Multiple melting in blends of isotactic and atactic poly(β-hydroxybutyrate)

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The phenomenon of multiple melting endotherms is investigated for the blend system isotactic/atactic poly(β-hydroxybutyrate) (PHB) for solvent-cast and melt-crystallized samples. It is shown that a melt/recrystallization process is operative for both methods of blend preparation. The overall melt behaviour is rationalized in terms of annealing of as-formed crystals and recrystallization of this material. Variations in d.s.c. scan profile with blend composition are ascribed to changes in the magnitude of the recrystallization exotherm. The crystallinity of the isotactic phase is shown to be invariant with composition. It is demonstrated that the solvent-cast blends are not fully miscible prior to the first melt.

(Keywords: poly(β-hydroxybutyrate); blends; multiple melting)

INTRODUCTION

The blending of polymers is a relatively inexpensive route to improving the properties of a polymeric material. Recently there has been much interest in the blending of semicrystalline and amorphous polymers. For these systems miscibility can be operative in the amorphous phase and the manifestations of such miscibility can be observed through the semicrystalline portion. This can take the form of melting point changes, changes in the kinetics of crystallization, variations in the level of crystallinity, and changes in the lamellar thickness and morphology.

We have been interested in the blending of bacterial poly(β-hydroxybutyrate) (PHB), with a synthetic version of the same polymer. The former is a semicrystalline polymer with a stereoregular isotactic configuration[1,2] while the latter can be produced with a range of tacticities[3,4]. We have focused our attention on the atactic, amorphous version of synthetic PHB prepared from racemic β-butyrolactone.

Thermal analysis, especially differential scanning calorimetry (d.s.c.) is widely used in the study of semicrystalline polymers as well as their blends. Quite frequently this gives rise to the observation of multiple melting endotherms. There has been much discussion in the literature as to the possible sources of such multiple melting peaks. The earliest rationalization for such behaviour was the presence of two or more groups of crystals with different morphologies (e.g. lamellar and extended-chain) or lamellar thicknesses[5-10]. Another view of the problem holds that the multiple peaks are due to a recrystallization process occurring during the d.s.c. scan wherein a polymer sample melts, then recrystallizes and melts a second time[11-20]. The superposition of two (or more) melting endotherms and the intervening crystallization exotherm gives rise to the multiple melting peaks.

One of the earliest and perhaps the best-studied example of multiple melting is that of isotactic polystyrene. Initially the multiple melting peaks observed in d.s.c. or differential thermal analysis were attributed to different morphologies, namely chain-folded crystals and extended-chain crystals[21]. However, later studies incorporating the effect of heating rate confirmed that a recrystallization process was operative[12,13].

More recently, multiple melting endotherms have been observed in the thermal analysis of poly(aryl ether ether ketone) (PEEK). This case seems particularly complex as there appears to be evidence to support both a melt/recrystallization process[19,20] as well as a mechanism based on two crystal populations[9]. Interestingly, optical microscopy used in conjunction with thermal analysis has shown that both processes may be operative[22], that is, the low-melting material may undergo a partial recrystallization and melt along with the higher-melting material. Furthermore, it has recently been shown[23] that the occurrence of melt/recrystallization is dictated by the temperature at which crystallization of PEEK is carried out.

While much has been published on multiple melting in single-component systems, relatively little has been reported on this phenomenon in blend systems[24-30]. Multiple melting has been reported for melt-crystallized isotactic PHB[31] as well as single crystals[32]. In the present work we examined this phenomenon in blends of isotactic and atactic PHB which had been melt-crystallized as well as samples prepared by evaporation of a common solvent. It will emerge that multiple melting can be observed in both cases and is very much affected by blend composition.

EXPERIMENTAL

Sample and blend preparation have been described previously[33]. Briefly, bacterial PHB (Marlborough Biopolymers, Billingham, UK) was purified by reprecipitation from *N,N*-dimethylformamide (DMF) into diethyl ether.

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Gel permeation chromatography (g.p.c.) analysis using polystyrene standards was performed in chloroform and yielded $M_w = 445\,000$, $M_n = 137\,000$. Synthetic, atactic PHB (Polysar Rubber Corporation, Sarnia, Ontario, Canada), prepared from racemic β-butyrolactone using a $ZnEt_2/H_2O$ catalyst[4,34–36], was purified by reprecipitation from chloroform into diethyl ether. G.p.c. analysis in chloroform showed $M_w = 21\,000$, $M_n = 11\,000$. The tacticities of these polymers, as determined by solution ^{13}C n.m.r., have been reported previously[37]. Solvent-cast blends were prepared from 1% solutions in chloroform which were filtered and the solvent evaporated overnight at room temperature. The resultant thin films (approximately 10 μm thick) were dried for 24 h under vacuum at room temperature.

Melting experiments were performed on a Perkin–Elmer DSC7, equipped with an intracooler. Samples were sealed in aluminium pans. Weights of approximately 0.5 mg were used for melting-point measurements and 2 mg or more for enthalpy measurements. Unless otherwise indicated, samples were heated at 20°C min^{-1} under a nitrogen atmosphere. Melt-crystallized samples were prepared by heating the solvent-cast blends 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^{-1} to an isothermal crystallization temperature, where they were allowed to crystallize for 1 h. The samples were then heated at 20°C min^{-1} to record the melting point. High purity indium and octadecane were used as temperature calibration standards, and energy calibration was performed using indium.

All melting points were recorded as the peak temperature. In heating rate experiments, melting points were corrected for instrumental thermal lag by using the indium leading edge technique[38,39].

