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Temperature dependence of cocrystallization and phase segregation in blends of poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)

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Abstract

The phase structure of the miscible blends of poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHB-HV) has been analyzed through DSC measurements and the observations of spherulite growth. Melting temperature and spherulite growth rate of the blends changed depending on the blend composition, which indicates that the extent of phase segregation increases as the HV content of PHB-HV increases from 0 to ca. 30 mol% and as the crystalline temperature increases from 90 to 120°C. When the HV content of PHB-HV is very low, the PHB/PHB-HV blend shows complete cocrystallization. The PHB content in the crystalline phase is similar to the whole composition of the blend. As the HV content of PHB-HV or the crystallization temperature increases, the PHB-HV content in the cocrystalline phase decreases. As a result, a large amount of PHB-HV chains are remained in the miscible amorphous phase between the PHB lamella when the HV content of PHB-HV is over 20% and the PHB-HV content of the blend is large. These PHB-HV chains may form the second and third crystalline phases, which are the PHB-HV crystal and the cocrystals with the PHB chains remaining in the amorphous phase. These data suggest that the cocrystallization of PHB and PHB-HV is induced by the entrapment of the PHB-HV chains near the growing front of the crystals by the PHB chains being about to crystallize. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Cocrystallization; Phase segregation; Poly(3-hydroxybutyrate)

1. Introduction

In melt-miscible blends of two semicrystalline polymers, phase segregation may, in a greater or lesser extent, precede crystallization. As a result, the blends can potentially form many microstructures varied on the morphological level, to which the component polymers are closely mixed [1–13]. The component polymers may cocrystallize in a single lamellae or form separate lamella or the crystallization of one component may suppress the crystallization of the other. The separate lamella may coexist in a fibril or form separate fibrils. In the latter case, the amorphous region between lamella may contain both components or only the component forming the lamella. The situation for the spherulite level or larger must be similar to the fibril level. Kinetic parameters (rates of crystallization, molecular mobility and so on) together with thermodynamic parameters (miscibility, free energy loss upon cocrystallization and so on) control the microstructure formation in a complex manner. Therefore, thermal history is one of the most important factors for controlling the phase structure of crystalline/crystalline polymer blends.

In previous papers, we analyzed the miscibility and the phase structure of the blends of poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHB-HV) by DSC thermal analysis, the observation of spherulite growth [14], and solid-state high-resolution ^{13}C NMR spectroscopy [15]. PHB-HV copolymers keep high crystallinity throughout a range of compositions from 0 to 100%HV due to the isomorphous behavior [16,17]. So, PHB/PHB-HV blends form a crystalline/crystalline polymer blend system. In the melt, PHB was immiscible with PHB-HV of high HV content, while it was miscible with PHB-HV of low HV content. In the immiscible blends, both component polymers, PHB and PHB-HV, crystallized independently from the separate melt phases and, as a result, formed the same microstructure as the pure component. On the other hand, in the miscible blends, the structure of the crystalline phase varied depending on the HV content of PHB-HV. For the blends of PHB and PHB-HV with very low HV content, PHB-HV cocrystallized with PHB and the

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Table 1
PHB and PHB-HV used as blend components

Sample[a]	Source	HV (mol%)[b]	$M_n \times 10^{-5}$ [c]	M_w/M_n [c]
PHB	KN06707KN	0	1.1	2.2
PHB-7%HV	PSM-17	7	4.7	1.6
PHB-11%HV	Po-16	11	2.3	1.8
PHB-16%HV	Po-16	16	3.0	1.7
PHB-20%HV	HW06302PV	20	2.9	1.7
PHB-28%HV	HW06302PV	28	2.1	1.7

[a] Fractionated by a mixed solvent of chloroform/heptane from the source shown in the second column.
[b] Determined by ^{1}H NMR spectroscopy.
[c] Determined by GPC.

composition in the crystalline phase was similar to the blend composition. As the HV content of PHB-HV increased, the degree of cocrystallization decreased, i.e. the PHB-HV content in the PHB crystalline phase decreased. When the HV content of PHB-HV exceeded ca. 20 mol% and the PHB-HV content of the blend was large, both the PHB crystalline phase and the cocrystalline phase were formed.

