Crystallization and Melting Behavior of Blends Comprising Poly(3-hydroxy butyrate-*co*-3-hydroxy valerate) and Poly(ethylene oxide)

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ABSTRACT: Blends of poly(3-hydroxy butyrate-*co*-3-hydroxy valerate) (PHBV) and poly(ethylene oxide) (PEO) were prepared by casting from chloroform solutions. Crystallization kinetics and melting behavior of blends have been studied by differential scanning calorimetry and optical polarizing microscopy. Experimental results reveal that the constituents are miscible in the amorphous state. They form separated crystal structures in the solid state. Crystallization behavior of the blends was studied under isothermal and nonisothermal conditions. Owing to the large difference in melting temperatures, the constituents crystallize consecutively in blends; however, the process is affected by the respective second component. PHBV crystallizes from the amorphous mixture of the constituents, at temperatures where the PEO remains in the molten state. PEO, on the other hand, is surrounded during its crystallization process by crystalline PHBV regions. The degree of crystallinity in the blends stays constant for PHBV and decreases slightly for PEO, with ascending PHBV content. The rate of crystallization of PHBV decreases in blends as compared to the neat polymer. The opposite behavior is observed for PEO. Nonisothermal crystallization is discussed in terms of a quasi-isothermal approach. Qualitatively, the results show the same tendencies as under isothermal conditions. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2776–2783, 2006

Key words: polymer blends; poly(3-hydroxy butyrate-*co*-3-hydroxy valerate); poly(ethylene oxide); crystallization

INTRODUCTION

Biodegradable and biocompatible polyesters have attracted a great deal of interest because of their potential applications in different fields as polymers, for biodegradable packaging or medical use. The natural polyesters, such as poly(3-*R*-hydroxy butyrate) (PHB) and poly(3-*R*-hydroxy butyrate-*co*-valerate) (PHBV),[1–6] as well as the synthetic biodegradable polyesters, like poly(ε-caprolactone) (PCL) or poly(tetramethylene succinate) (PTMS),[7,8] are highly crystalline polymers. PHB and PHBV suffer from extended thermal decomposition slightly above the melting temperature,[9] and their mechanical performance is limited by the high degree of crystallinity. Blending with conventional thermoplastics may lead to materials with improved mechanical properties and help to overcome the disadvantages of PHB-based polymers.[10] In that context, knowledge on the phase behavior of the polymer mixtures and on the crystallization behavior of the constituents in blends is an important aspect for tailoring of properties of such systems.

Blends consisting of two crystalline polymers of different chemical structure might be miscible in the molten state, but usually form phase-separated structures in the solid state. Examples of such systems are PHB/poly(ethylene oxide) (PEO),[11–14] PHB/poly(vinylidene fluoride),[15] poly(L-lactide acid)/poly(butylene succinate-*co*-butylene carbonate),[16] PTMS/PEO,[17] or poly(ethylene succinate)/PEO[18] blends. An important aspect in that context concerns the influence of the respective second component on the crystallization process of the constituents.

For PHB/PEO blends, it was inferred from glass transition temperatures and melting point depression that the constituents are miscible in the molten state.[11–14] Miscibility of the polymers in the amorphous state was also supported by results of viscosity studies and of light scattering on blend solutions.[19,20] Melting points of PHB and PEO differ by around 100°. It causes that the polymers in the blends crystallize independently of each other. Crystallization of PHB is characterized by the fact that PEO is mobile when PHB crystallizes. It is rejected from the site of PHB crystallization to intra- and interspherulitic regions. The spherulite growth rate of PHB, studied under isothermal conditions, decreases with increasing PEO content, which points toward miscibility of the constituents in the molten state. At sufficiently low tem-

TABLE I
Characteristics of PHBV and PEO

Polymer	Source	$\overline{M}_w$ (kg/mol)	$\overline{M}_w/\overline{M}_n$[a]	T_g[b] (°C)
PHBV	Aldrich	400[a]	2.06	2
PEO	Acros	100	1.91	−55

[a] Molecular mass determined by gel permeation chromatography (GPC) in chloroform at 25°C.
[b] This study, determined by DSC.

peratures also PEO crystallizes, and the mixture forms a crystalline/crystalline system in the solid state. A similar situation occurs in blends of PHBV and PEO.