RESULTS AND DISCUSSION

Solvent-cast blends

In *Figure 1a* are shown d.s.c. thermograms obtained at 20°C min^{-1} for blends prepared by casting from chloroform. Two melting peaks are observed at all compositions studied; however, the scan profiles change with composition. The low-temperature peak is better resolved and smaller relative to the high-temperature peak as the content of atactic PHB increases. When the atactic PHB content reaches 75%, there is evidence of an exotherm between the two endothermic peaks. This is indicative of a melt/recrystallization process. *Figure 1b* is a similar plot for the melt-crystallized case, which is treated below. The areas under the peaks have not been normalized to the total amount of isotactic component present so as not to obscure the scan profiles of samples high in atactic content.

Heating-rate studies were performed on the solvent-cast blends in order to further examine this process. *Figures 2a* and *b* show the results of such experiments for the 100% isotactic sample and the 50/50 blend, respectively. The observed changes in scan profile with heating rate support the view that the samples undergo a melt/recrystallization process. The low-temperature peak is presumably that of the as-formed crystals while the higher-temperature peak is due to the melting of crystals which have recrystallized. Most notable is the high heating rate necessary to overcome the reorganization process, which appears to be quite rapid in these samples.

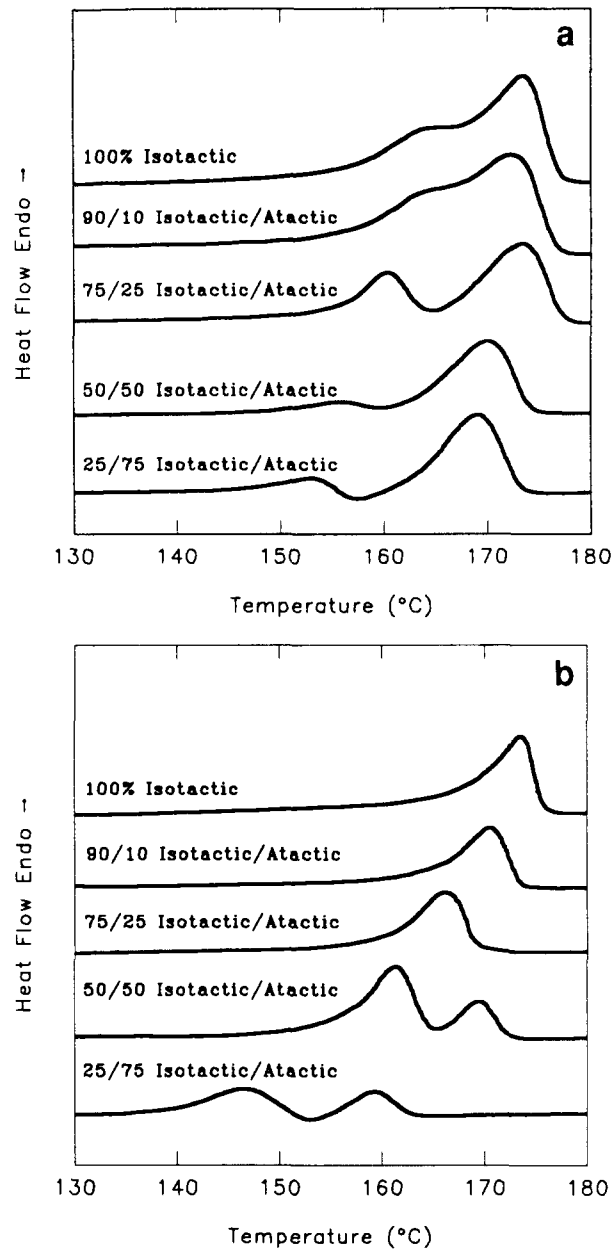

Figure 1 D.s.c. scans at 20° min^{-1} of isotactic/atactic PHB blends (a) solvent-cast and (b) melt-crystallized

For samples run at a 'normal' scan rate of 10 or 20°C min^{-1} the peak due to the as-formed crystals is hardly visible.

There is some ambiguity in the literature in the use of the terms 'annealing' and 'recrystallization'. The process of recrystallization implies partial melting of crystals followed by their crystallization using unmelted crystals for nucleation. Because the recrystallized material is formed at a higher temperature than its precursor, it also has a higher melting temperature. In contrast, annealing generally refers to the process of crystal perfection and thickening by treatment at a temperature above that at which the crystals were originally formed but below their melting point. While the outward manifestations of the processes of annealing and recrystallization can be the same, namely an increase in crystalline melting point, we will show subsequently that the two processes do not necessarily go hand in hand.

Figures 3a and *b* illustrate, for the solvent-cast blends, the variation in the total enthalpy of fusion, ΔH_f, as

