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Melting and Crystallization in Bacterial Poly(β-hydroxyvalerate), PHV, and Blends with Poly(β-hydroxybutyrate-*co*-hydroxyvalerate)

Robert P. Pearce and Robert H. Marchessault*

Department of Chemistry, McGill University, Montreal, Canada H3A 2A7

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ABSTRACT: The melting and crystallization behavior of bacterial poly(β-hydroxyvalerate), PHV, is reported and compared to the companion bacterial polyester poly(β-hydroxybutyrate), PHB. The equilibrium melting point, T^0_m, measured by the Hoffman–Weeks method is found to be 130 °C. A glass transition temperature of −16 °C is proposed as representative of amorphous PHV. Spherulitic growth kinetics are analyzed using the Lauritzen–Hoffman model, and kinetic parameters are extracted. Crystallization is found to occur within regime II. Melting and crystallization in blends of PHV with a copolymer P(HB-*co*-HV) containing 77 mol % HV are reported and discussed within the context of cocrystallization. Finally, it is shown that PHV and PHB are phase separated in the melt. The implications of this result in terms of current views of isodimorphism in the P(HB-*co*-HV) system are discussed.

Introduction

The importance of the bacterial copolyester poly(β-hydroxybutyrate-*co*-hydroxyvalerate), P(HB-*co*-HV), owes to its biodegradability combined with a wide range of physical properties.[1-3] Most studies of P(HB-*co*-HV) have focused on compositions rich in butyrate (HB) content[4-9] since the commercially available material is generally restricted to compositions between 0–30 mol % HV. This is an economic imperative for the supplier since yield decreases as the propionic acid cofeed, which generates valerate in the fermentation, is increased.[10] However, alternative substrates have allowed Doi *et al.* to broaden the composition range of the copolyesters produced by *Alcaligenus eutrophus*, which has been extended to 95 mol % HV.[11,12]

The P(HB-*co*-HV) system exhibits the phenomenon of isodimorphism, as evidenced by the maintenance of a high level of crystallinity over a wide range of compositions.[4,5,13-17] A minimum in the melting point versus composition curve occurs at an HV content of approximately 40 mol %; wide-angle X-ray measurements have shown that this composition corresponds to the changeover from the PHB lattice to the PHV lattice for HV contents in excess of 40 mol %.[4,14,16]

More recently, the bacterially produced homopolymer PHV was isolated for the first time by Steinbüchel *et al.*[18] using the microorganism *Chromobacterium violaceum*. This polymer is important as it represents a reference point for understanding some of the special properties of the isodimorphic P(HB-*co*-HV) system. A synthetic, racemic version of PHV was prepared from DL-β-ethyl-β-propiolactone by Yokouchi *et al.*[19] and later by Bloembergen *et al.*[20] The latter authors also synthesized racemic analogues of P(HB-*co*-HV) copolyesters and demonstrated that these samples exhibit isodimorphism, similar to the stereoregular bacterial system.[10]

The purpose of this article is to present some results obtained on the crystallization and melting behavior of bacterial PHV. This semicrystalline polymer has been shown to be isotactic in its chain configuration[18] with a glass transition temperature T_g of −11 °C and a melting point of approximately 107 °C for a solvent-cast film, in close agreement with values reported for the synthetic, racemic polymer.[19,20] The X-ray diffraction pattern has also been shown to be identical to that of the stereoblock synthetic polymer.[18] The present work will describe the measurement of the equilibrium melting point of bacterial PHV and will present an analysis of the spherulitic crystallization kinetics, making use of the Lauritzen-Hoffman theory of secondary nucleation.[21] In addition, some results pertaining to blends of PHV with PHB as well as P(HB-*co*-HV) will be presented and discussed in the context of isomorphism.

