Insertion-Crystallization-Induced Low-Temperature Annealing Peaks in Melt-Crystallized Poly(l-Lactic Acid)

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Annealing of poly(l-lactic acid) (PLLA) at temperatures lower than the temperature of primary melt-crystallization leads to appearance of distinct low-temperature annealing peaks in subsequently recorded calorimeter heating scans. Reason is continuation of crystallization by growth of crystals of lower stability as formed during primary crystallization. The assignment of low-temperature annealing peaks to crystallization is based on a robust analysis of the decrease of the heat capacity of the semicrystalline structure slightly above the glass transition temperature and its correlation with the corresponding enthalpy of crystallization. Comparison of the form of annealing peaks with classical enthalpy-recovery peaks obtained on devitrification of the glassy amorphous phase of semicrystalline PLLA supports the interpretation regarding the origin of annealing peaks.

1. Introduction

Melt-crystallization of polymers is a multistep process proceeding via crystal nucleation followed by growth.[1–3] In case of poly(l-lactic acid) (PLLA), formation of lamellae is expected which arrange within spherulites as typical superstructure of crystals and surrounding amorphous phase.[4–6] Both crystal nucleation and growth exhibit a distinct temperature dependence such that nucleation is fastest at 80–100 °C,[6–9] i.e., slightly above $T_g$, while the crystal-growth rate shows maxima at about 120 and 110 °C[5,6,10,11] associated with the formation of different crystal polymorphs. Crystallization at temperatures higher than about 120 °C leads to exclusive growth of α-crystals, while at temperatures lower about 100 °C formation of disordered ω'-crystals is observed.[12,13] In between these temperatures, growth of both phases may be detected.

Primary crystal growth, which may considered finished after a space-filled spherulitic superstructure is evident, often is followed by secondary crystallization.[14,15] Such secondary crystallization involves a stabilization of crystals formed on primary crystallization, e.g., by thickening and internal perfectioning.[16,17] Crystal stabilization often, though not throughout, is observed at the temperature of primary crystallization or at higher temperatures. It proceeds at a much lower rate than primary crystal growth and causes an upward shift of the melting temperature.[18–20] Another process, which may occur at temperatures lower than the primary crystallization temperature, is the growth of smaller crystals in regions not occupied by the initially grown lamellae.[21] Such regions may be located inside the lamellar stacks,[22,23] then often called insertion crystallization,[21] or in regions where crystallization at higher temperature was not possible.[24] Again, formation of smaller crystals in inter-lamellar regions occurs at lower temperature than primary crystallization since only then stability criteria (critical size of nuclei) favor their development. Typically, insertion crystallization involving growth of small crystals at temperatures lower than the primary crystallization temperature, thus being of lower stability, is connected with additional low-temperature melting events on subsequent heating, often denoted as so-called annealing peaks.[25,26] Note, similar small melting peaks, sometimes also called annealing peaks, may be observed after low-temperature isothermal crystallization,[27] with their smallness caused by melting, immediately followed and superimposed by recrystallization (melting–recrystallization–remelting).[28,29]

Melt-crystallization of polymers often is paralleled by the formation of a rigid amorphous fraction (RAF). The development of an RAF is caused by the covalent linkage of crystals with the surrounding amorphous phase and the associated constraint

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of adaption of any number of microconformations of amorphous chain segments near the crystal surface.\textsuperscript{[30–36]} The RAF often develops at the crystallization temperature, and immediately vitrifies as a result of the change of the global semicrystalline morphology and not during cooling to below a specific temperature.\textsuperscript{[37–40]} In other words, the RAF associated with a particular crystal is in an immobilized state as long as this crystal exists.\textsuperscript{[41]} Furthermore, the RAF related to a specific crystal is expected depending on both the temperature of primary crystallization and subsequent structural reorganization as these parameters control the crystal morphology/surface structure.\textsuperscript{[42–46]}

