Electronic Supplementary Material (ESI) for Soft Matter.

Distinct dynamics of structural relaxation in the amorphous phase of poly(L–lactic acid) revealed by quiescent crystallization

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Electronic supporting information

E.S.I. 1: RAF content for various theoretical enthalpies of melting of PLLA

Largely different values are reported in the literature for the theoretical enthalpy of melting of PLLA. Righetti et al. [1] summarized that the values proposed in the literature for the theoretical enthalpy of melting of a 100% crystalline PLA range between 82 and 203 J/g, because in most cases, a direct link with the crystalline α'- or α–form has not been considered. In the **Table SI 1** are given, for semi–crystalline PLLA crystallized from the melt during 600 minutes, the values of X_c and X_{RAF} calculated by using different values of $\Delta H_m°$ mentioned in [1]. It is observed that $X_c + X_{MAF}$ could exceed 100 % for $\Delta H_m°$ = 82 J/g and $\Delta H_m°$ = 93 J/g when crystallizing at 149 °C, although $\Delta H_m°$ = 93 J/g gives consistent values for X_c and X_{RAF} when crystallizing at 89 °C. On the other hand, $\Delta H_m°$ = 203 J/g leads to X_c = 23 % when crystallizing at 89 °C, which is hardly consistent with the maximum degree of crystallinity usually reported for PLLA either from calorimetric techniques or X–Ray diffraction.

In the present study, we used the temperature dependence of $\Delta H_m°$ proposed by Righetti et al. [1], which leads to $\Delta H_m°$ = 111.1 J/g for α'–crystals melting at T_m = 160 °C and $\Delta H_m°$ = 149.7 J/g for α–crystals melting at T_m = 200 °C. In this approach, the polymorphism of PLLA is considered, which is of interest when performing FSC since the scanning rate in FSC is high enough to prevent any kind of reorganization of the α'–form into the α–form. Uncertainties on X_c, X_{MAF}, and X_{RAF} are obtained from reproducibility, but also include any error related to the choice of the baseline for the calculation of both ΔCp and ΔH_m.

Table SI 1: X_c and X_{RAF} for various values of theoretical enthalpy of melting.

		This article		$\Delta H_m°$ = 82 J/g		$\Delta H_m°$ = 93 J/g		$\Delta H_m°$ = 203 J/g	
PLLA	X_{MAF} (%)	X_c (%)	X_{RAF} (%)	X_c (%)	X_{RAF} (%)	X_c (%)	X_{RAF} (%)	X_c (%)	X_{RAF} (%)
T_c = 89 °C	43 ± 2	42 ± 4	15 ± 6	57 ± 2	0 ± 6	50 ± 2	7 ± 6	23 ± 2	34 ± 6
T_c = 149 °C	46 ± 2	48 ± 4	6 ± 6	89 ± 2	/	78 ± 2	/	36 ± 2	18 ± 6