In this paper, the phase structure of the miscible PHB/PHB-HV blends is further analyzed through the DSC measurements and the observation of spherulite growth. We focus on the dependence of the phase structure on the crystallization temperature (i.e. thermal history) and on the process of the cocrystallization. We discuss how kinetic parameters, together with thermodynamic parameters, work on the structural formation.

2. Experimental

2.1. Materials

PHB (lot number KN06707KN) and PHB-22%HV (lot number HW06302PV) were purchased from Aldrich Co. PHB-7%HV (lot number PSM-17) and PHB-16%HV (lot number Po-16) were provided by ICI. Recently, it has been reported that PHB-HV extracted from bacteria has a broad chemical composition distribution (CCD) and/or a polymodal CCD [18,19]. In this study, PHB-HV samples were prepared by fractional precipitation of as received PHB-HV. Fractionation of PHB-HV was done by precipitation using a mixed solvent of chloroform/heptane. One gram of as received PHB-HV was dissolved in 200 ml of chloroform, and 10 ml of heptane was added repeatedly until a very small amount of precipitate appeared. Then, the solution was left for 24 h at ambient temperature. The precipitate was separated by centrifugation and used as a fractionated sample. To the supernatant solution, heptane was further added and the precipitate was separated again. This procedure was repeated until any amount of heptane gave no precipitate. Five fractions were used in this study. The source and the molecular weight of fractionated PHB-HV samples are shown in Table 1. Blends of PHB and PHB-HV were prepared by slowly casting from chloroform solution on glass Petri dishes at room temperature.

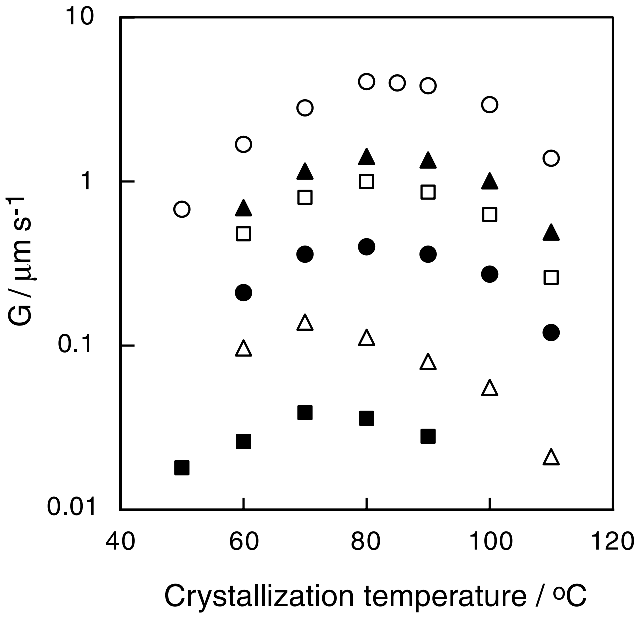

Fig. 1. Spherulite growth rate of PHB and PHB-HV as a function of crystallization temperature: PHB (open circle), PHB-7%HV (closed triangle), PHB-11%HV (open square), PHB-16%HV (closed circle), PHB-20%HV (open triangle), and PHB-27%HV (closed square).

2.2. Analytical procedures

DSC measurements were carried out using a SEIKO EXSTAR6000 system equipped with a SEIKO DSC 220U. Samples were 1–3 mg of films held between aluminum pans. The samples were melted at 195°C for 1 min, quenched to a selected crystallization temperature, kept for 3–6 h and reheated up to 200°C. The DSC curve of the reheating process was recorded. Unless otherwise indicated, a heating rate of 20°C min^{-1} was used. Melting temperature was determined from the maximum of the endothermic peak. Spherulite growth was observed with an Olympus BX90 polarized microscope equipped with a Mettler FP82HT hot stage. Film samples were heated to 195°C, kept at this temperature for 1 min and then cooled to a selected temperature where they were crystallized isothermally. Spherulite growth rates were taken as the slope of the linear plot of spherulite radius versus time.