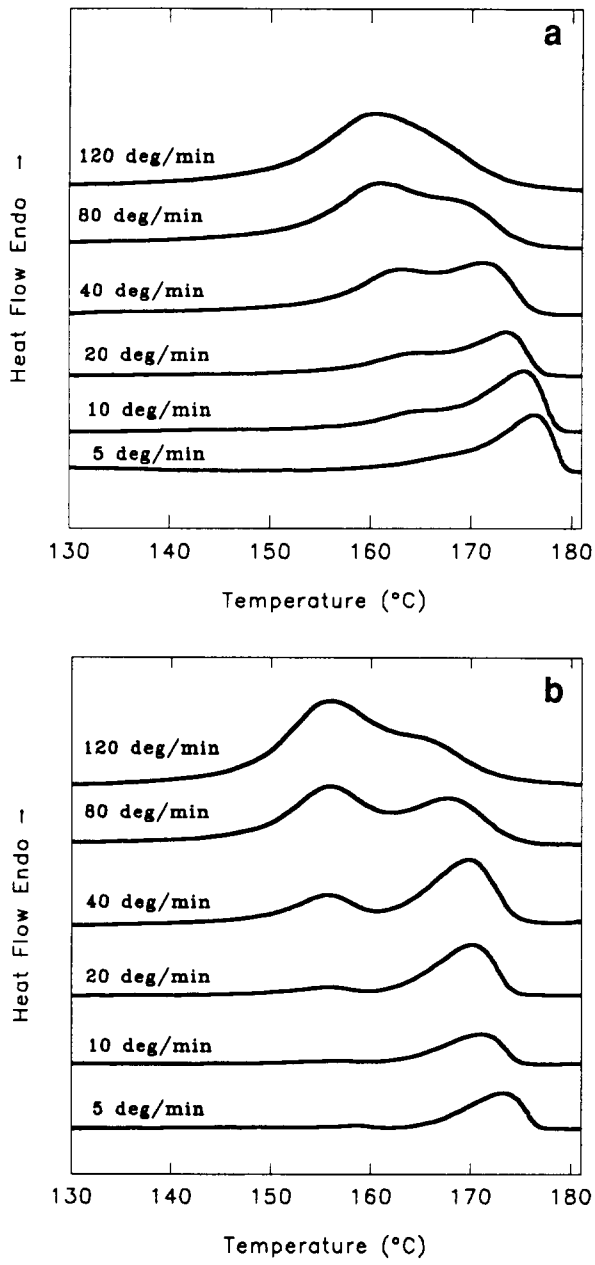

Figure 2 Effect of heating rate on d.s.c. scans of (a) 100% isotactic PHB and (b) 50/50 isotactic/atactic PHB, solvent-cast samples

obtained for the overall blend, and the degree of crystallinity, X, of the isotactic PHB component. The latter was calculated assuming $\Delta H_f = 146\,J\,g^{-1}$ (ref. 40) for a 100% crystalline sample and:

$$X = \frac{\Delta H_f(J\,g^{-1})}{146w}$$

where w is the weight fraction of isotactic PHB in the blend. Quite remarkable is the result that the isotactic PHB component maintains its level of crystallinity over all compositions investigated. This is despite the fact that the kinetics of crystallization are significantly reduced upon addition of the atactic polymer, as previously shown[33].

In the literature it has been suggested that there is a direct link between the amount of crystallinity developed in a blend of a semicrystalline polymer with an amorphous polymer and the variation in the glass transition temperature T_g of the system[25,26,41]. Essentially, as crystallization proceeds, the crystallizable component segregates from the amorphous phase. If the T_g of the amorphous component is greater than that of the crystallizable component, this process can continue until the T_g of the mixture reaches the temperature at which crystallization is occurring. At this point the crystallization process ceases. Typically, the level of crystallinity of the semicrystalline component remains constant up to a critical concentration of the second component, then drops sharply beyond this composition. This has been seen in the systems poly(ε-caprolactone)/poly(vinyl chloride)[25] and poly(ε-caprolactone)/poly(styrene-*co*-acrylonitrile)[26], as well as in several poly(vinylidene fluoride)-based blends[41]. In the case of the isotactic/atactic PHB system, both components have identical T_g values of approximately 4°C, so that crystallization of the isotactic component can proceed unimpeded, albeit at a slower rate[37].

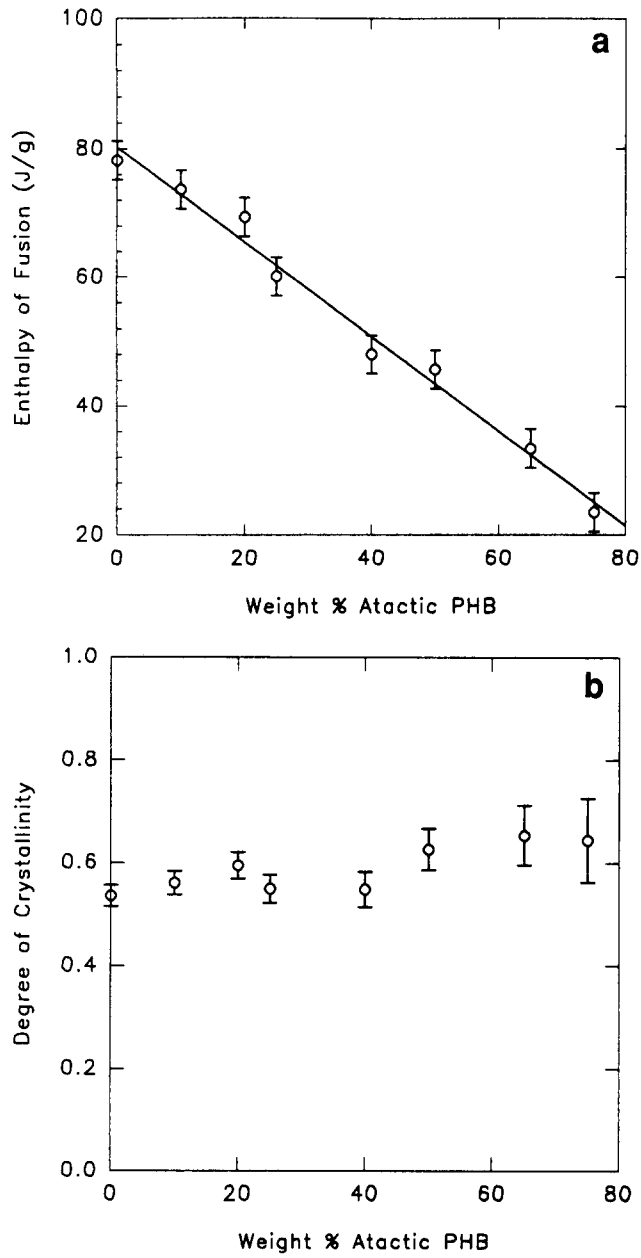

Figure 3 Overall enthalpy of fusion (a) and degree of crystallinity (b) of the isotactic component in solvent-cast blends of isotactic/atactic PHB