E.S.I. 2: FSC in-situ crystallization kinetics of PLLA at 89 and 149 °C

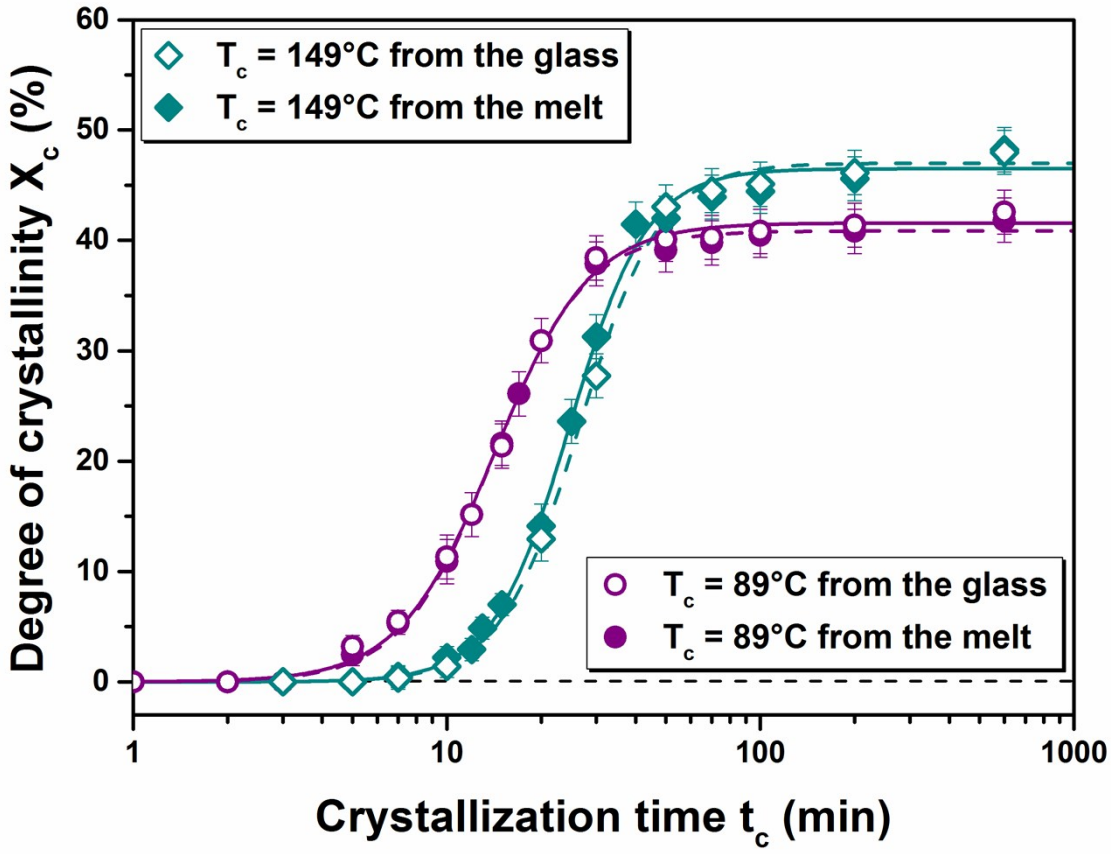

Figure SI 1: PLLA crystallization kinetics from glass and melt at 89 °C and 149 °C.

The crystallization kinetics of PLLA (**Figure SI 1**) shows that independently on the path to crystallization, i.e., from melt or glass, the crystallization at 89 °C starts about one decade before the crystallization at 149 °C. This is consistent with the PLLA half–time of melt–crystallization dependence with temperature which is longer for isothermal crystallization at 150 °C than at 90°C, as reported by Androsch et al. [2]. Besides the plateau characterizing the maximum of crystallinity is higher when crystallization is performed at 149 °C.

E.S.I. 3: Glass transition of amorphous and semi–crystalline PLLA obtained upon cooling

