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Melting temperature evolution of non-reorganized crystals. Poly(3-hydroxybutyrate)

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ABSTRACT

In the present study the correlation between the melting behaviour of poly(3-hydroxybutyrate) (PHB) original, non-reorganized crystals and the crystallinity increase during isothermal crystallization is presented and discussed. Since the reorganization processes modify the melting curve of original crystals, it is necessary to prevent and hinder all the processes that influence and increase the lamellar thickness. PHB exhibits melting/recrystallization on heating, the occurring of lamellar thickening in the solid state being excluded. The first step of the study was the identification of the scanning rate which inhibits PHB recrystallization at sufficiently high T_c. For the extrapolated onset and peak temperatures of the main melting endotherm, which is connected to fusion of dominant lamellae, a double dependence on the crystallization time was found. The crystallization time at which T_{onset} and T_{peak} change their trends was found to correspond to the spherulite impingement time, so that the two different dependencies were put in relation with primary and secondary crystallizations respectively. The increase of both T_{onset} and T_{peak} at high crystallization times after spherulite impingement was considered an effect due to crystal superheating and an indication of a stabilization process of the crystalline phase. Such stabilization, which produces an increase of the melting temperature, is probably connected with the volume filling that occurs after spherulite impingement.

1. Introduction

The microbially synthesized poly(3-hydroxybutyrate) (PHB) is an environmentally friendly polymer that has been object of increasing interest in the last decades because of its biodegradabilty and biocompatibility [1]. PHB is a semicrystalline, isotactic polymer with a relatively high crystallinity, which makes it a tough and quite brittle material.

The intrinsic fragility, together with the very low resistance to thermal degradation during processing has limited up to now the practical applications of plain PHB, even because it was found that both the incorporation of different hydroxyalkanoate monomeric units and the mixing with different polymers improve markedly the thermal and mechanical properties of the material [2–4]. Notwithstanding, poly(3-hydroxybutyrate) is a good candidate for the study of some aspects of polymer crystallization and melting. In fact, PHB is an extremely pure material, not containing catalyst residues, which could promote heterogeneous nucleation, being commercially produced by a batch fermentation process [5]. During crystal nucleation a very small number of nuclei are generally produced in pure PHB [6,7]. This makes poly(3-hydroxybutyrate) a model polymer for the quantitative estimation of time-dependent effects in polymer crystallization and melting.

Differential scanning calorimetry (DSC) is the most widely used experimental technique for the study of crystallization and melting behaviours of polymers, but the interpretation of a DSC melting profile of a semicrystalline polymer is generally not straightforward due to underlying transformations (crystal thickening and/or perfecting, recrystallization) that often occur simultaneously with fusion during a typical heating experiment. The extent of these processes is highly influenced by the heating rate and depends on the reorganization rate of the firmly coupled amorphous and crystalline regions. For polymers undergoing reorganization via crystal thickening and melting/recrystallization, the measured melting temperature increases with lowering the heating rate [8]. Since reorganization and recrystallization are processes slower than melting, a major effect on the melting behaviour is observed at low heating rates. The melting/recrystallization process is more pronounced in samples crystallized at low temperatures, and progressively reduce with increasing the crystallization temperature, since the original crystals, progressively more perfect, have less tendency to melt and recrystallize during a DSC scan [9]. Conversely, the melting temperature of polymers that do not undergo reorganization should decrease with decreasing the heating rate. In this

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case the increase of the measured melting temperature with the heating rate has to be ascribed to thermal lag and/or superheating [10].

The purpose of this study is to find a correlation between the evolution of the melting behaviour of original, non-reorganized, PHB crystals and the crystallinity increase during isothermal crystallization. Since the reorganization processes modify the melting curve of the original crystals, it is necessary to prevent and hinder all the processes that influence and increase the lamellar thickness. Poly(3-hydroxybutyrate) exhibits melting/recrystallization upon heating, whereas no crystal perfection via lamellar thickening in the solid state takes place [11–13]. Necessary, but not sufficient condition for the lamellar thickening is the existence of some segmental dynamics within the lamellar crystal, generally called α_c-relaxation process [14]. For this class of polymers, which includes, among others, polyethylene, polypropylene, poly(oxymethylene), poly(oxyethylene) etc., the increase of the melting temperature by isothermal thickening occurs according to a logarithmic law with respect to time [15]. For polymers that melt and recrystallize, as PHB, the melting temperature of original crystals can be obtained by preventing reorganization, which can be achieved by operating at high crystallization temperatures and high heating rates [16].

2. Experimental part

Poly(3-hydroxybutyrate) (PHB) with molar mass M_n = 260,000 g mol^{-1} and M_w/M_n = 1.6, was purchased from Sigma–Aldrich Corp. The polymer had the consistency of fine powder and was used as received without further purification.

DSC measurements were performed with a Perkin-Elmer Differential Scanning Calorimeter DSC7 equipped with an Intracooler II as refrigerating system. Dry nitrogen was used as purge gas at a rate of 30 mL min^{-1}. The instrument was calibrated at 5 K min^{-1} in temperature, energy and heat flow rate with high purity standards (indium, naphthalene, cyclohexane and sapphire) according to the procedure for standard DSC. For heating rates ranging from 1 to 90 K min^{-1}, the extrapolated onset of the indium melting was found to occur within a temperature interval of 0.15 K, which proves that, being superheating negligible for indium melting [17], the thermal inertia of the instrument (*i.e.* the delay in the heat transport from the heater to the sample) is negligible.

