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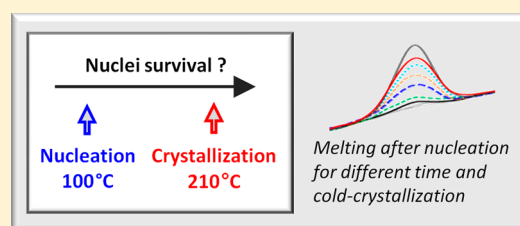
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ABSTRACT: Tammann's two-stage crystal nuclei development method has been applied to gain information about the kinetics of formation and the stability of homogeneous crystal nuclei in poly(ethylene terephthalate). The method requires rapid cooling of the relaxed melt to different nucleation temperatures close to the glass transition, in order to allow isothermal formation of homogeneous nuclei. Nuclei formation is then probed by fast heating of the system after predefined nucleation times to the growth-stage temperature where, according to the classical nucleation theory, nuclei grow to crystals connected with a measurable change of latent heat. For polymers, this picture does not hold. Homogeneous nuclei melt during the transfer from the temperature of their formation to the growth temperature as was proven by analysis of the melting behavior of even more stable crystals grown at the nucleation temperature. Though melting on heating, it is proposed that remnants of both nuclei and crystals, due to incomplete dissolution, allow very rapid reestablishing of slightly larger and more stable nuclei. This way, similar to the melting–recrystallization–remelting mechanism of polymer crystals of low stability on heating, the initially formed nuclei keep their overcritical size up to temperatures 100 °C, or even higher, above the nucleation temperature by continuous increase of their size.



INTRODUCTION

The recent introduction of fast scanning chip calorimetry (FSC) for analysis of polymer crystallization provided evidence for predominance of different mechanisms of primary crystal nucleation at different supercooling of the melt. The analysis of the crystallization rate in a wide range of temperatures revealed for numerous polymers including isotactic polypropylene (iPP),^{1–3} polyamides (PA),^{4–6} or poly(butylene terephthalate) (PBT)^{7–9} a bimodal dependence, that is, observation of a high- and low-temperature maximum of the crystallization rate, with the latter typically observed at temperatures about 30–50 °C above the glass transition temperature. These maxima were associated with heterogeneous and homogeneous crystal nucleation, that is, to formation of crystal nuclei on pre-existing surfaces/heterogeneities or in the bulk phase, respectively.¹⁰ For other polymers like poly(ϵ -caprolactone) (PCL)¹¹ or poly(ethylene terephthalate) (PET)¹² different nucleation mechanisms were identified by a strong asymmetry of the temperature-dependence of the gross crystallization rate, or the independence of the crystallization rate at high melt supercooling on the presence of purposely added nucleators, respectively.

The presumption of different nucleation mechanisms active at different supercooling of the melt, derived from the experimental observation of low- and high-temperature crystallization-rate maxima, has been supported by analyses of the semicrystalline morphology of samples crystallized at

different temperature which identified largely different nucleation densities. For example, an estimation of the nucleation density of PBT on crystallization at low and high supercooling of the melt revealed values of 10^6 and 10^{15} nuclei/mm³, respectively, with the increase occurring in a rather narrow temperature interval.⁹ Note that the nucleation density of 10^{15} nuclei/mm³ at high supercooling of the melt allowed estimation of the rate of homogeneous crystal nucleation of at least 10^{16} nuclei/mm³/s, which, however, is larger than the nucleation rate of 3×10^5 nuclei/mm³/s estimated for polyethylene from droplet-crystallization experiments,¹³ but lower than the value of 10^{22} nuclei/mm³/s from molecular dynamics simulations.¹⁴

Because of the large nucleation density in the case of crystallization at high melt supercooling, there is then observed formation of rather small ordered domains which are not forming a higher-order superstructure.^{6,9,15–18} A nucleation density of 10^{15} nuclei/mm³ corresponds to a distance between the centers of nuclei, roughly, of 5–10 nm. Because of the very small distance between the nuclei, lamellae cannot grow but nearly isometric crystals of nodular shape, with coalescence of these small crystals (Ostwald ripening) being strongly suppressed by the observed large rigid amorphous fraction.

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It is reasonable to suggest that a homogeneous nucleation mechanism is valid on crystallization at high supercooling. This suggestion is in accordance with the analysis of crystallization of heterogeneity-free droplets, which only crystallize at temperatures in the vicinity of the low-temperature crystallization-rate maximum of samples containing heterogeneous nucleators/impurities, and which yield a similar semicrystalline morphology and density of primary crystal nuclei as impurity-containing samples when crystallized at high supercooling.^{19,20} Further evidence for homogeneous crystal nucleation at high melt supercooling has been provided by the establishment of a link between the time scales of the densification of the glass and the formation of nuclei, as has been reported in detail elsewhere.^{21,22}