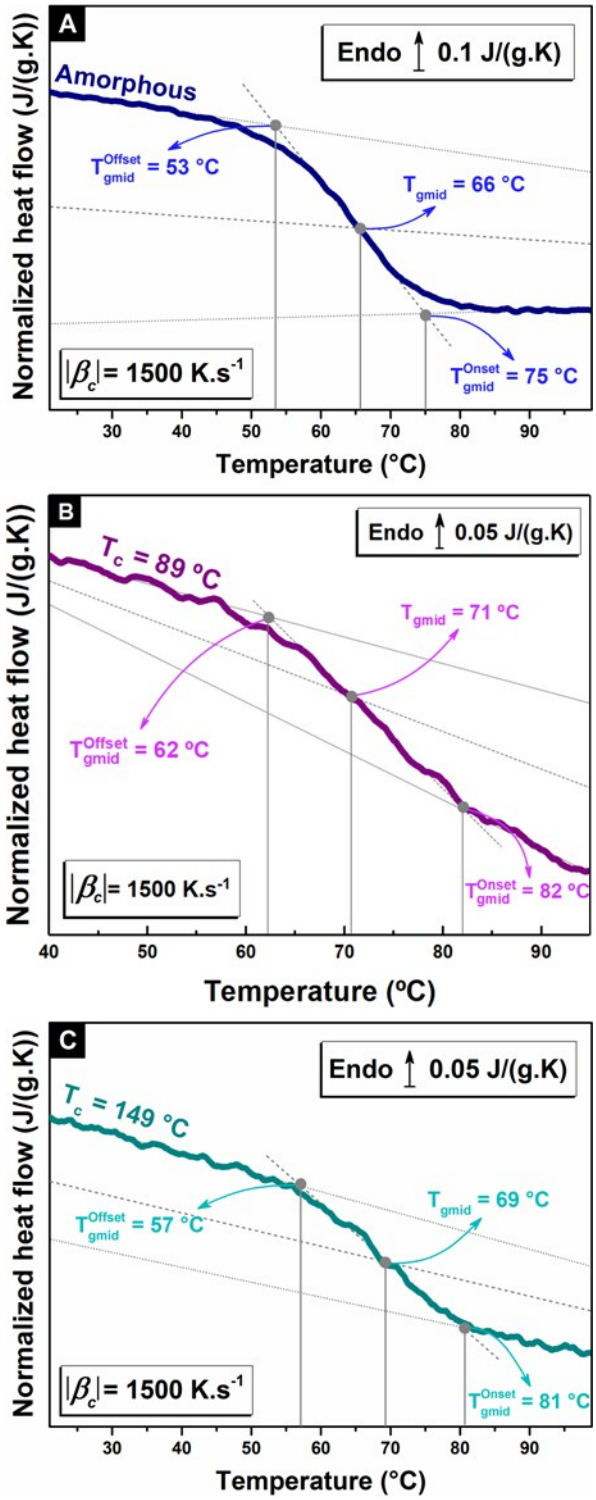

Figure SI 2: Glass transition signature of initially amorphous PLLA **(A)**, and PLLA crystallized from glass for 200 minutes at T_c = 89 °C **(B)**, and T_c = 149 °C **(C)**, obtained upon cooling at 1500 K s^{-1}.

The glass transition $T_{g\ mid}$ was obtained for amorphous PLLA ($T_{g\ mid}$ = $T_g^{0}{}_{mid}$ = 66 °C), and for PLLA crystallized from glass at T_c = 149 °C for 200 minutes ($T_{g\ mid}$ = 69 °C), by directly cooling the samples at 1500 K s^{-1} from the melt (**Figure SI 2**). To obtain a clear view of the glass transition of PLLA crystallized from glass during 200 minutes at T_c = 89 °C (**Figure SI 2**), the sample has undergone an additional heating ramp up to 120 °C.

Figure SI 3 shows the cooling from 120 °C to -60 °C and the subsequent heating from -60 °C to 250 °C, (step 1). Then a second procedure was performed without additionally heating the sample to 120°C (step 2). The comparison between the two heating runs from -60 to 250 °C shows no difference. This seems to indicate that the microstructure of PLLA was not significantly modified by the additional heating from the crystallization temperature to 120 °C. The $T_{g\ mid}$ value for PLLA crystallized from glass at T_c = 89 °C for t_c = 200 minutes was 71 °C. Thus the MAF is more constrained by the annealing at 89 °C.

It is worth mentioning that $T_{g\ mid}$ is always lower than the midpoint of the glass transition signature obtained upon heating $T_{\ mid\ heat}$. This is related to the thermal lag, which increases with the scanning rate. In a study by Monnier et al. [3], it has been checked in terms of fictive temperature, fragility, and physical aging that the correction for static and dynamic thermal lags upon heating, leads to find values for fictive temperature, which are consistent with those measured upon cooling.