Experimental Section

The bacterial PHV sample used was kindly supplied by Professor A. Steinbüchel, Institut für Mikrobiologie der Georg-August-Universtät Göttingen, Göttingen, Germany, and had been produced by the microorganism *C. violaceum*.[18] The sample had a viscosity-average molecular weight of 133 000 as measured in chloroform using values of the Mark–Houwink coefficients for PHB.[22] This approximation is consistent with the similarity in repeat structure for PHB and PHV. A copolyester, P(HB-*co*-HV), with an HV content of 77 mol % was kindly supplied by Professor Y. Doi, Tokyo Institute of Technology, and had been isolated from *A. eutrophus*.[11,12] All compositions were measured by solution ^{1}H NMR.

Samples for DSC analysis were cast from 1% solutions in chloroform which were filtered onto Teflon. The solvent was allowed to evaporate overnight, and the resultant films were dried for 24 h under vacuum at room temperature.

DSC measurements were performed on a Perkin-Elmer DSC7, equipped with an intracooler system. Isothermal crystallization experiments were performed using approximately 0.5 mg of sample, sealed in aluminum pans. These were heated under a nitrogen atmosphere to a temperature 15 °C above the melting peak temperature, held there for 1 min, and quenched at a nominal rate of 200 °C/min to a preselected crystallization temperature, where they were held isothermally. The crystallization time at each temperature was minimized in order to avoid effects due to isothermal thickening. Typically, samples were allowed to crystallize for 5–10 min. They were then heated directly to 120 °C, and the melting point was recorded at the peak temperature. Unless otherwise stated a heating rate of 40 °C/min was employed.

Samples for optical microscopy were prepared by filtering stirred chloroform solutions onto cleaned glass cover slips. The solvent was then evaporated as described above.

Measurements of the spherulitic growth rates by optical microscopy were performed using a Nikon Optiphot polarizing microscope equipped with a Linkham THMS 600 hot stage. Samples were heated on the hot stage at 20 °C/min to a

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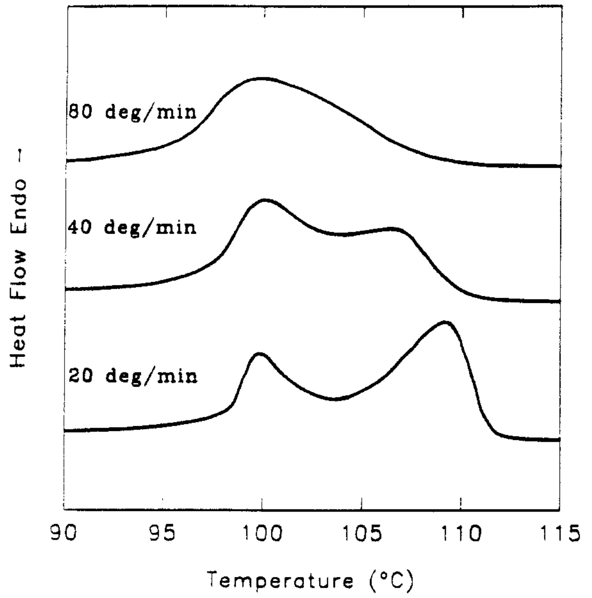

Figure 1. Variation of DSC scan profile with heating rate for bacterial PHV melt crystallized at 75 °C.

temperature 15 °C above the DSC melting peak temperature. The samples were held at this temperature for 1 min and then quenched at 130 °C/min to an isothermal crystallization temperature. Spherulitic growth was monitored under crossed polars using a video camera mounted on the microscope. The images were recorded on video tape, and the JAVA (Jandel Scientific) image analysis software was used to determine spherulite size at various times. Typically, 15–20 readings were made for each spherulite and linear growth rates were obtained with correlation coefficients of 0.99 or better by plotting size as a function of time. New samples were used for each run.

Results and Discussion

Melting Behavior of PHV. The Hoffman–Weeks[23] technique was used to estimate the equilibrium melting point T^0_m of bacterial PHV. By this technique, the variation of the observed melting point T_m with isothermal crystallization temperature T_c is measured. According to Hoffman and Weeks,[23]

$$T_m = T^0_m\left(1 - \frac{1}{\gamma}\right) + \frac{T_c}{\gamma} \tag{1}$$

where $\gamma > 1$ and T^0_m is obtained from a plot of T_m as a function of T_c by extrapolating the linear data until intersection with the $T_m = T_c$ line.

