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Irregularly shaped DSC exotherms in the analysis of polymer crystallization

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Summary

This article details a study of irregularly shaped DSC exotherms of poly(3-hydroxybutyrate) (PHB) developed during isothermal and non-isothermal crystallization. Due to the extreme purity of the polymer, PHB crystallization is mainly initiated by homogeneous nucleation, with the formation of very large spherulites, especially under slow nucleation conditions. When the number of growing spherulites is low, the evolution of latent heat is very sensitive to every act of nucleation as well as to the space limitations in the process of growth, resulting in non-monotonous development of latent heat, with sudden increases and decreases in crystallization rates. This results in non conventional DSC exotherms, under given crystallization conditions, characterized by spikes or shoulders associated to nucleation of new spherulites.

Introduction

The experimental determination of polymer crystallization kinetics with differential scanning calorimetry (DSC) is a well established method. Generally, a polymer sample is heated to about 20-30°C above the melting point, kept for a time sufficient to destroy all traces of previous crystalline order, then rapidly cooled to the desired crystallization temperature and there maintained until completion of the phase transition. When analyses are instead conducted in non-isothermal conditions, the polymer sample is cooled at a constant rate until crystallization is completed [1-7]. Crystallization kinetics is sometimes analyzed also after quenching the material to below the glass transition, then heated (cold crystallization) [1,6]. In all cases, the latent heat evolved during the transition is recorded as a function of time or temperature. Partial integration of the area beneath the DSC exotherm provides the kinetics of development of latent heat under the experimental conditions of analysis. These data allow to derive important information on the process of polymer crystallization.

Despite being a well established procedure, a general predictive model for crystallization kinetics, universally valid for all polymers, has not been developed yet. Even information gained on a given polymer sample might not be transferable to other samples of the same polymer, since small variations in molecular microstructure, molecular mass distribution, presence of additives, etc., may significantly affect the phase transition kinetics. Therefore, for each polymer batch it is necessary to perform precise determinations of crystallization kinetics.

Some analyses of this type, conducted on a microbial polyester, namely the poly(3-hydroxybutyrate) (PHB), are described in this contribution. It will be shown that, under some specific experimental conditions, irregularly-shaped DSC curves are developed during both isothermal and non-isothermal crystallization. Non-conventional DSC exotherms are sometimes observed in multicomponent systems, when the crystallizable polymer is dispersed into very small droplets: under this morphology, fractionated crystallization can occur, if heterogeneities that can start nucleation are confined into a portion of the segregated droplets, and crystallization starting from homogeneous nuclei prevails in the remaining material [1]. To our knowledge, multiple DSC exotherms arising from delayed nucleation in a fraction of the material have been observed only in phase-separated polymer blends or copolymers, but no report has been published to date on homopolymer systems.

Experimental part

Materials

Poly(3-hydroxybutyrate) (PHB) with molecular mass 435,000 Da was purchased from Aldrich Chemical Company, Inc. It was used both as received (in powder form), or as compression-molded sheet.

Preparation of compression-molded samples

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-30, and with a Perkin-Elmer Pyris 1 DSC. Both instruments were 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, to minimize problems due to thermal lags. 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 [1-4,8-10].

Before crystallization analyses, each PHB specimen was melted for 3 min at a temperature ranging from 185 to 200°C. The specific thermal treatments preceding crystallization analyses are detailed in the text for the various samples. Crystallization was analyzed in both isothermal and non-isothermal conditions. For non-isothermal analyses, the sample was cooled to room temperature at a constant rate, ranging from 0.5 to 15°C/min. For isothermal crystallization studies, after melting PHB was rapidly cooled to the desired crystallization temperature at a rate of 100°C/min, then maintained at this temperature for a time sufficient for completion of the phase transition.

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 melted with the same thermal treatment described above for DSC studies.

Results and discussion

Figure 1 illustrates the heat-flow rate profiles of poly(3-hydroxybutyrate) samples, measured during cooling from the melt at rates ranging from 0.5 to 15°C/min. Before cooling, the samples were melted at 193°C for 3 min. It is evident from Fig. 1 that the onset and maximum of crystallization peak shift to lower temperatures with increasing cooling rate. It is also seen in Fig. 1 that the heat flow rate plots obtained at relatively low cooling rates (below 5°C/min) do not have the smooth bell-shaped appearance typical of polymer crystallization curves, but displays some irregularities. Conversely, for higher cooling rates, the DSC curves become smoother without any irregularities in the heat-flow rate exotherms, with latent heat regularly developed during crystallization, as illustrated in Figure 1.