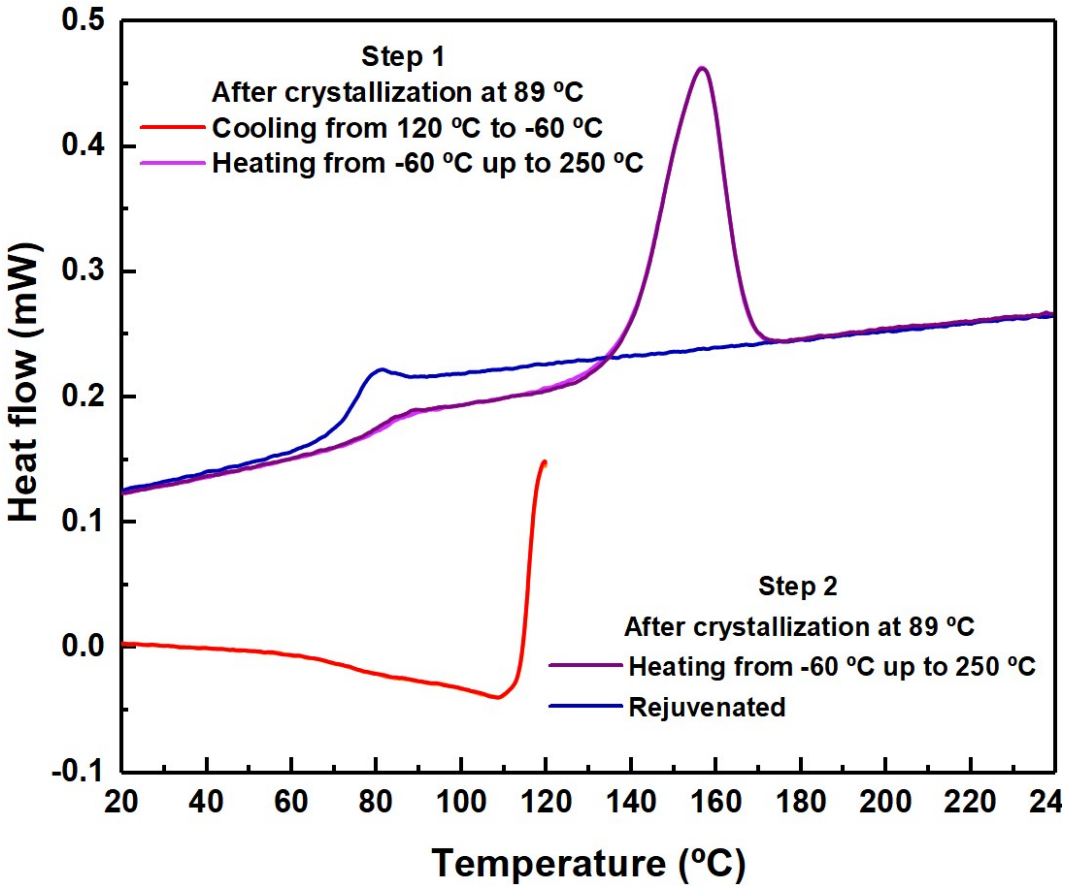

Figure SI 3: Glass transition signature from FSC of PLLA crystallized from glass during 200 minutes at T_c = 89 °C measured upon cooling and heating at 1500 K s^{-1}.

E.S.I. 4: Onset of structural relaxation

In **Figure SI 4** the onset of structural relaxation is determined for amorphous PLLA, and PLLA crystallized from the glassy state, at respectively 89 and 149 °C, for 200 minutes, according to the procedure published by other authors [4]. The sample was cooled from the melt, down to different aging temperatures T_{ag}, then aged for t_{ag} = 10 minutes. When the aging was performed above the onset of structural relaxation, PLLA did not undergo structural relaxation, so the curve obtained from the subsequent FSC scan perfectly superimposed to the curve of a non–aged sample, which was obtained from successive cooling and heating steps at the same rate, equal to 1500 K s^{-1}. When PLLA underwent structural relaxation, the subsequent FSC scan did not superimpose to the curve of the non–aged sample. According to **Figure SI 4**, the onset of structural relaxation is localized at about 72 °C, being the same in amorphous and semi–crystalline PLLA. Surprisingly, the temperature for which PLLA leaves equilibrium during cooling is not directly related with the microstructure. Moreover, since the glass transition occurs in a domain of temperature, $T_{Struc.\ Relax.}^{Onset}$ is not exactly consistent with $T_{g\ mid}$, being slightly (for PLLA crystallized at 89 °C) or significantly (for amorphous PLLA) higher.