This technique must be used with caution as complications can arise due to annealing and recrystallization. In the case of PHV there was a marked tendency toward multiple melting peaks following isothermal crystallization. However, by simply varying the heating rate it was evident that the low-temperature melting peak was that corresponding to the crystals formed at T_c while the high-temperature peak was due to material which had recrystallized during heating in the DSC. This is seen in Figure 1 for samples crystallized at 75 °C and subsequently melted. As the scan rate is increased, the low-temperature peak becomes larger at the expense of the high-temperature peak, indicative of a melt/recrystallization process. This is commonly observed in the thermal analysis of semicrystalline polymers and has recently been reported in PHB and blends of PHB.[24,25] The process of recrystallization tends to be more important for thinner crystals formed at larger undercoolings.[26]

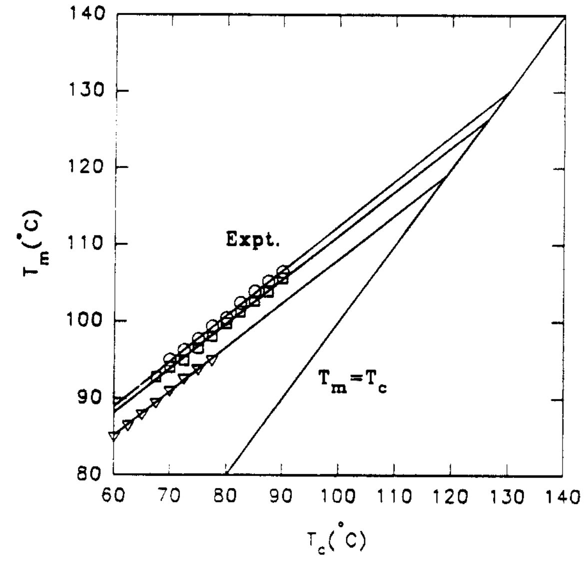

Figure 2. Hoffman–Weeks plots for bacterial PHV (○), P(HB-*co*-HV) 77 mol % HV (▽), and a 50/50 blend of both (□).

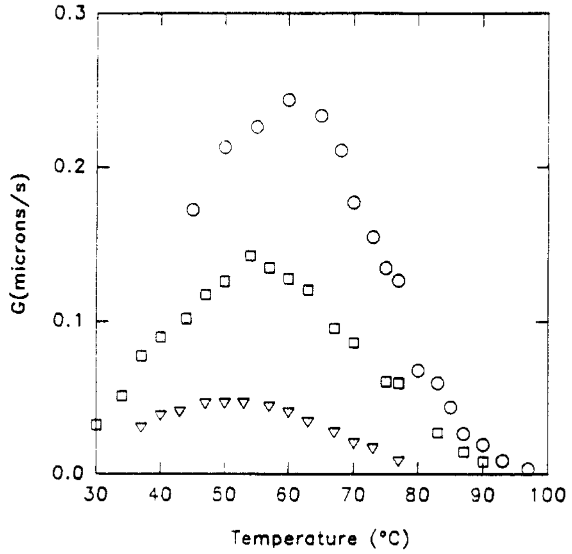

Figure 3. Spherulitic growth rates for bacterial PHV (○), P(HB-*co*-HV) 77 mol % HV (▽), and a 50/50 blend of both (□).

Figure 2 shows the Hoffman–Weeks plot for bacterial PHV. Also shown are plots for a P(HB-*co*-HV) sample of composition 77 mol% HV and a 50/50 blend of this copolymer with PHV, to be discussed later. Good linearity is obtained for PHV, and extrapolation to the line $T_m = T_c$ yields $T^0_m = 130$ °C. This compares to values obtained for PHB of 203 °C[27] and 200 °C,[28] obtained using the same methodology.

