Optimization of melting conditions for the analysis of crystallization kinetics of poly(3-hydroxybutyrate)

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Abstract: Studies of kinetics of polymer crystallization are generally performed by heating the material above the melting point, in order to erase previous thermal and mechanical history, followed by rapid cooling to the desired crystallization temperature or by cooling at a constant rate. For poly(3-hydroxybutyrate) this procedure implies some degradation of the polymer chain, which starts below the onset of melting. In this article the effects of melting conditions on the subsequent crystallization kinetics are discussed. It is shown that in order to sufficiently cancel memories of previous crystalline order of the analyzed PHB, it is necessary to bring the material at a temperature higher than 192 °C. Thermal treatments conducted at lower temperatures are not sufficient to destroy all solid aggregates, and crystallization of PHB has an anticipated onset of crystallization due to nucleation occurring via self-seeding. The chain degradation attained upon exposure at high temperatures has much lesser influence on crystallization kinetics than incomplete melting, with some effects detectable on the spherulitic morphology and on the final degree of crystallinity.

Introduction

Poly(3-hydroxybutyrate) (PHB) is a natural thermoplastic polyester with mechanical properties comparable to synthetic polymers. It has been produced since 1925 by bacterial fermentation, which takes place in the presence of a wide variety of bacteria [1]. At least 75 different genera of bacteria have been known to accumulate PHB as intracellular granules. Under limited nitrogen and in the presence of an abundant source of carbon, some bacteria can accumulate up to 60–80% of their weight in PHB [2].

PHB is fully biodegradable and biocompatible, with potential applications in packaging and agriculture as biodegradable films [3-5], in pharmaceutical industry as drug release material [6-8], and in medicine as biocompatible resorbable implant material [9-10]. However, until now there is no large commercial production of PHB goods because of its cost being higher than commodity polymers, narrow processability window and brittleness. Very low resistance to thermal degradation seems to be the most serious problem related to industrial processing of PHB. Since the melting temperature of PHB is around 170-180 °C, the processing temperature should be at least 180-190 °C. However, at these temperatures thermal degradation of PHB proceeds very quickly. The degradation reaction involves chain scission,

which causes a rapid decrease in molecular weight. At higher temperatures above 300 °C, degradation results in low molecular mass compounds [11-13].

The easy degradation creates problems also in the analysis of phase transitions of PHB. In order to study crystallization kinetics, it is necessary to melt the polymer sample before subsequent crystallization. The temperature of the melt and the time the polymer spends in the melt are designated to erase previous thermal history, so that all traces of existing crystal nuclei are destroyed. If the melting temperature or the holding time in the melt are too low, upon subsequent cooling the remaining partially ordered crystalline portions can act as predetermined athermal nucleation sites, resulting in an enhancement of the overall crystallization rate. This phenomenon is known as "self-nucleation" or "self-seeding" [14]. Only if all residual nuclei in the melt are eliminated, it is possible to conduct reliable analysis of crystallization kinetics, as crystal growth results only from the nuclei formed via thermal fluctuations or heterogeneously, but not by self-nucleation from non-completely melted crystallites. It was shown in [15, 16] that the total destruction of crystallites in polymers is a relatively long process. Alfonso and Ziabicki [15] estimated the activation energy for erasing of crystal memory as 89 $\pm$7 kJ/mole, which is higher than the typical values of activation energy for self-diffusion in polymers [15]. However, for PHB removal of all traces of previous crystal order implies partial degradation of the polymer chain, which occurs to a higher extent with the increase of melting temperature and time [12]. Degradation induces a decrease of molecular mass, which, in turn, affects the crystallization rate [14].

For these reasons, for a quantitative analysis of the crystallization process of PHB it is essential to properly choose the conditions of melting before crystallization. The selected thermal history should ensure the complete melting of the polymer to avoid self-seeding, and at the same time the minimum possible degradation of the material should be attained. A recent article reports the effect of melt processing conditions on crystallization behavior of PHB and its blends [18]. It was found that an increase in temperature and time of melt processing leads to a higher extent of the degradation process, with a shift of the crystallization temperature to lower values caused by the decrease of molar mass induced by chain degradation. We will show that, more than chain degradation, incomplete fusion plays a fundamental role in determining the crystallization kinetics of PHB. If the melting step that precedes crystallization is performed at a too low temperature, a large memory of previous crystalline order remains, which results in a large nucleation density that determines an anticipated onset of crystallization.