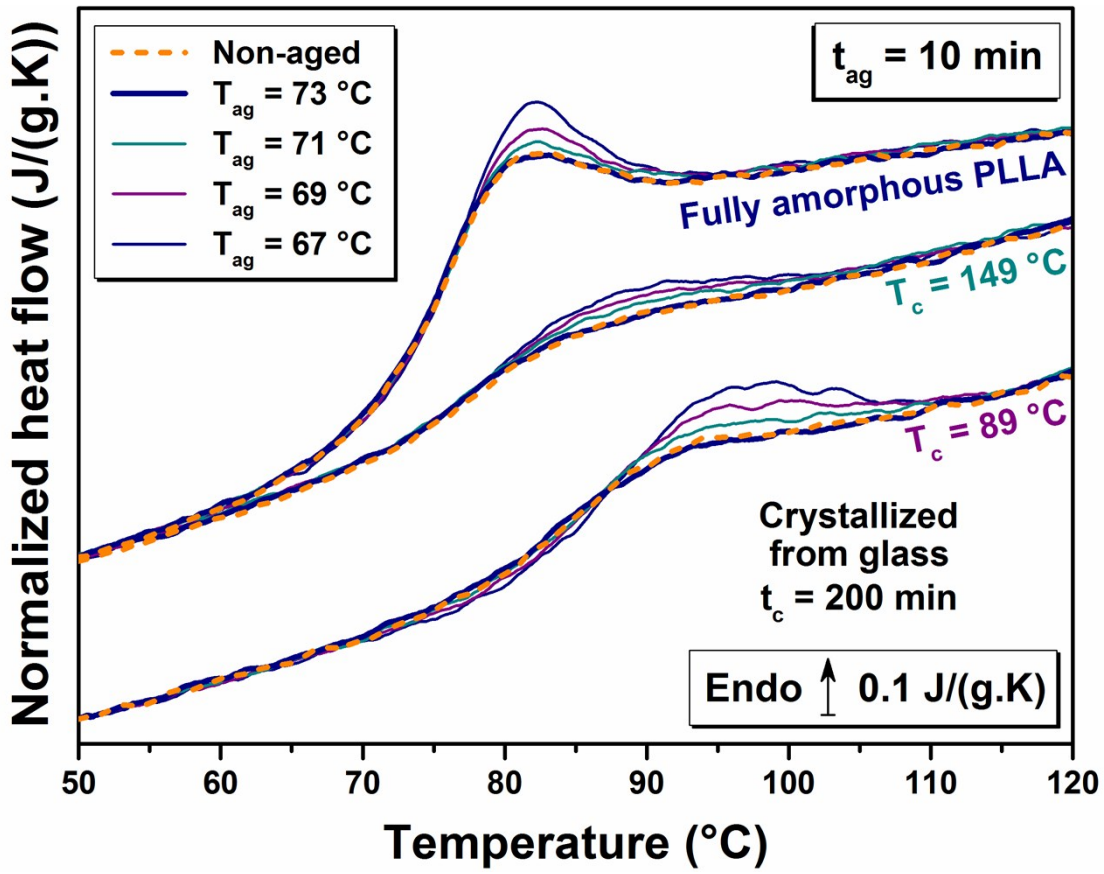

Figure SI 4 Heat flow curves normalized to both sample mass and heating rate of amorphous and semi-crystalline PLLA aged for t_{ag} = 10 minutes at T_{ag} = [73, 71, 69, and 67] °C. The semi-crystalline PLLA have been obtained by crystallizing amorphous PLLA from the glassy state for 200 minutes at respectively 89 and 149 °C. For each PLLA, the curve of a non–aged sample is superimposed to the curves of aged samples.

E.S.I. 5: FSC curves of PLLA aged for 10 min from -3 to 72 °C

Figure SI 5 displays the FSC curves in the glass transition region after aging amorphous PLLA for t_{ag} = 10 minutes at different temperatures ranging from 72 down to -3 °C. The heat flow step remains unchanged; also the glass and liquid lines perfectly superimpose, suggesting that no change of microstructure occurs due to the repetitive crossing of the glass transition from the consecutive heating/cooling steps. Two regimes emerge regarding the enthalpy of recovery. When T_{ag} ranges from 72 down to 45 °C (in blue), the peak of the enthalpy recovery moves to higher temperatures and it increases in intensity with the decrease of the aging temperature T_{ag}. Conversely, when T_{ag} decreases from 45 down to -3 °C (in grey), the peak starts shifting to lower temperatures and its intensity decreases.