Crystallization Kinetics of PHV. Spherulitic growth rates were measured for PHV and are summarized in Figure 3. It is seen that the maximum growth rate is observed at a temperature of approximately 60 °C, corresponding to an undercooling, ΔT of 70 °C. In contrast, PHB exhibits its maximum growth rate at $T_c \approx 90$ °C, corresponding to $\Delta T \approx 110$ °C.[27,28] This may be a reflection of the wider range available between T^0_m and T_g for crystallization to occur in the case of PHB (199 °C) as compared to PHV (140 °C). It was not found possible to measure growth rates below 45 °C because nucleation was too dense. PHV spherulites exhibited banding similar to that previously reported for PHB.[28] However, PHV yielded smaller spherulites than PHB, due to a higher nucleation density. For example, at 75 °C the average

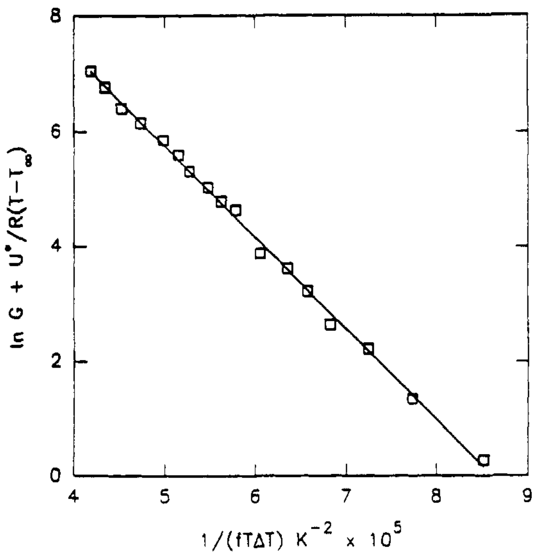

Figure 4. Lauritzen–Hoffman plot for bacterial PHV.

spherulitic radius for PHV was approximately 50 μm as compared to radii of 500 μm or more for PHB.[28]

In an attempt to extract values for the end-surface free energy, σ_e, and the work of chain folding, q, the Lauritzen–Hoffman model of secondary nucleation was used to analyze the growth rates, G:[21]

$$G = G_0 \exp\left(\frac{-U}{R(T - T_\infty)}\right) \exp\left(\frac{-K_g}{fT(\Delta T)}\right) \tag{2}$$

where the pre-exponential contains temperature-independent terms, U^* is the activation energy for transport of crystallizable segments to the crystallization front, T_∞ is the temperature below which such motion cases, T is the crystallization temperature, ΔT is the degree of undercooling, and f is a factor which accounts for the variation in the enthalpy of fusion Δh_f with temperature and is given by $f = 2T/(T^0_m + T)$. The nucleation constant K_g is given by[21]

$$K_g = \frac{n b_0 \sigma \sigma_e T^0_m}{\Delta h_f k} \tag{3}$$

where σ is the lateral surface free energy, b_0 is the molecular thickness, and k is the Boltzmann constant. The value of n in eq 3 depends on the regime of crystallization.[21,29] Regime I applies when each surface nucleation occurrence leads to rapid completion of the growth strip prior to the next nucleation event.[21] This corresponds to $n = 4$ and is obtained only at high crystallization temperatures. At lower temperatures, multiple surface nuclei form on the substrate. This is referred to as regime II and leads to $n = 2$. If crystallization occurs at still lower temperatures, the separation between the multiple nuclei characteristic of regime II reaches its minimum value. This is regime III and $n = 4$ in eq 3. Such a discrete variation in the parameter n with range of crystallization temperature can lead to the observation of regime transitions, manifested as abrupt changes in slope when the quantity $\ln G + U^*/R(T - T_\infty)$ is plotted as a function of $1/fT(\Delta T)$.[21,29]

In order to utilize the Lauritzen–Hoffman model the quantity $\ln G + U^*/R(T - T_\infty)$ was plotted as a function of $1/fT(\Delta T)$ while U^* and T_∞ were varied to maximize the correlation coefficient. The best fit for bacterial PHV, shown in Figure 4, was obtained from $U^* = 1550$ cal/mol and $T_\infty = 220$ K, the latter corresponding to $T_g - 43$ K. The value of the nucleation constant K_g extracted from the fit was 153 000 K².