Results and discussion

As mentioned above, heating poly(3-hydroxybutyrate) at temperatures close or above its melting point results in a decrease of molecular mass. Figure 1 illustrates the dependence of viscosity-average molecular mass (M_v) of PHB on temperature, for a residence time of 3 min. On the same plot, the M_v data of the as-received PHB powder and of the compression-molded sample are also reported. As expected, an increase of the temperature leads to a higher extent of degradation, with a corresponding decrease of molecular mass. The molecular mass of the initial powder sample decreases by about one half upon preparation of the compression-molded sheet, then subsequent thermal treatments conducted at even lower temperatures induce a further diminution of M_v, as quantified in Figure 1.
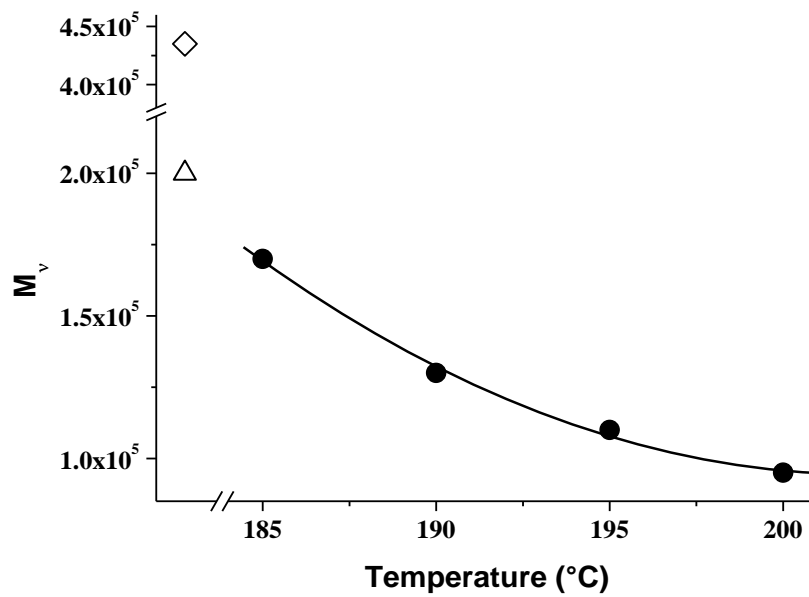
Fig. 1. Viscosity-average molecular mass as a function of temperature of melting, for a melting time of 3 min (closed circles). The open diamond and the open triangle represent the molecular mass of the as-received PHB powder and of the compression-molded sheet, respectively.
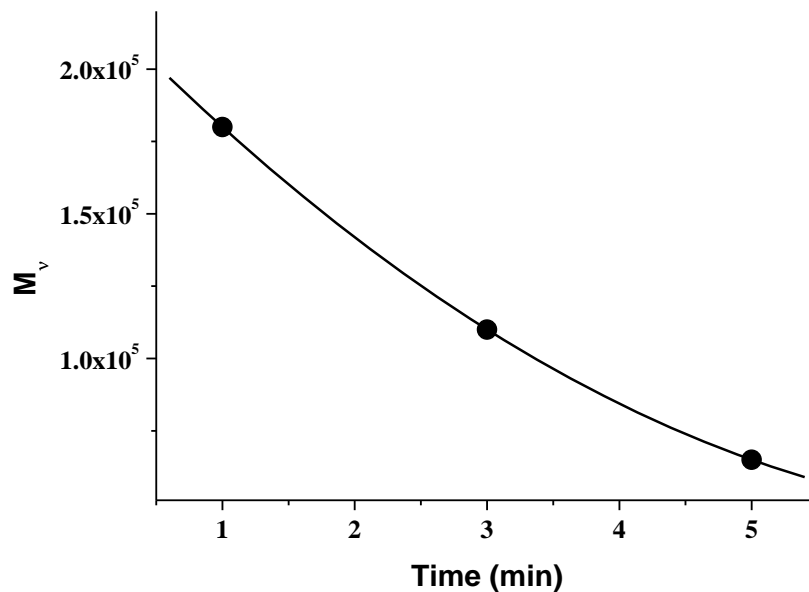

Fig. 2. Variation of the viscosity-average molecular mass upon duration of permanence at 195 °C.