The results of isothermal crystallization analyses of PHB, conducted at different temperatures (T_c), are depicted in Figure 2. Similarly to some of the curves registered at low cooling rates (Figure 1), isothermal crystallization data measured at relatively high temperatures, e.g. 100 or 110°C show an irregular trend. When crystallization is conducted at lower temperatures (T_c=80°C), the latent heat developed during the phase transition results in a rather smooth exothermic peak.

Non conventional DSC exotherms analogous to those presented in Figures 1 and 2 have sometimes appeared in the literature in the analysis of polymer crystallization. The reasons of the irregularities can be very different. As mentioned in the Introduction, fractionated crystallization in polymer blends or copolymers may lead to the appearance of crystallization exotherms with multiple peaks. In only a few cases bumped exotherms have been observed in homopolymers. An example is illustrated in Ref. 11, for non-isothermal crystallization of poly(L-lactic acid) (PLLA). When PLLA is cooled from the melt at various scanning rates, a sudden acceleration in phase transition kinetics is observed when a temperature of 118°C is reached. Unlike PHB,

the DSC curves obtained for PLLA in isothermal conditions display the conventional bell shape typical of polymer crystallization. In the case of PLLA the unusual appearance of DSC exotherms was attributed to a sudden acceleration in spherulite radial growth rate below 118°C, without any particular increase of nucleation rate, nor evidences of morphological changes revealable by optical microscopy [11]. However, for PHB there is no abrupt change in phase transition rate at a particular temperature as in PLLA.
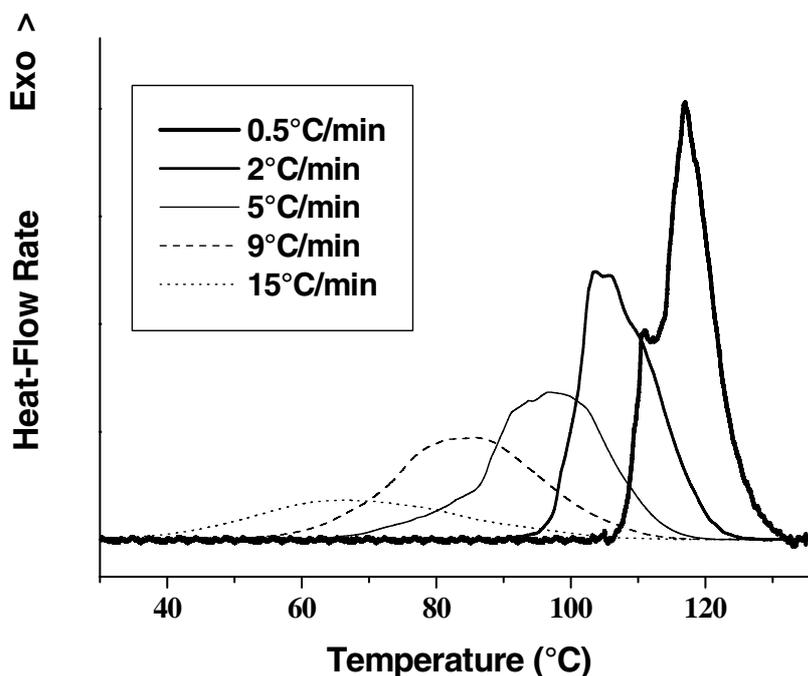

Figure 1. DSC thermograms of PHB powder crystallized at various cooling rates after melting at 193°C for 3 min. Measurements performed with Perkin-Elmer Pyris 1 DSC.

DSC exotherms with multiple maxima have been also reported for low molecular mass poly(ethylene oxide) (PEO), and explained as transient non-integral folding crystals that initially develop during crystallization, then transform to integral folding crystals through isothermal thickening or thinning [12]. Kinetics of the latter processes was found to occur only in oligomeric PEO, as the characteristic rates drastically slow down with increasing molecular mass [12-13]. However, poly(3-hydroxybutyrate) crystallizes according to integral folding, predominantly occurring by adjacent re-entry, folding in a zig-zag fashion alternately at approximately +45° and -45° to the a-axis [14-16]. In addition, X-ray analyses conducted on samples subjected to the same thermal history described in this manuscript, display no evidence of changes in crystal structure during the phase transition.