In this study, we report on thermal properties of PHBV and PEO in blends; the former polymer has a hydroxy valerate content of 12 mol %. Crystallization of the blend constituents is studied under both isothermal and nonisothermal conditions.

EXPERIMENTAL

Polymers

The bacterial random copolymer PHBV, containing 12 mol % of HV, and PEO were supplied by Aldrich Chemical Company and Acros Organics, respectively. The characteristics are listed in Table I.

Preparation of blends

Blends were prepared by casting from solutions with a total polymer content of 1 wt %. Chloroform was used as a common, nonselective solvent. The solvent was allowed to evaporate slowly at room temperature, and the resulting films were further dried under vacuum at 60°C for 3 days to remove residual solvent.

Calorimetric measurements

Crystallization behavior of both constituents was studied by differential scanning calorimetry (DSC). Isothermal crystallization behavior was monitored with a Perkin–Elmer DSC 7. For glass transition temperatures (T_g) and nonisothermal crystallization, a Perkin–Elmer Pyris 1 was used. The instruments were calibrated with indium standard. New samples, having a weight of about 6 mg, were used for each run. Thermal analyses were carried out under nitrogen.

Determination of glass transition temperature

After the samples were annealed at 175°C for 3 min and quenched in liquid nitrogen, the glass transition temperatures were measured in a DSC run, applying a heating rate of 20 K/min. The inflection point of the heat flow was taken as glass transition temperature.

Isothermal crystallization experiments

The samples were annealed at 175°C for 3 min. Afterward, the samples were cooled at a rate of 20 K/min to the respective crystallization temperature of PHBV, T_{c1}, and allowed to crystallize isothermally before further cooling down at the same rate to the desired crystallization temperature of PEO, T_{c2}. Isothermal crystallization temperatures, in the range between 100–110°C and 43–51°C, were applied for PHBV and PEO, respectively. Samples were crystallized for five half times at the respective crystallization temperatures. The half-time, $t_{0.5}$, of crystallization was determined experimentally as the time where 50% of the final crystallinity was reached.

Determination of melting points

Melting points were obtained after isothermal crystallization experiments by heating the samples from T_{c2}, with a heating rate of 10 K/min.

Nonisothermal crystallization experiments

After annealing at 175°C for 3 min, the samples were allowed to crystallize during runs with different constant cooling rates, s, ranging from 2 to 35 K/min.

Determination of spherulite growth rates

Polarizing optical microscope Zeiss Axiophot, equipped with a Linkam THMS 600 hot stage, coupled to a Linkam LNP cooling system, was used for monitoring growth rates. Samples were annealed for 3 min at 180°C, and cooled afterward at 20 K/min to the desired crystallization temperature of PHBV between 80 and 105°C. Radii of the spherulites were measured as a function of time using Soft Imaging System.

RESULTS AND DISCUSSION

Glass transition temperatures

Figure 1 shows the variation of glass transition temperature with blend composition. In the central range of composition, we could not detect glass transition temperatures, owing to insufficient suppression of crystallization during cooling and overlapping of cold crystallization with the glass transition region. However, the glass transition temperatures of the constituents are sufficiently separated from each other. Therefore, one may conclude from Figure 1 that the two polymers are miscible in the molten state, at least in the marginal composition ranges, where one of the components is in excess. This is supported by Fox equation, which agrees well with the experimental results. The fact that no T_g could be observed in the
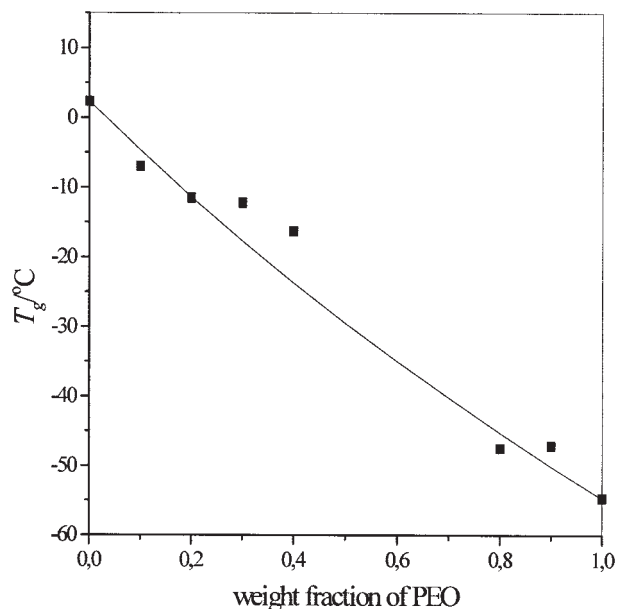
Figure 1 Glass transition temperatures of PHBV/PEO mixtures. The solid curve represents the Fox equation, with T_g^{PEO} = −55°C and T_g^{PHBV} = 2°C.

intermediate composition range could be also seen as an indication of limited miscibility of the constituents.

