and P(D-3HB). This result reflects the formation of homo-crystallites occurring separately in a melt-crystallized blend. In addition, it is interesting to note that the crystalline modification of homo-crystallites of neat P(L-3HB) and P(D-3HB) remained unchanged when M_w was lowered from 3.5×10^5 to 1.3×10^3 or 1.8×10^3 g mol⁻¹, which was in marked contrast to the results reported for neat L- and D-configured P(2HB) and P(2H3MB), for which a new crystalline modification was formed when M_w was lowered below 1.0×10^4 g mol⁻¹.^{3,4}

The X_c values of the samples were estimated from the WAXD profiles in Figure 2 and tabulated in Supplementary Table S1. The X_c values of neat P(L-3HB), P(D-3HB), their blend samples and as-received HMW P(D-3HB) were similar to one another and within the range of 73–79%, reflecting the synchronous formation of P(D-3HB) and P(D-3HB) homo-crystallites in the blend samples. If either P(L-3HB) or P(D-3HB) crystallized into homo-crystallites first and was followed by the other, the second polymer would crystallize between the previously formed homo-crystallites of the first polymer, and the homo-crystallite growth of the second polymer would be disturbed, resulting in lowered X_c values for the blend samples.

Differential scanning calorimetry

To investigate the effect of blending on thermal properties, DSC measurements were carried out (Figures 2c and d). A melting peak was observed at 176 °C for the as-received HMW P(D-3HB), which was in agreement with the reported value,^{11,12} whereas melting peaks were observed within a lower temperature range (92–122 °C) for the solution- and melt-crystallized neat P(L-3HB), P(D-3HB) and their blend samples. The low T_m values of the latter samples can be ascribed to their low molecular weights. The triple melting peak of the blend samples is the superimposition of the double melting peaks of the neat P(L-3HB) and P(D-3HB) samples, confirming their synchronous and separate homo-crystallization in the blend samples. The highest and lowest T_m values of the blend samples were lower than those of the neat P(L-3HB) and P(D-3HB) samples (Supplementary Table S1), indicating that the blending decreased the size of the homo-crystallites or disturbed the growth of P(L-3HB) and P(D-3HB) homo-crystalline lamellae. Here, we did not address the middle T_m values of the blend samples because of the overlap of the higher melting peak of the P(L-3HB) homo-crystallites and the lower melting peak of the P(D-3HB) homo-crystallites. The double peak observed for the neat P(L-3HB) and P(D-3HB) samples was attributable to the melting of imperfect crystallites and crystallites re-crystallized during DSC heating.

Polarized optical microscopy

To investigate the effect of blending on crystalline morphology and spherulite growth behavior, polarized optical microscopy was performed (Figure 3). Well-defined spherulites with Maltese cross and

periodic extinction along the radial direction were observed at $T_c = 60^\circ\text{C}$ for the neat P(L-3HB), P(D-3HB) and their blend, suggesting the orientation and periodic twisting of lamellae along the radial direction. Similar spherulites with Maltese crosses and periodic extinction were reported for P(D-3HB) with $M_w = 3.6 \times 10^5$ g and 24 monomer units.^{15,16} In the case of P(D-3HB) with 24 monomer units, the detailed dependence of periodic extinction and spherulitic shape on T_c are reported.¹⁶ The morphologies were maintained in neat P(L-3HB) and P(D-3HB) for T_c up to 75°C , although the periodic extinction became vague, whereas the Maltese cross and periodic extinction disappeared in the neat P(L-3HB), and periodic extinction was lost in neat P(D-3HB) at $T_c = 80^\circ\text{C}$. However, in the case of the blend, periodic extinction and the Maltese cross disappeared at $T_c = 70$ and 75°C , respectively, reflecting that the orientation and periodic rotation of P(L-3HB) or P(D-3HB) lamellae were disturbed at a relatively low T_c compared with neat P(L-3HB) and P(D-3HB) by the coexistence of P(L-3HB) and P(D-3HB) chains or the synchronous

Table 1 Molecular characteristics of P(L-3HB), P(D-3HB) and HMW P(D-3HB) used in the present study

Code	M_w^a (g mol^{-1})	M_w/M_n^a	$[\alpha]^{25}_{589}^b$ ($\text{deg dm}^{-1} \text{g}^{-1} \text{cm}^{-3}$)
P(L-3HB)	1.3×10^3	1.7	8.8
P(D-3HB)	1.8×10^3	1.8	-4.3
HMW P(D-3HB)	3.5×10^5	1.9	—

Abbreviation: HMW, high molecular weight.

