Glass transition in vapor deposited thin films of toluene

E. León-Gutierrez[a], G. Garcia[a], M.T. Clavaguera-Mora[a], J. Rodríguez-Viejo[a,b,*]

[a] Grup de Nanomaterials i Microsistemes, Departament de Física, Universitat Autònoma de Barcelona, Campus UAB, 08193 Bellaterra, Spain
[b] MATGAS Research Centre, Campus UAB, 08193 Bellaterra, Spain

ARTICLE INFO

ABSTRACT

We report on nanocalorimetric measurements of 50 nm thick toluene films at heating rates spanning 600 to 8×10^4 K/s. The films are grown from the vapour at 90 K directly onto the nanocalorimetric cell. The kinetic and thermodynamic stability of as-deposited films is higher than the stability of films cooled from the supercooled liquid at 2000 K/s. We also show that at those heating rates, the calorimetric T_g does not correlate with the relaxation time obtained by dielectric spectroscopy.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Many reports in the literature have dealt with the glass transition associated to organic glasses [1–5 and references therein]. While there are many organic liquids that may form a glass upon cooling, only few are simple enough that their intramolecular degrees of freedom can be ignored [6]. One of such simple molecules is toluene in which the only low-frequency intramolecular vibration is that of methyl rotation. Toluene also exhibits extremely high fragility with a fragility index $m = 105$ [7]. The super-Arrhenius dependence of the relaxation time when approaching the glass transition in supercooled toluene is well documented by several experiments including dielectric spectroscopy (DS) [7], deuteron-spin lattice relaxation [8] and microwave spectroscopy [9]. An ultrafast microcalorimetric study performed on micron thick toluene films obtained from the vapour has also been recently reported by Chonde et al. [10]. The heat capacity showed an unusually broad glass transition which may not be related to the fast rates but to the existence of temperature gradients within the sample, however the effect on the onset temperature was below the ± 5 K temperature uncertainty of the measurements. Interestingly, these authors found that the use of a relaxation time of 100 s at T_g for a heating rate, q, of 10 K/min did not provide a good comparison with the DS data of Döss et al. Instead they use the relation $\tau = 1 \, K/q$ to find a good correlation of their data with the relaxation time obtained by DS.

Recent measurements by Wang and Richter [11] provide data on the comparison between calorimetric and dielectric relaxation measurements on non-Debye and Debye-type liquids. For non-Debye liquids at moderate heating/cooling rates of 20 K/min the difference between the onset of the glass transition measured by calorimetry with respect to the kinetic glass transition (determined as the temperature at which the dielectric relaxation time equals 100 s) was between 1 and 3 K depending on the fragility of the liquid. Based on this small difference, the authors indicate that the definition of the kinetic glass transition temperature at $\tau = 100$ s, although arbitrary, provides a satisfactory correlation with calorimetric data. Johari and Aji [12] comment on the proper use of relaxation times determined using different techniques to compare ultraviscous liquid dynamics since they may be associated to different molecular/diffusive/rotational processes. They also point out that the use of a relaxation time of 100 s for the onset of the calorimetric glass transition associated to a heating rate of 20 K/min may not be a universal value to apply for the glass transition of all materials [12,13].

Nanocalorimetric measurements using microfabricated chips permit a good control of temperature differences within the sample region, a negligible thermal lag and a differential scheme that enables an extremely high resolution [14–17]. Previous works by Efremov et al. [18,19] have shown the suitability of the technique to analyze the glass transition on ultrathin polymer films.

Glassy materials prepared from its vapour are usually considered to be more unstable than similar glasses obtained by quenching [20]. In addition, organic glassy films grown at low temperatures through the vapour phase have rarely been the object of analysis due to the difficulties inherent to in situ calorimetric measurements. The pioneering work of Swallen et al. [21] has shown the extraordinary stability of glasses of 1,3-bis-(1-naphthyl)-

5-(2-naphtyl)-benzene (TNB) and indomethacin (IMC) grown from the vapour at $T \sim 0.85 T_g$. The kinetic stability was remarkable and films grown in few hours from the vapour had the equivalent stability of ordinary glasses obtained from the liquid and aged for months below T_g. These authors observed a significant reduction of the enthalpy associated to the glass state, a decrease of the fictive temperature and an increase of the onset of the calorimetric glass transition. Ishii et al. have confirmed a stability increase for smaller molecules such as ethylbenzene [22].