3. Results

Fig. 1 shows the spherulite growth rates of PHB and the fractionated PHB-HV samples as a function of crystallization temperature. As is well known [20,21], with increasing HV content from 0 to 27% the spherulite growth markedly slows down and the maximum of the growth rate shifts to lower temperatures. The maximum growth rates of PHB and PHB-27%HV were observed at ca. 90 and 70°C, respectively. In this study, we have examined the crystallization of PHB/PHB-HV blends between 90 and 120°C. This temperature range is higher than the temperature of the maximum growth rate. The rate of crystal growth decreases with increasing the crystallization temperature for the samples in this study.

3.1. Blends forming one crystalline phase

The melting behavior of PHB/PHB-HV blends was analyzed by DSC measurements. In our previous paper [15], the composition in the crystalline phase of PHB/PHB-HV blends has been estimated by solid-state ^{13}C NMR spectroscopy. It has been concluded that the melting temperature of PHB/PHB-HV blends changes depending on the PHB-HV content in the crystalline phase. When the PHB-HV content in the crystalline phase is similar to that of the whole blend, the plot of melting temperature against the PHB-HV content of the whole blend yields a straight line. When the PHB-HV content in the crystalline region is smaller than the whole blend, this plot becomes convex upward. Therefore, the analysis of melting behavior provides the information about the phase structure of PHB/PHB-HV blends.

Most of the blends studied in this work showed two-peak melting behavior. We can see the typical behavior in Fig. 2(a), which is the DSC heating curves of 50/50 PHB/PHB-11%HV blend crystallized at 90–120°C. Two melting peaks were found in these curves. Two melting peaks are often observed on the melting curve of semicrystalline polymers and polymer blends. When we interpret the two-peak behavior, it is important to distinguish multiple peaks arising from phase-separated structures and those arising as a result of a melt/recrystallization process. We can differentiate between them by simply varying the heating rate. In a previous paper [14], the variation of DSC melting curve with heating rate was investigated for the same blend crystallized at 80°C. It was clearly shown that the relative area of the lower temperature peak increased with the heating rate, which indicated a melt/recrystallization process. The lower temperature peak corresponded to the melting of the crystals formed at the crystallization temperature while the higher temperature one was due to the crystals rearranged during heating in DSC apparatus. It has been also confirmed that the two-peak behavior of the other PHB/PHB-HV blends crystallized at 80°C arose from a melt/recrystallization process. Therefore, the two-peak behavior of the blends crystallized at 90–120°C in this study can be ascribed to a melt/recrystallization process.