^a M_w and M_n are weight- and number-average molecular weights estimated by gel permeation chromatography.

^bMeasured in chloroform.

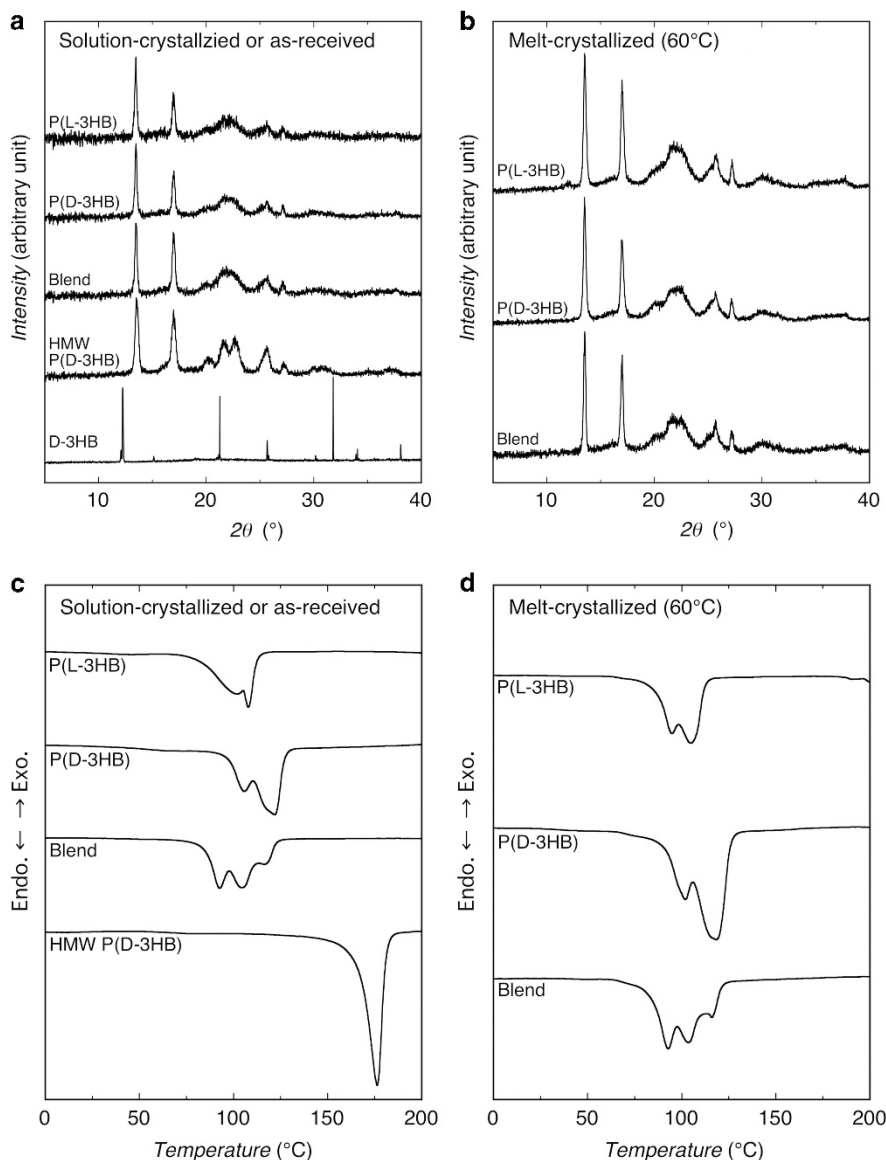


Figure 2 WAXD profiles (a, b) and DSC thermograms (c, d) of solution-crystallized (a, c) and melt-crystallized ($T_c = 60^\circ\text{C}$; b, d) neat P(L-3HB), P(D-3HB) and their blend, together with the profiles of as-received HMW P(D-3HB) and D-3-hydroxybutanoic acid (D-3HB; a, c). DSC, differential scanning calorimetry; HMW, high molecular weight; WAXD, wide-angle X-ray diffractometry.