Regarding the RAF of semicrystalline PLLA, numerous studies are available in the literature.\textsuperscript{[47–56]} Though quantitative comparisons are difficult, it seems that RAF-formation in PLLA depends on the crystallization temperature, such that on crystallization at temperatures higher than about 135 °C no RAF develops.\textsuperscript{[47,51]} In contrast, measurable amount is detected in particular after crystallization at temperatures lower than 120 °C, perhaps related to the \( \alpha/\alpha' \)-crystal polymorphism and the associated poorer crystal structure and morphology.\textsuperscript{[50,51]} In a similar temperature range, another related effect is observed for PLLA. Above about 115 °C, PLLA chains can perform helical jump motions within the crystals (crystal mobile), while this motion is not observed below this temperature (crystal fixed).\textsuperscript{[57]} The formation of RAF, probably requires fixation of the polymer chains in the crystal and is therefore only observed at temperatures where the PLLA crystals are in the fixed state.\textsuperscript{[38]} This is in agreement with the observation that for PLLA crystallized at high temperature, significant RAF is detected at \( T_g \), thus being formed during slow cooling. Possible reasons previously discussed are low-temperature vitrification of rigid amorphous structure developed during high-temperature crystallization, in line with the above said, or nondetectable crystallization during cooling connected with RAF formation.\textsuperscript{[51]}

In this study, we provide experiments showing that low-temperature annealing of PLLA crystallized at high temperature causes insertion crystallization, quantified by the area of annealing-induced enthalpy peaks in subsequently recorded calorimeter-heating scans and the corresponding decrease of the heat capacity slightly above \( T_g \). The experimental approach of correlating the enthalpy of crystallization with the vibrational heat capacity slightly above \( T_g \), we consider as a rather robust technique for estimation of the solid content. It does not require an elaborate determination of the heat-capacity step at \( T_g \) due to needed tangent constructions for extrapolating solid and liquid heat capacities from temperature-ranges outside the glass transition. The recently proposed origin of low-temperature annealing-induced enthalpic peaks in calorimeter heating scans, as being caused by insertion crystallization,\textsuperscript{[46]} but not relaxation of RAF developed at higher temperature is confirmed by an additional analysis of the form of these annealing peaks.\textsuperscript{[56,59–64]}

**2. Results and Discussion**

**2.1. Isothermal Primary and Secondary Crystallization**

Figure 1 shows the temperature–time profile of the initial melt-crystallization experiment at 140 °C. A rather high crystallization temperature of 140 °C was selected such to obtain crystals of high melting temperature and to have available a large temperature window, limited by \( T_g \) (60 °C) on the low-temperature side and the primary crystallization temperature (140 °C) on the high-temperature side, for subsequent low-temperature annealing experiments. Since crystal nucleation and growth of PLLA are slow at 140 °C, an additional nucleation step at 60 °C was inserted into the temperature–time profile. Though the nucleation rate is highest around 80–100 °C,\textsuperscript{[6–9]} the lower nucleation temperature of 60 °C is advantageous since nucleation and growth are well separated at this temperature. With the selected nucleation time of 300 s, formation of a sufficiently high number of nuclei and absence of crystal growth are warranted. For minimizing destruction of nuclei during their transfer to the crystallization temperature, a rather low transfer-heating rate of 100 K s\textsuperscript{-1} was used, in accord with results about heating-rate effects in Tammann’s two stage nucleation and growth experiments observed elsewhere.\textsuperscript{[9,55,66]} Crystallization at 140 °C was performed for time periods between 10\textsuperscript{3} and 10\textsuperscript{4} s, covering primary crystallization as well as secondary crystallization at identical temperature. After each crystallization experiment for a specific crystallization time, an analysis-heating scan was recorded allowing for estimation of the residual enthalpy of crystallization and the corresponding decrease of the heat capacity of the partially crystallized system. For accurate determination of heat-capacity differences, control-heating scans were recorded for re-estimation of the heat capacity of liquid/noncrystallized PLLA, effectively avoiding errors due to instrumental drift, in particular in experiments including long crystallization times.

