Kinetic arrest of front transformation to gain access to the bulk glass transition in ultrathin films of vapour-deposited glasses

Joan Ràfols-Ribé, Ana Vila-Costa, Cristian Rodríguez-Tinoco, Aitor Lopeandía, Javier Rodríguez-Viejo, Marta Gonzalez-Silveira[1]

Supplementary information

Transformation mechanism of single TPD layers

Prior to the capping experiments it is essential to understand how the single layers of IMC, TPD and TCTA glasses prepared at different deposition temperatures behave when measured using fast-scanning nanocalorimetry. When using fast-scanning calorimetry an ad-hoc normalization of the heat capacity curves needs to be used to identify the transformation mechanism and extract the velocity of the front when this is the dominant mechanism. The detailed explanation of the methodology is provided elsewhere[1]. Basically, we normalize the experimental heat capacity curves, C_p^{exp}, by the surface of the sample instead of its mass, using the following expression:

$$c_p^{norm}(T) = \frac{C_p^{exp}(T)}{\rho A} - c_p^g \xi_0 = \xi_l(T)\left(c_p^l - c_p^g\right) + \Delta h \frac{d\xi_l(T)}{dT} \qquad \text{(S1)}$$

where c_p^l and c_p^g refer respectively to the specific heat capacity of the liquid and the glass, Δh the excess enthalpy, ξ_0 is the total thickness of the sample and ξ_l is the film thickness already transformed to liquid which is a function of time and temperature and can be expressed as $\xi_l(T) = m_l(T)/\rho A$, where ρ is the density of the material and assumed constant, *A* is the surface and m_l is the mass of the sample that has already transformed to liquid.