In order to reduce temperature gradients, the sample mass was kept as small as possible, approximately 3.5 mg. This weight is the minimum quantity of PHB that allows to cover completely the bottom of the DSC pan (diameter: 6 mm). A very small number of nuclei are generally produced during PHB nucleation process at high T_c's [7]. In this condition, as it was observed in some preliminary tests, if the thickness of the sample is not regular and uniform, a slowdown of the spherulite growth can occur, with consequent non-reproducibility of the crystallinity developed. A fresh sample was employed for each analysis, in order to minimize problems caused by thermal degradation of the material.

Before the analyses, each PHB sample was heated to 466 K at a rate of 30 K min^{-1} and maintained at this temperature for 3 min with the aim of destroying all traces of previous crystalline order [18]. Successively the samples were cooled to the desired crystallization temperature at a nominal rate of 200 K min^{-1}. At each T_c the length of the isothermal step was varied in order to obtain several samples with different crystalline degree. After partial or complete crystallization, the melting behaviour was recorded by heating the sample directly from T_c up to 463 K at various heating rates (see below).

3. Results and discussion

3.1. Optimization of the scanning rate

In case of polymers that melt and recrystallize during a DSC heating scan, it is necessary to prevent crystal reorganization, in order to obtain the melting temperature of original crystals. This can be achieved by operating at sufficiently high crystallization temperatures and high heating rates [16]. Thus, as first step, it is necessary to individuate the scanning rate which inhibits recrystallization of PHB at sufficiently high T_c.

PHB crystallization rate has a maximum at about 363 K [19,20]. Preliminary tests revealed that at $T_c < 388$ K it is impossible to stop crystallization before completion of the transition, as crystal growth continues during the successive heating scans, therefore analysis on the melting behaviour of PHB after isothermal crystallization was carried out at T_c's higher than 388 K.

In order to define of the most favorable heating rate, crystallizations at 393 K with samples of weight approximately constant was performed (sample mass = 3.5 ± 0.2 mg). A constant sample weight guarantees the same thermal lag relative to the mass (as detailed below). The specific heat capacity (c_p) of PHB in the melting region at various heating rates after complete isothermal crystallization (40 min) at 393 K is illustrated in Fig. 1. The corresponding heat flow rate curves are shown in the insert of Fig. 1. A multiple melting behaviour is observed, which includes a main peak at about 435 K, connected to the fusion of dominant lamellae developed during primary crystallization, a shoulder at about 415 K and a final endotherm at 442 K, in agreement with literature data [21]. The peak at 442 K originates from melting of polymers chains recrystallized during the heating scan, since it is visible only at the lower scanning rates. The shoulder at about 415 K is associated to the fusion of less stable crystals, developed probably during the secondary crystallization process, which can perfect on heating, as the intensity of the shoulder reduces with reducing the heating rate [22]. The c_p curves of Fig. 1 reveal that the main peak shifts progressively to higher temperatures with increasing the heating

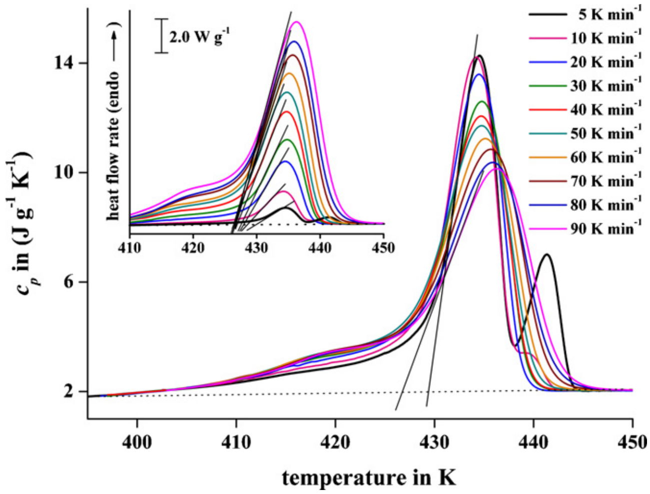

Fig. 1. Specific heat capacity of PHB in the melting region at various heating rates (5, 10, 20, 30, 40, 50, 60, 70, 80, 90 K min^{-1}) after complete isothermal crystallization (40 min) at 393 K. (The melting behaviour at 5 K min^{-1} is drawn with a thicker line to make it more evident.) The lines tangent to the steepest part of the main peak rising side of the curves recorded at 5 and 90 K min^{-1} are also drawn. In the insert the same melting behaviour is reported as heat flow rate curves. All the lines tangent to the steepest part of the main peak rising side are also drawn. The dotted lines are the baselines for the melting process. The intersection between the tangents and the baseline defines the extrapolated onset temperature of the main peak (T_{onset}). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

rate; its intensity decreases, whereas its width raises. The enthalpy involved in the process does not change significantly with the heating rate (about 102 J g^{-1}, which corresponds to a crystallinity of approximately 70%, being the heat of fusion of 100% crystalline PBH 146 J g^{-1} [23]).