As pointed out above, non conventional DSC curves have been sometimes reported in the literature in the analysis of crystallization of multicomponent systems. In isotactic
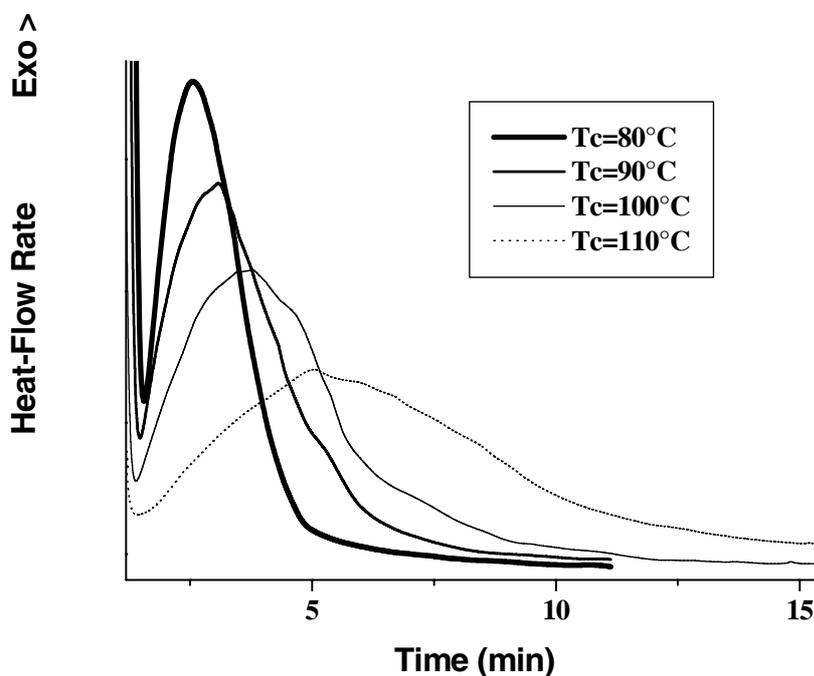
Figure 2. DSC thermograms of PHB powder during isothermal crystallization at 80 and 100°C, after melting at 193°C for 3 min. Measurements performed with Perkin-Elmer Pyris 1 DSC.

polypropylene/polycarbonate blends, when polypropylene is the dispersed phase, multiple exothermic peaks observed during non-isothermal crystallization were found to arise from homogeneous nucleation in droplets with diameter lower that 20 μm [17]. Similar processes were detected in isotactic polypropylene/polystyrene blends [18], in polyamide/polystyrene blends [19], and in some other phase-separated systems where the crystallizable component is confined into small droplets, and the available heterogeneities are segregated into a small portion of the droplets [20]: in such systems crystal formation is delayed in the remaining heterogeneity-free domains, as crystal growth starts from homogeneous nuclei. This results in the appearance of multiple peaks in the DSC exotherms, associated to homogeneous and heterogeneous nucleation.

Similarly to the phase-separated multicomponent systems, for poly(3-hydroxybutyrate) the irregular shape of the heat-flow rate curves shown in Figures 1 and 2 may be caused by non monotonous development of latent heat during the crystallization. As mentioned above, PHB is commercially produced by a batch fermentation process, hence is an extremely pure material, not containing catalyst residues and other impurities, peculiar to synthetic polymers, that can promote heterogeneous nucleation [16,20-22]. The nucleation process is mostly homogeneous, resulting in formation of a very small number of very large spherulites. This situation takes place especially when the polymer is crystallized at high temperatures, where the rate of homogeneous nucleation is low, as exampled in Figure 3.
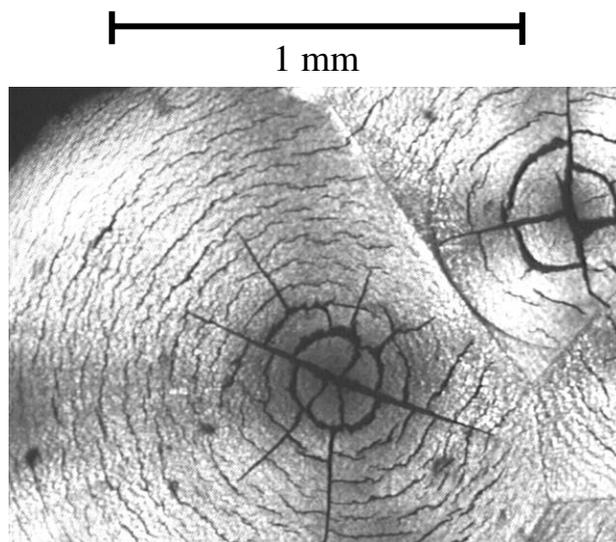
1 mm

Figure 3. Optical micrograph (crossed polars) of PHB film, crystallized during cooling at 5°C/min, after melting at 200°C for 3 min.