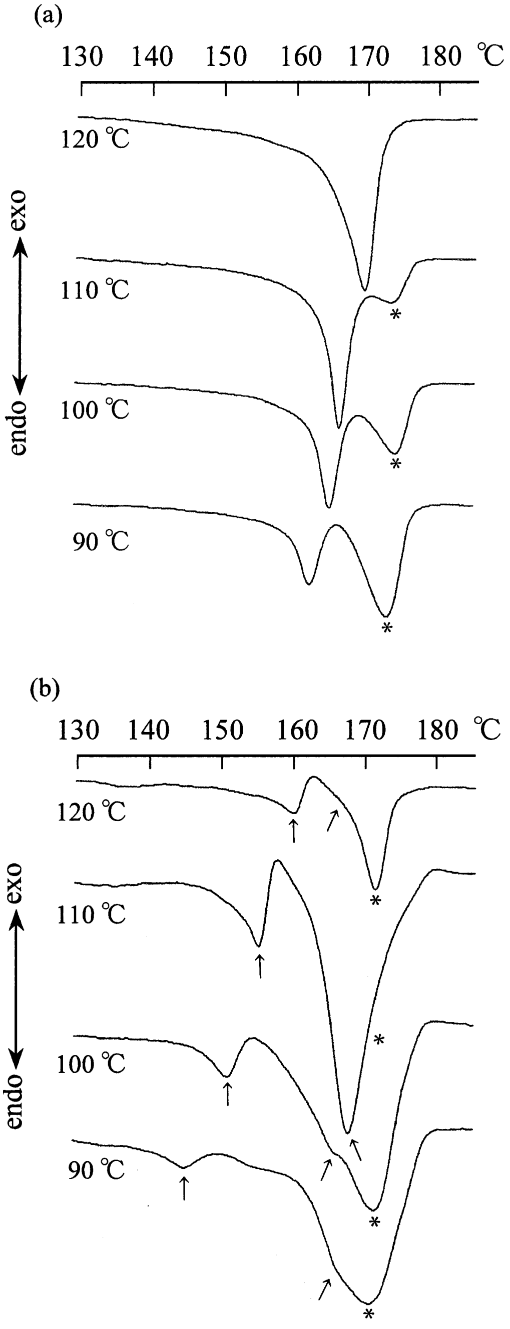

Fig. 2. DSC heating curves of PHB/PHB-HV blends crystallized at 90–120°C: (a) 50/50 PHB/PHB-11%HV; (b) 25/75 PHB/PHB-27%HV. Peaks marked with an arrow and an asterisk indicate the melting of the crystals formed at the selected crystallization temperature and melt/recrystallization process, respectively.

Fig. 3(b) shows the variation in the melting temperature with PHB-HV content for PHB/PHB-11%HV blends crystallized at 90–120°C. The blends crystallized at a temperature in this range formed only one crystalline phase. The melting temperature of the blends lay on a straight line connecting the melting temperatures of the component polymers, PHB and PHB-11%HV. The linear relationship between melting temperature and blend composition indicates that at any blend composition and at any temperature between 90 and 120°C PHB-11%HV cocrystallized with PHB and the PHB-HV content in the crystalline region was similar to the blend composition [15]. The blends of PHB and PHB-7%HV also showed similar behavior, indicating that PHB and PHB-7%HV cocrystallized in these blends (see Fig. 3(a)). Fig. 3(d) shows the melting