In order to obtain values for σ_e and q it is necessary to assign a crystallization regime. This is straightforward in the case of PHB where a regime II → III transition is evident.[27,28] However the situation is not so obvious for PHV. By applying the Lauritzen Z-test[30]

$$Z \approx 10^3 (L/2a)^2 \exp[-X/T(\Delta T)] \tag{4}$$

where L is the substrate width and Z is a dimensionless parameter, it is possible to test for regimes I and II. The procedure consists in using eq 4 to calculate values of L. To test for regime I, the substitution $X = K_g$ is made and the condition $Z \leq 0.01$ is applied.[30] When these criteria are applied to PHV, a value of $L \leq 0.1$ Å is obtained, which is unacceptably low.[21] Hence regime I can be eliminted. To test for regime II the substitution $X = 2K_g$ is made and the condition $Z \geq 1$ is applied.[30] For PHV this yields $L \geq 3 \times 10^5$ Å at a crystallization temperature of 100 °C and $L \geq 120$ Å at a temperature of 50 °C. These values are consistent with crystallization within regime II.

The choice between regimes II and III can be made on the basis of calculated values of σ_e, which can be obtained using eq 3. It is first necessary to obtain an estimate for Δh_f, the heat of fusion for a fully crystalline sample of PHV. For a synthetic version of PHV, Δh_f has been estimated to be 131 J/g.[31] This agrees well with a value of $\Delta h_f = 128$ J/g obtained for a bacterial P(HB-*co*-HV) sample with 95 mol % HV.[17] From the crystal structure of synthetic PHV, $a_0 = 5.0$ Å and $b_0 = 9.3$ Å.[19] The crystalline density has been calculated to be 1.28 g/cm³,[19] and this yields $\Delta h_f = 1.67 \times 10^8$ J/m³ for PHV.

Calculation of $\sigma\sigma_e$ assuming regime II crystallization yields a value of 471 erg²/cm⁴. To evaluate σ_e the empirical expression[32]

$$\sigma = \alpha(\Delta h_f)(a_0 b_0)^{1/2} \tag{5}$$

is used. On the basis of the constant α, there are two classes of polymers. High-melting polyesters such as poly(pivalolactone) and PHB have $\alpha \approx 0.25$,[33] while another class, including polyethylene and other vinyl polymers, have $\alpha \approx 0.1$.[33] Use of $\alpha \approx 0.25$ in eq 5 yields $\sigma = 28.5$ erg/cm² and $\sigma_e = 16.5$ erg/cm². The latter value corresponds to a work of chain folding, q, given by[21]

$$q = 2a_0 b_0 \sigma_e \tag{6}$$

of only 2.2 kcal/mol of folds. The quantity q has been shown to vary with chain structure and is found to be approximately 5 kcal/mol for moderately flexible chains such as polyethylene and around 7 kcal/mol for chains with bulky side groups such as polystyrene and poly(pivalolactone).[21] For PHB a value of $q = 5.1$ kcal/mol has previously been obtained,[27] and it is difficult to justify a value much lower than this for PHV, which has a longer side group.

If $\alpha = 0.1$ is used in eq 6, values of $\sigma = 11.4$ erg/cm², $\sigma_e = 41.1$ erg/cm², and $q = 5.5$ kcal/mol of folds are obtained. These values are more reasonable and add to the growing evidence that not all linear polyesters have $\alpha \approx 0.25$. Hoffman *et al.* have indicated that poly(ε-caprolactone) should be considered as a modified vinyl polymer with $\alpha = 0.1$.[33] Goulet and Prud'Homme also found $\alpha = 0.1$ to be an appropriate choice for caprolactone copolymers.[34]

It is clear that there is need for a better understanding of the molecular parameters which govern the choice of α.