Data about the kinetics of formation of homogeneous crystal nuclei at high supercooling of the melt may be gained by application of Tammann's two-stage crystal nuclei development method, introduced more than hundred years ago.²³ The method induces the formation of nuclei at high supercooling of the melt and subsequent isothermal growth at higher temperature. As such, this method utilizes the often largely different temperatures of maximum rate of primary crystal nucleation and crystal growth, which is needed since formation of nuclei, typically, cannot be followed in situ by calorimetry, microscopy, or scattering experiments. In other words, if the right experimental conditions are chosen, this method allows detection of nuclei which were formed at low temperature by growing them at higher temperature to crystals, being connected with a measurable change of latent heat proportional to the nuclei density. Tammann's crystal nuclei development method was initially applied to gain knowledge about nucleation and crystallization of organic liquids, and was later on applied to study silicate glasses,^{23–25} it has rarely been used to analyze homogeneous nucleation in polymers. This is also due to the fact that it is often impossible to adjust well-defined states of amorphous structure free of crystals and nuclei as part of the nucleation experiment, requiring both reproducible and fast cooling of the relaxed melt to low temperatures where homogeneous nucleation is predominant. Furthermore, it needs to be assured that after nuclei formation the system is transferred to the temperature of growth at rather high rate to prohibit the formation of additional nuclei or even crystal growth during heating. FSC has been proven to be a superior tool to obtain information about the kinetics of homogeneous crystals nucleation, as Tammann's nuclei development method has recently been applied for analysis of a few polymers including isotactic polybutene-1 (iPB-1),²¹ poly(lactic acid) (PLA),^{26,27} PA 6,²² and PCL.²⁸ However, it may also be noted that due to the high demands of Tammann's crystal nuclei development method regarding the temperature–time profiles to realize, the rather long experimentation time needed, as well as shortcomings as dissolution of nuclei during their transfer to the development stage,²⁵ alternative nonisothermal methods have been proposed.^{29,30}

The present study concerns the analysis of formation of homogeneous crystal nuclei in PET, and their detection employing Tammann's nuclei development method using FSC. As far as we are aware, Tammann's nuclei development method has not yet been used to characterize the crystallization behavior of PET, though crystal nuclei formation at high supercooling of the melt and in the glassy state and its effect on the formation of a semicrystalline structure at elevated temperature have been identified early for this polymer via

other techniques with limited but logical conclusions.^{31–33} For example, though PET crystallizes on cooling only at rates lower than about 1 °C/s,³⁴ it has been found that cooling the melt at rates up to 100 °C/s leads to nuclei formation, which then accelerated subsequent isothermal crystallization at 100 °C.³³ It was shown furthermore that annealing of quenched PET below or near the glass transition temperature causes a decrease of the cold-crystallization temperature during subsequent heating,^{31,32} and leads to an increase of the number of spherulites growing at elevated temperature,³¹ with both phenomena explained by nuclei formation at low temperatures.

In the present work it is attempted to continue and expand the previously performed studies about nuclei formation in PET at high supercooling of the melt and in the glass, by employing FSC. It is the aim to qualitatively test the general approach of using Tammann's nuclei development method to gain information about the kinetics of homogeneous nuclei formation in this polymer, but also to contribute to the recently started discussion of the thermal stability of nuclei;^{11,28} it is still not proven whether nuclei formed in the nucleation-stage of Tammann's nuclei development experiment melt during the transfer to the growth stage or if they survive and even grow. However, this is not important as long as the enhanced crystallization at the growth stage is observed, which allows one to draw conclusions about the nuclei development at the nucleation stage.^{11,21,22,26–28} In order to contribute to the discussion of the thermal stability of homogeneous nuclei, in this work Tammann's nuclei development method has been modified such that at the nucleation-stage temperature annealing has been extended to observe not only nuclei but also crystals whose melting behavior on heating to the growth stage then also provides information about the nuclei stability. The **Results and Discussion** is structured such that in the first part the temperature–time profile of the FSC crystal nucleation experiments is explained. This is followed by a presentation of basic data about the kinetics of isothermal and nonisothermal crystallization, which are needed for the design and understanding of the nucleation experiments performed. In the third and final part the specific nuclei-development experiments according to Tammann are introduced, followed by a discussion of the results.

■ EXPERIMENTAL SECTION

In the present study we employed an Eastar MN052 PET homopolymer grade from Eastman Chemical (USA). It is a neat medical grade with high flow characteristics, and an intrinsic viscosity of 0.74 dL/g,³⁵ delivered in form of pellets. Specimens for the FSC analysis were prepared using a SLEE microtome to obtain thin sections with a thickness of 15 μm, which then were reduced in their lateral size to about 100 μm using a scalpel and a stereomicroscope.