In a former preliminary work [23], we proposed a novel setup combining thermal evaporation in ultrahigh vacuum conditions with in situ measurements of the heat capacity of thin films. This setup is being used for the analysis of the glass transition in ultra-thin and/or thin organic glasses. The proposed procedure includes several advantages with respect to conventional systems such as the ability to carry out in situ measurements, to explore a large variety of heating rates and the high sensitivity which allows the measurement of few nanometer thick films where size effects may become important. In the present analysis a wide range of heating rates is explored, i.e. 600 to 8×10^4 K/s, that enables a comparison with data extracted from different techniques/approaches that probe the relaxation times at different time scales. We show that the calorimetric data obtained at ultrafast heating rates on toluene films directly obtained from the vapour or on films fast-cooled from the supercooled liquid, do not correlate directly to data obtained from dielectric spectroscopy when using the relation that for a heating rate of 10 or 20 K/min the relaxation time associated to the calorimetric glass transition is 100 s.

2. Experimental

Precise description of the set-up used for the in situ nanocalorimetric analysis is described elsewhere [23]. Highly pure commercial ($\geq 99.98\%$) toluene was introduced in the UHV main chamber hold at $\approx 10^{-9}$ mbar through a high-precision leak valve to control the quantity of vapour phase condensed in the substrate surface. The deposition temperature is controlled by a PT100 sensor and fixed at 90 K. As formerly described [23], the films were grown on the platinum heater/sensor of a microdevice based on a 180 nm thick SiN$_x$ membrane suspended on a silicon frame. Immediately after condensation of the amorphous films, scans are performed by heating the nanocalorimeters up to the desired temperature at heating rates varying from around 600 to 8×10^4 K/s. At sufficiently fast heating rates, the final C_p value is obtained after several corrections described in detail in Refs. [14–16]. From the experimental data and using the heat capacity of the supercooled liquid of bulk samples at 160 K [24], we estimate the mass of the film. In the present study and for all the samples, we fixed the film thickness as well as the growth rate, around 50 nm and 0.01 nm/s, respectively. The influence of several parameters, such as deposition temperature, growth rate and final thickness, which has recently been found to play a significant role in the layers properties, is out of the scope of the present paper and will be analyzed in further work. Prior to the experiments, the microchips are calibrated individually in an external cryostat and the resistance at room temperature, as well as the temperature coefficient of resistance, TCR, are determined. In order to benchmark the accuracy of the T_g values determined in the present study we measured the melting temperature of crystalline thick films of methanol and compare it with the tabulated value ($T_m = 175.4$ K) [25]. The measured value is 176 ± 1 K, and do not vary with film thickness neither with heating rates confirming the goodness of our calibration. Note that in these calibration tests, the thickness of the methanol layers was largely increased to ensure a bulk and well-known behaviour.