The effect of melting time on molecular mass is illustrated in Figure 2 for the temperature of 195 °C. A progressively lower molecular mass results upon increase of the residence time at high temperatures, and a reduction of more that one half is

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attained when the permanence of the PHB sample is extended from 1 to 5 min. Similar diminutions of M_v with the extension of thermal treatment were obtained also at the other investigated temperatures. The trends of the data shown in Figures 1 and 2 are in good agreement with the data on the effects of exposure of PHB to high temperature reported in the literature [1].
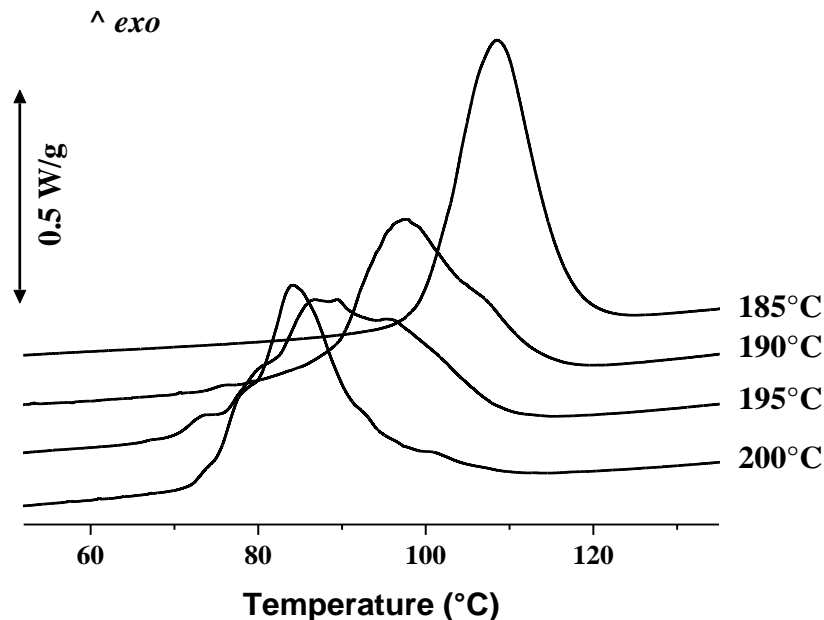

Fig. 3. Heat-flow rate plots of PHB upon cooling at 5°C/min, after melting at the indicated temperatures for 3 min.

The influence of melting conditions on crystallization behavior is illustrated in Figure 3; the results of DSC analyses conducted upon cooling at a rate of 5 °C/min after melting PHB at various temperatures for 3 min are displayed. When the polymer is melted at 185 °C, crystallization starts around 121 °C. An increase in the temperature of melting results in a corresponding delay of the phase transition, as the onset point is shifted to lower temperatures. The shift of crystallization with the increase of temperature of thermal treatment before crystallization has been reported also in ref. 18, and attributed to degradation: melting PHB at high temperatures leads to a degradation process that causes a delayed crystallization [18]. However, degradation of PHB induces a decrease in molecular mass, which is expected to lead not to a delay, but to an acceleration of the crystallization kinetics, as it results in an increase in both nucleation and growth rates [14]. The rate of lateral growth of a polymer crystal is inversely dependent on molecular mass, as diffusion of chains towards the crystal growth front becomes more difficult as the chains become longer [14, 19]. For PHB the decrease of spherulite growth rate with molecular mass was probed by Alfonso et al. [20]. Similarly, the rate of formation of primary nuclei is controlled by chain sliding diffusion, which requires disentanglement of molecular chain within the interface between the nucleus and the melt, and also results in an inverse dependence of nucleation rate on molecular mass [21].