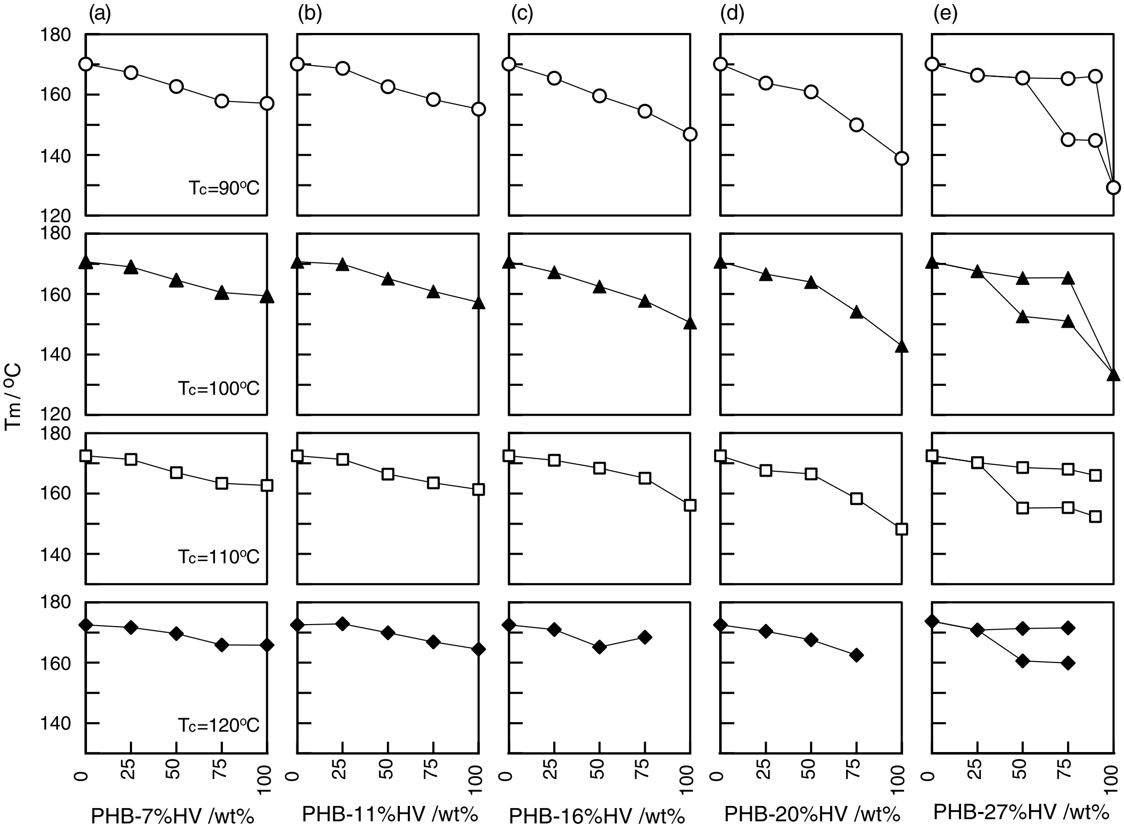

Fig. 3. Melting temperature of PHB/PHB-HV blends crystallized at 90°C (open circle), 100°C (closed triangle), 110°C (open square), and 120°C (closed diamond) as a function of PHB-HV content of the blend: (a) PHB/PHB-7%HV; (b) PHB/PHB-11%HV; (c) PHB/PHB-16%HV; (d) PHB/PHB-20%HV; (e) PHB/PHB-27%HV.

temperature of PHB/PHB-20%HV blends crystallized at 90–120°C. Melting was not observed for PHB-20%HV kept isothermally at 120°C because this copolymer did not crystallize at this temperature within 6 h (which is the sample preparation condition of this study). Though the melting temperature of the blends crystallized at 90–110°C still lay between the melting temperatures of the component polymers, it was rather close to the melting temperature of PHB. This observation indicates that the main component of the crystalline region was PHB [15]. In these blends, phase segregation occurred, i.e. PHB-HV molecules escaped from the growing front of the crystals before crystallization.

Fig. 3(c) shows the melting temperature of PHB/PHB-16%HV crystallized at 90–120°C. For the samples crystallized at 90 and 100°C, the relation between melting temperature and blend composition was similar to that of PHB/PHB-7%HV and PHB/PHB-11%HV. The melting temperature of the blends lay on a straight line connecting the melting temperatures of the components. Therefore, PHB-16%HV cocrystallized with PHB in these blends. On the other hand, the blends crystallized at 110°C showed the behavior similar to the PHB/PHB-20%HV blends. The plot of melting temperature versus PHB-HV content of the blend became convex upward. So, as the crystallization temperature increased, the melting temperature of the PHB/PHB-16%HV blends became close to the melting temperature of PHB. This observation indicates that the composition in the crystalline phase changes depending on the crystallization temperature. The PHB-16%HV content in the crystalline region decreased as the crystallization temperature increased. So, the phase structure of the PHB/PHB-HV blends is affected by crystallization temperature.

The phase structure of the PHB/PHB-HV blends forming one crystalline phase has been further investigated through the observation of spherulite growth by a polarized microscope. In a previous paper [14], it has been confirmed that the logarithm of the spherulite growth rate shows the blend-composition dependence similar to the melting temperature. Fig. 4 shows the relation between the spherulite growth rate and the blend composition of PHB/PHB-HV blends crystallized at 90–110°C. For PHB/PHB-7%HV and PHB/PHB-11%HV, the logarithm of the growth rate lay on a straight line connecting the growth rate of the components. PHB/PHB-16%HV blends crystallized at 90 and 100°C also showed similar behavior. For PHB/PHB-16%HV blends crystallized at 110°C and PHB/PHB-20%HV blends, this plot became convex upward. Therefore, the logarithm of growth rate shows the composition dependence similar to the melting temperature, which supports the phase structure predicted from the melting temperature. The PHB-HV

