Supplementary Information

Suppression of the transformation front

Figure S1 shows the calorimetric traces of capped TPD glasses with different thicknesses at two different deposition temperatures. The overlap of the transition of the capped samples regardless of their thickness is an indicator that this transition follows a homogeneous process throughout the volume of the sample.

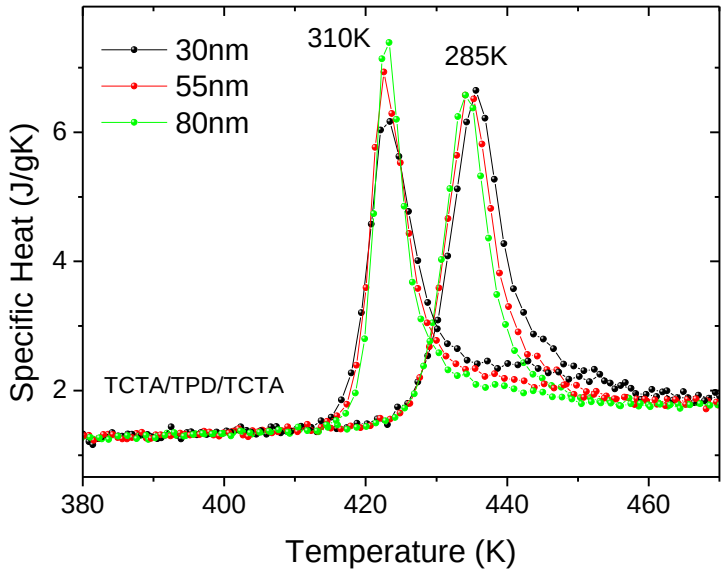

Figure S1: Specific heat traces obtained during a heating ramp at 3.5x10^4 K/s for the glass transition of capped TPD films of different thicknesses, prepared at two deposition temperatures (310 K and 285 K).

Formation of liquid regions in thicker samples

We have also verified that the observation of a distinct calorimetric peak associated to the liquid (overshoot at T=380 K) during annealing above Tg is similar for thicker film stacks (30/300/30), as shown in Figure S2.

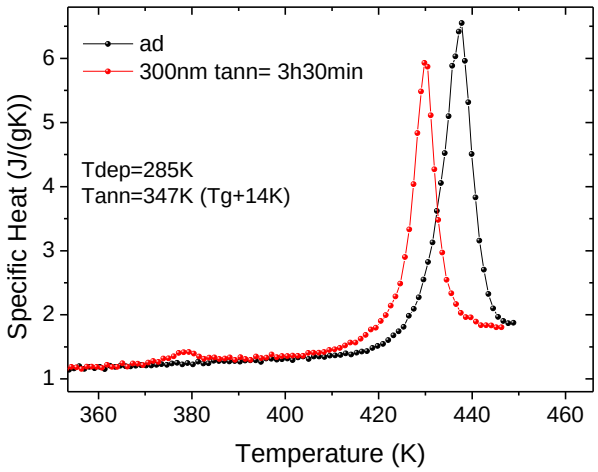

Figure S2: Specific heat traces obtained during a heating ramp at 3.5x10^4 K/s for the glass transition of capped TPD films of 300 nm. In black, the as deposited sample, in red a sample annealed for 3h and 30 min at 347 K.

<u>Front versus bulk mechanism</u>:

We have also grown much thicker stable materials (40-50 m thick) (see supplementary material at Vila-Costa et al. [1]). They transform into the liquid following a bulk process. This is easily inferred from transformation time, t_trans, that in these highly stable glasses was around 2 1/2h, while if the transformation was by surface fronts the time needed to transform should be 10-15 larger (taken v 0.2 nm/s at Tg+14K). It is interesting to note the same occurs in our thin film stacks. If surface fronts were responsible for the transformation a 60 nm film would transform in around 5 min, while ttrans is between 3-8 h depending on the stability of the TPD layer. t_trans of the TCTA/TPD (60nm) /TCTA is roughly similar to the t_trans of the 50 micrometers thick film.

References

1. Vila-Costa, A. *et al.* Nucleation and Growth of the Supercooled Liquid Phase Control Glass Transition in Bulk Ultrastable Glasses. *Phys. Rev. Lett.* **124**, (2020).