and separate formation of homo-crystallites in the spherulites. In the case of high-molecular-weight PLLA and PDLA, periodic extinction was lost, but Maltese crosses remained in the blends.⁷

The radial growth rate of the spherulites (G) and the induction period for spherulite growth (t_i) were estimated from polarized optical

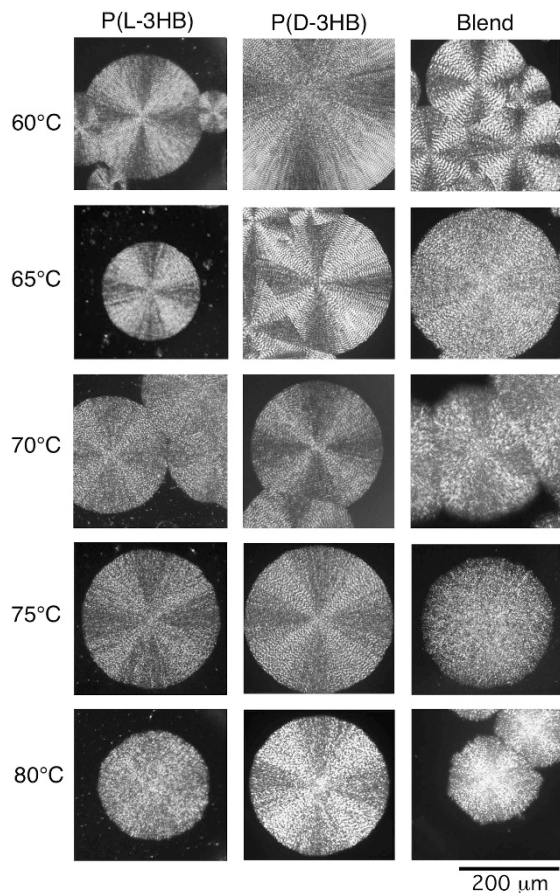


Figure 3 POM photographs of neat P(L-3HB), P(D-3HB) and their blend crystallized at different T_c values of 60–80 °C from the melt; neat P(L-3HB) crystallized at 60, 65, 70, 75 and 80 °C for 37, 32, 22, 78 and 110 s; neat P(D-3HB) crystallized at 60, 65, 70, 75 and 80 °C for 10, 25, 75, 82 and 56 s; and the blend crystallized at 60, 65, 70, 75 and 80 °C for 165, 240, 180, 110, 240 and 390 s. POM, polarized optical microscopy.

photographs and are plotted in Figures 4a and b as a function of T_c . The G values of the blend (20–36 $\mu\text{m min}^{-1}$) were much lower than those of neat P(L-3HB) (58–136 $\mu\text{m min}^{-1}$) and P(D-3HB) (97–159 $\mu\text{m min}^{-1}$). The relatively low G values of the blend strongly suggest that the selection of chains with one type of configuration on the growth sites of homo-crystallites in the mixed polymers of P(L-3HB) and P(D-3HB) delayed the homo-crystallization. The results of the morphologies and G strongly reflect the incorporation of both P(L-3HB) and P(D-3HB) homo-crystallites into the same spherulites. However, in the case of the homo-crystallization of the high-molecular-weight PLLA/PDLA blends from the melt, a very small difference was observed between the G values of the blend and neat PLLA or PDLA.⁷ It is likely that PLLA- and PDLA-chain-rich domains were formed by the melting of the homo-crystallites of PLLA and PDLA, respectively, and remained even after annealing above T_m , resulting in easy homo-crystallization in the blend without the selection of chains with one type of configuration on the growth sites at T_c below T_m . The G values of neat P(L-3HB) and P(D-3HB) were in good agreement with the values reported for P(D-3HB) with 24 monomer units for $T_c = 60$ –80 °C (91–161 $\mu\text{m min}^{-1}$),¹⁶ with $M_w = 3.6 \times 10^5 \text{ g mol}^{-1}$ for $T_c = 60$ –80 °C (70–252 $\mu\text{m min}^{-1}$),¹⁵ and with $M_w = 6.9 \times 10^5 \text{ g mol}^{-1}$ for $T_c = 60$ –80 °C (72–192 $\mu\text{m min}^{-1}$).¹⁷ The reported G values for P(D-3HB) and the values found in the present study reflect that the G values are not significantly altered by molecular weight, which is in marked contrast to the normal trend that segmental mobility increases with decreasing molecular weight, thereby elevating G . By contrast, the t_i of the blend was higher than the t_i of the neat polymers at $T_c = 80$ °C, reflecting disturbed nucleation. The T_c dependence of the G values was smaller for the blend than for neat P(L-3HB) and P(D-3HB), although we cannot give an appropriate reason for this finding.