Studies of the influence of melting conditions on the thermal behavior of other polymers that easily degrade at temperatures close to their melting point clearly indicate that a higher extent of thermal degradation accelerates crystallization. For instance, poly(L-lactic acid) undergoes thermal degradation above 180 °C, which occurs via random chain scission and is accompanied by a decrease of molecular mass, similarly to PHB [22-24]. When the melting temperature is raised from 200 to 210 °C, in the subsequent cooling scan conducted at a rate of 2 °C/min the crystallization temperature increases by about 2-3 °C [25]. From these considerations, it seems improbable that the shift of the onset of crystal growth of PHB with temperature of thermal treatment, shown in Figure 3, is to be ascribed to a decrease of molecular mass caused by chain degradation.
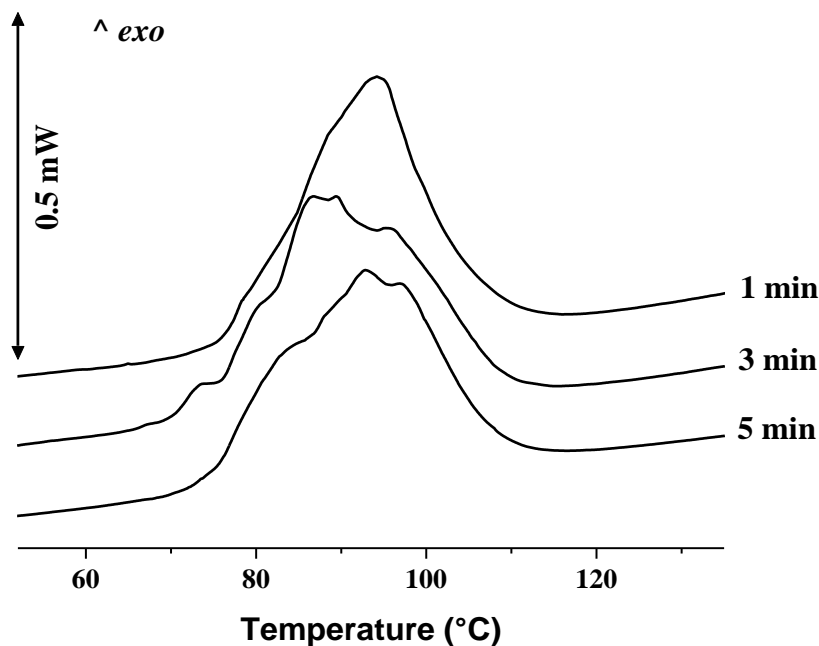

Fig. 4. Heat-flow rate plots of PHB samples upon cooling at 5 °C/min, after melting at 195 °C for the indicated times.

Further information comes from the analysis of the effect of permanence time at high temperatures on crystallization kinetics. Figure 4 presents the DSC curves determined upon cooling of PHB melted at 195 °C for different times. The DSC curves have a rather different shape, but all indicate that crystallization starts around 114-115 °C, independently of the time spent at 195 °C. The heat-flow rate plot gained after 1 min at 195 °C is rather smooth, whereas the curves obtained after 3 and 5 min at 195 °C are quite irregular, with the appearance of multiple spikes all along the course of the exothermic process. However, some spikes are visible also in the DSC curve measured after melting at 195 °C for 1 min, but are less pronounced than those in the other two plots of Figure 4. As demonstrated in Ref. 26, these spikes arise from non-monotonous development of latent heat during crystallization. Under given crystallization conditions, homogeneous nucleation can prevail in PHB because of the extreme purity of the polymer, with the formation of large spherulites. When the number of growing spherulites is low, the evolution of latent heat is largely affected