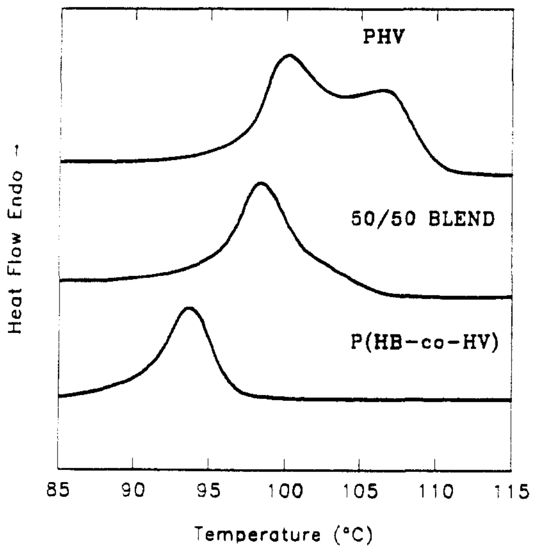

Figure 5. DSC traces after isothermal crystallization at 75 °C for bacterial PHV, P(HB-*co*-HV) 77 mol % HV, and a 50/50 blend of both.

For reasons already discussed, regime III can be eliminated as a possible crystallization regime since $n = 4$ in eq 3 yields values of $\sigma\sigma_e$, σ_e, and q which are half of those obtained by assuming regime II crystallization.

Blends of PHV and P(HB-*co*-HV). The phenomenon of isodimorphism, as observed in the P(HB-*co*-HV) system,[4] has been shown to lead to cocrystallization in blends of PHB and P(HB-*co*-HV) of low HV content.[24] In view of these results it was sought to investigate such behavior using PHV and P(HB-*co*-HV) of high valerate content. For this purpose melting and crystallization were examined in a copolymer P(HB-*co*-HV) of 77 mol % HV and a 50/50 blend of this copolymer with PHV.

Figure 5 shows DSC scans for 100% PHV and P(HB-*co*-HV) and a 50/50 blend of the two. The samples had been melted and then isothermally crystallized at 75 °C for 5 min. The scan for 100% PHV shows a prominent high-temperature peak which is due to material which has recrystallized (cf. above). Focusing on the low-temperature peak which is due to material formed at the crystallization temperature, it is seen that the 50/50 blend has a peak temperature which is between those of PHV and P(HB-*co*-HV), although close to that of PHV. To further elucidate this behavior, a Hoffman–Weeks experiment was performed and the results are shown in Figure 2. It is seen that over the entire range of crystallization temperatures investigated, the 50/50 blend consistently yields a melting point which is between those of PHV and P(HB-*co*-HV). Extrapolation to the line $T_m = T_c$ yields T^0_m = 119 °C for P(HB-*co*-HV), T^0_m = 126 °C for the 50/50 blend, and as reported above T^0_m = 130 °C for pure PHV. These data provide evidence for cocrystallization between PHV and P(HB-*co*-HV).

Crystallization kinetics were examined by measuring spherulitic growth rates for the three samples. Volume-filling spherulites were obtained at all temperatures investigated, and the results are presented in Figure 3. It is observed that the kinetics of crystallization in the case of the 50/50 blend are intermediate between those of PHV and P(HB-*co*-HV). Accompanying this is a shift in the temperature of maximum crystallization rate, G_{max}, to lower temperatures as the level of valerate in the system decreases. These results are also consistent with cocrystallization. It has been reported previously that in P(HB-*co*-HV) samples with levels of valerate between 55 mol % and 95 mol %, a decrease in HV content results in slower crystallization kinetics and a shift in G_{max} to lower T_c.[17]