As an example, Figure 2 shows fast scanning chip (FSC) analysis heating scans of PLLA crystallized at 140 °C for different periods of time, recorded using a rate of 500 K s\textsuperscript{-1}. The selected heating rate is sufficiently high to suppress cold-crystallization, and, as such, the observed enthalpy of melting \( \Delta h_m \) corresponds
to the enthalpy of crystallization \(\Delta h_c\) in the prior isothermal crystallization step. Though using an even higher heating rate is advantageous for increasing the signal/noise ratio, it is detrimental regarding thermal-lag effects, quantified elsewhere for the used instrument.[67–69] Data obtained on samples annealed at 140 °C for less than about 100 s reveal on subsequent heating the glass transition at around 68 °C, being slightly higher than typically observed in conventional differential scanning calorimetry (DSC) experiments.[70,71] due the higher heating rate,[72–74] and no further events. Annealing the sample longer than about 100 s permits crystallization as indicated with the melting event at temperatures close to 200 °C and the decrease of the heat-capacity step at \(T_g\) due to the reduced liquid fraction. The two vertical arrows at the melting peak (\(\Delta h_m\)) and at 90 °C \(c_p\) serve for illustration of quantification of the crystallization process, described in detail below.

With gray and blue coloring of curves, holding for crystallization times shorter and longer than 500 s, respectively, a qualitative change of the crystallization mechanism is indicated, associated with primary and secondary crystallization, as concluded from a plot of the enthalpy of crystallization as a function of the crystallization time, shown in Figure 3. Data points are averages of multiple measurements using different samples and sensors, for the sake of confirming reproducibility. Due to different sample masses, though only minor, absolute enthalpy values are different, and for this reason all data were normalized, based on the enthalpy of crystallization for 500 s (see blue arrow).

The measurements reveal the start of crystallization after about 100 s and completion of the primary crystallization step after around 500 s, with the rather fast crystallization caused by the prior nucleation step at 60 °C. Worth noting, melt-crystallization at 140 °C, with the crystallization temperature directly approached on cooling the quiescent melt, is much slower, with a crystallization half-time well above \(10^3\) s.[85,75] The slow and linear increase of the crystallization enthalpy with log time on crystallization longer than 500 s is assumed being related to crystallization stabilization.[16,17,76–82]

FSC curves, as exemplarily shown in Figure 2, are further analyzed regarding the crystallization-time dependence of the solid fraction above \(T_g\), conveniently derived from the heat capacity (see vertical arrow in Figure 2, denoted \(c_p\)). It is expected that \(c_p\) decreases as the enthalpy of crystallization increases during the crystallization process,[83,84] which is quantified with the data of Figure 4, showing the heat capacity at 90 °C as a function of the enthalpy of crystallization of PLLA at 140 °C. The different symbols represent analyses performed on different samples. Gray and blue colored symbols emphasize primary crystallization and secondary crystallization associated to crystal stabilization, respectively.

c_{\text{p,liquid}} decreases as the enthalpy of crystallization increases during the crystallization process,[83,84] which is quantified with the data of Figure 4, showing the heat capacity at 90 °C as a function of the enthalpy of crystallization at 140 °C. Again, both quantities are normalized allowing to show data obtained on different samples. Normalization of \(\Delta h_c\), again, was performed by dividing all data with the \(\Delta h_c\) value obtained on crystallization for 500 s, representing the approximate end of the primary crystallization process. Normalization of \(c_{\text{p,liquid}}\) values is based on the measured value of the heat capacity of liquid PLLA (\(c_{\text{p,liquid}}\)) at 90 °C and extrapolated value of the heat capacity of solid PLLA (\(c_{\text{p,solid}}\)), with the sample-mass effect considered by normalization with \(\Delta h_c\) (500 s).
corresponds either to the one-to-one transformation of liquid PLLA into crystals without formation of an RAF or, in case of formation of an RAF, to a constant ratio between crystallinity and RAF, as discussed in other studies.\cite{39,85}