The extrapolated onset of the main peak (T_{onset}), determined from the intersection of the baseline heat flow rate signal and the extrapolated tangent to the steepest part of the peak rising side, is found to decrease progressively with increasing the heating rate. Fig. 1 also shows the tangents to the specific heat capacity curves at the lowest and highest heating rates, 5 and 90 K min^{-1} respectively, to show how the extrapolated onset of the main melting peak varies with the heating rate. Since the rising sides of the main peak at the different heating rates are very close, the heat flow rate curves with the corresponding tangents are reported in the insert of the same figure. The analysis of the heat flow rate curves displays that the extrapolated onset of the main peak decreases progressively if the heating rate raises from 5 up to 50 K min^{-1}, whereas it remains almost constant for higher heating rates. The findings reveal that PHB crystals, developed at 393 K, undergo reorganization during fusion, because, with decreasing the heating rate, the onset of the main melting peak shifts to higher temperature. At heating rates higher than 50 K min^{-1} the recrystallization seems to be hindered, since the extrapolated onset temperature approaches a constant value, even if the peak temperature is found to increase. Actually the curves must be interpreted and corrected for the shift of the observed melting temperature caused by superheating and thermal lag, being the thermal inertia of the instrument negligible, as detailed in Section 2.

Superheating pertains to the increase of the melting temperature induced by the time dependence of the melting process, whereas thermal lag is connected with the presence of thermal gradients within the sample [10]. The thermal lag causes the broadening of the melting peak, with the consequence that the peak point shifts to higher temperatures with increasing the sample mass, the enthalpy of fusion and the heating rate [24–26]. On the contrary, the extrapolated melting onset is not affected by thermal gradients and depends only on superheating, *i.e.* on the kinetics of the melting process, and consequently only on the heating rate [10]. The onset of fusion is also independent of the recrystallization process, which starts just after the beginning of the transition [10]. Thus the extrapolated melting onset values (T_O), determined for all the curves from the intersection of the specific heat capacity curves and the tangent to the steepest part of the growing shoulder at 415 K (see Fig. 2), after correction for the superheating, should all correspond to the same temperature. As in Fig. 1, also in Fig. 2 only the tangents to the specific heat capacity curves at the lowest and highest heating rates, 5 and 90 K min^{-1} respectively, are shown, as the c_p curves in the shoulder region are very close and mostly overlapped. In the insert, to show details of tangents construction, the heat flow rate curves with all the corresponding tangents are displayed.

The effect of heating rate (β) on T_O has been quantified according to the following equation [10]:

$$\log\left(T_O\left(\beta\right)-T_c\right)=D+\alpha\,\log\beta \qquad (1)$$

where the parameter α is around 0.2 [10]. The equation holds for isothermally crystallized linear polymers and demonstrates that for $\beta\to0$, T_O approaches T_c. Fig. 3 shows the linear fit to the $(T_O(\beta)-T_c)$ data as a function of the heating rate for the melting of PHB completely crystallized at 393 K. The parameter α of the linear relationship $(\log(T_O(\beta)-T_c)=0.821+0.197\log\beta)$ is in excellent agreement with the expected value, which confirms the correctness of the procedure for the determination of the T_O values. Also the insert of Fig. 3 proves that T_O converges to T_c for $\beta\to0$. It is worth noting in Fig. 3 that the difference $(T_O(\beta)-T_c)$ slightly tends to saturate, as found and described previously [10]. The finding that the superheating approaches a constant value with increasing the heating rate constitutes a further verification of the accuracy in the tangent construction.

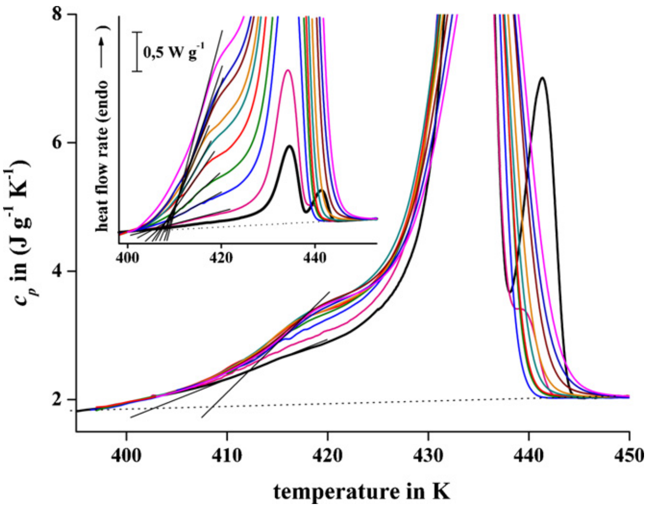

Fig. 2. Enlargement of Fig. 1. The legend is the same as Fig. 1. The lines tangent to the growing shoulder at about 415 K of the curves recorded at 5 and 90 K min^{-1} are also drawn. In the insert the same melting behaviour is reported as heat flow rate curves. All the lines tangent to the growing shoulder at about 415 K are also drawn. The dotted lines are the baselines for the melting process. The intersection between the tangents and the baseline heat flow rate defines the extrapolated onset temperature of the melting process (T_O). (The melting behaviour at 5 K min^{-1} is drawn with a thicker line to make it more evident.)

As a first approximation, the effect of superheating on the melting behaviour of PHB can be removed correcting the abscissa values of all the curves by a factor equal to the difference $(T_O(\beta)-T_c)$. All the resulting curves would show a melting process that starts at 393 K and possible differences in the melting behaviour at the various heating rates could be ascribed to different crystal reorganization occurring during the heating scans at different rates.