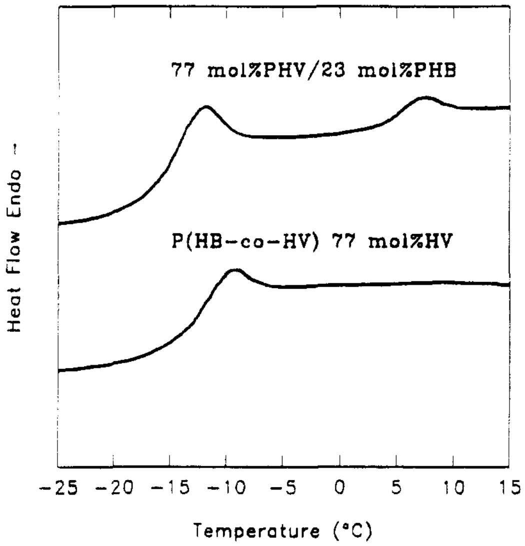

Figure 6. DSC traces after melt quenching for 77 mol % PHV/23 mol % PHB and P(HB-*co*-HV) 77 mol % HV.

The above observations suggest cocrystallization between PHV and P(HB-*co*-HV). Thus, simplistically, a 50/50 blend of the two is equivalent to a sample of P(HB-*co*-HV) with an intermediate amount of HV within both the amorphous and crystalline zones. It could be argued, however, that P(HB-co-HV) simply acts as a diluent for PHV, leading to a depression in T^0_m and slower kinetics of crystallization. However, the DSC results showed that the 50/50 blend achieved virtually the same level of crystallinity as PHV after isothermal crystallization at 75 °C, as revealed by similar enthalpies of fusion (40 J/g for the 50/50 blend and 44 J/g for PHV). Yet there was no evidence of a melting peak due to P(HB-*co*-HV). This implies that the addition of a noncrystalline diluent does not result in a decrease in overall crystallinity, which is unreasonable.[25,35,36] Furthermore, addition of P(HB-*co*-HV) to PHV resulted in a shift of G_{max} toward lower T_c. This is contrary to results obtained upon addition of noncrystallizable atactic PHB to bacterial PHB, where a shift of G_{max} toward *higher* T_c was observed.[27] Because of these considerations, it is apparent that the role of P(HB-*co*-HV) is not simply that of a noncrystalline diluent but rather it cocrystallizes with PHV.

Blends of PHV and PHB. Given the interest in the P(HB-*co*-HV) system and the evidence in the literature for isodimorphorism in this system, it seemed instructive to examine blends of the homopolymers PHB and PHV. For this purpose a blend of 77 mol % PHV/23 mol % PHB was chosen as it corresponded to the composition of the copolymer on hand.

The DSC scan obtained after quenching the blend from the melt is shown as the top trace in Figure 6. It is seen that individual T_g's of −16 and +4 °C are obtained for the blend. For comparison the corresponding DSC scan from a P(HB-*co*-HV) sample of the same composition is shown as the bottom trace in the same figure. In the latter case an intermediate T_g of −13 °C is obtained, in agreement with a previously reported value for a P(HB-*co*-HV) sample of similar composition.[37] These data indicate that while HV and HB segments are capable of accommodating each other in the crystalline phase when they are in the form of a copolymer, the two homopolymers phase separate in the melt. The latter observation may be rationalized in terms of thermodynamic arguments based on the free energy of mixing. However, more substantially, it suggests that the cocrystallization observed in the P(HB-*co*-HV) system may indeed be partially kinetic in origin, as suggested previously.[38]

Allegra and Bassi[39] have discussed the requirements for isomorphism in both random copolymer systems and blends. In the former case the requirements for isomorphous substitution are that the comonomer repeat units have similar volumes and shapes; the two must also possess closely related chain conformations. These requirements are met by the P(HB-*co*-HV) system. In particular, the two homopolymers PHB and PHV both crystallize in the form of a 2_1 helix, with fiber repeats of 5.96 and 5.56 Å, respectively.[19,40,41] This copolymer system is analogous to the system poly(3-methyl-1-butene-*co*-4-methyl-1-pentene). In the latter instance the presence of one extra methylene unit in the side chain leads to isodimorphism,[42] as it does in the P(HB-*co*-HV) system.