### 2.2. Low-Temperature Annealing Below and Above the Glass Transition Temperature

Figure 5 shows the temperature–time profile of low-temperature annealing experiments performed below (blue) and above \( T_g \) (red). The pathways of nucleation and primary crystallization are unchanged compared to the experiments discussed above. Samples crystallized at 140 °C for 500 s were cooled at a rate of 1000 K s\(^{-1}\) to 100, 90, and 80 °C, where the previously formed PLLA crystals are in the crystal-fixed state, and isothermally annealed for different periods of time between 10\(^3\) and 10\(^4\) s. After annealing, analysis heating scans were recorded at rates of 500 and 1000 K s\(^{-1}\), for determination of \( \Delta h_c \) and \( c_p \) (90 °C) as a function of the annealing conditions. Note that compared to earlier studies of low-temperature annealing in poly(butylene terephthalate) (PBT)\cite{56} and poly(butylene succinate) (PBS),\cite{26} only a single annealing step at a preselected temperature was performed but not sequential annealing at different temperatures. For the sake of comparing the nature of the annealing peaks in the subsequently recorded heating scans, whether these are melting peaks or enthalpy-recovery peaks, PLLA was cooled after completion of primary crystallization at 1000 K s\(^{-1}\) to 50 °C, i.e., to below \( T_g \), and similarly annealed for up to 10\(^3\) s.

Low-temperature annealing at a temperature between \( T_g \) and the temperature of primary crystallization causes appearance of low-temperature annealing peaks in subsequently recorded heating scans and to a further decrease of \( c_p \) (90 °C). As an example, Figure 6 shows FSC heating scans recorded after primary crystallization of PLLA at 140 °C for 500 s and subsequent low-temperature annealing at 100 °C for different time. With increasing annealing time, the area of the annealing peak increases, and its maximum shifts to higher temperature. The onset temperature, in contrast, seems less affected. In other words, during isothermal annealing decreases the enthalpy of the system, as in any crystallization process. Simultaneously with the increase of the area of the annealing peak decreases the heat capacity above \( T_g \) which is shown at an enlarged scale in the inset.

The annealing-induced decrease of the heat capacity slightly above \( T_g \) indicates further solidification of system. Together with the observed decrease of the enthalpy, as detected with the annealing peaks, it is straightforward assuming that new crystals formed. Interpretation of the annealing peaks as being caused by relaxation of an RAF is contradicted by the suggestion of absence of RAF formation on crystallization at temperatures higher than 135 °C\cite{47,51} and the decrease of the heat capacity at 90 °C. RAF formation on annealing at 100 °C is not excluded as a reason for the decrease of \( c_p \) (90 °C), which, however, may only occur in conjunction with crystal formation. Quantification of the correlation between the increase of the enthalpy of crystallization during annealing and corresponding decrease of the heat capacity at 90 °C, i.e., increase of the solid fraction, is provided with Figure 7. Gray colored data refer to primary and secondary crystallization at 140 °C, discussed above with Figure 4, while yellow, orange, and red symbols represent data associated with low-temperature annealing at 80, 90, and 100 °C up to 10\(^4\) s, respectively, after completed isothermal primary crystallization at 140 °C. While it seems settled that further solidification of the system occurs during low-temperature annealing, a clear and unambiguous effect of the annealing temperature is not detected, requiring further, optimized experiments. However, the data suggest a slightly stronger decrease of \( c_p \) (90 °C) with increasing crystal fraction (see red vs gray line). Reasons may be RAF formation in parallel to crystal formation or, more likely, a lower specific enthalpy of crystallization of crystals forming during low-temperature annealing. While crystallization at 140 °C leads to formation of \( \alpha \)-crystals, insertion crystallization at temperatures equal to or lower than
100 °C causes formation of α'-crystals with a lower specific enthalpy of crystallization of the bulk crystal phase.\(^{[59–63,89]}\) Isothermal crystallization experiments (not shown) were performed between 120 and 140 °C on one side, and between 80 and 100 °C on the other side, yielding α- and α'-crystals, respectively. Regardless of low-temperature nucleation steps, there was observed a strict linearity of the dependence of the solid fraction on the crystallization enthalpy, with different slopes according to the polymorphism-controlled different specific enthalpy of crystallization of the bulk crystal phase in these two temperature ranges, confirming an earlier crystallization experiment reported elsewhere.\(^{[88]}\)