After correction of the temperature, the specific heat capacity curves of Fig. 1 assume the aspect represented in Fig. 4 and shown in a detail in Fig. 5. By comparison with Fig. 1, it emerges that the location of the main peak, reduces in temperature with increasing

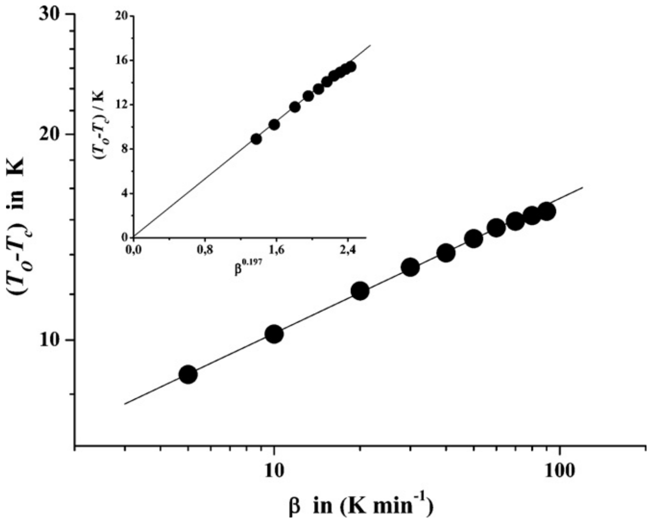

Fig. 3. Experimental difference $(T_O(\beta)-T_c)$ for the melting process of PHB crystallized at 393 K as a function of the heating rate. Both the quantities are on logarithmic scale. The linear fit is also drawn. In the insert the same difference $(T_O(\beta)-T_c)$ is depicted as a function of $\beta^{0.197}$ (see text).

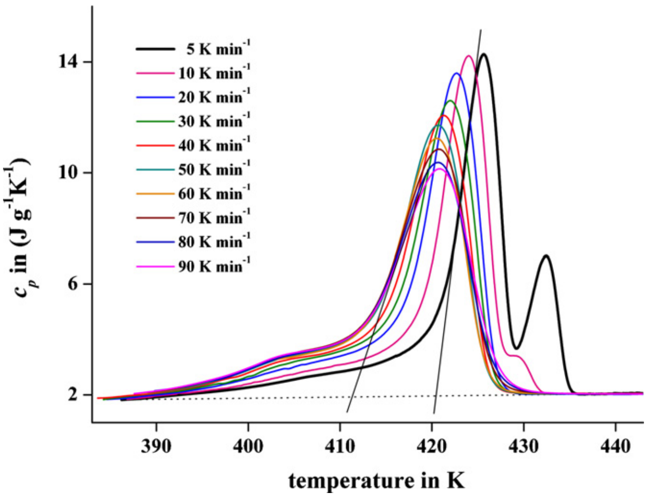

Fig. 4. Corrected specific heat capacity of PBH in the melting region at various heating rates (5, 10, 20, 30, 40, 50, 60, 70, 80, 90 K min^{-1}) after complete isothermal crystallization (40 min) at 393 K. The lines tangent to the steepest part of the main peak rising side of the curves recorded at 5 and 90 K min^{-1} are also drawn.

the heating rate. (In Fig. 4 only the tangents to the rising side of the main peak at the lowest and highest heating rates, 5 and 90 K min^{-1} respectively, are depicted whereas all the tangents are reported in the enlargement of Fig. 5.)

The extrapolated onset temperature of the main peak (T_{onset}) decreases progressively and significantly if the heating rate raises from 5 up to 60 K min^{-1}. For heating rates higher than 60 K min^{-1} T_{onset} is approximately constant, which reveals that for PHB crystals, grown at 393 K, the recrystallization is seriously hindered at heating rates equal or higher than 60 K min^{-1}, as the extrapolated onset temperature approaches an almost constant value.

As the kinetics of the melting process is ruled by the movement of the crystalline-amorphous interface, the differences between the measured (superheated) and the respective true values of T_O and T_{onset} could be dissimilar [10,27]. A higher concentration of crystalline defects and topological constraints could produce a higher superheating for the fusion of secondary lamellae with respect to the dominant ones. In this case, the temperature correction applied in Figs. 4 and 5 could be too high as regards the main peak; however smaller correction factors would make all the curves closer to each other, confirming that the scanning rate of 60 K min^{-1} may be sufficient to hinder recrystallization during heating.

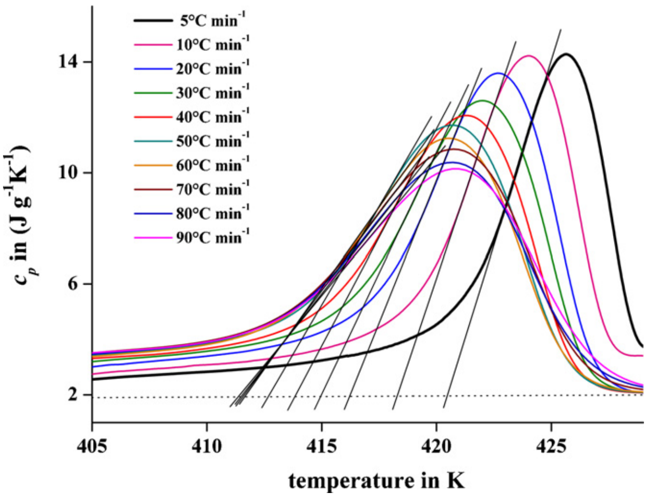

Fig. 5. Enlargement of Fig. 4 in the main peak region. All the tangent lines to the rising side of the main peak are also drawn. The dotted line is the baseline for the melting process. The intersection between the tangents and the baseline defines the extrapolated onset temperature of the main peak (T_{onset}).