FSC analyses were performed using a power-compensation Mettler-Toledo Flash DSC 1 which was connected to a Huber intracooler TC100 for fast cooling and subambient temperature operation. The calorimeters were purged with dry nitrogen gas at a flow rate of 35 mL/min. Before loading of the sample, the FSC sensor was conditioned and temperature-corrected according to the instrument manual. To improve the thermal contact between the sensor and the sample, a droplet of highly viscous Wacker silicon oil AK 60,000 was placed on the heatable area of the sample calorimeter and equally distributed using a single-hair tool to form a thin film. The oil was then subject to repeated heating and cooling until absence of any drift of the heat-flow rate signal. Subsequently, the sample was placed on the sensor, with the first heating scan performed at a rate of 10 °C/s to allow slow melting and adjustment of good thermal contact to the sensor. The sample mass of about 130 ng was determined by

comparison of the absolute heat of crystallization in units of J, obtained in the FSC, with the mass-specific heat of crystallization in units of J/g, obtained using a calibrated PerkinElmer differential scanning calorimeter DSC 7 on slow cooling at identical rates of 0.033, 0.083, and 0.167 °C/s (2, 5, and 10 °C/min). Note that the FSC heat of crystallization has been determined by analysis of the heat of melting of the crystals formed on slow cooling, using a high heating rate of 1000 °C/s, which results in a good signal-to-noise ratio and suppresses cold-crystallization.

RESULTS AND INITIAL DISCUSSION

Temperature–Time Profile of Nuclei Development Experiments According to Tammann. Figure 1 shows

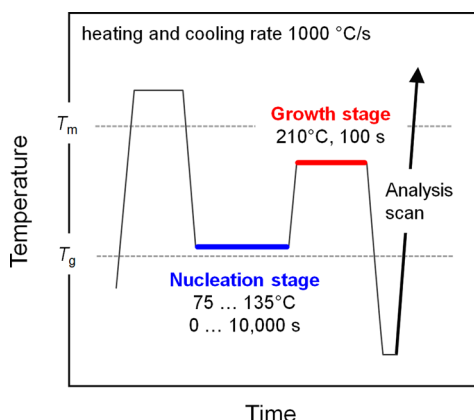


Figure 1. Temperature–time profile of FSC experiments used to obtain kinetic data about nuclei formation in PET according to Tammann's two-stage crystal nuclei development method. The positions of the melting temperature T_m and glass transition temperature T_g are indicated.

schematically the temperature–time profile of FSC experiments realizing Tammann's two-stage crystal nuclei development method for analysis of the nucleation behavior of PET. The sample was heated to 320 °C and isothermally held at this temperature for 0.5 s in order to obtain a relaxed melt and then cooled at a rate of 1000 °C/s to the temperature of intended nuclei formation, that is, to the nucleation stage. In this work, nucleation experiments were performed at temperatures between 75 and 135 °C, for time periods up to 10 000 s. Note that we observed vitrification of the melt of PET on cooling at 1000 °C/s at about 80 °C, that is, nucleation was performed at temperatures near and slightly higher than the glass transition temperature T_g . Then, the sample with a specific nucleation history was transitioned to the growth stage at 210 °C using an identical rate of 1000 °C/s, to allow isothermal crystallization for a period of 100 s. It has been tested in preliminary experiments that isothermal annealing of the relaxed melt at 210 °C for a period of 100 s, that is, of the PET melt which was directly cooled to the growth temperature, does not lead to crystallization. As such, it proves that crystal nucleation at 210 °C is very slow and the observed growth of crystals during annealing at 210 °C for 100 s in samples subjected to the temperature–time profile shown in Figure 1 is due to formation of nuclei in the nucleation stage.

Kinetics of Isothermal and Nonisothermal Crystallization. Prerequisite for analysis of crystal nucleation by Tammann's crystal nuclei development method is knowledge of the kinetics of both nonisothermal and isothermal crystallization of the polymer under investigation, in order to properly

design and interpret the two-stage nuclei development experiments. Half-times of primary crystallization of the PET grade of the present study have been measured as a function of temperature by interruption of the isothermal crystallization process after predefined crystallization time, and measurement of the fraction of formed crystals via their enthalpy of melting on subsequent heating; plotting the enthalpy of melting as a function of the crystallization time yields then conversion–time curves, used for the determination of crystallization half-times.

Figure 2 shows examples of such conversion–time curves obtained on isothermal melt crystallization at temperatures

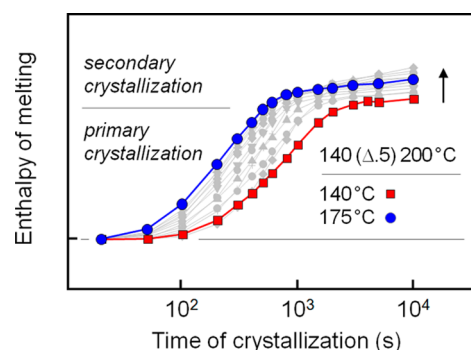


Figure 2. Enthalpy of melting after crystallization at different temperatures between 140 and 200 °C as a function of the crystallization time. The enthalpy of melting corresponds to the enthalpy of crystallization in the preceding crystallization-step, and its dependence on time yields information about the crystallization half-time.