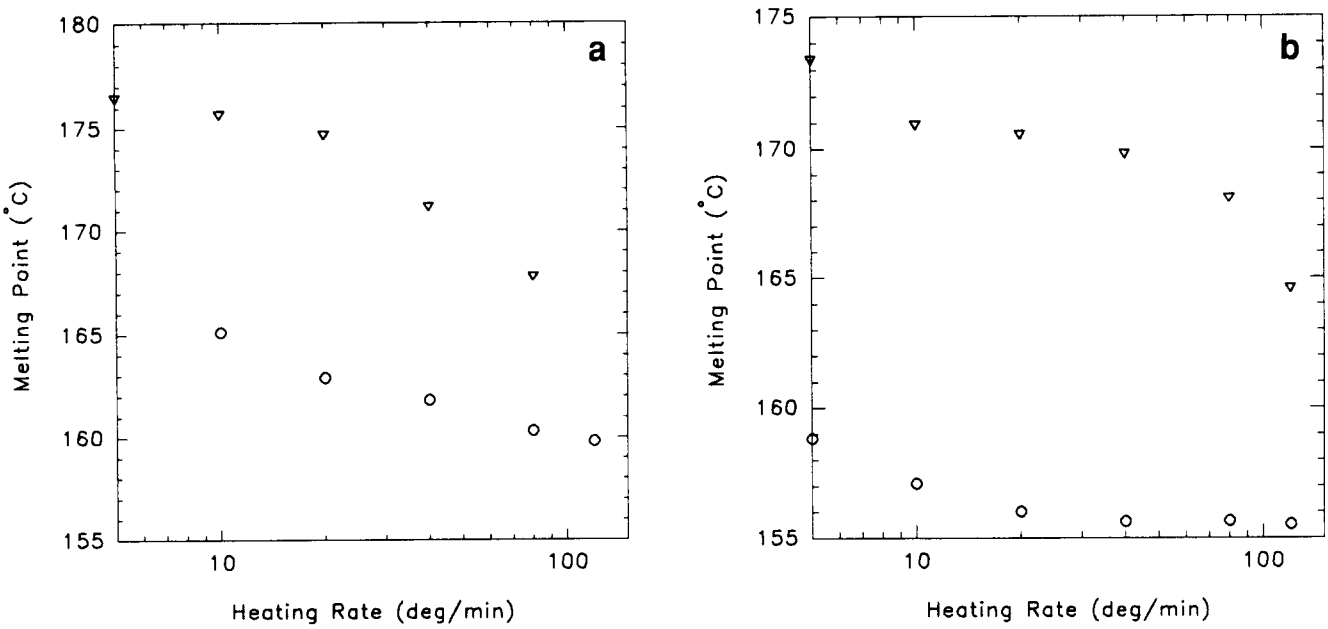

Figure 4 Effect of heating rate on melting temperatures for (a) 100% isotactic PHB and (b) 50/50 isotactic/atactic PHB, solvent-cast samples