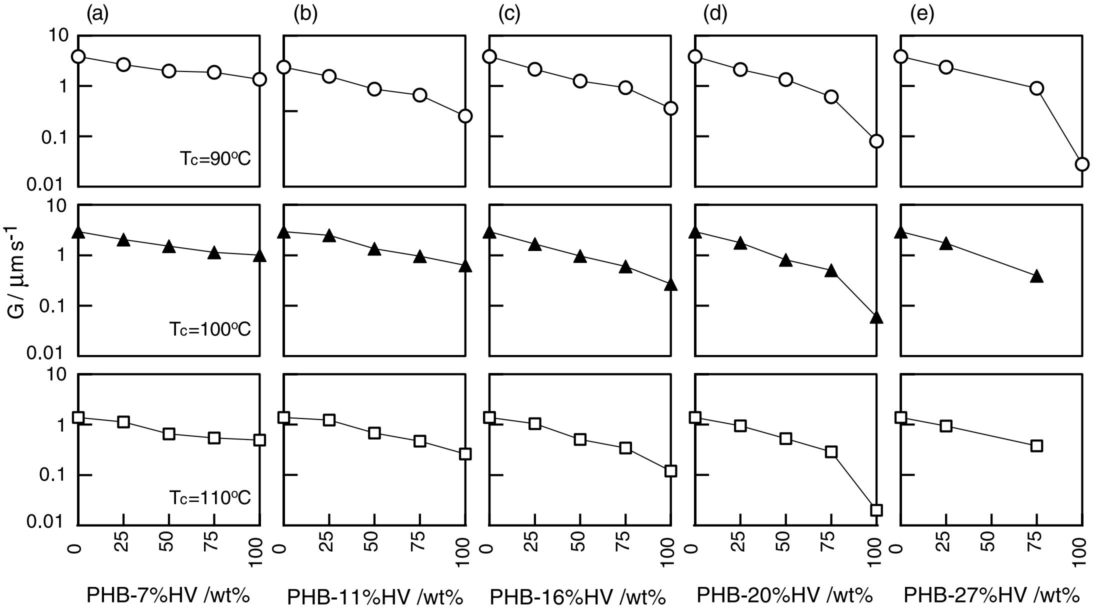

Fig. 4. Spherulite growth rate of PHB/PHB-HV blends crystallized at 90°C (open circle), 100°C (closed triangle), and 110°C (open square) as a function of PHB-HV content of the blend: (a) PHB/PHB-7%HV; (b) PHB/PHB-11%HV; (c) PHB/PHB-16%HV; (d) PHB/PHB-20%HV; (e) PHB/PHB-27%HV.

content in the crystalline region decreases as the HV content of PHB-HV increases and as the crystallization temperature increases.

3.2. Blends forming two crystalline phases

Some PHB/PHB-27%HV blends had three peaks on the DSC melting curve. Fig. 2(b) shows the DSC heating curves of 25/75 PHB/PHB-27%HV blend crystallized at 90–120°C. They had three melting peaks (two peaks and one shoulder at a side of the higher temperature peak). The origin of three-peak behavior has been analyzed by varying the heating rate. Fig. 5 shows the DSC heating curves of 10/90 PHB/PHB-27%HV blend at heating rates of 20 and 30°C min^{-1}. It is apparent that the relative height of the highest temperature peak increased with decreasing the heating rate. Thus, the highest temperature peak is due to a melt/recrystallization process, while the lowest and middle temperature peaks are the true melting peaks of the crystals formed at the crystallization temperature.

Fig. 3(e) shows the relationship between the positions of the middle and lowest temperature peaks and the blend composition of PHB/PHB-27%HV. The position of the middle temperature peak was as high as the melting temperature of pure PHB, indicating that this peak is due to the melting of the PHB crystals. The lower temperature peak lays between the melting temperatures of PHB and PHB-27%HV. This result strongly suggests that the lowest temperature peak is due to the melting of the cocrystals.

The mechanism of crystal formation in the PHB/PHB-27%HV blends has been further investigated. The DSC heating curves were recorded for 10/90 PHB/PHB-27%HV crystallized for various periods of time at 90°C (Fig. 6). As the time for crystallization increased from 3 to 60 min, the melting enthalpy became larger, showing the growth of crystals. The fact that the melting curve of the sample crystallized for 300 min is similar to that of the sample crystallized for 60 min shows that the crystallization was completed within 60 min. It is interesting that the ratio of the area of the middle temperature peak to that of the lowest temperature peak is independent of the crystallization time. This means that the cocrystals and the PHB crystals grow simultaneously in the blend.

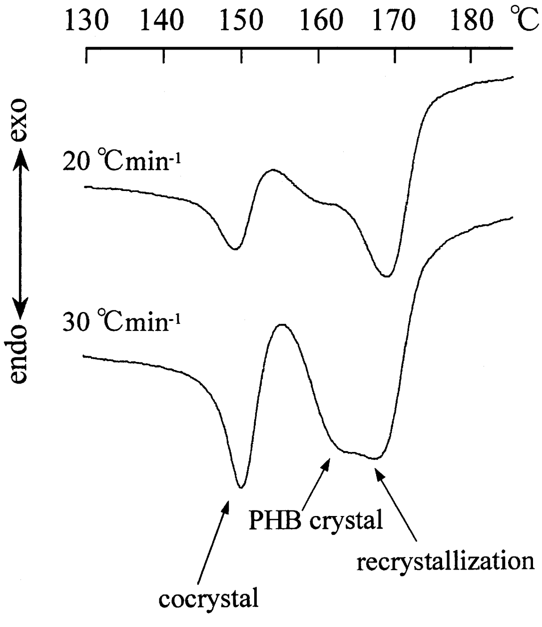

Fig. 5. DSC heating curves of 10/90 PHB/PHB-27%HV blend crystallized at 90°C at heating rates of 20 and 30°C min^{-1}.