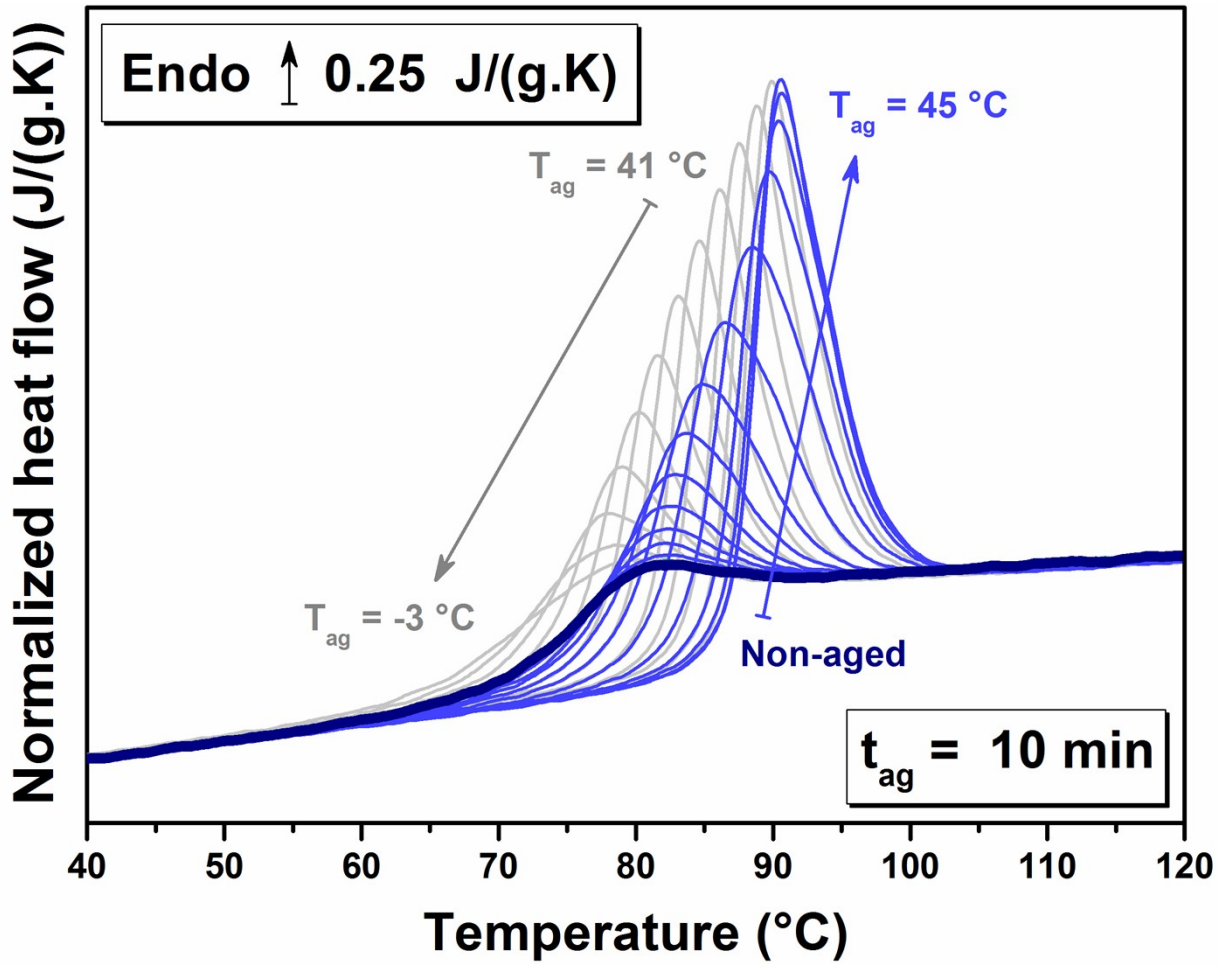

Figure SI 5: Heat flow curves normalized to both sample mass and heating rate of amorphous PLLA aged for t_{ag} = 10 minutes at different temperatures ranging from 72 down to -3 °C. The curve of a non–aged amorphous PLLA is also presented.

Figure SI 6 shows the results of physical aging experiments performed on initially amorphous PLLA that has been crystallized for t_c = 200 minutes at T_c = 89 °C (**A**) and T_c = 149 °C (**B**). The FSC scans exhibit profiles in the glass transition domain for semi–crystalline PLLA, similar to amorphous PLLA.