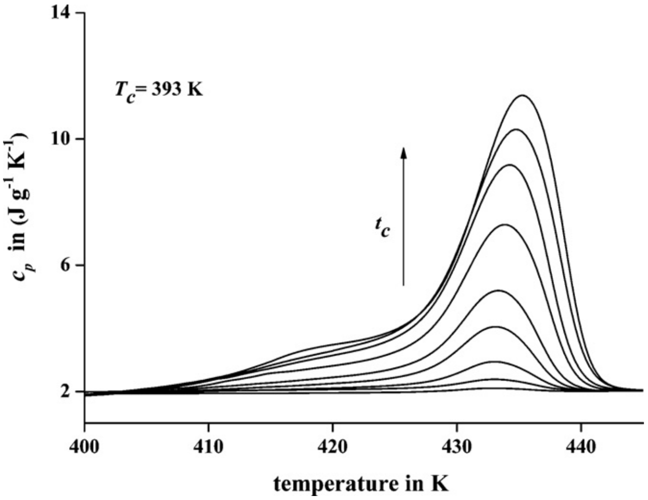

Fig. 6. Specific heat capacity of PHB in the melting region at 60 K min^{-1} after isothermal crystallization at T_c = 393 K (t_c = 2, 3, 4, 5.5, 7, 9, 12, 20, 40 min).

On the basis of these considerations, it was decided to conduct the study of the melting behaviour of PHB at the rate of 60 K min^{-1}, in order to prevent the recrystallization process.

3.2. Melting temperature evolution after partial crystallization

Fig. 6 collects some c_p curves of PHB in the melting region, measured at 60 K min^{-1} after different crystallization times (t_c) at T_c = 393 K. The curves show that after short crystallization times, the melting behaviour is constituted mainly by only one peak, but with increasing t_c, a shoulder appears on the low-temperature side, about 15–20 K below the main peak, growing progressively in intensity. The same behaviour is exhibited by the c_p curves after various crystallization times at different T_c's (Fig. 7). The finding confirms that the shoulder is connected to the fusion of less stable crystals, which develop mostly in presence of more perfect crystals and melt earlier due to their lower stability.

The extrapolated onset temperatures of the main peak, measured after different crystallization times at various T_c's, are reported in Fig. 8 as a function of the crystallization time t_c in logarithmic scale, as proposed in ref. [10]. T_{onset} initially decreases with t_c, then tends to raise slightly again.

Besides the onset temperature, also the peak temperature (T_{peak}) show a double dependence, as evidenced in Fig. 9, in which the peak temperatures are reported as a function of the crystallization time t_c. An increase of the slope of T_{peak} vs. log t_c is observed at the same t_c values at which T_{onset} data reverse their trends. The double dependence is exhibited also if the peak temperatures are plotted as a function of $(m\Delta h_m\beta)^{1/2}$ (Fig. 10). This quantity is approximately the measurement of the T_{peak} increase caused by the thermal lag. In fact according to the theory of differential scanning calorimeters, for a simple and pure substance, for which T_{onset} corresponds to the true melting temperature, the broadening of the peak due to thermal lag is proportional to the square root of heating rate, thermal resistance (R) and enthalpy involved in the process [24–26]:

$$T_{peak} - T_{onset} = \left(2Rm\Delta h_m\beta\right)^{1/2} \qquad (2)$$

where m is the sample mass and Δh_m is the enthalpy of fusion per gram. In case of polymers, the onset temperature does not represent the true melting temperature of the material because of the broad

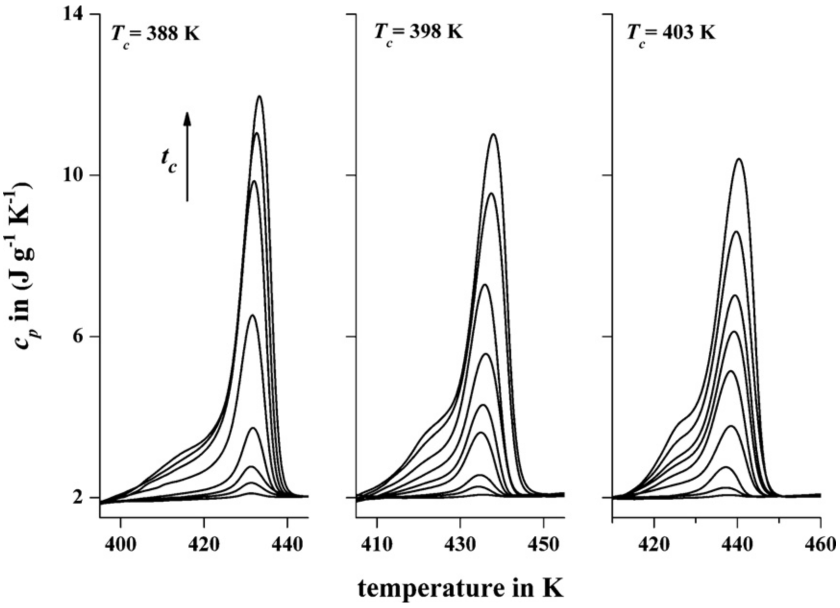

Fig. 7. Specific heat capacity of PHB in the melting region at 60 K min^{-1} after isothermal crystallization at T_c = 388 K (t_c = 1, 1.5, 1.8, 2.5, 4, 6, 9, 25 min), T_c = 398 K (t_c = 4, 6, 8, 11.5, 15, 18, 25, 35, 75 min), T_c = 403 K (t_c = 10, 18, 20, 30, 40, 50, 60, 90, 150 min).