3. Results and discussion

The final temperature of the heating scans was limited below the onset of non-reversible processes, including sublimation, allowing many consecutive scans under identical heating/cooling conditions. In Fig. 1, we compare the thermal behaviour of toluene films on heating at several heating rates for the as-deposited sample from the vapour, AD, and a sample fast-cooled from the supercooled liquid, FC. For a clearer comparison the curves are normalized with respect to the heat capacity of the liquid. The upscan of the AD sample is a single scan that corresponds to the first scan after deposition. The measure is representative of many first scans performed on multiple equivalent samples. The upscan of the FC sample corresponds to the second and subsequent scans that are performed with identical heating/cooling conditions. The heat capacity data associated to FC samples is typically the average of 50 consecutive scans to improve the signal-to-noise ratio. As fast-cooled samples are annealed above T_g, the previous thermal history is erased and they are always representative of a sample cooled from the liquid at a rate of 2000 K/s. On the contrary, in the as-deposited sample the thermal history includes the deposition conditions without further aging. In both cases, the heating scan from the as-deposited or from the fast-cooled sample was initiated a few seconds after reaching the desired starting temperature. We note that the scan shape derived from our nanocalorimetric setup is comparable to data obtained from other accurate nanocalorimetric analysis [18] and bulk data on toluene [24]. If we use the temperature width as a measure of the quality of the scan, as suggested by Johari [26], we find $\Delta T_{endo} \sim 5$–9 K, and $\Delta T_{endo}/T_g$ equal to 0.038–0.064, which compares to a value of 0.025 obtained from conventional DSC on bulk toluene. We extract the onset of the glass transition temperature, T_{on}, by drawing the intersection of a linear fit of the C_p in the glassy state and the rise in C_p. Reproducibility of the onset temperature from different scans at identical heating rates on samples deposited under identical conditions agreed within 1.5 K from scan to scan. This is stated as the temperature error of our measurements. T_{on} values determined at 5×10^4 K/s are 139 ± 1.5 and 131 ± 1.5 K for the AD and FC samples, respectively. Another sample obtained by slowly cooling from the liquid at a rate of 5 K/min had a T_{on} of 135 ± 1.5 K. These values are substantially higher than those measured with slower heating rates 1–10 K/min on conventional glasses: 117.5 K [24]. The influence of the heating rate on the
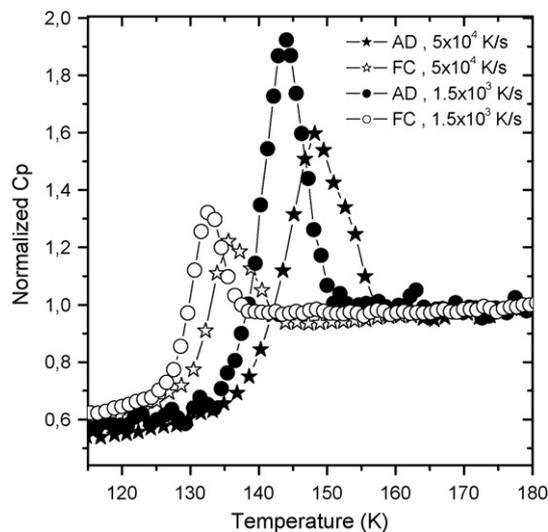
Fig. 1. Normalized heat capacity versus temperature for AD and FC samples at two heating rates of 1.5×10^3 and 5×10^4 K/s. (Normalisation was performed by fixing $C_p = 1$ at the liquid region, i.e. from 165 to 175 K.)

heat capacity rise in toluene is also shown in Fig. 1, where two different heating rates, 1.5×10^4 and 5×10^4 K/s, are directly compared. A clear indication of the different thermal histories between as-deposited and fast-cooled samples arises from the exaggerated overshoot of the as-deposited films which is reminiscent of the high heating and preparation method inherent to the first scans.

Integration of the heat capacity yields the enthalpy upon heating and is used to obtain the fictive temperature, T_f. The enthalpies associated to the glass and supercooled liquid states were found independent of the heating rate. The difference in thermodynamic stability between AD and FC glasses is clearly observed when plotting their enthalpy versus temperature (Fig. 2). The vapour deposited sample has lower enthalpy confirming its higher thermodynamic stability. T_f is defined as the temperature of the intersection of the linearly extrapolated equilibrium liquid (dotted line in Fig. 2) and glass $H(T)$ curves. T_f is 116 ± 2 K for the AD sample and 124 ± 2 K for the FC sample. The lower fictive temperature of the as-deposited film compared to the FC glass confirms its higher thermodynamic stability. The higher T_f of the FC films is inherent of the fast cooling rate. The improved stability of vapour deposited glasses has been explained in terms of the large mobility of the surface molecules during the deposition process [21]. The toluene layers of this study were prepared at 90 K, which corresponds to a temperature of $T_g - 27$ K or $0.77T_g$, slightly below the $0.85T_g$ value measured by Kearns et al. [27] as the one giving the highest stability. It is also interesting to note that the T_{on} is higher than T_f even in the unstable samples. We associate this behaviour to the ultrafast heating rates used in the present study. We also measure the jump in heat capacity from the glass to the supercooled liquid in toluene, $\Delta C_p = 0.52 \pm 0.02$ J/(g K), which closely agrees with the bulk value extrapolated at 130–140 K [24].