In the case of blends, however, there are two additional requirements for cocrystallization, viz. miscibility in the melt and similar rates of crystallization for the component polymers.[39] In the case of PHB/PHV blends, violation of the first of these requirements precludes the possibility of cocrystallization. However, in the case of blends of PHV and P(HB-*co*-HV) employing a copolymer with 77 mol % HV, the observation of cocrystallization implies that the two requirements are met.

Since crystallization kinetics are very much dependent on copolymer composition for the P(HB-*co*-HV) system,[17] it is clear that the presence or absence of cocrystallization will depend very much on the relative compositions of the constituent polymers present in a blend.

It has previously been reported that the T_g values for the P(HB-*co*-HV) system vary systematically from +4 to −16 °C as the HV content changes from 0 to 95 mol %.[37] However, the T_g of 100% PHV has been reported as approximately −11 °C.[18] This value was confirmed in the present work and seems, at first glance, to violate the usual monotonic variation of T_g with composition in random copolymer systems.[43] However, the value of T_g can depend to a large extent on the level of crystallinity and typically increases with crystallinity due to a decrease in chain mobility.[44] For example, isotactic polystyrene and poly(ethylene terephthalate) exhibit an increase in T_g of approximately 10 °C as crystallinity increases from 0 to about 40%.[45] Hence the somewhat higher value of T_g as measured in PHV can be attributed to the difficulty in quenching the sample from the melt sufficiently fast to avoid crystallization. This is consistent with the results reported in the previous section on the crystallization kinetics of PHV, where it was found impossible to obtain data below 45 °C due to a high nucleation density.

In contrast to the case of 100% PHV, blends of PHV with PHB as well as with P(HB-*co*-HV) of low valerate content yielded lower T_g's of approximately −16 °C (unpublished data). It appears that the problem of PHV crystallization during melt quenching is alleviated in the case of blends. The value of −16 °C agrees well with a predicted value of −17 °C for PHV obtained from data on P(HB-*co*-HV) copolymers.[37] In view of these observations the real value of T_g for amorphous PHV is probably closer to −16 °C than the previously reported value of −11 °C.[18]

Summary and Conclusions

This report has focused on various aspects of melting and crystallization for bacterial PHV. The equilibrium melting point has been evaluated to be 130 °C. This should permit a better understanding of the melting point variation in the P(HB-*co*-HV) system, as most theories of melting point variation in copolymers require values for T^0_m of both homopolymers.[46,47] In the past, studies have tended to focus on copolymers rich in HB since data were available on the melting of PHB. Such studies can now be extended to copolymers with high HV content.

The analysis of crystallization kinetics for PHV has yielded values of σ_e = 41 ergs/cm^2 and q = 5.5 kcal/mol of folds. It has been suggested that the latter parameter is that which correlates best with repeat unit structure.[33] The value of q for PHV compares with q = 5.1 kcal/mol of folds for PHB[27] and suggests that the effect of the added methylene unit in the side group of PHV is not significant in terms of the work required to make a fold. By comparison, introduction of a bulky side group such as a phenyl ring in polystyrene increases q from 5.3 kcal/mol in polyethylene to 7.1 kcal/mol.[33]

The results obtained on blends of PHV with P(HB-*co*-HV) are consistent with previous studies which have shown that cocrystallization can occur in P(HB-*co*-HV)-based blends.[24,48] Furthermore, it has been shown that the homopolymers PHB and PHV are phase-separated in the melt. This suggests that isomorphism, as it is observed in the P(HB-*co*-HV) system, is a delicate balance between thermodynamic aspects which govern miscibility and kinetic aspects which determine the inclusion of comonomer segments in the crystals.

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