We estimated the nucleation constant (K_g) and the front constant (G_0) using the nucleation theory established by Hoffman *et al.*,¹⁸ in which G can be expressed by the following equation:

$$G = G_0 \exp[-U^*/R(T_c - T_\infty)] \exp[-K_g/(T_c \Delta T f)], \quad (1)$$

where U^* is the activation energy for the transportation of segments to the crystallization site, R is the gas constant, T_∞ is the hypothetical temperature at which all motion associated with viscous flow cease and f is the factor expressed by $2T_c/(T_m^0 + T_c)$ that accounts for the change in the heat of fusion as the temperature is decreased below T_m^0 . Figure 4c illustrates the $\ln G + 1500/R(T_c - T_\infty)$ plots as a function of $1/(T_c \Delta T f)$ using the T_g and T_m^0 values reported for P(D-3HB) (4 and

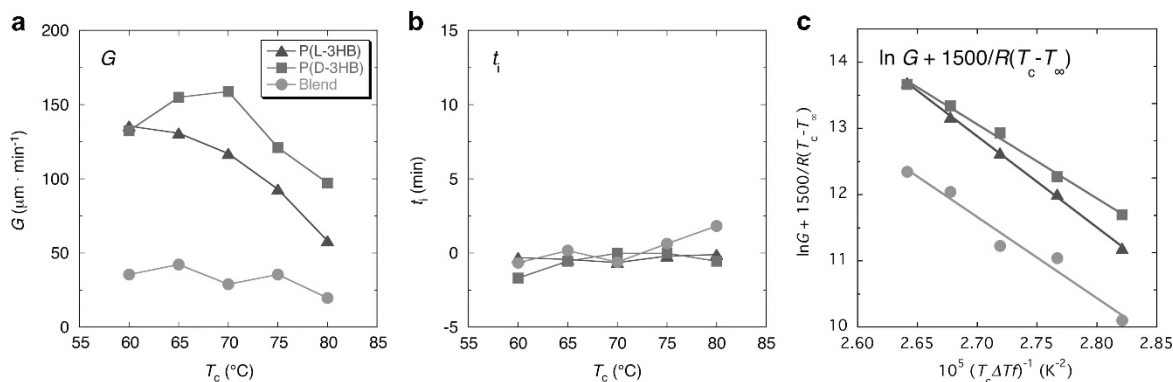


Figure 4 (a) Radial growth rate of spherulites (G), (b) induction period for spherulite growth (t_i) of neat P(L-3HB), P(D-3HB) and their blend as a function of T_c and (c) $\ln G + 1500/R(T_c - T_\infty)$ of neat P(L-3HB), P(D-3HB) and their blend as a function of $1/(T_c \Delta T f)$. A full color version of this figure is available at *Polymer Journal* online.

197 °C, respectively),^{15,17} the universal values of $U^* = 1500 \text{ cal mol}^{-1}$ and $T_\infty = T_g - 30 \text{ K}$. The plots in Figure 4c give K_g as a slope and the intercept $\ln G_0$ (Supplementary Table S2). Only one K_g value was observed for neat P(L-3HB), P(D-3HB), and their blend, indicating the presence of a nucleation mechanism within the T_c range considered in the present work. The blend K_g value ($1.23 \times 10^6 \text{ K}^2$) was between the values for neat P(L-3HB) ($1.38 \times 10^6 \text{ K}^2$) and P(D-3HB) ($1.12 \times 10^6 \text{ K}^2$). The similar K_g values of neat P(L-3HB), P(D-3HB) and their blend indicate that the nucleation mechanism remained unchanged by blending.