According to the literature, the maximum in homogeneous nucleation rate of poly(3-hydroxybutyrate) occurs around 60°C [16]. When crystallization of PHB is conducted at high cooling rates, the nucleation density is rather large, as a consequence of the shift of the phase transition to low temperatures [3]. This results in a high number of simultaneously growing spherulites, and the development of new crystallites during the phase transition, typical of homogeneous nucleation, has a very limited influence on the rate of evolution of latent heat. Conversely, at low cooling rates, crystallization of PHB is initiated at high temperatures by a very small number of isolated spherulites. In such a system with only few growing spherulites, the evolution of latent heat is extremely sensitive to every act of nucleation as well as to a space limitation during growth of spherulites. It results in upward and downward turns of the DSC signal at the corresponding time, visible as shoulders or spikes in the plot. The non-conventional shape of the DSC curves determined at low cooling rates, exhibited in Figure 1, is thus explained. Similarly, isothermal crystallization conducted at low T_c results in a smooth shape of the crystallization exotherm, as shown in Figure 2, because of the large number of spherulites nucleated in the same time range. At higher T_c, the low number of growing spherulites, coupled with progressive nucleation of new ones, leads to the rather irregular shape of the DSC curve illustrated in Figure 2 for $T_c \geq 90$°C.

The effect of nucleation kinetics on the non-conventional appearance of crystallization exotherms of PHB can also be evinced from the plots of Figure 4, that report the DSC curves measured during cooling of PHB at a rate of 5°C/min, after melting at various temperatures. As will be detailed in a forthcoming paper, heating to a temperature below 193°C results in incomplete melting of PHB crystals [23]. This largely enhances the nucleation rate in the subsequent cooling scan, revealed by the shift of the onset of the crystallization curve with decreasing pretreatment temperature. When PHB is melted at 185°C, during the following cooling at 5°C/min a very high number of spherulites start to grow simultaneously as a consequence of selfnucleation process

on non-completely melted crystallites. Conversely, when PHB is crystallized after melting at 195°C, nucleation from homogeneous melt prevails, resulting in the bumped shape of the heat-flow rate exotherm. Fusion conducted at intermediate temperature (190°C) leads to the appearance of some shoulders, less pronounced than in the crystallization curve gained after melting at 195°C, due to the different nucleation density [23]. It needs to be underlined that repetition of experimental analyses under conditions of complete melting of PHB crystals (i.e. at temperatures of at least 193°C) lead to crystallization exotherms with the same overall appearance, with bumps developing at slightly different temperatures, as expected for homogeneous nucleation coupled with low nucleation density.
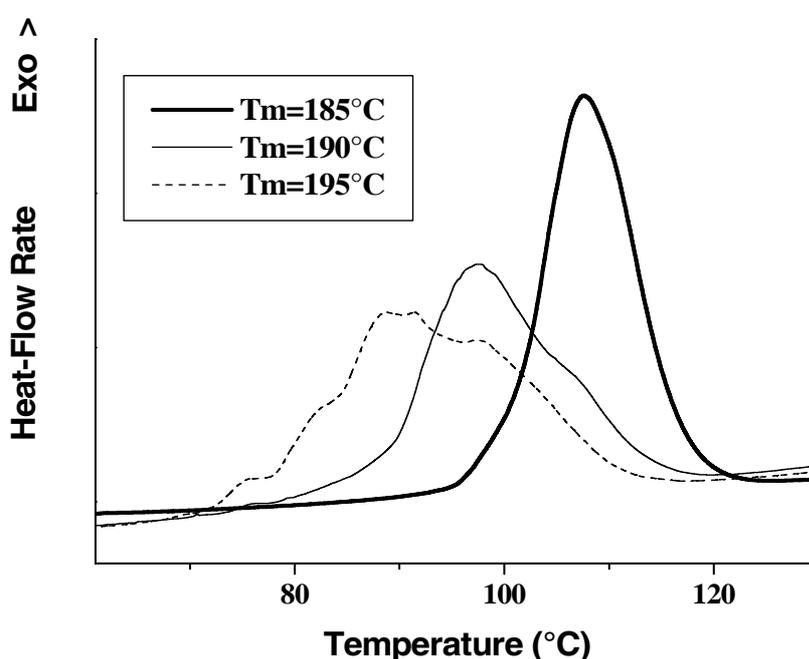

Figure 4. DSC thermograms of PHB film, measured during crystallization at 5°C/min, after melting for 3 min at the indicated temperatures. Measurements performed with Mettler DSC-30.