To obtain a more reliable understanding of the kinetics of vapour-deposited glasses, we performed a systematic analysis of the heating rate behaviour of thick toluene films. We further compare the behaviour between samples directly obtained from the vapour and cooled from the liquid at 2000 K/s (Fig. 3). In nanocalorimetry at medium-to-fast heating rates the residence time of the sample around the glass transition region is of the order of ms. For the rates used in the present analysis the time needed to go through the glass transition region, i.e. ~20 K, is 0.25–40 ms. Consequently, for a sample with identical thermal history higher temperatures are required to reach equilibrium at those heating rates. Fig. 3 shows that under the present conditions of much faster heating than cooling the calorimetric relaxation times differ
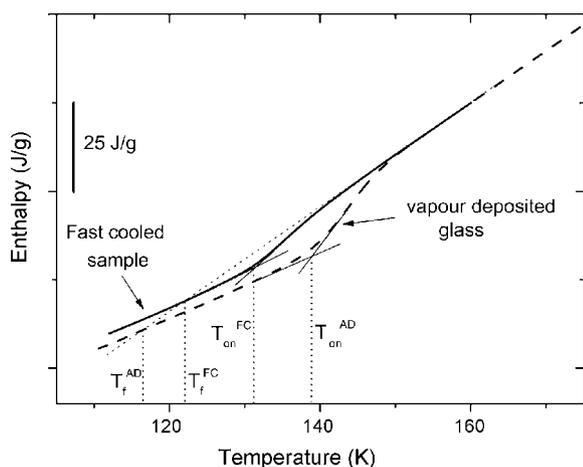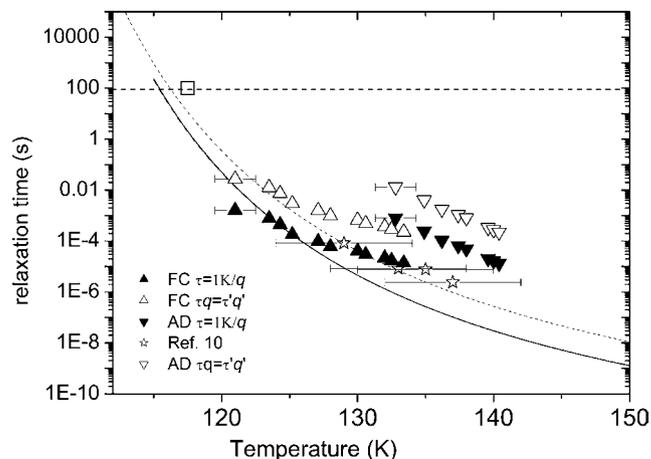
Fig. 3. Plot of the relaxation time of toluene versus temperature for AD and FC samples. Continuous and dashed lines correspond to data from Döss et al. [7] and Hinze and Sillescu [8], respectively. The square was obtained from calorimetry at a rate of 10 K/min [23]. The stars are data from Chonde et al. [10] using the relation $\tau = 1$ K/q. Horizontal dashed line is for $\tau = 100$ s. Down (up) triangles refer to AD (FC) samples with relaxation times calculated by the two expressions quoted in the graph.

from those obtained by dielectric relaxation. If we use the relation $\tau^* q = 100$ s*10 K/min, where τ is the relaxation time associated to a heating rate, q, the data from both techniques differ by 3-to-5 orders of magnitude depending on the stability of the thin film (AD versus FC samples). To add to this, we note that the difference between DS and deuteron spin-alignment experiments [7] yielded a one order of magnitude variation in time constants, i.e. in supercooled toluene the mechanical relaxation time is longer than the relaxation time characteristic of the dipolar motion. Johari [12] notes that the calorimetric relaxation time at T_g may not have a universal value for all the materials and therefore a direct comparison between standard calorimetry and DS may be unreliable. In fact the DS data of Döss et al. yields a $T_{g,diel}$ at 100 s which is 2 K below the normally accepted calorimetric glass transition of toluene obtained by DSC at a heating rate of 10 K/min, $T_g = 117.5$ K [24] (square in Fig. 3). We also plot for comparison in Fig. 3 the data obtained on toluene thick films by Chonde et al. [10] using ultrafast microcalorimetry and applying the relation $\tau = 1$ K/q. Solid symbols represent data obtained by using the same relation as Chonde et al. for FC (up triangle) and AD (down solid triangle). Open symbols are determined by using the definition that the calorimetric relaxation time is 100 s at T_{on} for a heating scan of 10 K/min. The averaged 50 nm thick toluene samples used in the present study behave similarly to the micron thick films also grown from the vapour in Ref. [10]. Although molecular dynamics simulations have shown that the relaxation times may be strongly influenced by the interaction with the surface [28–30], we do not observe a significant dynamic effect on the relaxation time of the FC samples due to the thickness of the films.