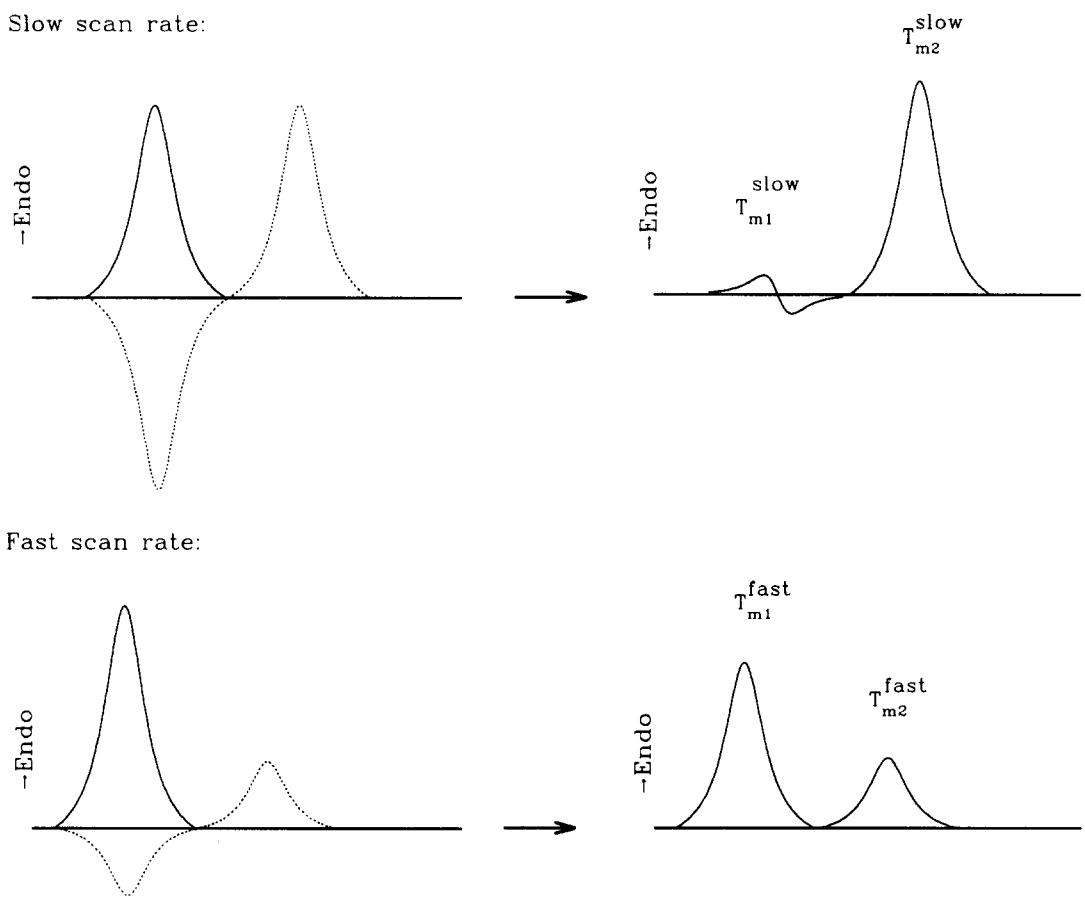

Figure 5 Schematic representation of effect of heating rate on multiple melting in isotactic/atactic PHB blends incorporating the role of annealing prior to the first melt. Solid curves represent low-temperature melting endotherm, dashed curves represent recrystallization exotherm and high-temperature melting endotherm: $T_{m1}^{slow} > T_{m1}^{fast}$, $T_{m2}^{slow} > T_{m2}^{fast}$

A plot of the peak temperatures for the low-temperature (T_{m1}) and high-temperature (T_{m2}) endotherms from *Figure 2 versus* heating rate are shown in *Figure 4*. A striking trend emerges, namely that the melting points decrease continuously, even at a high heating rate such as 120°C min^{-1}. This implies that annealing is phenomenologically dominant over superheating in these samples over the range of heating rates investigated[17].

To understand the variation in melting points and relative peak heights with heating rate, consider the schematic in *Figure 5*. This is based on the model of Rim and Runt[26] to explain multiple melting in the system

poly(ε-caprolactone)/poly(styrene-*co*-acrylonitrile). However, in the case of our blend system the effect of crystal annealing prior to the first melt endotherm has been incorporated. Hence at a slow scan rate there is ample time for both annealing prior to the first melt and for melted crystals to recrystallize, as shown by the large exotherm and subsequent second melting endotherm. The overall result is a relatively small first endotherm and the presence of an exotherm between the two endotherms. When a fast scan rate is employed the first endotherm is shifted to lower temperature since the as-formed material has less opportunity to thicken prior to the first melting peak. There is also less time for recrystallization. The net effect is a relatively large first melt endotherm which is shifted to a lower temperature than the corresponding endotherm in the case of a slow scan rate. The latter is also true of the second endotherm due to recrystallized material.

In comparing the scans obtained at $20°C\,min^{-1}$ in *Figure 1a* for solvent-cast samples, it is apparent that blends with higher amounts of atactic material exhibit a decrease in the relative size of the low-temperature endotherm. As illustrated above, this is a reflection of a larger recrystallization exotherm between the melting endotherms. If the exotherm is large enough, it can actually be observed directly, as in the case of the 75% atactic PHB sample (cf. above). Lemstra *et al.*[12] have proposed that all else being equal, the rate of recrystallization should decrease as T_m increases, since the degree of undercooling decreases. This explanation has merit in the case of the isotactic/atactic PHB system. Certainly the lower melting points observed are intimately linked to a decrease in lamellar thickness or degree of order as well as a thermodynamic depression.

The data in *Figure 4* suggest that the as-formed crystals of the 50/50 blend are less prone to annealing than those of the 100% isotactic sample. This is evidenced by the levelling off of the T_{m1} values for heating rates beyond $20°C\,min^{-1}$ in the case of the 50/50 sample, while those for the 100% isotactic sample continue to decrease over the whole range of scan rates. It is reasonable to suppose that the presence of the atactic component inhibits the thickening of the semicrystalline component. This has been suggested previously[42] for the blend system PEEK/poly(ether imide). There are two rationales for such behaviour. First, if the non-crystallizable component has a higher T_g than the crystallizable component, the interlamellar amorphous zones in a miscible blend of the two will also exhibit a higher T_g than that of the pure semicrystalline material. This will result in a stiffer matrix with less chain mobility, and hence thickening is impeded[42]. Clearly, this picture is not relevant to the system under study here as both components have identical T_g values[37]. Alternatively, the lattice model of Kumar and Yoon[43] shows that the non-crystallizable component is present in the interphase between the crystal surface and the interlamellar amorphous zones. This should result in the additional energy requirement of expulsion of the non-crystallizable component upon thickening of the lamellae.

It is notable that while the as-formed crystals in the blend samples appear less prone to annealing than those in the 100% isotactic sample, their tendency towards recrystallization is actually higher (cf. above). This suggests that annealing and recrystallization are separate processes in these samples. This will also be evident from the data obtained on melt-crystallized samples.

Melt-crystallized blends

In any study involving polymer blends, a central question which arises is that of miscibility. In previous publications[33,44] the system isotactic/atactic PHB has been shown to be miscible in the melt, as revealed through a depression in the equilibrium melting point. The case of the solvent-cast system is less clear.

In order to shed some light on this problem a series of experiments was performed on the pure isotactic PHB and a 60/40 blend of the isotactic/atactic PHB system. Both samples had been prepared by solvent casting from chloroform. The goal was to examine the effect of residence time in the melt on the subsequent melting after isothermal crystallization at a temperature of 120°C for 1 h. The results can be seen in *Figure 6*. While the 100% isotactic sample shows no apparent effect of melt-residence time on the subsequent melting point, a different trend emerges in the case of the blend. Here, the melting point after isothermal crystallization shows a depression of approximately 3°C and reaches a plateau after about 0.7 min in the melt. These data suggest that the solvent-cast blends are not fully miscible prior to melting. However, given the very short period of time in the melt necessary for the two polymers to blend on a molecular scale, any phase separation of the two polymers in the solvent-cast samples must be on a very small scale[30].