between 140 and 200 °C. It can be seen that within the temperature range presented crystallization is fastest at 175 °C (blue circles) while it is slower at both higher and lower temperatures. The curves of Figure 2 reveal furthermore by the change of the slope the time-ranges of fast primary and slow secondary crystallization in the early and final stages of the crystallization process, respectively.¹⁰ The half-times of crystallization reported here refer to the primary crystallization process, and are shown in Figure 3 as a function of the crystallization temperature. As was already concluded from visual inspection of the conversion–time curves of Figure 2, the data of Figure 3 illustrate that melt-crystallization of the

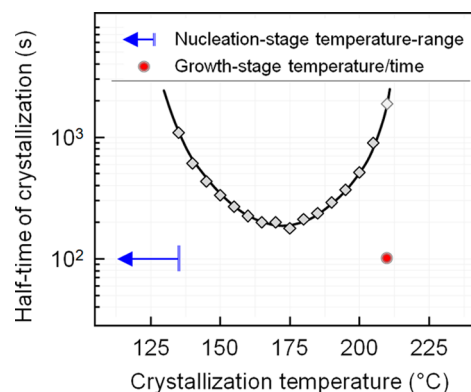


Figure 3. Half-time of primary crystallization as a function of temperature. The plot contains additional information about the temperature of nuclei formation and nuclei development/growth according to Tammann's two-stage crystal nuclei development method (see also Figure 1).

particular PET grade is fastest at around 175 °C which is in general agreement with data reported elsewhere.^{12,36} The minimum crystallization half-time is about 180 s, which also is in the wide range of data obtained on PET grades of different molar mass and synthesis routes.^{12,36–38} In addition to the crystallization half-time data, Figure 3 contains information about the range of temperatures at which it was attempted to gain data about the kinetics of crystal nucleation.

A requirement for application of Tammann's two-stage nuclei development method is nuclei formation at temperatures at which crystal growth ideally is completely absent or very delayed with respect to nuclei formation, in order to have available a rather large time interval for nuclei formation not superimposed by their growth. At temperatures lower than 135 °C the crystallization half-time rapidly increases with decreasing temperature with this temperature range selected for analysis of the kinetics of crystal nucleation (see horizontal blue arrow in Figure 3). The red circle indicates the temperature of the crystal growth stage. For the case of melt-crystallization in which the relaxed melt is directly transferred from a temperature higher than the equilibrium melting temperature to 210 °C, the formation of crystals is not observed with 100 s since nuclei are missing. If the formation of a large number of nuclei in the isothermal nucleation-stage occurs, subsequent crystallization at 210 °C will be enhanced such that crystal formation can be detected within the preselected crystallization time of 100 s.

Knowledge about the kinetics of nonisothermal melt-crystallization of the particular PET grade used is required since it must be assured that crystals and nuclei are not already forming during cooling the relaxed melt to the nucleation stage. Figure 4 is a plot of the enthalpy of crystallization of the specific

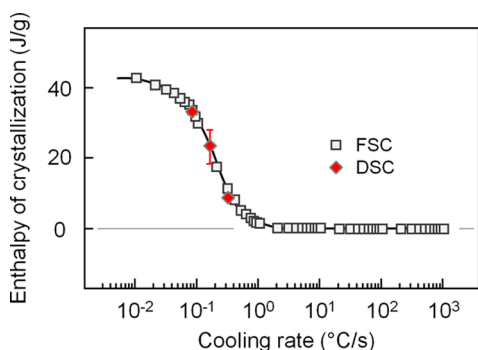


Figure 4. Enthalpy of crystallization as a function of the cooling rate. Data have been measured by FSC (squares) and by DSC (red diamond symbols).

PET used in this work as a function of the cooling rate. FSC analysis of the enthalpy of crystallization of the crystals forming during cooling the polymer at different rates relied on the measurement of their enthalpy of melting during subsequent heating since detection of crystallization peaks in the cooling scans was impossible due to the large noise-to-signal ratio. The obtained absolute enthalpies of crystallization were converted into specific enthalpies of crystallization using data collected with a DSC and employing samples of known mass (red diamond symbols). The data of Figure 4 reveal that cooling the PET grade of this study at rates faster than about 1 °C/s suppresses crystallization, with this value being in line with earlier reports in which critical cooling rates to suppress

crystallization of less than 1.6 °C/s (100 °C/min)³³ and about 2³⁴ and 10 °C/s¹² were suggested.