Crystallinity

The blend constituents crystallize successively and independently to an excellent approximation. They do not form mixed crystals. Therefore, melting enthalpies are used to characterize the crystallinity of the blends. Selected results for melting enthalpies obtained for the blends after isothermal crystallization are shown in Figure 2. To compare crystallinities of the constituents, we introduce the relative degree of crystallinity $\Delta H_m/\Delta H_{ref}$, with ΔH_{ref} being the melting enthalpy of 100% crystalline material. We use for the reference quantities the following values, ΔH_{ref}^{PHBV} = 109 J/g[21] and ΔH_{ref}^{PEO} = 188.3 J/g.[22] With these values and the data plotted in Figure 2, we get degrees of crystallinity of 50% for PHBV and 75% for PEO after crystallization under the indicated conditions. Moreover, the linear decrease of melting enthalpy of PHBV with PEO content in blends, as shown in Figure 2, demonstrates that the degree of crystallinity of PHBV is constant in the blends. The amorphous melt of PHBV and PEO does not influence the degree of crystallinity of PHBV developing in isothermal crystallization. PEO, on the other hand, crystallizes when surrounded by crystalline PHBV. With increasing content of PHBV in the blends, this leads to marked reduction of the degree of crystallinity of PEO as compared to the neat polymer, i.e., the existence of crystalline PHBV hampers the

development of PEO crystallinity in blends under isothermal crystallization conditions.

Melting behavior

The approach of Hoffman–Weeks was applied for determining equilibrium melting temperatures, T_m^0, of the blend constituents.[23] Accordingly, the equilibrium melting temperature follows from