by every act of nucleation, as well as by space limitations in the process of growth, resulting in non-monotonous development of latent heat, with sudden increase or decrease of heat flux. This produces irregular DSC exotherms, characterized by spikes or shoulders associated to nucleation of new spherulites or to spherulite impingement. Also some of the DSC curves illustrated in Figure 3, namely those gained after melting at 195 and 200 °C are rather irregular, indicating that fusion conducted at these temperatures favor growth of a limited number of spherulites. The different shapes of the DSC curves of PHB samples subjected to the various thermal treatments suggest that the melting conditions influence nucleation of PHB. When the polymer is maintained at high temperatures for a time sufficient to completely melt the material, crystallization is mainly initiated by a limited number of heterogeneities followed by sporadic homogeneous nucleation, which results in growth of only a few spherulites, as typical for PHB. Conversely, when the thermal treatments are conducted at relatively low temperatures, some partially ordered chain portions may remain in the melt, which speeds up the onset of crystallization during the subsequent cooling as a result of self-nucleation. A high number of spherulites is expected to develop, compared to crystallization conducted after melting at high temperatures. In such conditions, latent heat is continuously evolved during the phase transition, without any sudden macroscopic acceleration or deceleration of the phase transition rate, which results in smooth and narrow DSC exotherms, as seen in Figure 3 for the crystallization monitored after melting PHB at 185 °C for 3 min.
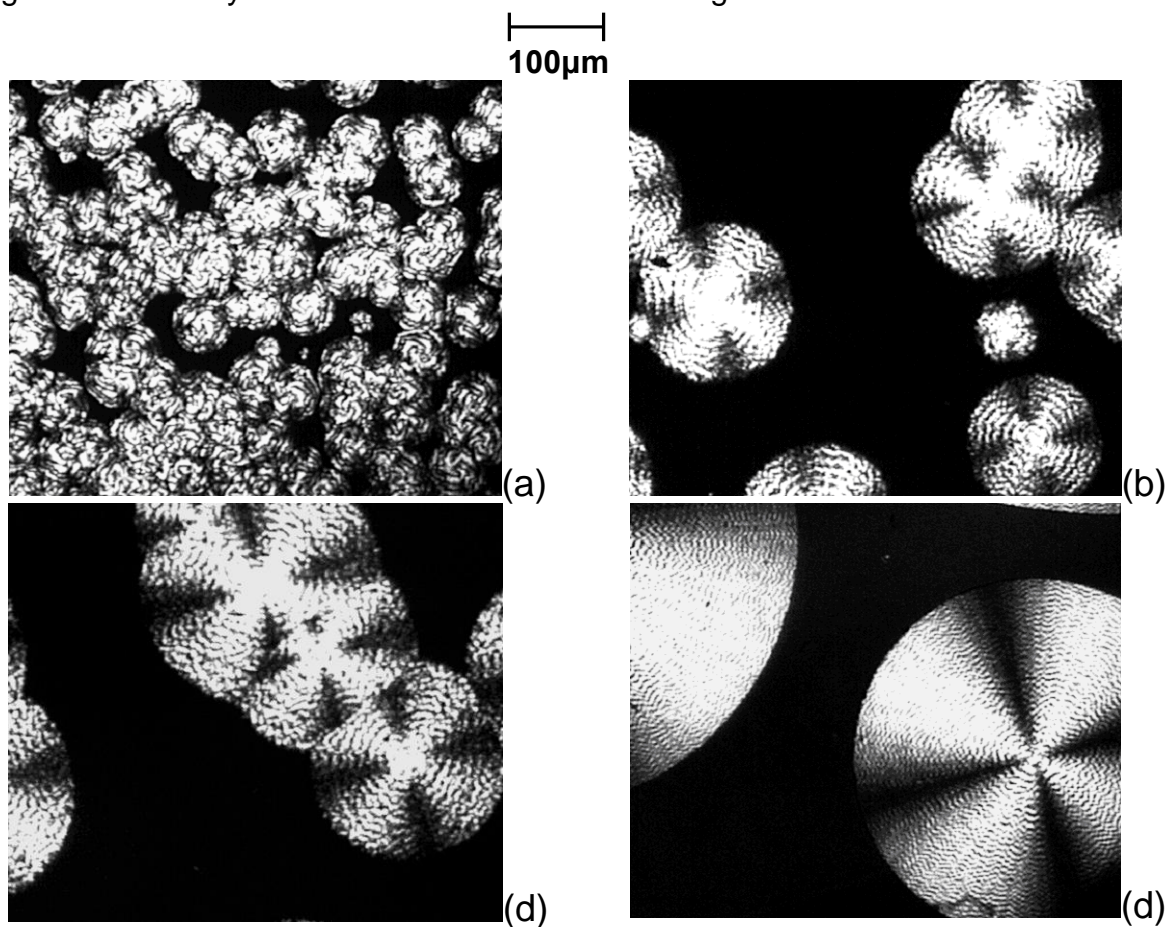

Fig. 5. Optical micrographs (crossed polars) of PHB during cooling at 5 °C/min after melting at various temperatures for 3 min: (a) 185 °C; (b) 190 °C; (c) 192 °C; (d) 195 °C.