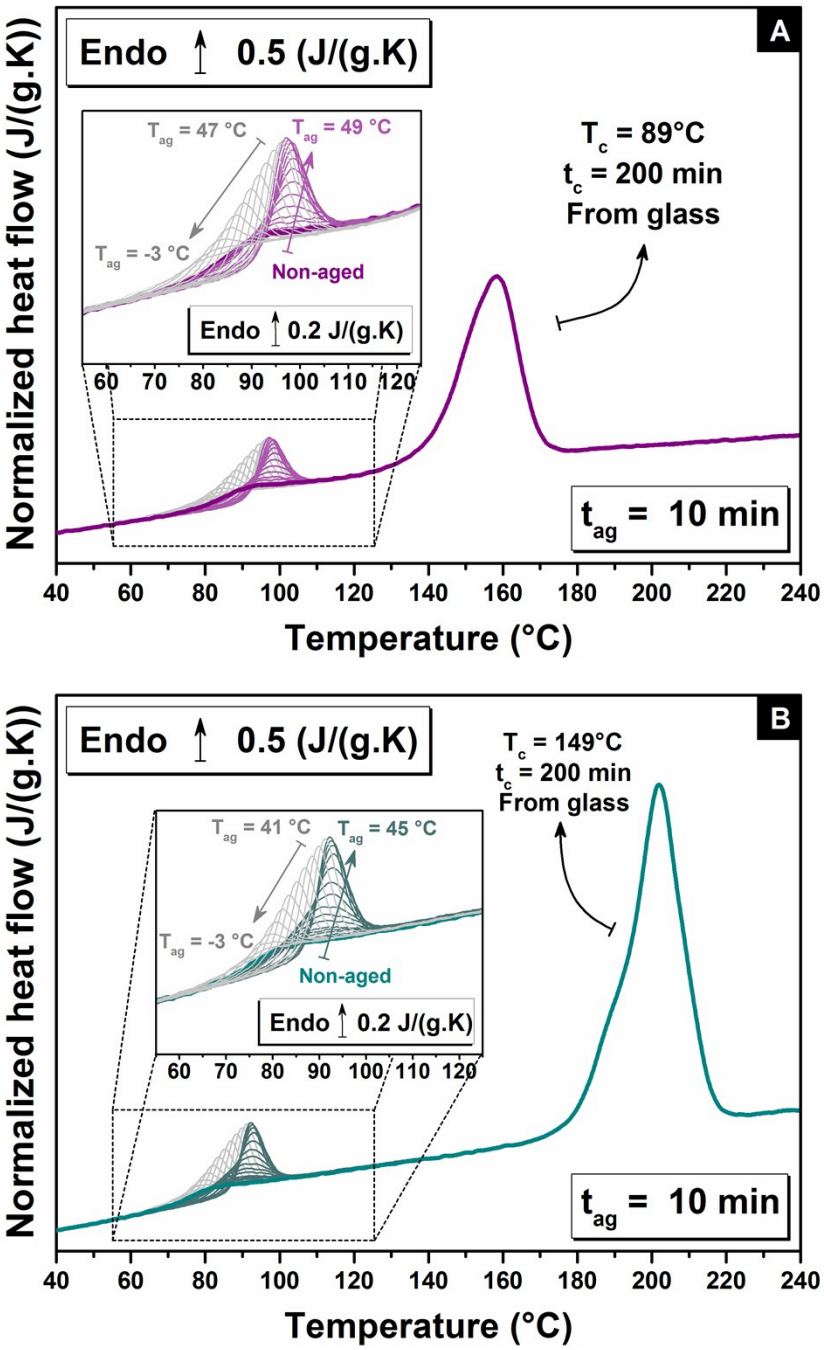

Figure SI 6: Heat flow curves normalized to both sample mass and heating rate of initially amorphous PLLA samples crystallized from glass for 200 minutes at T_c = 89 °C **(A)** and T_c = 149 °C **(B)**, then aged for t_{ag} = 10 minutes at different temperatures ranging from 72 down to -3 °C. A focus on the glass transition is given in the **Insets**. The curves of non–aged amorphous PLLAs are also presented.

E.S.I. 6: Enthalpy of recovery before rescaling of PLLA aged for 10 min from -3 to 72 °C

The enthalpy of recovery calculated from the FSC curves of amorphous and semi–crystalline PLLA is presented in **Figure SI 7**. The onset of structural relaxation is the same and the two regimes are distinct independently on the microstructure, but the enthalpy of recovery is higher in amorphous PLLA for aging temperatures less than 60 °C.

The enthalpy of recovery in semi–crystalline PLLA is lower because of lower amorphous content and/or mobility restrictions. Discriminating these two effects is not possible from this only figure. Therefore, rescaling procedures have been performed by normalizing the enthalpy of recovery to the content of amorphous phase undergoing the structural relaxation (see main text). The participation of the RAF in the structural relaxation is assumed in this study, so the rescaling has been done to the only MAF and to the whole amorphous phase (MAF + RAF).