$$T_m = \alpha T_c + (1-\alpha)T_m^0 \tag{1}$$

where parameter α represents a stability parameter that depends on lamellar thickness and crystal perfection. After isothermal crystallization for five half times at the desired crystallization temperatures, the melting points of the polymers were detected by heating the samples at a rate of 10 K/min. Hoffman–Weeks plots for PHBV in blends with PEO are shown in Figure 3. Since PHBV exhibits a double melting peak, the data refer to the lower melting point, because only the lower melting point varied with crystallization temperature. Analogous plots for PEO are presented in Figure 4. Qualitatively, we note a slight decrease in
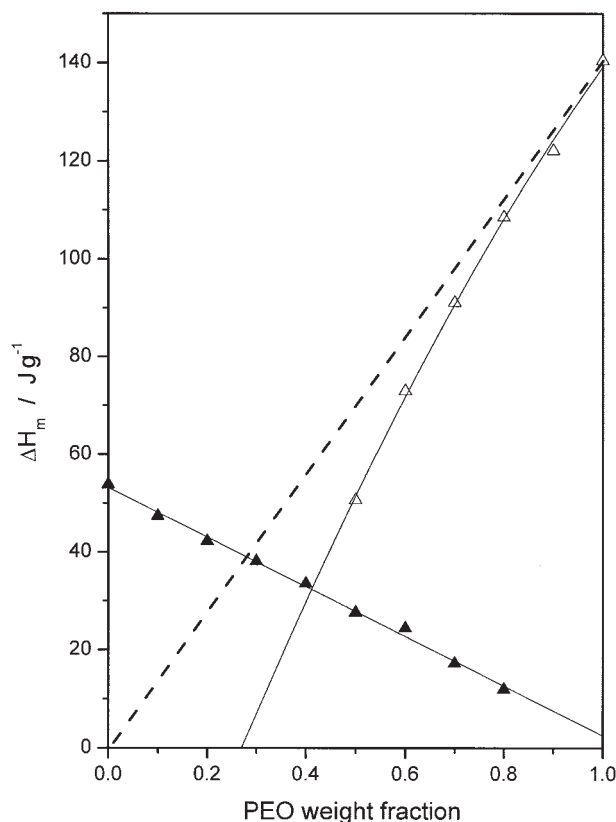
Figure 2 Melting enthalpy, ΔH_m, of PHBV and PEO in blends after isothermal crystallization for five half times at T_{C1} = 104°C and T_{C2} = 44°C, respectively. Markers: ▲, PHBV; △, PEO.
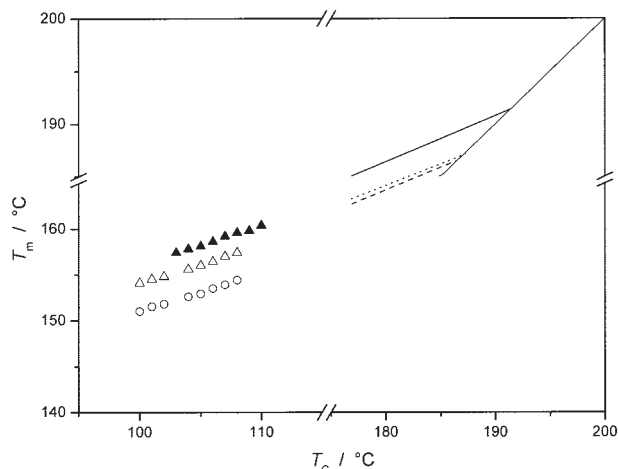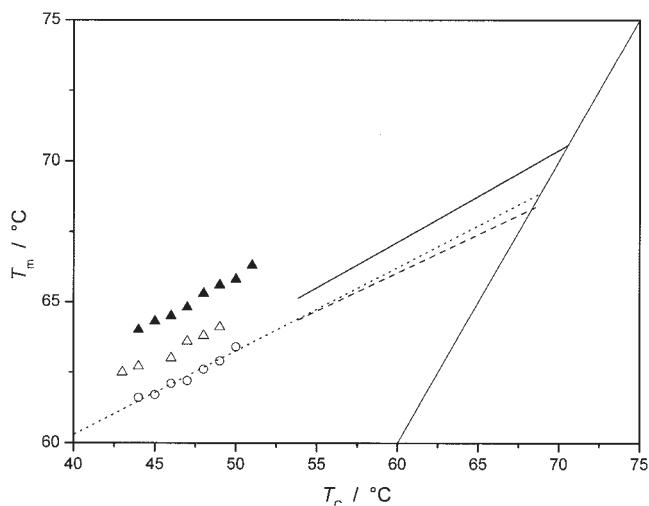
Figure 3 Hoffman–Weeks plots for PHBV in blends with PEO. The experimental data points are displaced, whereas the regression curves are at the original position. ▲ 100/0, data displaced by +5°C, solid regression curve; △ 80/20, data displaced by +3°C, dashed regression curve; ○ 50/50, data at original position, dotted regression curve.

melting temperature for both constituents in blends, which supports miscibility of the two polymers.

The equilibrium melting points estimated for pure PHBV and pure PEO are 190 and 71°C, respectively. The parameter α was found close to 0.4 for PHBV and close to 0.3 for PEO in all systems. The value for PHBV agrees well with $\alpha = 0.35$ found in Ref. 24.

Kinetics of isothermal crystallization

Under conditions studied, the two constituents are crystallizing in different situations. The constituents

Figure 4 Hoffman–Weeks plots for PEO in PHBV/PEO blends. The experimental data points are displaced, whereas the regression curves are at the original position. ▲ 0/100, data displaced by +2°C, solid regression curve; △ 18/82, data displaced by +1°C, dashed regression curve; ○ 25/75, data at original position, dotted regression curve.

TABLE II
Avrami Exponents and Rates of Crystallization for PHBV and PEO in Blends at $T_{C1} = 104$°C and $T_{C2} = 44$°C

PHBV/PEO	n	$t_{0.5}^{-1}$ (min^{-1})
PHBV		
100/00	1.78	0.87
80/20	2.05	0.70
60/40	2.07	0.59
50/50	1.99	0.52
40/60	2.01	0.35
PEO		
00/100	2.17	1.96
10/90		1.31
40/60		2.85
50/50		3.64

Crystallization temperatures T_{C1} and T_{C2} correspond to undercoolings $\Delta T = 86$ K for neat PHBV and $\Delta T = 27$ K for neat PEO.

are miscible in the molten state. When we lower the temperature, PHBV starts to crystallize out of the homogeneous system. Hence, no problem arises with application of Avrami equation. PEO, on the other side, crystallizes in a phase-separated system. It crystallizes in the presence of PHBV crystallites, which means, phase boundaries may influence crystallization kinetics of PEO. This influence is not taken into account in Avrami equation. Therefore, we characterize the rate of PEO crystallization by reciprocal half-time of crystallization, which can be defined independently of Avrami equation, and take pure PEO as the reference for crystallization of PEO in blends.