Crystalline species in enantiomeric polyester blends

In the present work, homo-crystallites were formed separately and synchronously in a well-defined enantiomeric P(3HB) blend. Furthermore, only homo-crystallites were formed in our preparatory study of a well-defined enantiomeric blend of HMW P(D-3HB) and oligomeric P(L-3HB). Stereocomplexation in enantiomeric polymer blends has been reported for α -substituted optically active polyesters such as PLA,^{1,2} P(2HB),³ P(2H3MB)⁴ and P(2HM2MB)⁵ and β -substituted optically active polyesters such as P(3H44DCH) and P(3H44DCP)⁶ (Figure 1). The P(3HB) used in the present study was a β -substituted optically active polyester. Although stereocomplexation of the α -substituted optically active polyesters PLA, P(2HB), P(2H3MB) and P(2HM2MB) was confirmed by both WAXD and DSC, stereocomplexation of P(3H44DCH) and P(3H44DCP) was monitored by DSC but not by WAXD. However, there has been no report of the stereocomplexation of a β -substituted optically active polyester in which stereocomplexation was confirmed by WAXD, although stereocomplexation was strongly suggested by the DSC results.⁶

P(3HB) is a β -substituted optically active polyester with identical side chains (methyl groups) to those of an α -substituted optically active polyester, PLA. A stereocomplex is formed in the enantiomeric polymer blend of PLA but not P(3HB). It is expected that a rigid planner structure based on a sp^2 carbonyl carbon adjacent to a chiral α -carbon promotes the stereocomplexation of PLA, which is in marked contrast to the structure of P(3HB), in which a chiral α -carbon is connected to a carbonyl carbon via a flexible methylene unit (Figure 1), thereby reducing structural rigidity. Moreover, P(D-3HB) homo-crystallites are reported to have C–H...O=C hydrogen bonds, which are stronger than those of PLLA homo-crystallites and different from the bonds of PLLA/PDLA stereocomplex crystallites and PLLA homo-crystallites.¹⁹ It is probable that because of the specific strong types of hydrogen bonds of P(L-3HB) or P(D-3HB) that the P(L-3HB) and P(D-3HB) chains in the enantiomeric blend cannot form stereocomplex crystallites with more stable hydrogen bonds than those of the homo-crystallites of P(L-3HB) or P(D-3HB). Moreover, it is likely that P(L-3HB) and P(D-3HB) cannot form stereocomplex crystallites with more stable chain conformations and packing than the homo-crystallites.

It is believed that for the crystallization of enantiomeric polymer blends, stereocomplexation rarely occurs. However, there are few reports regarding the exclusive homo-crystallization of well-defined enantiomeric polyester blends,⁷ whereas there are numerous reports regarding the stereocomplexation of enantiomeric polyester blends.^{1–6} To elucidate the relationship between stereocomplexation ability or homo-crystallizability and molecular structure, it is crucial to accumulate data for the stereocomplexation ability or homo-crystallizability of different enantiomeric polymer blends crystallized with various procedures and conditions. As reported for enantiomeric PLA and P(2HB) blends, crystalline species depend on molecular

weights and crystallization procedures and conditions.¹ Low-molecular-weight enantiomeric PLA and P(2HB) blends are known to enhance stereocomplexation, whereas the main crystalline species for high-molecular-weight enantiomeric PLA blends are homo-crystallites.¹ For example, for high-molecular-weight enantiomeric PLA blends, various methods such as the orientation and addition of another polymer are proposed to promote stereocomplexation and suppress homo-crystallization.²⁰ Therefore, although stereocomplexation was not observed for the low-molecular-weight enantiomeric P(3HB) blend in the present study, varying the molecular weights and the crystallization procedure and conditions may promote stereocomplexation.

CONCLUSIONS

In solution- and melt-crystallization of the blend, P(L-3HB) and P(D-3HB) chains crystallized synchronously and separately into homo-crystallites but not stereocomplex crystallites. In the case of the blend, the orientation and periodic rotation of lamellae in the spherulites disappeared at a relatively low T_c compared with neat P(L-3HB) and P(D-3HB); the nucleation for spherulite growth was disturbed and the size and the G of the homo-crystallites were decreased by the synchronous and separate homo-crystallization and the coexistence of P(L-3HB) and P(D-3HB) homo-crystallites in the spherulites. However, synchronous and separate homo-crystallization in the blend and the coexistence of P(L-3HB) and P(D-3HB) homo-crystallites in the spherulites did not affect the X_c and nucleation mechanism.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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Supplementary Information accompanies the paper on Polymer Journal website (<http://www.nature.com/pj>)