For the design of the nuclei development experiment according to Tammann, besides proof of absence of crystallization during cooling the melt, it must furthermore be warranted that homogeneous nuclei are not developing during both cooling the melt to the nucleation stage and heating to the growth stage; only then the crystallization behavior at the growth stage can be correlated to isothermal nuclei formation during the low-temperature nucleation stage. In this work, the melt has been cooled at a rate of 1000 °C/s to the nucleation stage and then heated at an identical rate to the growth stage, after prior isothermal nuclei formation. Absence of nuclei formation during cooling to the nucleation stage and heating to the growth stages has been proven by comparing the crystallization kinetics of a sample which was cooled directly from 320 °C to the growth temperature of 210 °C, with that of a sample which, prior isothermal crystallization at 210 °C, was cooled at 1000 °C/s to below T_g and reheated at the same rate. The observed data did not reveal an acceleration of the crystallization process due to the short-time low-temperature treatment. Summarizing, under the here employed conditions the prerequisites for applying Tammann's two-stage nuclei development method are fulfilled for PET. These are (i) the nucleation rate at the development temperature is negligible compared to the nucleation rate at the nucleation stage; (ii) the growth rate at the nucleation stage is orders of magnitude lower than the nucleation rate; (iii) the thermal treatment at cooling and heating rates of 1000 K/s does not lead to formation of nuclei without an isothermal treatment at the nucleation stage.

Application of Tammann's Two-Stage Crystal Nuclei Development Method. Figure 5 shows a set of FSC curves of

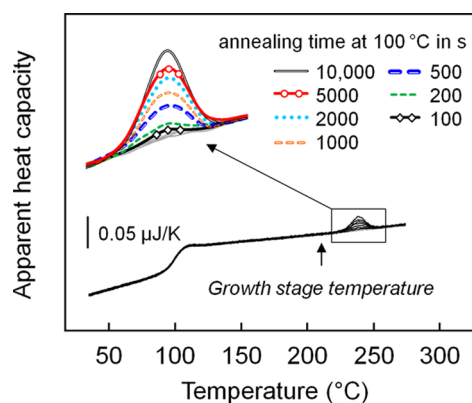


Figure 5. Apparent heat capacity of PET of different thermal history as a function of temperature, obtained on heating at 1000 °C/s. The relaxed melt was cooled at a rate of 1000 °C/s to the nucleation-stage temperature of 100 °C and annealed for different time, as indicated in the legend. After annealing, the samples were heated at 1000 °C/s to the growth-stage temperature of 210 °C and annealed for 100 s. The heating scans were then recorded after recooling to −60 °C. The inset shows the melting peak at a different, enlarged scale.

PET samples of different nucleation history, obtained on heating at 1000 °C/s; in Figure 1, in which the temperature–time profile of Tammann's nuclei development experiments was shown, such heating scans were labeled “analysis scan”. In the example of Figure 5, the relaxed melt was cooled at a rate of 1000 °C/s to the nucleation-stage temperature of 100 °C and annealed for different time between 10 and 10 000 s. After

annealing, the samples were heated at 1000 °C/s to the growth-stage temperature of 210 °C and allowed to crystallize for 100 s. The heating scans were then recorded after recooling to −60 °C.

The FSC curves of Figure 5 show with the heat-capacity increment the glass transition at around 100 °C and then, at about 240 °C, an endothermic melting peak for samples which were annealed at 100 °C longer than 100 s. Annealing shorter than 100 s at 100 °C did not lead to crystallization within 100 s at 210 °C, and the FSC curves of such samples do not show a melting peak (see gray curves in the inset). Though the area of the melting peak in the FSC curves of the samples which were annealed 100 s or longer at 100 °C is rather small, there is detected a systematic increase of its area with the time of prior annealing at the nucleation-stage temperature of 100 °C (see inset). The increase of the melting-peak area, that is, of the enthalpy of melting with the time of prior annealing at 100 °C is caused by an increasing number of homogeneous crystal nuclei at the nucleation-stage temperature. As such, the evolution of the area of the melting peak in the analysis scans recorded subsequent the two-stage crystal nuclei development experiment provides an information about the kinetics of crystal nucleation, further discussed below.

The set of FSC heating curves shown in Figure 5 is representative for two-stage crystal nuclei development experiments with the nucleation-stage temperature being between 75 and 100 °C. In this range of nucleation temperatures, the formation of crystals was not detected within the frame of the maximum annealing time of 10 000 s but the formation of crystal nuclei which accelerated the crystallization process at 210 °C. At higher nucleation-stage temperatures, within the window of analyzed annealing times up to 10 000 s, both the formation of nuclei and their growth at identical temperature was allowed, as is demonstrated with the bottom set of FSC heating curves in Figure 6. The relaxed melt was cooled at a rate of 1000 °C/s to 125 °C and then annealed for different time as is indicated in the legend, before recooling to −60 °C and recording of the analysis heating scan. The heating curves of samples annealed for periods of time less than 500 s do not show a melting peak which would indicate formation of crystals. If the annealing time, however, is increased to 500 s or longer, then a melting peak is detected with its area increasing with annealing time, providing information about the progress and the kinetics of crystallization, as was also demonstrated with Figures 2 and 3. Melting of crystals formed at 125 °C occurs well below 200 °C, as it is assigned to the low-temperature part of the observed double melting peak. However, heating at the selected rate of 1000 °C/s allows reorganization of the initially formed crystals which then melt around 200 °C (the high-temperature part of the double melting peak).^{39,40}