It is worth noting that the shape of the DSC curves gained after melting at high temperatures is not reproducible when the sample under analysis is changed. Repetition of experimental analyses under conditions of complete melting leads to crystallization exotherms with the same overall appearance, but with bumps and spikes developing at slightly different temperatures. This is because of the statistical nature of homogeneous nucleation in a polymer characterized by a very low nucleation density. This explains the differences in the appearance of the exotherms in Figure 4, and also the slight differences in the temperature range where crystallization takes place.

An analysis of the nucleation density of PHB after melting at various temperatures, conducted by polarized optical microscopy, is presented in Figure 5. When melting is performed at 185 °C, a high number of spherulites develop, as shown in Figure 5-a. An increase of the temperature of thermal treatment that precedes crystallization leads to a lower density of nucleation, as illustrated in Figures 5-b to 5-d. A drastic decrease of the number of growing spherulites is attained when the temperature of melting is raised to at least 192-193 °C.
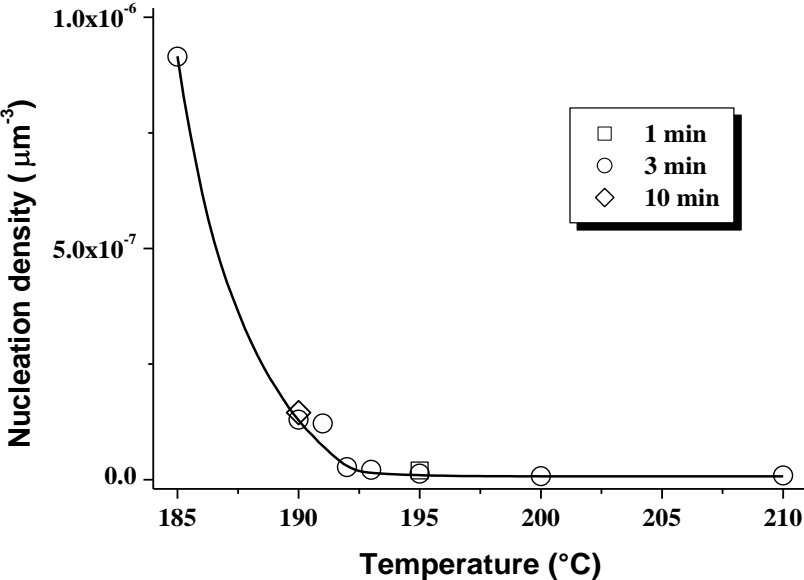

Fig. 6. Nucleation density of PHB after completion of crystallization at 5 °C/min as a function of temperature of preceding thermal treatment for the indicated times.

The data gained by the optical microscopy analysis of nucleation density as a function of the thermal history are summarized in Figure 6 which shows the final nucleation density of PHB after cooling at 5 °C/min as a function of melting temperature. It is seen in Figures 5 and 6 that melting below 192 °C for 3 minutes is insufficient for complete melting of the crystals, resulting in relatively high nucleation density during the subsequent crystallization, as a result of self-nucleation. As shown in Figures 5 and 6, a large memory of previous crystal order remains in the melt upon exposure at T < 192 °C. The residual chain portions pertaining partial crystalline order act as nucleation centers and result in a high nucleation density and a small spherulite size. This effect is higher for thermal treatments conducted at lower

temperatures, and results in an anticipated onset of crystallization, as quantified in Figure 3. For samples melted at T>192 °C, nucleation density approaches low levels indicating complete melting of crystals.

