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Supplementary Information for: Reaching the ideal glass transition by aging polymer films

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Isothermal enthalpy recovery As a showcase, DSC heating scans recorded after different aging times at 248 K are shown in Figure 1. A pronounced broad overshoot, increasing in intensity with the aging time, is evident. The inset of Figure 1 shows the aging time dependence of the recovered enthalpy and the corresponding values of T_f. At the longest aging times the amount of recovered enthalpy is about 23 J/g. In such time scale, that is, several days, this amount is considerably larger than normally observed in conventional glasses. T_f reaches a plateau value of 295 K, after the longest aging time.

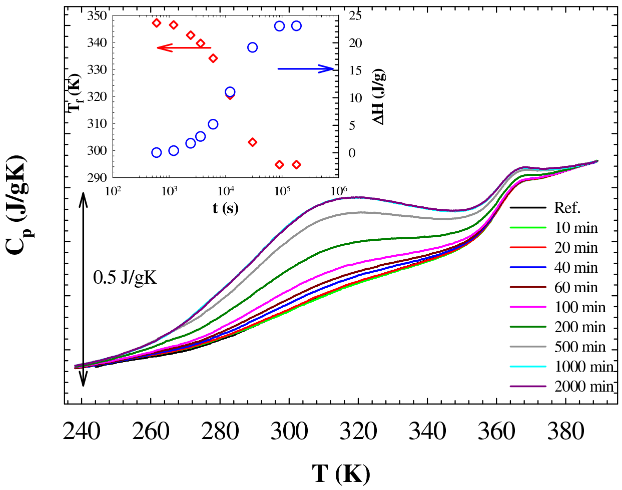

Fig. 1 Heat capacity as a function of temperature for 30 nm PS films annealed at 248 K at the indicated aging time. The reference curve corresponds to a sample heated up just after cooling. The inset shows the resulting recovered enthalpies (right axis) and T_f(s) (left axis) as a function of the aging time.

Specific heat: 30 nm films vs. bulk An important aspect of the present study regards the equivalence of the equilibrium thermodynamics of 30 nm PS films with the bulk polymer. Hence, in order to define the thermodynamic diagram when cooling 30 nm PS films at 20 K/min, the specific heat was determined. This is shown in Figure 2 (brown line) after correction of the baseline. The experimental specific heat is compared to the glass and melt specific heats reported in the ATHAS databank[1], also shown in Figure 2 (blue and red lines respectively). As can be seen, once the specific heat of the present study of the glass and the melt are taken at sufficiently low and high temperatures respectively (below ∼ 260 K and above ∼ 355 K), the 30 nm thick sample exhibits melt and glass specific heats equal to those of bulk PS. The former result agrees with previous studies showing that the equilibrium thermodynamics is essentially bulk-like for freestanding films as thin as 30 nm[2–6].

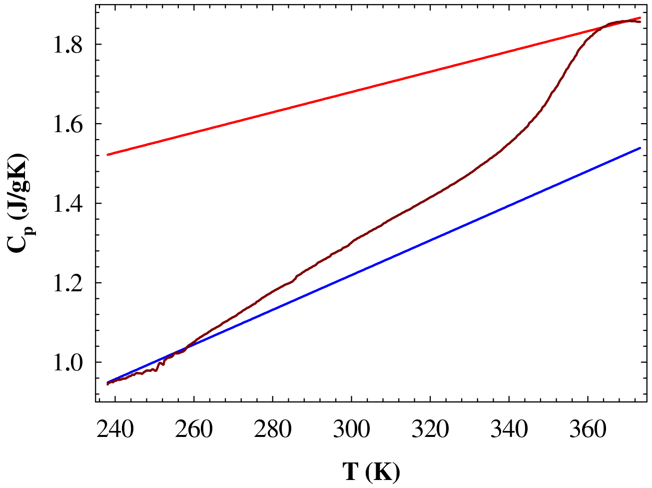

Fig. 2 Heat capacity as a function of temperature of 30 nm thick PS films cooled down at 20 K/min (brown line), melt (red line) and glass (blue line) bulk PS.

Two steps recovery of equilibrium The presence of two molecular mechanisms driving the 30 nm thick PS toward equilibrium and its analogy with bulk glass formers constitutes a crucial ingredient to achieve the ideal glass transition. In bulk glass formers, this has been recently found studying the isothermal enthalpy recovery in several polymers[7]. Achieving information on the presence of multiple mechanisms, and their corresponding thermodynamic states in metastable equilibrium, generally requires experimentally demanding observation time scales. However, there exist numerous experimental studies on the enthalpy recovery of different glasses, showing a plateau with partial re-

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covery[8–16]. In all these cases, the amount of recoverable enthalpy, determined from the knowledge of the melt and glass specific heats – providing the specific heat jump – and the distance from the glass transition ($T_g - T_a$), is *always* considerably larger than the enthalpy actually recovered at a plateau. Importantly, this is the case even in one study where the total amount of recoverable enthalpy is erroneously evaluated[11] due to an underestimation of the specific heat jump: $\Delta C_p = 0.475$ J/gK versus a value of 0.625 J/gK reported by Wunderlich and co-workers[17], on the basis of several estimations meeting the standards of acceptable data. Furthermore, several studies exist on both polymeric[18,19] and non-polymeric glass formers[20,21] showing the existence of intermediate plateaus before total recovery of equilibrium is achieved.

Here, the analogy between 30 nm thick PS and the corresponding bulk polymer for what concerns how the two mechanisms of equilibration act is presented showing unpublished results on isochronal enthalpy recovery experiments on bulk PS (5 days aging) at different temperatures. These data are plotted in Fig. 3 together with analogous data for 30 nm thick PS films aged for 480 min at different temperatures (already shown in the inset of Fig. 2 of the main manuscript). In both cases, the presence of two maxima in the plot of the recovered enthalpy as a function of temperature is indicative of the presence of two mechanisms of relaxation. However it is worth of remark that: i) the time scale of observation to achieve separation of the two time scales of equilibration is significantly larger for bulk PS than 30 nm films; ii) even with such a difference in the time scales of observation, the separation of the two maxima in the enthalpy is considerably more marked in the 30 nm thin films than in bulk PS.

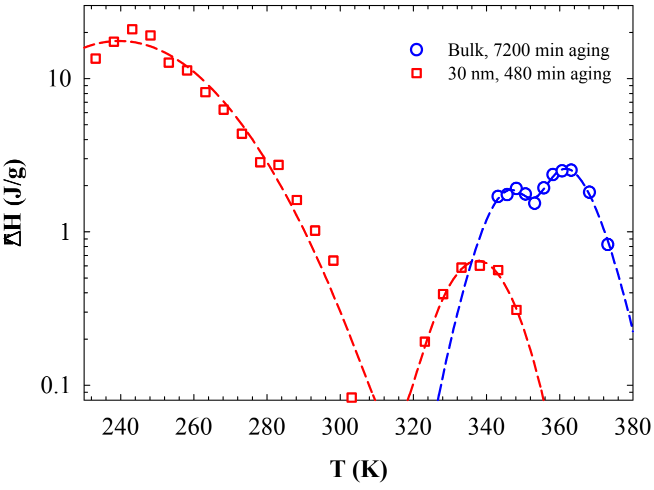

Fig. 3 Recovered enthalpy as a function of aging temperature for 30 nm thick PS films and bulk PS aged for 480 min and 5 days, respectively. Dashed lines are guides to the eye

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