In the center part of Figure 6 is shown an FSC heating curve of a PET sample which initially was cooled from 320 °C at a rate of 1000 °C/s to 125 °C and annealed/crystallized for 10 000 s; the corresponding melting curve was shown in the lower part of Figure 6. Then, after crystallization, the semicrystalline sample was heated at 1000 °C/s to 210 °C, and held at this temperature for 0.01 s, before recooling to −60 °C. The subsequently recorded heating scan does not show a melting peak, which leads to the conclusion that all crystals formed during annealing at 125 °C for 10 000 s first reorganized and then melted during heating to 210 °C at a rate of 1000 °C/s. This experiment was performed for all samples which crystallized during annealing at the nucleation-

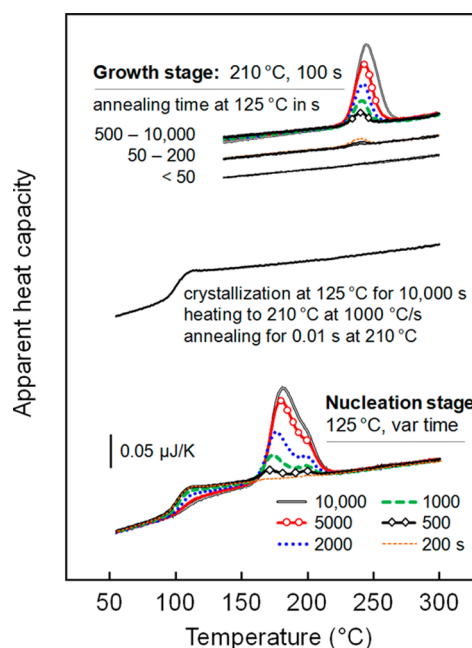


Figure 6. Apparent heat capacity of samples of different thermal history as a function of temperature, obtained on heating at 1000 °C/s. Bottom set of curves: The relaxed melt was cooled at a rate of 1000 °C/s to 125 °C and annealed/crystallized for different time, before recooling to −60 °C, and subsequent collection of the shown FSC curves. Depending on the annealing time, the FSC curves show an endothermic peak which is due to melting of crystals formed at 125 °C. Center curve: The relaxed melt was cooled at a rate of 1000 °C/s to 125 °C and annealed/crystallized for 10 000 s; the melting of crystals formed at 125 °C is shown with corresponding double-line black curve in the bottom data set. Then, after crystallization, the semicrystalline sample was heated at 1000 °C/s to 210 °C, and held at this temperature for 0.01 s, before recooling to −60 °C. The afterward obtained shown FSC heating curve does not show melting, indicating that all crystals melted on the transfer of the system from 125 to 210 °C. Top set of curves: The relaxed melt was cooled at a rate of 1000 °C/s to 125 °C and annealed/crystallized for different time. Subsequent the nucleation/crystallization step at 125 °C, the samples were heated at 1000 °C/s to 210 °C, and held at this temperature for 100 s, to allow growth of nuclei. As before, the samples were then recooling to −60 °C, to perform the shown final analysis heating scan.

stage temperature, in order to ensure that the samples did not contain crystals after the transfer to the growth-stage temperature.

In the top part of Figure 6, finally, are shown three sets of FSC heating curves obtained after the two-stage nucleation and growth experiment. Prior heating, the relaxed melt was cooled at a rate of 1000 °C/s to 125 °C and annealed/crystallized for different time as is indicated at the left-hand side of the various curves. Subsequent the nucleation/crystallization step at 125 °C, the samples were heated at 1000 °C/s to 210 °C, and held at this temperature for 100 s, to allow crystal growth. If annealing at 125 °C was performed for periods of time less than 50 s then there is not observed crystallization at 210 °C within 100 s, as is concluded from the absence of melting in the analysis scan (see bottom set of curves). If the time of annealing at 125 °C is between 50 and 200 s then there is detected formation of rather low amount of crystals as is seen by the appearance of small melting peak around 240 °C (center set of curves). It is important to note that during annealing at 125 °C for 200 s, or shorter time, crystals did not form (see also

the set of curves in the lower part of Figure 6), that is, crystallization at 210 °C is based on the formation of crystal nuclei at 125 °C only. However, if the annealing time at 125 °C exceeds 200 s, then nuclei grow to crystals during the nucleation stage and melt around 200 °C (see bottom part of Figure 6). Heating of such samples to 210 °C followed by annealing for 100 s reveals a tremendous increase of the overall crystallization rate, as is detected with the large melting peaks in the analysis scans in the upper set of curves in the top part of Figure 6.