Interestingly, while the solvent-cast blends do not appear to be fully miscible, they actually exhibit melting points which are below those of the isothermally crystallized samples. For example, the 50/50 blend prepared by casting from chloroform has a melting point of approximately 155°C when measured at a high scan rate to inhibit annealing, while the melt-crystallized sample of the same composition has a T_m of about 163°C. This reflects the larger undercooling entailed by solvent casting at room temperature as compared to melt crystallization at 115°C. Of course, this ignores the role of the chloroform solvent as a diluent for the isotactic PHB, but it seems safe to assume that this effect is not so large as to overcome the 95°C difference between the temperature of preparation for the solvent-cast samples and the melt-crystallized samples.

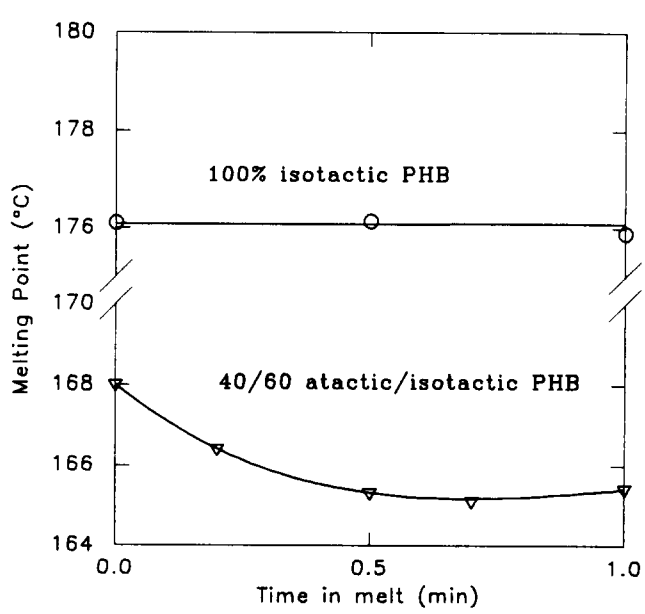

Figure 6 Effect of melt residence time on melting point for melt-crystallized samples of isotactic PHB and 40/60 atactic/isotactic PHB

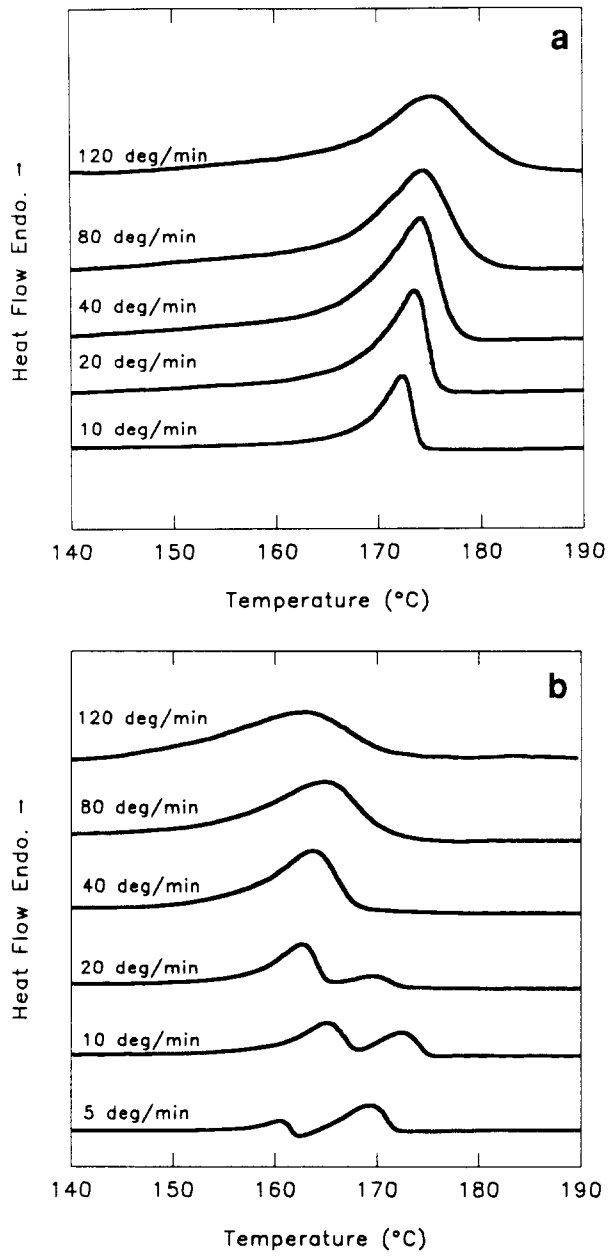

Figure 7 Effect of heating rate on d.s.c. scans of (a) isotactic PHB and (b) 50/50 isotactic/atactic PHB melt-crystallized samples

The phenomenon of melting and recrystallization followed by remelting can also be seen in melt-crystallized blends of isotactic/atactic PHB, as illustrated in *Figure 1b* for scans at 20°C min^{-1} of samples with various compositions following isothermal crystallization at 115°C for 1 h. The trend is similar to that observed in the case of solvent-cast blends. Samples with higher amounts of atactic material show a greater tendency towards recrystallization and remelting.

Heating-rate studies performed on melt-crystallized samples are illustrated in *Figures 7a* and *b* for 100% isotactic PHB and a 50/50 blend of isotactic/atactic PHB, respectively. From the scans taken of the 50/50 blend it can be seen that, as in the case of the solvent-cast blends, the second melting peak decreases in magnitude as the heating rate is increased. This indicates that a melt/recrystallization process is operative. At 5°C min^{-1} there is evidence of an exotherm between the two melt endotherms. While the sample of 100% isotactic PHB does not show any evidence of multiple melting, this is not the case if the crystallization is carried out at a lower temperature[31].