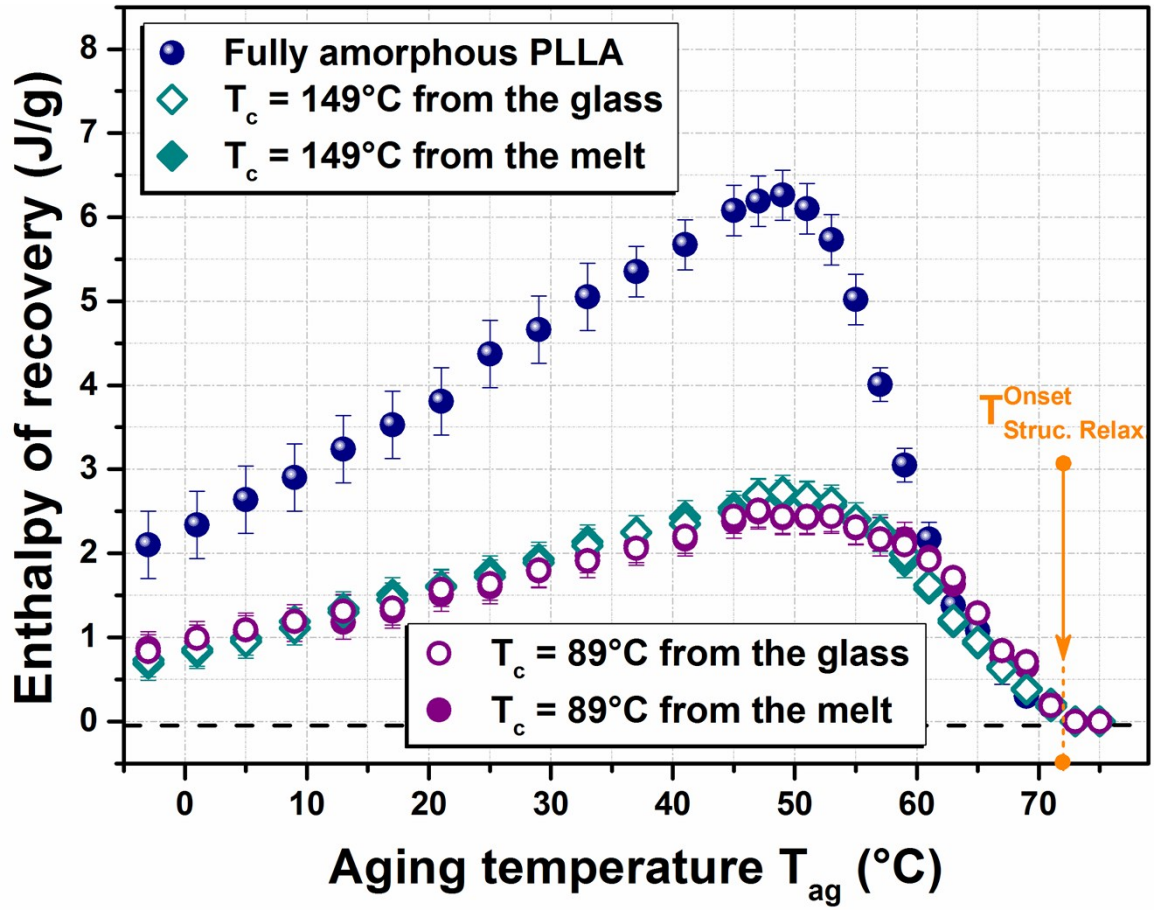

Figure SI 7 Enthalpy of recovery as a function of aging temperature for amorphous and semi–crystalline PLLA (t_c = 200 minutes) aged during t_{ag} = 10 minutes. The onset of structural relaxation at 72 °C is indicated by an arrow.

References

[1] M.C. Righetti, M. Gazzano, M.L. Di Lorenzo and R. Androsch, *Eur. Polym. J.*, 2015, **70**, 215−220.
[2] R. Androsch, M. L. Di Lorenzo and C. Schick, *Eur. Polym. J.*, 2016, **75**, 474–485.
[3] X. Monnier, A. Saiter and E. Dargent, *Thermochim. Acta*, 2017, **658**, 47–54.
[4] V.M. Boucher, D. Cangialosi, A. Alegría, J. Colmenero, *Macromolecules* 2012, **45**, 5296–5306.