distribution of crystallites stability. Eq. (1) can be substituted by:

$$T_{peak} - T_{peak,o} = \left(2Rm\Delta h_m\beta\right)^{1/2} \tag{3}$$

where $T_{peak,o}$ is the peak temperature extrapolated to zero mass and heating rate, with the instrumental effects that cause broadening removed. A double linear trend can be evidenced in Fig. 10 at each crystallization temperature: T_{peak} values increase linearly up to a $(m\Delta h_m\beta)^{1/2}$ value approximately equal to 3, then the slope raises, the trend remaining substantially linear.

Since the heating rate and mass are constant for the measurements detailed in Figs. 8–10, the broadening of the peak should depend only on the enthalpy involved in the melting process. The slope change which is observed in the T_{peak} vs. $(m\Delta h_m\beta)^{1/2}$ plots occurs at a Δh_m value of about 40–50 J g^{-1}. From the analysis of the enthalpy of fusion as a function of the respective crystallization time (Fig. 11) one can see that a value of 40–50 J g^{-1} corresponds approximately to the inflection point of the Δh_m sigmoidal curves. Also the crystallization times at which T_{onset} and T_{peak} data reverse their trend correspond to the inflection points of the Δh_m curves (Figs. 8, 9, 11). The Δh_m inflection point, which is symptomatic of a slowing of the crystallization process, is usually associated with spherulite impingement [28,29]. As an example, Fig. 12 shows the kinetic analysis of the isothermal crystallization at 393 K, according to the commonly used Avrami equation: [30]

$$\ln[-\ln(1-w_c)] = n\ \ln k + n\ln(t_c - t_o) \tag{4}$$

where w_c is the relative crystallinity, depicted in insert B, n is the Avrami coefficient, which is related to the type of nucleation and geometry of crystal growing, k the overall kinetic constant, t_c the crystallization time and t_o the induction time for the crystallization process. The time at which the function ln[−ln(1 − w_c)] deviates from linearity, indicated by an arrow, usually corresponds with the time at which the minimum of the crystallization heat flow rate exotherm is observed (insert A). The non-linear trend of the Avrami function is connected with the so-called secondary crystal-

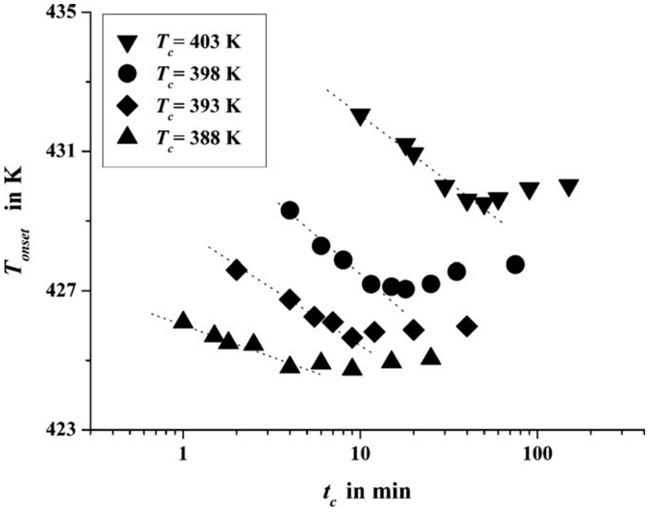

Fig. 8. Extrapolated onset temperature of PHB main peak measured at 60 K min^{-1} after various crystallization times at the indicated T_c's as a function of the crystallization time (t_c) on logarithmic scale. The dashed lines are a guide for the eye.

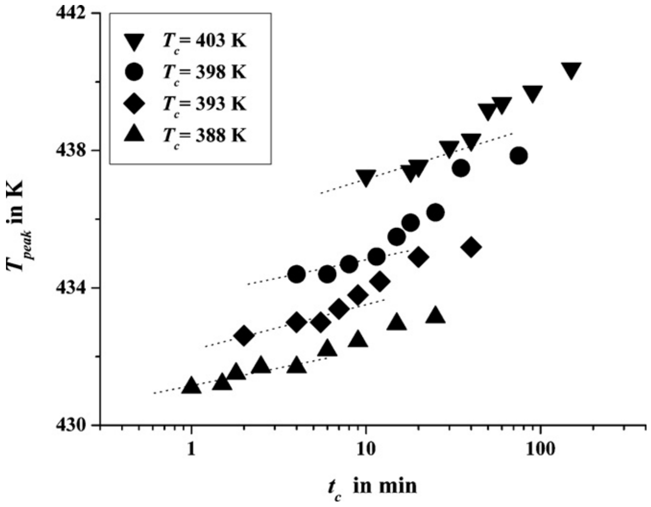

Fig. 9. Peak temperature of PHB main peak measured at 60 K min^{-1} after various crystallization times at the indicated T_c's as a function of the crystallization time (t_c) on logarithmic scale. The dashed lines are a guide for the eye.