[1] Corresponding author: marta.gonzalez@uab.cat

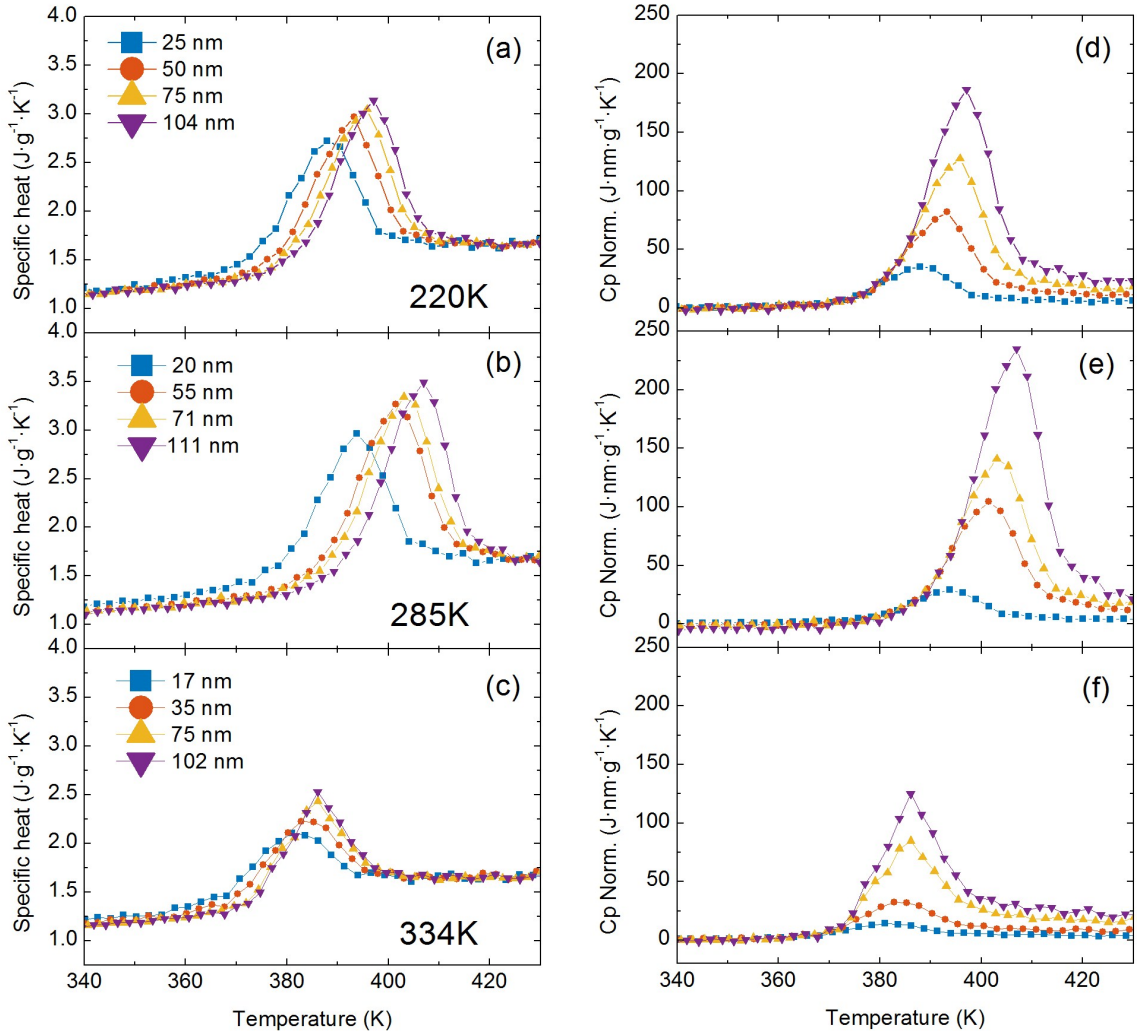

Figure S1: Left panels: specific heat curves for TPD films obtained at different deposition temperatures: (a) 220 K (0.66T_g), (b) 285 K (0.86T_g) and (c) 334 K (T_g). Right panels: curves obtained by normalizing the same heat capacity data from the left panel using equation S1. The legend indicates the thickness of the films.

Figure S1 shows the calorimetric traces for TPD films of different thicknesses deposited at 220 K, 285 K and 334 K, both normalized by the total mass of the sample and using equation S1. As we have thoroughly analyzed in previous studies[2–4], after normalizing the heat capacity trace by the total mass of the sample, a shift to lower temperatures of the calorimetric peaks corresponding to the thinner films is characteristic of a transition dominated by a heterogeneous mechanism. When applying the ad-hoc normalization, the overlap of the onset of the transformation shows that the films transform to the supercooled liquid via a parallel front whose velocity is independent of the film thickness.

Transformation mechanism of capped IMC thin film glasses

Figure S2 shows the calorimetric traces of capped and single films IMC deposited at different temperatures. For each deposition temperature, we present the glass transition of films of different thickness. It can be clearly seen how capping the IMC films results in a glass transition that takes at higher temperatures. Moreover, the overlap of the transition of the capped films with different thickness is an indication that the transformation is taken place simultaneously in all the volume. The glass transition in capped IMC films takes place, therefore, via a homogeneous transformation mechanism.