Overall crystallization kinetics of PHBV is discussed in terms of Avrami equation:[25]

$$-\ln[1 - X(t)] = K(T)t^n \tag{2}$$

where normalized crystallinity $X(t)$ is defined as the ratio of conversion at time t and the final conversion, ratio of peak areas $a(t)/a(\infty)$. Avrami plots for PHBV in blends as well as for pure PEO according to eq. (2) were strictly linear in a certain range of time (correlations: 0.999. . . 0.998). Deviations from linearity or from eq. (2) occurred for PHBV, above a degree of conversion of around 85%, and for pure PEO at around 95% conversion. As mentioned before, we determine solely the half-time of crystallization for PEO in blends. Therefore, we convert here parameters n and K for PHBV also in half-time $t_{0.5}$ after

$$t_{0.5} = \left(\frac{\ln 2}{K}\right)^{1/n} \tag{3}$$

Table II gives selected examples of Avrami exponents and reciprocal half times for crystallization of PHBV and PEO in blends. The Avrami exponents, n,
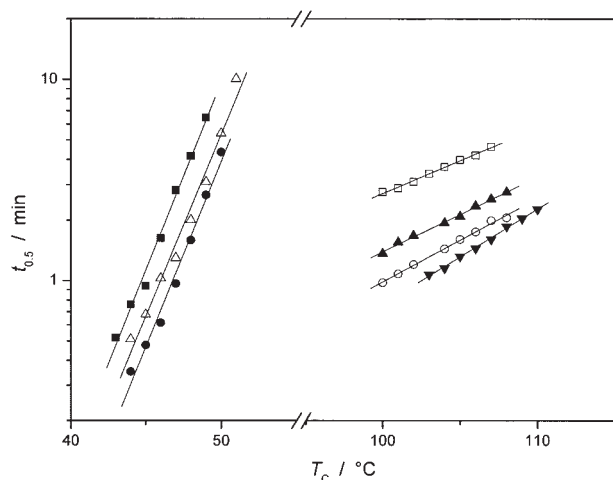
Figure 5 Half-time of isothermal crystallization versus crystallization temperature for PHBV and PEO in PHBV/PEO blends. PHBV: (▼) 100/0, (○) 80/20, (▲) 50/50, (□) 20/80. PEO: (△) 0/100, (■) 10/90, (●) 40/60.

were found close to 2 for PHBV and also for pure PEO. We observe that the rate of crystallization of PEO exceeds that of PHBV, although the undercooling of PEO is less than that of PHBV. Moreover, the rate of crystallization of PHBV decreases with increasing amount of PEO, whereas the crystallinity of PHBV does not change in the blends (*cf*. Fig. 2). The opposite behavior may be recognized for PEO.