Data as were shown in Figure 6 are representative for experiments with the nucleation-stage temperature being between 105 and 135 °C. In the early stage of annealing there occurs nuclei formation which then is followed by their growth to crystals on extended annealing; at nucleation-stage temperatures lower than 105 °C, only formation of nuclei was observed within 10 000 s but no growth was detected. The qualitatively different crystallization behavior/kinetics after the transfer of systems initially containing either only nuclei, or nuclei and crystals to the growth-stage temperature is quantified with Figure 7. It shows the enthalpy of crystallization

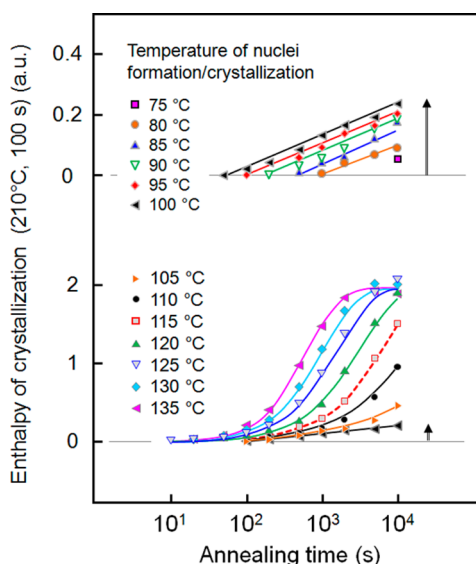


Figure 7. Enthalpy of cold-crystallization at 210 °C for 100 s as a function of the time of annealing at different nucleation-stage temperatures, as indicated in the legend. In the upper and lower parts are shown data obtained on PET with the nucleation-stage temperature being between 75 and 100 °C and between 105 and 135 °C, respectively. The data set related to nucleation at 100 °C (black triangles) is shown in both parts of the Figure, in order to illustrate the different maximum enthalpy of crystallization during annealing for 100 s at 210 °C, after annealing below and above 100 °C for 10 000 s.

at 210 °C for 100 s as a function of the time of annealing at different nucleation-stage temperatures, as indicated in the legend. In the upper part are shown data obtained on PET with the nucleation-stage temperatures being between 75 and 100 °C, which contained only nuclei at the end of the nucleation stage. In the lower part of Figure 7, correspondingly, are shown data obtained after annealing between 105 and 135 °C, which then contained nuclei or crystals at the end of the low-temperature annealing step, depending on the annealing time. The data set related to nucleation at 100 °C (black triangles) is shown in both parts of the Figure, in order to illustrate the

different maximum enthalpy of crystallization after annealing below and above 100 °C for 10 000 s.

Regarding nucleation experiments performed between 75 and 100 °C, the crystallization-enthalpy data of Figure 7 reveal that a decrease of the nucleation-stage temperature in the discussed temperature-window is connected with a decrease of the nuclei-formation rate. This dependence of the nucleation rate on temperature is expected since it is known that homogeneous nucleation is often fastest slightly higher than T_g (≈ 75 °C for PET), and decreasing with decreasing temperature.^{11,26,27}

Nuclei formation at temperatures higher than 100 °C is accompanied or rapidly followed by crystal growth, complicating the analysis of its kinetics and hiding the expected decrease in nucleation rate after passing the maximum with increasing temperature. Though crystals forming at the nucleation-stage temperature melt during the transfer of the system to the growth stage, there is observed a distinct increase of the crystallization rate which is proportional to the degree of crystallinity. The link between the crystal fraction formed during annealing at low temperature and the cold-crystallization kinetics at 210 °C is emphasized with Figure 8. It shows with

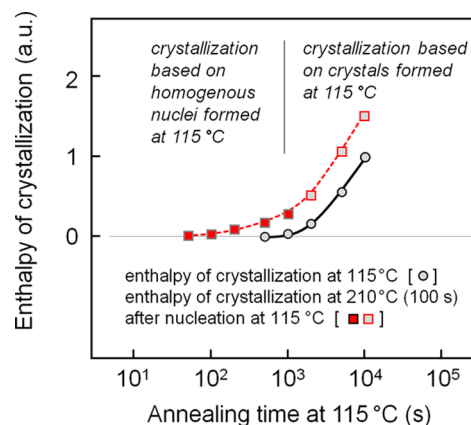


Figure 8. Enthalpy of cold-crystallization of at 210 °C for 100 s as a function of the time of annealing at 115 °C (squares, red dash-line), and enthalpy of melt-crystallization at 115 °C as a function of the crystallization time (circles, black solid line).

the squares and dashed line the enthalpy of cold-crystallization at 210 °C for 100 s as a function of the time of prior annealing at 115 °C (see also the square symbols and dashed line in the bottom part of Figure 7), and with the circles the enthalpy of melt-crystallization at 115 °C as a function of the crystallization time. For samples annealed at 115 °C and then cold-crystallized at 210 °C for 100 s, it is observed that annealing shorter than about 1000 s is connected with an only minor increase of the crystallization rate at 210 °C. In this time interval, crystallization is not detected at 115 °C, that is, the increase of the cold-crystallization enthalpy at 210 °C is due to nuclei which formed at 115 °C, similar as in all experiments related to the data sets in the top part of Figure 7. In contrast, if the annealing time at 115 °C exceeds 1000 s then there is observed a tremendous increase of the crystallization rate at 210 °C, which can be correlated to the prior formation of crystals at the nucleation-stage temperature, quantified with the circles in Figure 8.