There is a major difference between the heating-rate studies carried out on melt-crystallized and solvent-cast blends. In the former case a heating rate of 40°C min^{-1} is sufficient to effectively impede recrystallization and subsequent remelting. This is in contrast to the solvent-cast samples, where even a heating rate of 120°C min^{-1} was insufficient to overcome the reorganization process. This indicates that the reorganization is inherently more rapid in the case of the solvent-cast samples. A second difference between the samples prepared by the two techniques is illustrated in *Figure 8*, where peak temperatures for the melt-crystallized samples of 100% isotactic PHB and 50/50 isotactic/atactic PHB are plotted as a function of heating rate. Whereas the solvent-cast blends showed clear evidence of annealing prior to the first melting endotherm, the melt-crystallized samples do not. In fact the melting points are approximately invariant with

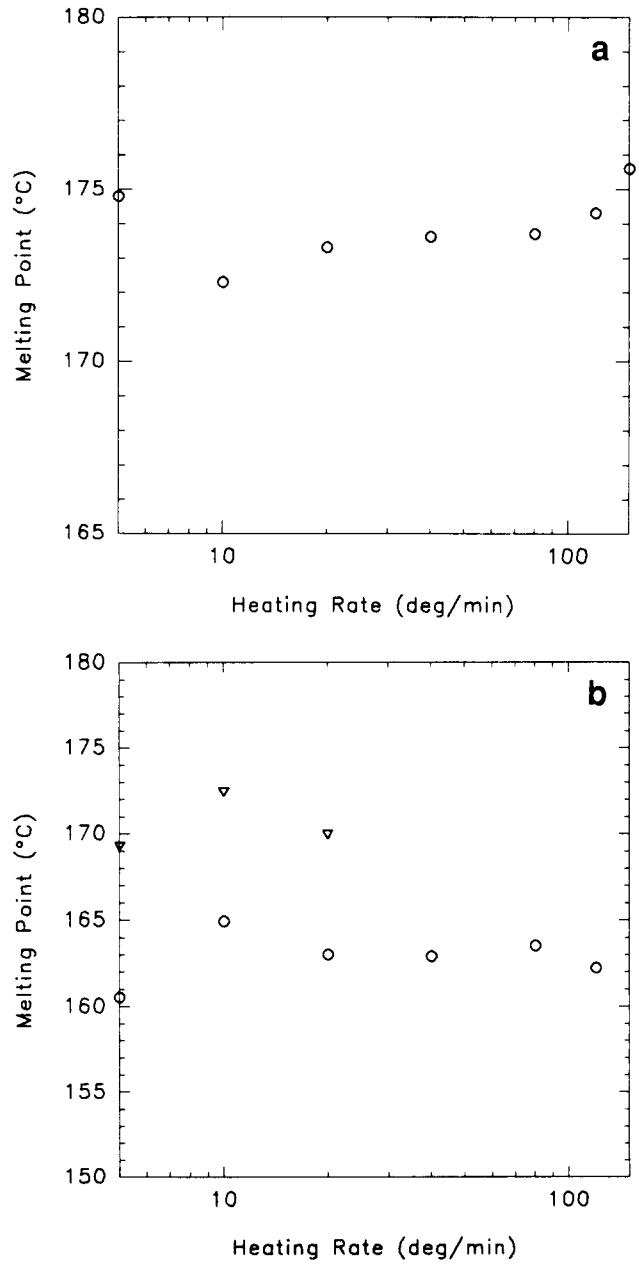

Figure 8 Effect of heating rate on melting point for (a) isotactic PHB and (b) 50/50 isotactic/atactic PHB melt-crystallized samples

heating rate. This result suggests that annealing prior to melting and recrystallization do not necessarily go hand in hand. The fact that the melt-crystallized samples show no sign of annealing must reflect their inherently thicker crystals. This should come as no surprise considering that they were grown at a much lower undercooling than the solvent-cast samples.

The degree of crystallinity following isothermal crystallization has been measured for the various compositions, and the results are summarized in *Figure 9*. It is again seen that the presence of the atactic component does not inhibit the level of crystallinity attained by the isotactic component. This in turn implies that on the time-scale of crystallization there is no impediment to disentanglement of the isotactic chains as they are 'reeled-in'[45] from the miscible melt.

Considering a given blend composition, 50/50, and varying the temperature of isothermal crystallization yields the results shown in *Figure 10* after subsequent melting at 20°C min^{-1}. It is seen that samples formed at lower crystallization temperatures have a greater propensity towards recrystallization. This is almost certainly a reflection of a lowering of the melting points for samples crystallized at larger undercoolings.

Effect of annealing prior to d.s.c. scan

The results on solvent-cast and melt-crystallized blends suggest that melting followed by recrystallization can occur even in the apparent absence of annealing. It is unclear, however, whether the converse is true. In fact, it has been suggested that the process of crystal annealing can involve both solid-state processes, such as changes in defect concentration and lamellar fold length, as well as melting followed by recrystallization[46]. However, one final piece of evidence should illustrate that recrystallization and annealing should be thought of as separate processes for the system under study. In *Figure 11* is shown a d.s.c. scan obtained at 20°C min^{-1} of a solvent-cast sample of isotactic PHB which had been previously annealed at a temperature of 130°C for 2 h. In comparing this scan with that in *Figure 1a*, for a sample