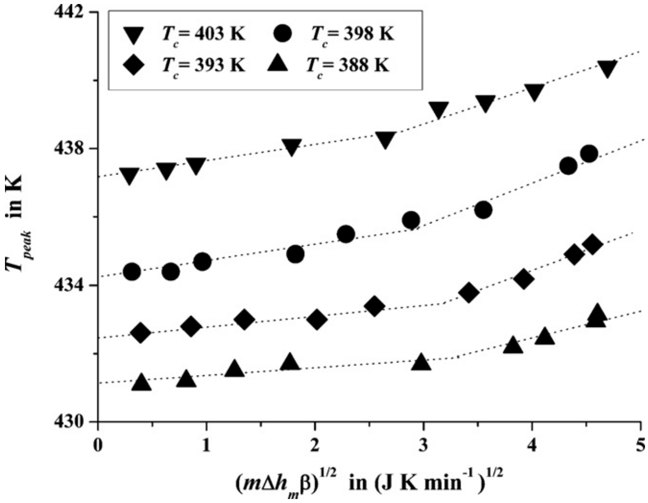

Fig. 10. Peak temperatures of PHB measured at 60 K min^{-1} after various crystallization times at the indicated T_c's as a function of $(m\Delta h_m\beta)^{1/2}$. The dotted lines are a guide for the eye.

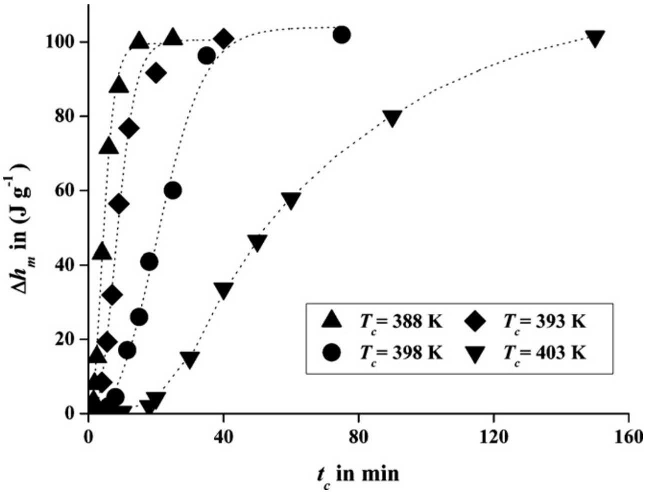

Fig. 11. Enthalpy of fusion of PHB as a function of the crystallization time at the indicated T_c's. The dotted lines are a guide for the eye.

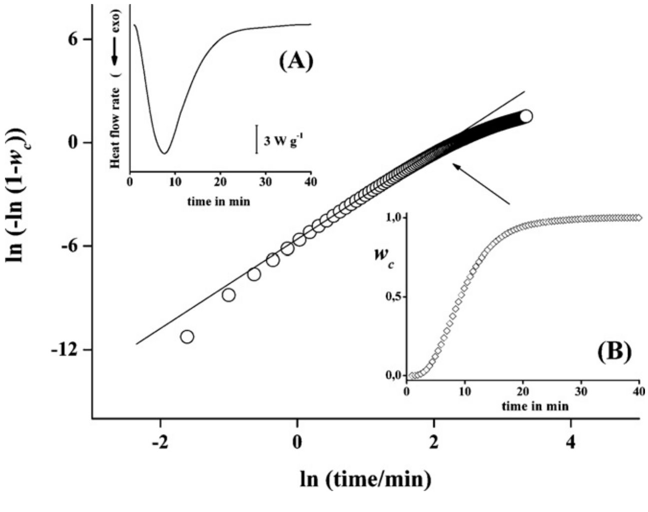

Fig. 12. Avrami plot for PHB crystallized at 393 K. Insert (A): DSC isothermal crystallization curve of PHB at 393 K. Insert (B): relative crystallinity as a function of time for the PHB isothermal crystallization at 393 K.

lization, that mainly occurs starting from the inflection point of the w_c curve and implies an increase of the crystallinity degree through the growth of defective crystallites [31].

The findings of Figs. 8–10 indicate that different mechanisms of crystalline growth operate during the crystallization process of PHB. Before spherulite impingement, mainly dominant lamellae grow unhindered and well separated one from the other [32]. The first crystals that develop at the beginning of the crystallization are more perfect, successively the crystalline growth occurs through the formation of crystals with a higher defect concentration, as indicated by the extrapolated onset temperature that decreases with increasing the crystallization time. The rise of T_{peak}, which is monitored simultaneously with the T_{onset} decrease, has to be ascribed to the enthalpy effect on the peak broadening [24–26]. After spherulite impingement, dominant lamellae continue to grow and form in quite free spaces, as indicated by the intensity of the main peak that keeps on increasing (Figs. 6 and 7). At the same time, smaller and less perfect (subsidiary) lamellae develop diffusely, accommodating between the larger and more perfect dominant lamellae [33]. This process gives origin in the melting behaviour to the shoulder, located about 15 K below the major peak, whose weight increases with the crystallization time. Since the slope change of the T_{onset} and T_{peak} vs. t_c curves occurs in correspondence with the beginning of the secondary crystallization, it seems likely that the two different trends are connected to the primary and secondary crystallization processes respectively, as also found for the melting peak temperatures of linear polyethylene and ethylene–styrene copolymers, even if for these polymers the increase of the melting temperature during the secondary crystallization stage originates by the lamellar thickening process [15,34].