Considering the relaxation character of crystal destruction, it is obvious to expect some time dependence of the process of removing crystal residues that may cause self-seeding [15-17]. At this stage of analysis we show only as a illustration that the time of erasing of crystal memories depends strongly on the temperature, being long below equilibrium melting temperature, T_m^o, and very short above. The equilibrium melting temperature was experimentally determined by Al-Salah (190 °C) [27], by Avella et al. (194 °C) [28] and by Organ et al. [29], who show the molecular dependence of T_m^o with T_m^o = 186 °C for a PHB with molecular weight ca. 100.000. It is seen in Fig. 6 that an increase of time at 190 °C from 3 to 10 minutes does not significantly reduce the nucleation density as a result of self-seeding process, whereas at 195 °C 1 minute is sufficient for approaching low nucleation density typical for erasing crystal memory. Optical microscopy observations agree well with DSC data. As seen in Figure 4, the change of the melting time between 1 and 5 minutes at 195 °C, being in the range for complete erasing of crystal memory as can be deduced from Fig. 6, does not affect the temperature range of crystallization peak (within the experimental errors). The only difference is the shape of the DSC exotherm, with the appearance of discontinuities in the development of latent heat, that become more pronounced for residence times at 195 °C higher than 1 min. On the other hand, the DSC exotherms shown in Figure 4 refer to PHB samples with different initial molecular mass, as shown in Figure 2, as a consequence of the different duration of the exposure at 195 °C. Despite the largely different molecular mass, all the three samples crystallize within the same temperature range upon cooling at the same constant rate. This excluded that the decrease of molecular mass caused by a different extent of chain degradation produces a shift of the crystallization temperature.

Despite the minor effects on crystallization kinetics of PHB, thermal degradation influences the spherulitic morphology. PHB spherulites are characterized by a maltese cross and circular bands [1]. An increase of the temperature of fusion induces development of PHB spherulites with progressively lower band spacing, as shown in Figure 5. For PHB [1,32], as well as for other polymers [30-31], the band spacing increases with molecular mass, which, in turn, decreases with the temperature of fusion that precedes the crystallization step. Hence a higher temperature of melting causes growth of PHB spherulites with circular bands characterized by lower spacing.

The effects of thermal treatment on crystallinity degree (w_C) of PHB is exhibited in Figure 7. An increase of the temperature of fusion causes a decrease of w_C, which seems to level off at temperatures around 195 °C. This kind of dependence can be explained by crystal order remaining after melting at low temperatures, favoring thus not only nucleation of the crystals via self-seeding, but also the overall amount of crystal phase that develops upon cooling. The plateau in crystallinity values in the temperature range where complete melting of PHB crystals is attained confirms the role that incomplete melting plays in development of PHB crystals. The increase of w_C with time of melting can be ascribed to the different extent of thermal degradation of the material caused by the varied thermal history, which affects the molecular mass.
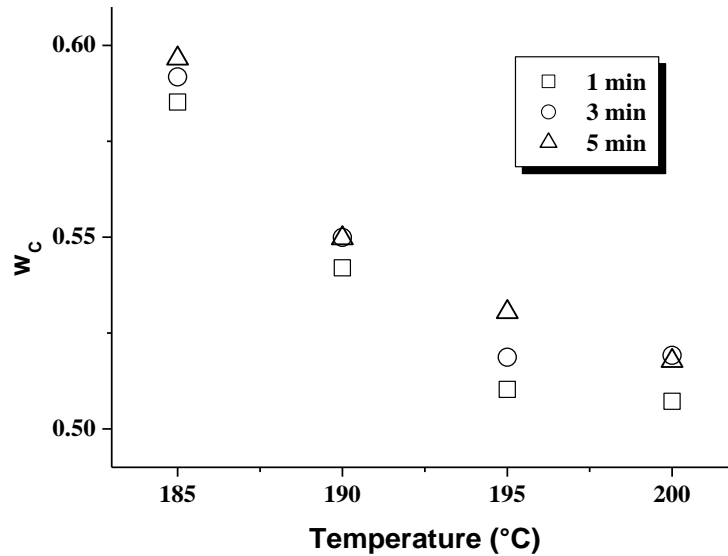
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Fig. 7. Variation of the final crystallinity as a function of melting temperature and time after cooling at 5 °C/min.

As mentioned above, molecular mass is known to influence the rate of growth of polymer crystals, as a lower molecular mass generally results in a higher crystal growth rate [14]. When PHB is maintained for relatively large times at a given temperature above the melting point, large thermal degradation induces some considerable decrease of molecular mass. Polymer chains are shorter, and can more easily diffuse towards the growing crystals, favoring development of higher amounts of crystal phase.