Half times of crystallization versus crystallization temperature are presented in Figure 5. For constant blend composition, half times of PHBV and PEO as well increase exponentially with crystallization temperature in the range of temperatures studied. As stated earlier, the figure also demonstrates decrease in the rate of PHBV crystallization, with increasing PEO content at T_c = const. Figure 6 shows in more detail the composition dependence of reciprocal half-time at constant crystallization temperature for the two constituents. In the range where PHBV forms the excess component, its rate of crystallization decreases exponentially with PEO content. Deviations from exponential behavior occurred above 50 wt % of PEO. The decrease of PHBV crystallization rate with increasing PEO content indicates that the components are miscible in the molten state. The crystallization rate of PEO decreases, as compared to neat PEO, when small amounts of PHBV are added. With increasing amount of PHBV, a pronounced increase in the crystallization rate of PEO was observed, indicating nucleating activity of crystalline PHBV. Qualitatively, the same results were found in blends of PCL and PEO.[26]
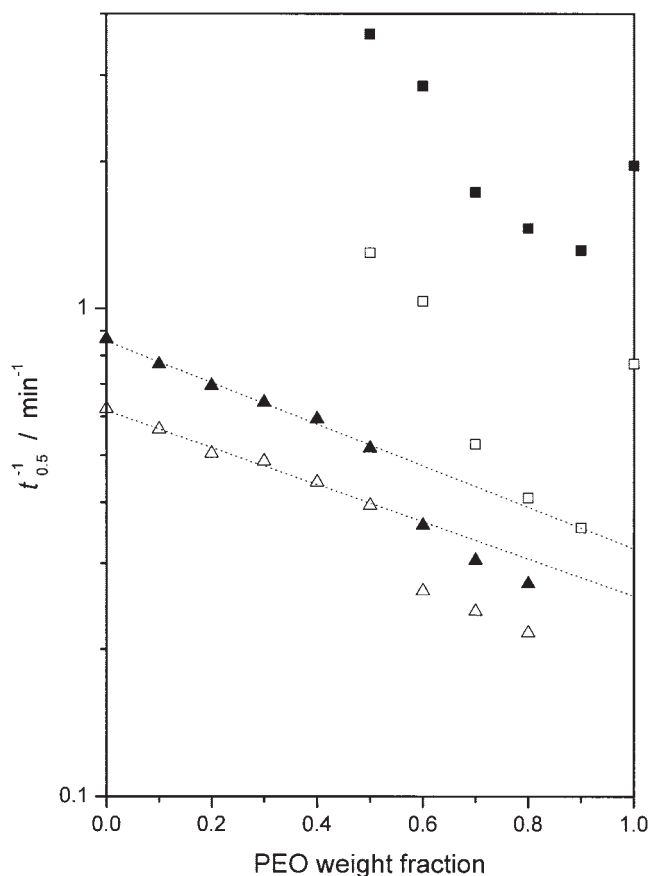
Spherulite growth rate of PHBV

The spherulite growth rate, G, of PHBV in blends with PEO has been studied under isothermal conditions.

Rates for crystal growth of PEO in blends could not be detected. For PHBV, the spherulite radius R increased linearly with time, for all temperatures and blend compositions investigated.

The temperature dependence of G turned out to be qualitatively the same as the one depicted in Figure 5 for half-time of crystallization of PHBV versus temperature. For PHB, the growth rate G was found to be 8 μm/min at 130°C.[9] Extrapolation of the result found for PHBV, $G(\mu m\ min^{-1}) = 7080\ exp\ (-\vartheta/19.8°C)$, to 130°C yields around 10 μm/min, in reasonable agreement with the former value. These values are in excellent agreement with data reported in Ref. 12 for PHB, 8 μm/min, and[22] for PHBV, 9 μm/min.

Figure 7 shows the spherulite growth rate of PHBV as a function of blend composition for different crystallization temperatures. Again, we recognize similarities to the corresponding rates of Figure 6. Deviations from exponential behavior in Figure 7 are more pronounced than in Figure 6. We may conclude that decrease of reciprocal half-time and spherulite growth rates with increasing content of PEO provides direct support for miscibility of the components in the mol-

Figure 6 Reciprocal half times of PHBV and PEO as functions of weight fraction of PEO for different crystallization temperatures. PHBV: (▲) 104, (△) 107°C. PEO: (■) 44, (□) 47°C.
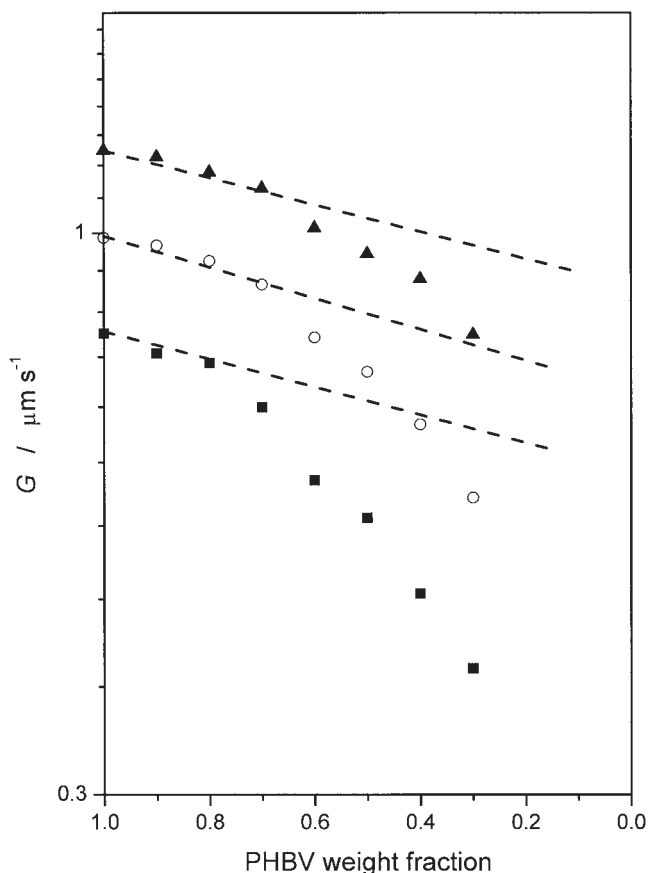
Figure 7 Radial growth rate, G, of PHBV spherulites in PHBV/PEO blends as a function of blend composition at different crystallization temperatures. Crystallization temperature: ■ 100°C, ○ 96°C, ▲ 92°C.