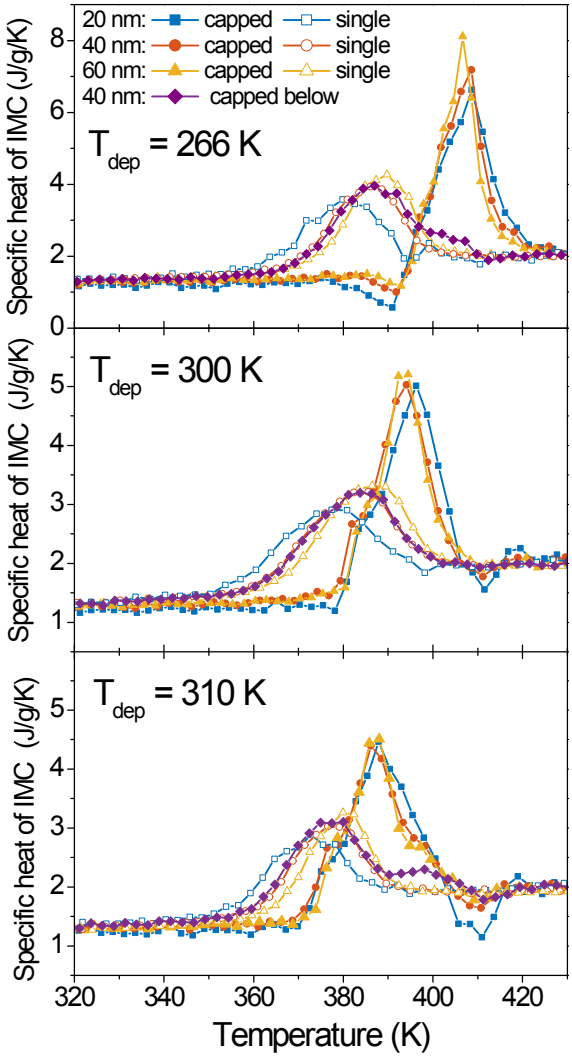

Figure S2. Calorimetric trace glasses of IMC deposited at (a)266 K (0.85T_g), (b)300 K (0.95T_g) and (c) 310 K (0.98T_g). The curves correspond to single (void symbols) and capped layers with configuration TPD/IMC/TPD (filled symbols). Different symbols indicate different IMC thicknesses, as labelled in the legend. Dispersion in thickness is around 10% maximum from the values in the legend. TPD films are always 20 nm thick. The diamonds correspond to an IMC/TPD bilayer configuration. The dashed black lines in panel (a) determine the onset of devitrification for the capped layers

Calorimetric study of TCTA glassy thin films

TCTA has also been thermally characterized using fast-scanning nanocalorimetry. Figure S3 shows the nanocalorimetric trace for single TCTA layers deposited at different temperatures. As was previously seen for other vapor deposited glasses, TCTA exhibits a calorimetric trace typical of a propagating front transformation, inferred from the apparent onset shift that the specific heat curves exhibit as a function of the sample's thickness (curves not shown). The onset of the devitrification, seen in the inset of Figure S3 is taken as the onset of the front and is analogous to comparing the onsets of samples with different thickness. The limiting fictive temperature, Tf, has been calculated as the intersection of the extrapolated enthalpy of the supercooled liquid with the enthalpy curve yield by integration of the specific heat curves[5]. Figure S3 reflects a similar behavior to what we have seen for TPD, IMC, toluene and many other organic glass formers[6], i.e. a clear dependence of the stability on the deposition temperature, with a maximum of stability around 0.85Tg. In this case, this maximum of both kinetic and thermodynamic stability corresponds to a substrate temperature around 360 K.