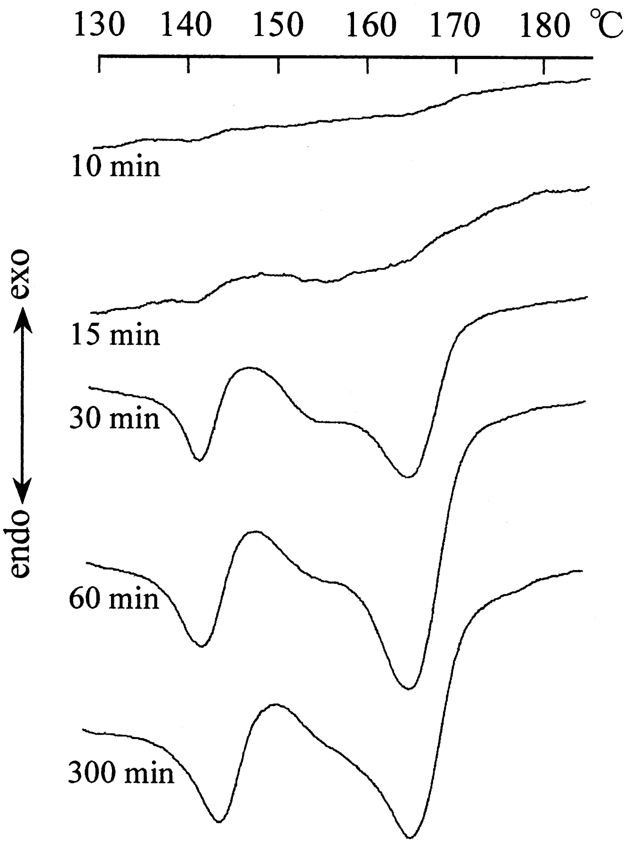

Fig. 6. DSC heating curves of 10/90 PHB/PHB-27%HV blend crystallized at 90°C for various periods of time.

The phase structure and crystallization process of PHB/PHB-27%HV have been further analyzed through the observation of spherulite growth by polarized microscope. In the melt state, a homogeneous phase was observed for all the PHB/PHB-27%HV blends. No evidence of liquid–liquid phase separation was visible. At every blend composition and at every crystallization temperature, the spherulites grew at a constant rate until they impinged on each other. No evidence of partitioning of the component polymers, PHB and PHB-27%HV, between the melt and the spherulites was observed. So, PHB crystals and the cocrystals coexist in a spherulite.

Fig. 4(e) shows the relation between the spherulite growth rate and the blend composition for PHB/PHB-27%HV blends. The growth rate is plotted in logarithmic scale. The melting temperature of PHB-27%HV is so low that the spherulite growth of the copolyester could not be observed at 100°C and higher. As shown in Fig. 1, the maximum of the spherulite growth rate of PHB-27%HV was observed at ca. 70°C. The growth rate of PHB-27%HV at 90°C was 0.028 μm min^{-1} and the growth rate at a temperature higher than 90°C must be slower than this rate. Therefore, in logarithmic scale, the growth rate of the PHB/PHB-27%HV blends crystallized at 90, 100, and 110°C were close to that of PHB rather than that of PHB-27%HV. This result, together with the fact that the cocrystals and the PHB crystals grow simultaneously (Fig. 6), indicates that the crystallization rate of cocrystals is similar to that of PHB.