ten state. In a two-phase melt, growth rate should be independent of blend composition. We note, for blends containing less than 30% of PHBV, spherulites grow in irregular shape. This prevents precise measurements of the diameter of PHBV spherulites.

Kinetics of nonisothermal crystallization

For nonisothermal crystallization studies, crystallization was monitored at various cooling rates as mentioned in the Experimental part. The discussion will be given in terms of the procedure proposed in Ref. 8.

Avrami eq. (2) describes crystallization under isothermal conditions. Generally, one cannot expect a power law of that type for nonisothermal crystallization, with cooling rate s = const, since the rate constant K of eq. (2) is a function of temperature. However, one may expect quasi-isothermal behavior for conversions $X_T(s)$ belonging to a series of nonisotherms, each characterized by a constant cooling rate, and determined at a certain temperature T = const. In generalization of eq. (2), we characterize nonisother-

mal crystallization at different constant cooling rates, s, by the quasi-isothermal approach:

$$- \ln[1 - X_T(s)] = K(T)$$
$$\times \left(\frac{\Delta T}{s}\right)^n \quad \text{at } T = \text{const and } s \neq \text{const} \quad (4)$$

where the temperature difference is the difference between onset temperature and temperature T of interest, $\Delta T = T_{onset} - T$ with $T < T_{onset}$. After eq. (4) we describe a series of nonisotherms by parameters K and n determined under conditions as indicated. The conversion X_T is detected at temperature T = const and each conversion X_T refers to a different cooling rate s = const. Hence, eq. (4) characterizes a quasi-isothermal process having for each X_T a different thermal history.

Figure 8 shows conversions $-\ln(1-X)$ versus $\Delta T/s$ for PHBV in 80/20 PHBV/PEO blends for various constant cooling rates, s. Completely analogous results were found for crystallization of PEO in blends, indicating that crystallization of the constituents proceeds independently. The onset temperature, T_{onset}, was selected as the temperature where the conversion amounted to $X = 0.01$. Conversions for T = const are also indicated in the figure. It can be seen that the experimental data obey the power law after eq. (4) to a very good approximation. For the temperature indicated in the figure (91°C), the nonisothermal process can be characterized after eq. (4) by the parameters n = 1.64 and $K^{1/n}$ = 1.68 min^{-1}. Moreover, we recognize that only cooling rates within a limited range contribute to the power law at a constant temperature. In the example shown in Figure 8, cooling rates vary in the
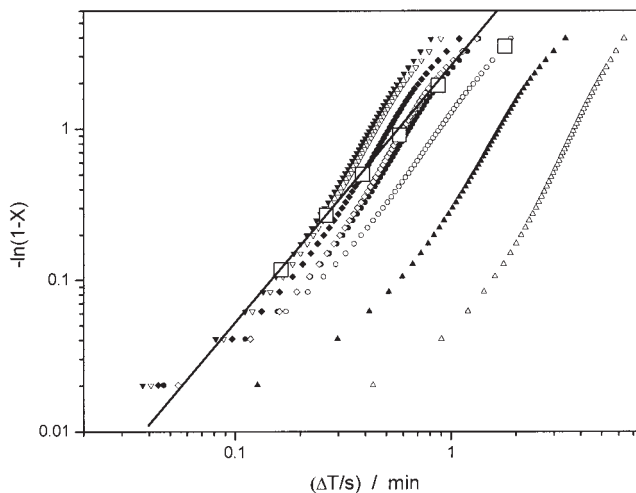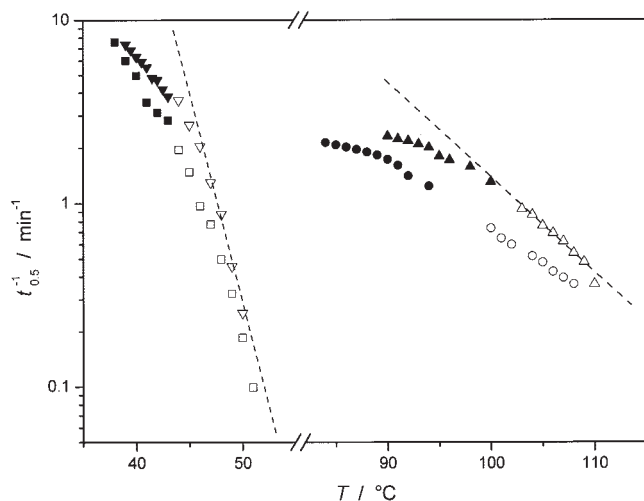