According to experimental evidences, a number of polymers are characterized by dominant and subsidiary lamellae with equal thickness, as for example poly(4-methylpentene-1) [35]. On the contrary, for other polymers like poly(ethylene terephthalate) or poly(ethylene ether ketone), the dominant lamellae are thicker than the later developed subsidiary lamellae [36–39]. There are two models describing the spatial distribution and organization of dominant and subsidiary lamellae respectively: the dual lamellar stack model (with dominant and subsidiary lamellae in separate stacks) and the lamellar insertion model (with subsidiary lamellae inserted between the dominant lamellae within the same stack) [37]. Poly(3-hydroxybutyrate) likely belongs to the first series, with dominant and subsidiary lamellae of equal thickness, since from small-angle X-ray scattering measurements the lamellar thickness was found to remain constant for the entire isothermal crystallization at various temperatures (398 ≤ T_c ≤ 418 K), which also indicates that primarily formed crystals do not thicken during the whole isothermal crystallization process [13]. In addition, in the same study it was proven that secondary crystallization occurs in PHB during the later stage of isothermal crystallization, in competition with the continuous primary crystallization, confirming the observations here made in Fig. 6, and that secondary crystals form in the amorphous layers between the primarily formed lamellar crystal stacks [13].

Notwithstanding that (i) PHB crystals are distinguished by constant thickness, not increasing with time [13], (ii) recrystallization is hindered at the heating rate of 60 K min^{-1}, T_{onset} is found to raise slightly at high crystallization times, after spherulite impingement, in the same t_c range in which T_{peak} shows an enhanced slope (Figs. 8–10).

A tentative explanation of the results could yield to hypothesize a "stabilization" process of the crystalline phase, as it has been recently suggested for the isothermal crystallization of poly(ε-caprolactone) and syndiotactic polypropylene, studied by means of a pulsed dynamic mechanical technique [40]. For poly(ε-caprolactone), for example, a melting temperature increase of a few degrees was found to occur during crystallization at 331 K: the event starts when the crystallinity degree is approximately equal to 50% of the final value and continues up to the end of crystallization [40]. The study proved that the degree of stabilization is zero at the beginning of the crystallization process and increases fast during the secondary crystallization. The findings of the present study on PHB are in perfect agreement with the results on poly(ε-caprolactone): the extrapolated onset temperature of the PHB main melting peak, which is found to decrease during the primary crystallization, discloses that no stabilization occurs at low crystallization times. On the contrary, at high crystallization times the PHB crystalline phase might undergo a stabilization process, as the extrapolated onset temperature of PHB main melting peak inverts its trend at a crystallization time corresponding approximately to the spherulite impingement time.

The probability that the T_{onset} and T_{peak} increase originates from crystal improvement through the reduction of defects at the interfaces of the crystalline regions, should be quite small at high and progressively increasing crystallization times, considering that, owing to the high crystallinity degree achieved by the PHB samples, the reorganization of the crystalline segments would be rather hindered by the possible presence of vitrified rigid amorphous regions coupled with the crystals [41].

Conversely, for polymers that do not thicken at the solid state, as poly(ε-caprolactone), syndiotactic polypropylene and poly(3-hydroxybutyrate), and that do not recrystallize, the elevation of the melting temperature at high crystallization times could be explained considering that after spherulite impingement, both dominant and subsidiary lamellae are located in geometrically more restricted areas. Topological constraints could produce an increase of the energy barrier for the movement of the crystalline-amorphous interface, inducing an enhanced thermal stability of the crystals, whose melting temperature raises [27]. It might therefore be an effect due to crystal superheating. In effect it was proven that superheating depends on crystallization conditions, specifically temperature and time, and that it decreases progressively for $t_c \to 0$ [10], because fusion of very small crystalline areas, quite perfect and without constraints and restrictions, can occur with a reduced energy barrier for the crystalline-amorphous interface movement. The progressive increase of the crystals extension can yield to a stabilization of the crystalline phase: such stabilization process is connected with volume filling that occurs after spherulite impingement and perhaps it is an event common to other polymers.

4. Conclusions

The study of the melting behaviour of poly(3-hydroxybutyrate) original non-reorganized crystals as a function of crystallization time is presented and discussed in this paper. For polymers that melt and recrystallize during heating, like PHB, the melting temperature of original crystals can be obtained by operating at high crystallization temperatures and high heating rates. The first step of the study was the identification of the scanning rate which inhibits the PHB recrystallization process at sufficiently high T_c. It was found that the heating rate of 60 K min^{-1} is sufficient to prevent the recrystallization that occurs simultaneously with fusion. Successively the melting behaviour of PHB after various crystallization times at different T_c was collected. The dependence on the crystallization time of the extrapolated onset and peak temperatures of the main melting peak, which is connected to the fusion of dominant lamellae, resulted double, even if different. In particular the crystallization time at which T_{onset} and T_{peak} change their trends was found to correspond to the spherulite impingement time, so that the two different dependences were put in relation with primary and secondary crystallizations respectively. The increase of both T_{onset} and T_{peak} at high crystallization times after spherulite impingement was considered to be an indication of a “stabilization” process of the crystalline phase, as was found to occur also in other polymers, as for example poly(ε-caprolactone) and syndiotactic polypropylene. The elevation of the melting temperature at high crystallization times has been explained tentatively considering that after spherulite impingement topological constraints for both dominant and subsidiary lamellae can produce an elevation of the energy barrier for the movement of the crystalline-amorphous interface, which in turn can generate an increase of the melting temperature and the crystal stability. As a result it can be affirmed that the progressive increase of the crystals extension yields to a stabilization of the crystalline phase.

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