Conclusions

Polymer crystallization is sensitive to the initial structure that is produced during melting. This point is of special importance for polymers where the process of total melting is relatively long and is accompanied by molecular degradation. In the case of PHB, degradation in the temperature range of fusion is rather fast. The most common interpretation of the changes of crystallization behavior of PHB after various thermal treatment is attributed to degradation [e.g. 18]. Our experimental results have shown that crystallization of PHB is much more affected by incomplete melting than by chain degradation attained upon exposure at high temperatures. Our results indicate that some of the effects reported in literature as caused by degradation are rather related to non-completely melted structures. At this stage of analysis we have shown that in order to sufficiently cancel memories of previous crystalline order, it is necessary to melt PHB at a temperature higher than 192 °C. It is anticipated that this temperature can be varied slightly with the initial structure of the material before melting (size and degree of perfection of crystals).

The temperature needed for erasing of crystal memory, 192 °C, is 16 °C higher than the peak of fusion of apparent crystal structure as registered by DSC at a rate of at 10 °C/min. This difference can be applied as an alternative measure of the optimal conditions of melting of PHB. The statement often seen in the literature, although usually not supported by experimental details, that weaker conditions of melting (190

°C for 1-5 minutes) are sufficient for destroying the previous thermal history and avoid self-seeding [33-36] should be seen in this view.

Considering the relaxation character of crystal destruction we plan in a future to analyze quantitatively the process of erasing of crystal memory in PHB with estimation of the activation energy.

Experimental part

Materials

Poly(3-hydroxybutyrate) (PHB) with molecular mass 435,000 Da was purchased from Aldrich Chemical Company, Inc. Before analyses PHB was dried under vacuum for 16 h, then compression-molded with a Carver Laboratory Press at a temperature of 200 °C for 2 minutes, without any applied pressure, to allow complete melting. After this period, a load of 0.5 ton was applied for 2 min, then the sample was cooled to room temperature by means of cold water circulating in the plates of the press.

Calorimetry

Crystallization analyses of PHB were conducted with a Mettler DSC 822. The instrument was calibrated in temperature with high purity standards (indium and zinc), and in heat-flow-rate with heat of fusion of indium. Dry nitrogen was used as purge gas at a rate of 30 ml/min. For each measurement a fresh sample was always used, to minimize problems arising from thermal degradation of the polymer.

In order to reduce temperature gradients, the sample mass was kept small and approximately equal to 3 mg, so that problems due to thermal lags are reduced as much as possible. Crystallization is an exothermic process and the heat developed during the phase transition may cause some local heating and create thermal gradients within the sample. As a consequence, phase transitions can occur at temperatures that do not correspond to those detected by the instrumentation. The thicker the sample, the more critical this problem is, especially when crystallization is conducted under non isothermal conditions [37-38].

Before crystallization analyses, each PHB specimen was melted for a time ranging from 1 to 5 min at a temperature varying from 185 to 200 °C, then cooled to room temperature at a rate of 5 °C/min. Final crystallinity of polymer was determined assuming the heat of fusion of a 100% crystalline PHB equal to 146 J/g [32].

Optical Microscopy

Morphological analyses were performed with a Zeiss polarizing optical microscope equipped with a Linkam TMHS 600 hot stage. Photomicrographs were taken using a JVC TK-1085E Video Camera coupled with the software Image-Pro Plus 3.0. Dry nitrogen was used as purge gas in the hot stage during all measurements and thermal treatments. Before crystallization analyses, PHB was subjected to the same thermal treatments described above for DSC studies.

Molecular mass analysis

Molecular mass of PHB, both as received and after thermal treatments at various temperatures and times that lead to partial or complete melting of PHB crystals, was determined by viscosity analysis using the Mark–Houwink-Sakurada equation [39]:

$$\bar{\eta} = KM_\nu^\alpha$$

where $K = 0.012$ mL·g^{-1} and $a = 0.77$ [40]. Measurements were conducted at 25 °C, using chloroform as solvent.

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