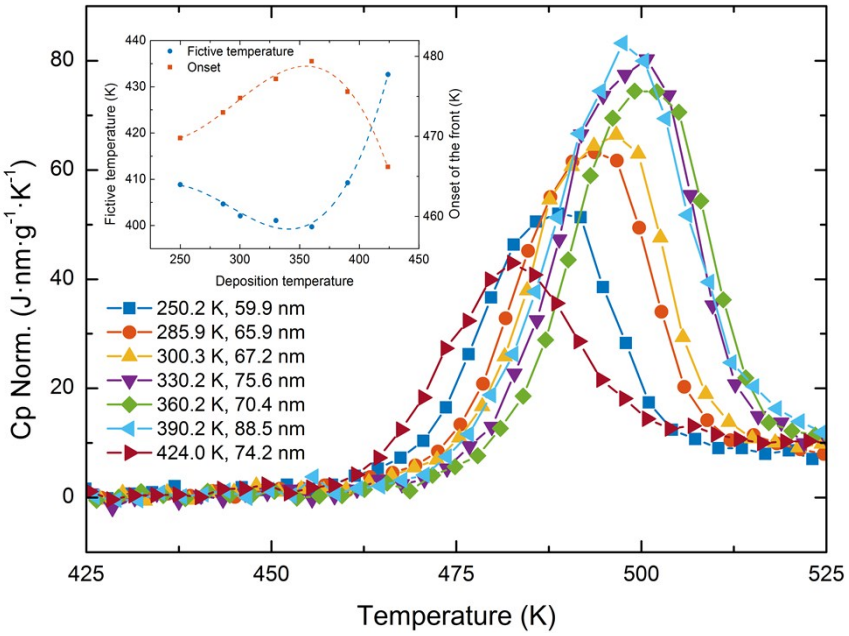

Figure S3. TCTA calorimetric trace for samples deposited at different temperatures (as indicated in the legend). Due to the dispersion in the thicknesses of the different samples, the heat capacity is normalised using equation S1. INSET: Shows the fictive temperature (blue circles, left axis) and onset temperature of the front (orange squares, right axis) as a function of deposition temperature. Lines are merely a guide-to-the-eye. Like many other organic glass-formers, it shows a maximum of stability around 0.85Tg, corresponding to 360 K in this case.

Evolution of the bottom TCTA glassy thin films during the deposition of the multilayer stack

TCTA capping films have been obtained at a deposition temperature which does not correspond to the one that yields the most stable glass. This glass can, therefore, age towards a more stable state during the deposition of the subsequent films, TPD and the top layer of TCTA. To evaluate the relevance of this aging on the TCTA bottom film we have performed isothermal treatments at 285 K and 325 K to single layers of TCTA. Figure S3 shows the specific heat trace of an as-deposited TCTA film and of TCTA thin films which have been aged during different times at 285 K and 325 K. As can be seen in the figure, the difference in the specific heat traces with and without the aging treatment at 285 K is very small. Even after 25 minutes of aging, the onset and peak position remain unchanged, although the area has slightly increased. On the other hand, at 325 K the aging is noticeable. However, the aging of the TCTA bottom layer does not apparently modify the capping properties of this layer, considering the results presented in figure 4 where we see the same effect when capping TPD deposited at 325 K and 285 K (where almost no aging is present).

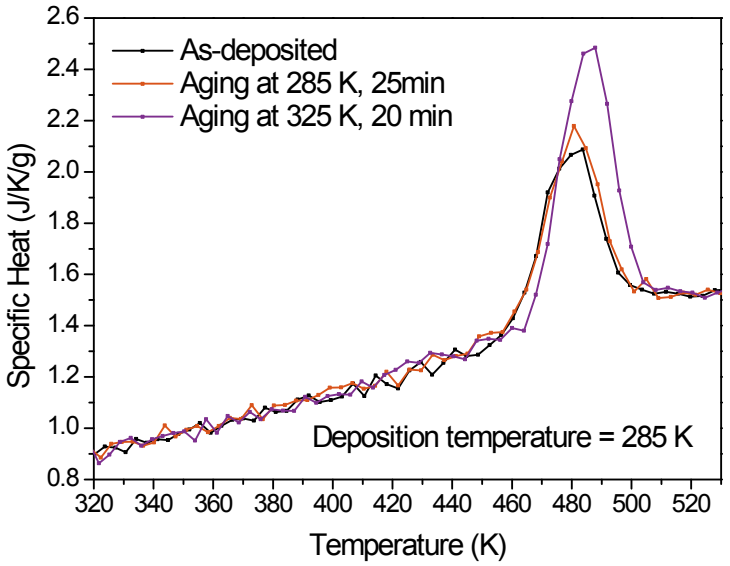

Figure S4. Calorimetric trace for thin TCTA films deposited at 285 K after different annealing treatments. The annealing times correspond to the deposition time of the thickest TPD film.

References

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