■ FINAL DISCUSSION AND CONCLUSIONS

In the present work a first successful attempt has been made to apply Tammann's two-stage crystal nuclei development method for analysis of homogeneous crystal nucleation in the specific case of PET. Tammann's two-stage crystal nuclei development method includes fast cooling of the relaxed melt to low temperature to allow isothermal formation of homogeneous nuclei as a function of time, followed by heating of the system to elevated temperature where the nuclei, or remnants of them, can grow to detectable sizes. Though the experimental approach of Tammann to obtain data about the kinetics of crystal nucleation has recently been applied for several polymers, reliable data about the thermodynamic stability of nuclei are not available yet; note that according to the classical nucleation theory, formation of crystal nuclei of supercritical size is connected with a decrease of the free enthalpy of the system, with the individual nuclei then possessing a thermodynamic stability limit. However, since the total enthalpy of nuclei formation is low, both their development during annealing and disappearance upon heating cannot directly be measured by calorimetry.

It is experimentally proven that the formation of nuclei at low temperature accelerates cold-crystallization at elevated temperature. However, it is an open question whether the nuclei formed at low temperature can be transitioned to the growth temperature, or whether this heating-step is connected with a change of their structure and morphology. Depending on the heating rate applied, the nuclei may melt and disappear on heating, reorganize by growth and increase their stability, or even may be superheated and maintain metastability for a certain period of time.

In order to shed further light into the stability of crystal nuclei, Tammann's nuclei development approach has been modified in extension to earlier work such that not only nuclei but also crystals with measurable latent heat were formed at the nucleation-stage temperature. These crystals were then employed to probe the upper limit of the thermal stability of homogeneous nuclei formed at identical temperature. In the example-experiment of Figure 6, in which first nuclei and then also crystals were formed at 125 °C, subsequent heating revealed melting of the crystals at temperatures below 200 °C. With the justified assumption that nuclei with a less favored surface-to-volume ratio are of lower stability than crystals it is concluded that all nuclei are melting during the transfer to the selected growth-stage temperature of 210 °C. This notwithstanding, the cold-crystallization rate increases proportional to the annealing time at low temperature, confirming the kept link between the time-dependent nucleation density at 125 °C and the crystallization rate at an almost 100 °C higher temperature. It is therefore assumed that melting of the crystal nuclei on their transfer from the nucleation stage to the growth stage is as incomplete as the melting of crystals, preserving a not completely disordered liquid/melt and allowing very rapid reformation of slightly larger and more stable nuclei. The data of Figure 7 suggest that the nucleating effect of homogeneous nuclei is maintained at an even 130 °C higher temperature than their formation temperature; for example, it has been shown that nuclei formation at 80 °C accelerated the cold-crystallization at 210 °C.

As evidenced for PET above, nuclei melt/disorder on the way to the development temperature. Then there may be expected self-seed effects in analogy to numerous performed

crystallization experiments starting with a melt containing incompletely destroyed crystals.⁴¹ For such a melt memory effect, one would expect that with higher heating rate for the transfer from the nucleation stage to the growth stage the nucleating effect could survive to higher development temperatures. However, this possibility was disproven by just the opposite behavior of PCL nuclei.²⁸

In order to explain all these observations we propose a new model explaining the stability of polymer nuclei on heating, namely, a melting/disordering–reorganization process with continuously increasing size and stability of the nuclei on heating, similar to the melting–recrystallization processes seen for many polymer crystals. Such a complex reorganization process would straightforward explain the increase of the crystallization rate, even at highly elevated temperature.

For small molecules it is assumed that overcritical nuclei may grow on the way from the nucleation to the development temperature, keeping overcritical size all the time. For polymers such process seems not possible since the nuclei formed at low temperature are so small and unstable that they will melt/disorder a few ten °C above the nucleation temperature. This must occur since even the larger and more stable crystals with detectable heat of fusion melt below the development temperature as was shown with the data in Figure 6. But similar to the melting–recrystallization process of polymer crystals the nonisotropic melt, just after disordering of the nucleus, may reform a slightly more stable nucleus within very short time. Only at heating rates above 200 000 K/s such a process seems to be suppressed as was shown for PCL.²⁸ The presented data on PET nucleation, crystallization and melting strongly support such a melting/disordering recrystallization process for crystal nuclei in polymer cold crystallization. To the best of the authors' knowledge, such a process was not yet proposed.

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Notes

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