



Crystal reorganization of poly (butylene terephthalate)



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ABSTRACT

The kinetics of isothermal melt-crystallization of poly (butylene terephthalate) (PBT) has been evaluated in a wide temperature range from below the glass transition temperature T_g to close to the equilibrium melting temperature, using fast scanning chip calorimetry. Analysis of heating scans recorded after pre-defined crystallization times permitted gaining valuable information about the effect of crystallization on the glass transition, the cold-crystallization kinetics and stability of crystals formed at the crystallization temperature and during heating. As one of the main conclusions, it is suggested that reorganization on heating involves melting of crystals without formation of a completely relaxed and isotropic melt (at the length scale of a crystal) but a non-isotropic cluster of chain segments which turn into a more stable crystal by a fast click- but not classical secondary nucleation/growth-mechanism.

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1. Introduction

In recent years, using fast scanning chip calorimetry (FSC), it was possible to gain several new information about the crystallization behavior of poly (butylene terephthalate) (PBT), going beyond former knowledge gained by conventional differential scanning calorimetry (DSC), microscopy, or X-ray scattering. With the fast cooling and heating capacity of FSC, and the opportunity to measure fast first-order phase transitions it was possible to obtain data about crystallization rates at high supercooling of the melt, as well as to comprehensively evaluate the effects of cooling and heating rates on crystallization and crystal reorganization. Regarding the isothermal crystallization kinetics it was found that the crystallization rate shows a bimodal dependence on temperature, with distinct crystallization-rate maxima observed at about 140 and 75 °C [1–3]. Similar as in case of many other polymers [4–6], the bimodal temperature dependence of the crystallization rate is caused by a change of the nucleation mechanism, with heterogeneous nucleation dominating at low supercooling of the melt while

at high melt-supercooling homogeneous nucleation prevails [7]. In the specific case of PBT, the cross-over temperature between the different crystallization mechanisms occurs at around 120 °C. In contrast to isotactic polypropylene or polyamides [6], the nucleation mechanism does not affect the structure of the crystals; it has been shown in prior work [3] that independent on the crystallization temperature the α -modification is forming. Furthermore, regarding non-isothermal crystallization, fast-cooling experiments provided information that crystallization can completely be suppressed on cooling the relaxed melt faster than about 300–500 K/s to below the glass transition temperature T_g [2,3,8,9]. Due to the fast formation of homogeneous crystal nuclei at temperatures close to T_g , cold-crystallization on heating typically is much faster than crystallization on cooling the equilibrium melt being free of homogeneous nuclei. Consequently, by FSC it was quantified for PBT that the critical heating rate to suppress cold-crystallization is distinctly higher than the critical cooling rate to avoid crystallization on cooling, being about 10,000 K/s [8]. Finally, also the critical heating rate to suppress non-isothermal reorganization of crystals formed at low temperature close to 70 °C was determined, being above 100,000 K/s [8].

With the present work it is attempted to further complete crystallization studies on PBT, focusing on the analysis of FSC heating scans after isothermal crystallization in a wide range of temperatures between 25 and 200 °C. As such, temperatures below

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