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Density of heterogeneous and homogeneous crystal nuclei in poly (butylene terephthalate)

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ABSTRACT

Quantitative analysis of the nucleation density of poly (butylene terephthalate) using microscopy yielded values of 10^6 and 10^{15} nuclei mm^{-3} for the cases of heterogeneous and homogenous nucleation on crystallization at low and high supercooling of the melt, respectively. Fast scanning chip calorimetry revealed that the largely different nucleation densities cause two crystallization-rate maxima at 130 and 70 °C, with characteristic minimum crystallization times of the high- and low-temperature crystallization processes being about 1 and 0.1 s, respectively. It has furthermore been excluded by X-ray scattering that the low-temperature crystallization-rate maximum is due to the formation of a different crystal polymorph; independent of the supercooling there is observed formation of α-crystals. The crystallization study has been completed by analysis of the non-isothermal crystallization behavior, identifying a minimum critical cooling rate of about 10 K s^{-1} to avoid completion of the high-temperature crystallization process and to initiate crystallization at low temperature. For complete vitrification, the PBT melt needs to be cooled faster than 200 K s^{-1}.

1. Introduction

Since the introduction of fast scanning chip calorimetry (FSC) for the analysis of the crystallization behavior of polymers about ten years ago, [1–4] it has been shown on example of numerous polymers that there is a qualitative change of the mechanism of primary crystal nucleation on variation of the crystallization temperature (T_c). Due to its high cooling capacity and short time constant, FSC permits isothermal measurement of the rate of melt-crystallization in a wide range of temperatures from below the glass transition temperature (T_g) to close to the equilibrium melting temperature ($T_{m,0}$). Note that analysis of the kinetics of crystallization at high supercooling of the melt is often impossible on using conventional differential scanning calorimetry (DSC), since the sample may crystallize already on the approach of T_c when cooling at rather low cooling rate of at best few hundred K/min, or during not yet achieved instrumental steady state at the begin of the isothermal analysis stage [5,6]. FSC analysis of the crystallization rate of isotactic polypropylene (iPP) [7–9] and its random copolymers with 1-alkenes [10], of several aliphatic polyamides (PA), including PA 6 [11], PA 66 [12], and PA 11 [13], and of polyesters including poly(ε-caprolactone) (PCL) [14] or poly (butylene terephthalate) (PBT) [15–17] revealed a bimodal dependence on T_c, which has been explained with a transition from heterogeneous nucleation, evident at rather low supercooling, to homogeneous

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nucleation, evident at rather high supercooling of the melt. Though the interpretation of the low-temperature crystallization-rate maximum as being related to homogeneous nucleation is not yet unequivocally agreed upon [18], there seems consensus that it is caused by activation of a qualitatively different mechanism of crystal nucleation than is evident at low supercooling.

The assumption of a qualitative change of the mechanism of crystal nucleation on variation of T_c is strongly supported by analysis of the nucleation density of samples which have been crystallized at largely different supercooling, using microscopy. For iPP [19], PA 6 [20], and PA 11 [13] it has been shown that at low supercooling of the melt crystallization proceeds *via* spherulitic growth of only few nuclei to form laterally extended lamellae. At high supercooling of the melt, in contrast, due to the largely increased number of nuclei by several orders of magnitude, lateral growth of nuclei and formation of lamellae and spherulites was suppressed [13,20–25]. Unfortunately, for all of these polymers, besides the drastic increase of the nucleation density on increasing the supercooling above a critical value, there is simultaneously observed formation of a different crystal polymorph [26–28]. In other words, it cannot be excluded that the low-temperature maximum of the gross crystallization rate is then also be caused by an increased crystal growth rate.