It has been proposed for several polymers\(^{[59–63,89]}\) including PLLA,\(^{[56]}\) that endothermic annealing peaks in calorimeter heating scans, performed after low-temperature annealing of systems crystallized at higher temperature, may (partially) be caused by relaxation of RAF. In other words, the annealing peaks are in this case interpreted as enthalpy-recovery peaks. With the rather high crystallization temperature of 140 °C, and rapid cooling to annealing temperatures of 100 °C and lower, inhibiting nonisothermal secondary crystallization, RAF formation is considered unlikely. Even if there forms minor amount of RAF, denoting the observed annealing peaks as melting, rather than enthalpy-recovery peaks, however, is further supported by comparing the annealing-time evolution of the shape of endothermic peaks observed after annealing above and below \(T_g\).

Figure 8 shows sets of FSC heating curves recorded after annealing PLLA at 100 °C (top) and 50 °C (bottom) for different periods of time, as indicated in the legend. Prior annealing, all samples were crystallized for 500 s at 140 °C, and cooled at a rate of 1000 K s\(^{-1}\) to the respective annealing temperature. Worth noting, annealing semicrystalline PLLA for 10\(^4\) s at 50 °C, i.e., in the glassy state, allowed completion of enthalpy relaxation and caused crystal nucleation and growth, yielding a small endothermic peak in the heating scan at around 120 °C. This observation confirmed an earlier study of the nucleation kinetics in glassy PLLA,\(^{[90,91]}\) however, with the corresponding heating scan not shown in Figure 8, for the sake of clarity. Regarding the presentation of FSC curves obtained on samples annealed at 100 °C, it is important to report that curves were vertically shifted relative to each other, such to emphasize that the onset of the endothermic event hardly is a function of the annealing time. Referring to Figure 6, annealing at 100 °C causes further solidification of the system and a decrease of heat capacity above \(T_g\). The corresponding offset between the various heating curves was removed in Figure 8 by minor vertical shifting, for improved illustration of the annealing-time evolution of the annealing peak. Comparing the annealing-time evolution of endothermic peaks observed after annealing semicrystalline PLLA below and above \(T_g\) reveals that in both cases the peak maximum shifts to higher temperature but that the peak onset temperature remains approximately unchanged only in case of annealing above \(T_g\) (see upper set of curves). With increasing time of annealing the glass, devitrification on heating occurs at increasingly higher temperature, with the shift of the onset of the glass transition considered as a measure of the kinetic stability of the densified glass;\(^{[93]}\) even stronger effects were observed for vapor-deposited ultra-stable glasses.\(^{[93]}\)

Following the evaluation presented in ref. [86], the annealing-time dependence of the temperature of the maximum of the annealing peak is analyzed, shown in Figure 9 for the four different annealing temperatures, respectively. Regarding the annealing experiments performed between 80 and 100 °C (yellow, orange, and red data points), the observed linear dependency on the logarithm of the annealing time is in qualitative agreement with observations,\(^{[86,94–96]}\) focusing on the analysis of the kinetics of insertion crystallization. Most striking, however, is the different behavior when comparing the annealing experiments performed between 80 and 100 °C with the annealing experiment performed at 50 °C (blue data points). Despite also for the latter a linear increase of the “annealing-peak temperature” with the logarithm of the annealing time is observed, the slope is much lower than on annealing at higher temperature.
3. Conclusions

The study is considered a contribution to the ongoing debate of the origin of low-temperature endothermic peaks in DSC heating scans, observed after primary crystallization at rather high temperature, followed by annealing at lower temperature. Such endothermic peaks may be related to prior enthalpy relaxation of a glassy rigid amorphous fraction or continuation of the crystallization process, involving the formation of new, small crystals. To further shed light onto the question whether annealing peaks are caused by enthalpy relaxation or continued crystallization, PLLA has been crystallized at conditions not causing for- mation of an RAF at the temperature of primary crystallization. Though formation of a minor RAF during subsequent cooling is possible, its determination seems complicated. An analysis of the RAF via measurement of the heat-capacity increment at \( T_g \) and the enthalpy-based crystallinity does not yield a final answer because the specific enthalpy of melting of PLLA crystals is not precisely known (see Table 2 in ref. [7]).