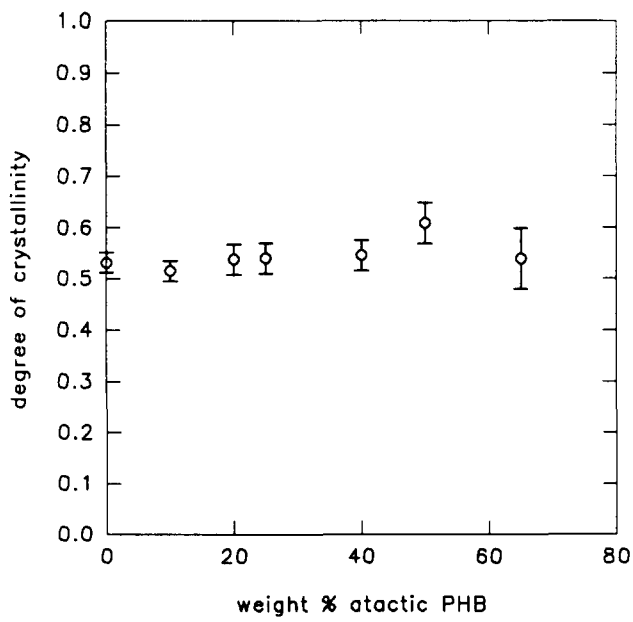

Figure 9 Degree of crystallinity of isotactic component in melt-crystallized blends of isotactic/atactic PHB

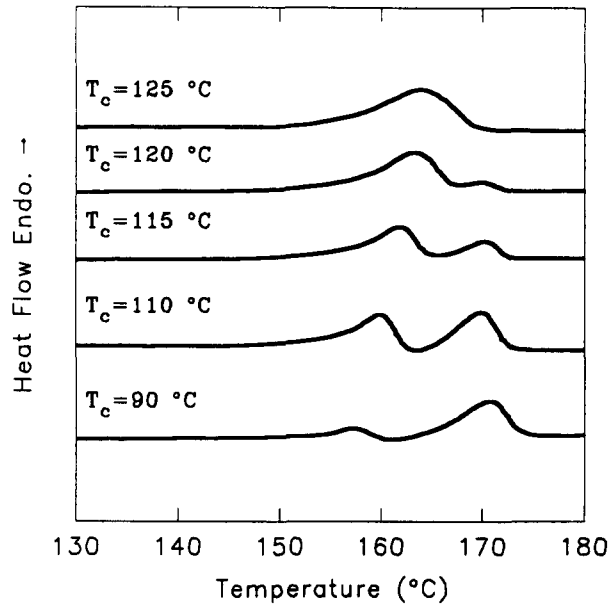

Figure 10 Effect of crystallization temperature on melting behaviour at 20°C min^{-1} for 50/50 isotactic/atactic PHB blend

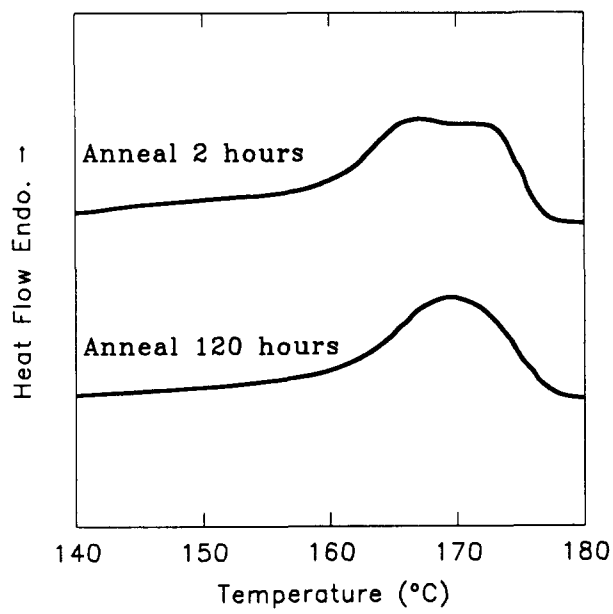

Figure 11 Effect of annealing at 130°C prior to d.s.c. scan at 20°C min^{-1} for solvent-cast 100% isotactic PHB

of the same composition which had not been annealed prior to the scan, it is clear that the effect of the annealing process is to increase the relative size of the low-temperature endotherm. This result is simply a reflection of the fact that the annealed crystals have a higher melting point and hence are less prone to recrystallization for reasons already discussed. Evidently, the appearance of a second, higher-temperature melting peak is not necessarily a reflection of annealing effects[31]. If the annealing is carried out for a longer time the crystal melting point will be high enough to avoid recrystallization altogether. This is seen in *Figure 11* for a sample annealed at 130°C for 120 h.

SUMMARY AND CONCLUSIONS

In this study it has been shown that the d.s.c. scan profile obtained for isotactic PHB and its blends with atactic

PHB is a reflection of the processes of annealing of as-formed crystals as well as melting followed by recrystallization and remelting. The multiple melting as it occurs in the blends is very much a function of both composition and preparation technique. It has been shown that the recrystallization process in solvent-cast blends is inherently faster than in the case of melt-crystallized blends. Furthermore, the latter samples showed no tendency towards annealing prior to the first melt while the blends prepared by solvent evaporation annealed even at high heating rates. The process of reorganization can be somewhat complex, as it depends on sample preparation, blend composition, temperature of crystallization, etc. However, the overall behaviour for this system can be rationalized in terms of variations in melting point.

The combined effects of annealing and recrystallization could lead to potential difficulties in obtaining meaningful melting points of polymer samples. Furthermore, analyses of melting-point depression for blends or copolymers which appear in the literature often assume that, in the presence of multiple peaks, it is the higher melting point or that corresponding to the larger peak which is the 'correct' value. Our original study[37] of the solvent-cast isotactic/atactic blends reported melting points obtained at a scan rate of 10°C min^{-1} and actually represent the melting of the recrystallized material. Given that the vast majority of d.s.c. melting points in the literature are obtained at scan rates of 10 or 20°C min^{-1}, these results suggest that scan rate experiments should be done more frequently when studying polymer melting.

ACKNOWLEDGEMENTS

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