It might be inferred that the irregularities in the heat flow rate exotherms are not related to peculiarities of phase transition but are caused by a high noise to signal ratio, which increases with decreasing scanning rates [24]. As shown in Figure 1, measurements conducted at low scanning rates, i.e. in the conditions of low heat flux, evidence some noise in the heat flow rate curves, even outside the phase transition range. This is especially evident for the sample that was analyzed during cooling at 0.5°C/min. However, the results presented in Figure 4, that were all determined at the same scanning rate, exclude a possible influence of noise on the irregular shape of the thermoanalytical curves. The DSC plots seen in Fig. 4 have largely different appearances, depending on the melting history and thus nucleation rate. Moreover, our measurements were conducted with different apparatuses: a power-compensation Perkin-Elmer Pyris 1 DSC (Figures 1 and 2), and a heat-flux Mettler DSC-30 (Figure 4). In both cases non-conventional shapes of DSC curves were detected.

A typical feature of poly(3-hydroxybutyrate) spherulites is the formation of circumferential cracks, as well as radial ones departing from the spherulite centers [25-27], like those shown in Figure 3. These cracks develop upon cooling, both during spherulite growth and after completion of crystallization, and arise from volume changes during crystallization, as well as from the different thermal expansion coefficient of the liquid and solid polymer [25-27]. It was recently shown that large shrinks of the polymer sample during analysis can worsen the thermal contact between pan and sample, and, in extreme cases, deform the pan. This may lead to spikes in the heat flow rate profile, and to erroneous heat capacity output [28]. However, the cracks in PHB spherulites appear not only during crystallization, but also during the progressive cooling after completion of the phase transition. Therefore, if the irregularities in the DSC curves were originated by cracks within the sample, bumps or spikes in the heat-flow rate curves would have been observed also after completion of crystallization. Since the heat flow rate plots are smooth outside the crystallization peak, as shown in Figure 1, the influence of cracks in PHB spherulites on DSC signal can be excluded.

Nucleation kinetics of polymers is generally quantified by optical microscopy, by measuring the time or temperature dependence of the number density of nuclei [1]. For poly(3-hydroxybutyrate), due to the very low nucleation density and the very large size of the spherulites, the area visualized under the optical microscopy may be not representative of the whole sample. Using the smallest possible enlargement, the maximum area visible under our optical microscopy is that shown in Figure 3. The number of PHB spherulites that are developed in this area is too small to provide quantitative reliable data. In the case of poly(3-hydroxybutyrate), under slow crystallization conditions, it becomes possible to gain information on nucleation kinetics also from calorimetric data, when the appearance of new spherulites is revealed by upward turns in the heat-flow rate signal, overlapping the main phase transition exotherm. Comparison of the area shown in Figure 3, where only 4 spherulites are visible, with that of typical DSC sample pans, that have a diameter of about 4-5 mm, may allow to determine the total number of spherulites that grow under the given crystallization conditions, as well as the timing of their starting growth, and possibly make a quantitative correlation of the shape of DSC curve with the amount of growing crystal at every temperature during analysis. Such an analysis needs further investigations.

Conclusions

Our study demonstrated that non-monotonous development of latent heat during PHB crystallization can produce irregularly-shaped DSC exotherms. Crystallization of PHB is initiated predominantly via homogeneous nucleation, which may result in a very low nucleation density, due to the extreme purity of the polymer. Since the average diameter size of PHB spherulites can be very large, especially when crystallization occurs at high temperatures, and their number very low, even the onset or end of growth of a single spherulite, in a sample that contains only a few growing ones, can produce significant variations of the crystallization rate, revealed as spikes or shoulder in the DSC curve. This finding may allow to correlate measurements of nucleation rates by the conventional optical microscopy methods, with the irregularities in the DSC exotherms, which analysis is currently under evaluation.

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