In this study, we present three results, which provide further evidence/indications that the endothermic peaks appearing after annealing PLLA at a lower temperature than primary crystallization occurred are due to melting of crystals formed during annealing.

i. Figure 7 shows the decrease of the heat capacity above the glass transition (at 90 °C) with annealing time, indicating continued solidification of the material. Such solidification may be caused by the unlike processes of isothermal vitrification of an existing RAF or new-RAF formation in conjunction with its vitrification at the annealing temperature. In no case, the decrease of the heat capacity can be caused by enthalpy relaxation of a preexisting RAF. Furthermore, in case of an isothermal vitrification of an RAF, on heating an upward step in the heat capacity is expected near the annealing temperature, and not an endothermic peak. This leaves continued crystallization at the annealing temperature and melting at the temperature of the annealing peak as the only reasonable explanation of the observed behavior. Despite crystallization-caused formation of RAF and its vitrification during isothermal annealing cannot be excluded, enthalpy relaxation of such RAF, as a rule, cannot occur at its temperature of formation.

ii. The endothermic peaks after annealing at temperatures above the glass transition (at 80, 90, and 100 °C) do not show a shift of their onset with annealing time, as shown in Figure 8. In contrast, the onset of the enthalpy-relaxation peak after annealing below \( T_g \) exhibits an easy to recognize shift to higher temperatures with annealing time. These observations, as well as (iii), point to different origins of the annealing and relaxation peaks, supporting the view that the annealing peaks are caused by continued crystallization.

iii. Despite the constant peak onset temperatures for annealing at 80, 90, and 100 °C (ii), the maximum of all peaks shifts with annealing time to higher temperatures. Figure 9 shows the time dependencies, which indicate an essentially linear increase with the logarithm of annealing time. Again, the shift for the peaks assumed to be due to crystallization is much stronger than the shift for the enthalpy relaxation peak, indicating different origins for both.

As such, we summarize as follows: Annealing PLLA at temperatures lower than the temperature of primary melt-crystallization leads to the appearance of distinct low-temperature annealing peaks in subsequently recorded calorimeter heating scans. The reason is a continuation of crystallization by the growth of crystals of lower stability as formed during primary crystallization, similar to PBT [82,86] or PBS [26]. The assignment of low-temperature annealing peaks to insertion crystallization is based on a robust analysis of the heat capacity of the semicrystalline structure slightly above the glass transition temperature and its correlation with the enthalpy of crystallization. Comparison of the form of annealing peaks with classical enthalpy-recovery peaks obtained on devitrification of the glassy amorphous phase of semicrystalline PLLA, as well as of the annealing-time dependence of the peak temperatures supports the interpretation regarding the origin of annealing peaks.

4. Experimental Section

The study was performed using a FSC calorimeter Flash DSC 1 (Mettler-Toledo, Switzerland), allowing for precise adjustment of nucleation and crystallization pathways due to its high cooling capacity in combination with the use of small samples [97]. Samples used had a mass between, roughly, 50 and 100 ng and were placed in the center of the heatable sec- tion of the FSC chip membrane where the temperature-distribution was homogenous. [98] Gold leaf of negligible addenda heat capacity was em- ployed, attached to the sensor membrane by a thin layer of silicone oil, as a mechanically decoupled substrate for the samples. This minimized straining the sensor membrane during cooling and heating due to the unavoidable mismatch between the thermal expansion of the sample and the sensor membrane. [99] PLLA homopolymer (d-isomer content <1.5%) with a molar mass and melt-flow rate of 120 kDa and 8 g/(10 min) (210 °C/2.16 kg), respectively, was obtained from Corbion Purac [100,101]. Details of the thermal protocols are provided below.
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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
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