While the increase of the nucleation density by several orders of magnitude within a narrow temperature range on decreasing the temperature is considered as evidence for a qualitative change of the nucleation mechanism, occurrence of homogeneous crystal nucleation at high supercooling of the melt has independently been proven by droplet experiments. Submicron size heterogeneity-free droplets of iPP [29,30] and PA 6 [31] were slowly cooled from the melt and then crystallized only at high supercooling, leading to a similar granular morphology as was observed in quenched samples which contained heterogeneous nucleators and which were crystallized close to T_g. As such, homogeneous crystal nucleation either may be enforced by quenching the melt, required to avoid crystallization *via* a heterogeneous nucleation mechanism at high temperature, or by absence of heterogeneous nucleators, as was achieved in droplet experiments due to the drastic decrease of the crystallizing volume, excluding presence of heterogeneities.

Analysis of the crystallization behavior of vitrified samples of PCL [14,32], PA 6 [33] and isotactic polybutene-1 (iPB-1) [34] revealed furthermore that during annealing of the glass there is first observed enthalpy relaxation, and only after its completion there is detected crystal nucleation followed by crystal growth. The decrease of the enthalpy of the glass to the value of the liquid state corresponds to a densification of the glass, involving cooperative rearrangement of molecule segments on a length-scale of few nanometers, eventually leading to formation of small clusters of parallel aligned chain segments, to be considered as homogeneous nuclei if being of supercritical size. For heterogeneous nucleation it would be expected that it proceeds faster than relaxation.

In the present work it is intended to continue/expand formerly performed FSC research of the crystallization behavior of PBT [15–17]. It has been found that on slow cooling at rates which are typically applied in conventional DSC PBT crystallizes within a single crystallization event at temperatures between 160 and 200 °C [35,36]. Increasing the cooling rate led to the expected shift of the crystallization temperature to lower temperature but also, if exceeding 40 K s^{-1}, to the detection of a fast low-temperature crystallization event at temperatures lower than 80 °C, depending on the cooling rate [16]. The critical cooling rate required to inhibit crystallization was found to be about 300 K s^{-1}. Isothermal analysis of crystallization of PBT at different temperatures revealed two crystallization-rate maxima at about 150 and 75 °C, with approximate half-times of crystallization of 0.6 and 0.2 s, respectively [15,16]. The bimodal appearance of the isothermal crystallization rate was attempted to be linked to the occurrence of two different glass transition temperatures at about 40 and 100 °C, related to the mobile and rigid amorphous fractions (MAF and RAF) of the amorphous phase, respectively. It was suggested that vitrification of the RAF around 100 °C slowed down the crystal growth rate, leading to the high-temperature crystallization-rate maximum at 150 °C. As a further reason for the bimodal appearance of the crystallization rate, a possible change of the crystal structure at high supercooling has been considered, for example due to the formation of an intermediate structure following Ostwald's rule of stages [37], similar as has been observed for poly(butylene naphthalate) [38]. Third, a change of the crystal morphology on temperature variation was discussed, based on the earlier detection of usual and unusual spherulites above and below about 200 °C, [39,40] however, as such not fitting the temperature in between the high- and low-temperature crystallization-rate maxima; note that in unusual spherulites the optical axes of the indicatrix are oriented 45° off the spherulites radius. Final conclusions regarding the observation of two crystallization-rate maxima at different crystallization temperatures were not drawn, and also a possible change of the nucleation mechanism was not considered. In view of the prior investigations of the nucleation and crystallization behavior of iPP, PA, and PCL, using FSC to assess the temperature range of high supercooling of the melt, it is intended to re-inspect the crystallization of PBT in order to further trace the not yet known origin of the low-temperature crystallization-rate maximum.

The paper is structured such that in the first two parts non-isothermal and isothermal FSC crystallization experiments are presented, confirming earlier findings regarding the crystallization kinetics of PBT. The assumption of a qualitative change of the mechanism of crystal nucleation on variation of the degree of supercooling the melt is then followed by a qualitative analysis of the semicrystalline morphology/nucleation density as a function of T_c, using polarizing optical microscopy (POM) to probe absence or presence of spherulitic crystal growth, and using atomic force microscopy (AFM) for analysis of the crystal morphology. Finally, it will be shown by X-ray scattering