Figure 8 Nonisothermal crystallization of PHBV in 80/20 PHBV/PEO blends. Cooling rates: (△) 2, (▲) 5, (○) 10, (●) 15, (◇) 20, (◆) 25, (▽) 30, (▼) 35 K/min. The open squares refer to 91°C.

range $15 \leq s \leq 35$ K/min. When the temperature T = const increases, the corresponding straight line shifts downward in Figure 8, i.e., data belonging to smaller cooling rates contribute to eq. (4) or the nonisothermal process shifts closer to isothermal conditions.

Plots of rate of crystallization, $t_{0.5}^{-1}$, versus temperature, presented in Figure 9, show this behavior quite clearly. One recognizes that rates of nonisothermal crystallization approach the rates of isothermal crystallization at sufficiently high temperatures. At low temperatures, conversions do not change very much with cooling rate; therefore, the corresponding rate is smaller than under isothermal conditions. The figure also shows that the rates of crystallization change with composition as, under isothermal conditions, for PHBV it decreases with increasing PEO content and for PEO it increases with ascending PHBV content. Selected rate constants for nonisothermal crystallization at constant temperature and for varying composition are compiled in Table III. Again the same qualitative behavior as for crystallization under isothermal conditions can be seen.

CONCLUSIONS

Measurements of glass transition temperatures point toward miscibility of PHBV and PEO in the amorphous state. After isothermal crystallization of the constituents at different crystallization temperatures, the degree of crystallinity of PHBV does not change in the blends, whereas the degree of crystallinity of PEO is slightly reduced in the blends. Support for miscibil-

TABLE III
Parameters for Dynamic Crystallization of PHBV and PEO in Blends at Constant Temperature

PHBV/PEO	n	$t_{0.5}$ (min)	R
At $T = 91°C$ for			
PHBV			
100/0	1.62	0.45	0.997
80/20	1.64	0.48	0.999
60/40	1.65	0.53	0.996
50/50	1.68	0.55	0.996
30/70	1.68	0.97	0.991
At $T = 42°C$ for			
PEO			
0/100	1.51	0.32	0.996
10/90		0.38	0.998
40/60		0.26	0.997
50/50		0.21	0.995

ity comes also from crystallization dynamics. Owing to the huge difference in melting temperatures of the constituents, the components crystallize consecutively in the blends. Under isothermal conditions, both the overall rate of crystallization and the growth rate of spherulites of PHBV decrease with increasing content of PEO. This indicates that spherulites develop from a homogeneous melt mixture. One also observes that the rate of PEO crystallization in blends increases under the influence of PHBV crystallites when the content of PHBV is sufficiently high. Nonisothermal crystallization of the constituents was examined under constant cooling rates. Discussion in terms of a quasi-isothermal approach shows that, in the range of low temperatures, rates of isothermal crystallization exceed that of nonisothermal crystallization. At sufficiently high temperatures, the rates approach each other. Qualitatively, the same tendencies for temperature and composition dependencies are observed as for isothermal crystallization.

Figure 9 Rates of isothermal and nonisothermal crystallization of PHBV and PEO in blends versus temperature. Open and solid symbols refer to isothermal and nonisothermal crystallization, respectively. Triangles, PHBV; circles, PHBV in 50/50 blends. Squares, PEO; inverse triangles, PEO in 50/50 blends.

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