4. Discussion

As shown in Section 3.2 and in our previous papers [14,15], the crystalline phase structure of miscible PHB/PHB-HV changed depending on the HV content of PHB-HV. As the HV content of PHB-HV increased from 0 to ca. 30 mol%, the extent of the phase segregation increased. When the HV content was very low, the blend showed complete cocrystallization. In these blends, the composition in the crystalline phase was similar to the blend composition. And as a result, the composition in the amorphous phase was also similar to the blend composition. As the HV content of PHB-HV increased, the PHB content in the cocrystalline phase increased and at last the crystalline phase contained little PHB-HV. In this case, a large amount of PHB-HV molecules and a small amount of PHB molecules were reminded in the miscible amorphous phase between the PHB lamella. These molecules often formed the second and third crystalline phases and those phases were the PHB-HV crystals and the cocrystals. PHB/PHB-27%HV was an example of such a case.

In this study, we have shown that the crystalline phase structure of miscible PHB/PHB-HV blends also depended on the crystallization temperature. The blends of PHB and PHB-HV with 16%HV showed cocrystallization at 100°C or lower temperature, while they showed phase segregation followed by crystallization of PHB at 110°C. So, the PHB-HV content in the crystalline phase decreases with the increase of the crystallization temperature.

It was reported that for PHB-HV containing 40% and lower HV, the crystallization rate [22] and spherulite growth rate [20,21] decreases with the increase of the HV content. So, in PHB/PHB-HV blends, PHB chains are probably set to crystallize before PHB-HV chains are. If the phase segregation between PHB and PHB-HV is slow compared with the crystallization of PHB, the PHB chains, that is about to crystallize at the growing front of a crystal (or a spherulite), may trap the PHB-HV chains in the neighborhood and drag it into the crystalline phase. The cocrystallization occurred in PHB/PHB-7%HV, PHB/PHB-11%HV, and PHB/PHB-16%HV may be explained by this hypothetical process. Therefore, the rate of spherulite growth and the rate of phase segregation have much effect on the cocrystallization. As the rate of phase segregation increases and/or the rate of spherulite growth of PHB decreases, the PHB-HV chains have more chance to escape from the growing front of crystals and, as a result, the PHB content in the crystalline phase becomes larger than the blend composition.

The rate of phase segregation and the rate of spherulite growth of the PHB/PHB-HV blends change depending on the HV content of PHB-HV and on the crystallization temperature. The fact that PHB and PHB-HV with high HV content is immiscible [23] reveals that the free energy of mixing of PHB/PHB-HV blends increases with the HV content of PHB-HV. As the free energy of mixing increases, the rate of phase segregation must increases. So, the rate of phase segregation increases with the increase of the HV content of PHB-HV. This explains the dependence of the phase structure on the HV content of PHB-HV in PHB/PHB-HV blends. In the temperature range higher than 90°C, the spherulite growth rate of PHB decreases as temperature increases. The mobility of polymer chain, of course, increases with temperature. So, the changes in the spherulite growth rate and the molecular mobility explain the temperature dependence of the phase structure of PHB/PHB-HV blends.

It has not been clear why two types of the crystalline phase, the cocrystals and the PHB crystals, form simultaneously in blends such as PHB/PHB-27%HV containing much PHB-27%HV. One possible idea is that at the growing front of spherulite, two types of lamella may not form exactly at the same time. PHB lamella may form at first. In such a case, PHB-HV must be ejected from the crystalline phase. In the melt state of the PHB/PHB-27%HV blends, a homogeneous phase was observed by polarized microscope. So, PHB-HV chains exist interlamella (and/or interfibrillar), intraspherulitic regions where they form homogeneous melt phase with uncrystallized PHB chains. As we consider the blend containing much PHB-27%HV, significant amount of chains are remained in the interlamella (and/or interfibrillar) melt phase. Therefore, another crystalline phase can grow in this PHB-HV-rich phase. The analysis of the crystallization rate by DSC measurement revealed that the apparent crystallization rate of the cocrystalline phase is similar to that of the PHB crystalline phase (see Fig. 6). This result indicates that the formation of PHB lamella is immediately followed by the crystallization of the PHB-HV-rich phase. This means that the crystallization of this PHB-HV-rich phase in the blends is much faster than the pure PHB-HV. The preceding PHB lamella probably reduce the mobility of molecules in the PHB-HV-rich melt phase. The reduction may make the PHB-HV-rich phase crystallize faster. So, the crystallization of the PHB-HV-rich phase may be induced by the PHB chains remained in this phase.

Acknowledgements

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