In the present report no measurements below 600 K/s were attempted, but we speculate the data should be closer to the values obtained by DS. The divergence in the time to reach equilibrium is mainly observed at temperatures much above the nominal T_g. We point out the differences observed between the nanocalorimetric data and the DS and deuteron-spin relaxation cannot be simply related to the different thermal histories of the sample. Whether it is certain that our samples show significant hysteresis due to the different heating/cooling conditions, the AD sample is thermodynamically equivalent to a sample cooled from the liquid at an extremely slow rate. As apparent from Fig. 3, FC and AD samples show a distinct behaviour which origin needs to be clarified but could arise from their difference in thermodynamic stability. What is observed is that in both FC and AD layers, the usually accepted

Fig. 2. Enthalpy versus temperature for the AD (dashed line) and FC (continuous line) samples obtained from integration of the heat capacity data at a heating rate of 5×10^4 K/s. The dotted line is an extrapolation of the liquid to infer the fictive temperature.

empirical relation between relaxation time and heating rate, to compare thermodynamic and dielectric measurements, yields an unsatisfactory correlation. This disagreement may arise, as already reported by other authors [12,13], from the fact that distinct time scales probed by the several techniques are in fact associated to different material properties.

A modification of the technique is under development to allow for broadband calorimetry at heating rates spanning at least 5 orders of magnitude with a lower bound set by the sensitivity and the sublimation of the sample.

4. Conclusions

We have shown that in situ nanocalorimetric measurements on toluene thin films provide a convenient tool to analyze the glass transition at heating rates well above those used in conventional calorimetry. The as-deposited and fast-cooled films show a remarkable different kinetic and thermodynamic stability. The as-deposited layers are more stable than samples fast-cooled from the liquid, i.e. they have a lower fictive temperature. In the explored heating rate range and using the empirical relation that correlates the relaxation time of 100 s with the onset of the calorimetric glass transition at a heating rate of 10–20 K/min our data does not agree with previous reports of the dielectric relaxation time.

Acknowledgements

References

 [1] S.M. Dounce, J. Mundy, H.-L. Dai, J. Chem. Phys. 126 (2007) 191111.
 [2] P.G. Debenedetti, F.H. Stillinger, Nature 410 (2001) 259–267.
 [3] C.A. Angell, Science 267 (1996) 1924–1935.
 [4] E. Donth, The Glass Transition: Relaxation Dynamics in Liquids and Disordered Materials, Springer-Verlag, Berlin, 2001.
 [5] J.C. Dyre, Rev. Mod. Phys. 78 (2006) 953–972.
 [6] G. Liu, M. Mackowiak, Y. Li, J. Jonas, J. Chem. Phys. 94 (1991) 239–242.
 [7] A. Döss, G. Hinze, B. Schiener, J. Hemberger, R. Böhmer, J. Chem. Phys. 107 (1997) 1740–1743.
 [8] G. Hinze, H. Sillescu, J. Chem. Phys. 104 (1996) 314–319.
 [9] V.A. Santarelli, J.A. MacDonald, C. Pine, J. Chem. Phys. 46 (1967) 2367–2375.
[10] M. Chonde, M. Brindza, V. Sadtchenko, J. Chem. Phys. 125 (2006) 094501.
[11] L.M. Wang, R. Richter, Int. J. Thermophys. 29 (2008) 2055–2061.
[12] G.P. Johari, D.P.B. Aji, J. Chem. Phys. 129 (2008) 056101.
[13] L.M. Wang, Y. Tian, R. Liu, R. Richert, J. Chem. Phys. 128 (2008) 084503.
[14] M.Y. Efremov, E.A. Olson, M. Zhang, Z. Zhang, L.H. Allen, Phys. Rev. Lett. 91 (2003) 085703.
[15] M.Y. Efremov, E.A. Olson, M. Zhang, S.L. Lai, F. Schiettekatte, Z.S. Zhang, L.H. Allen, Thermochim. Acta 412 (2004) 13–23.
[16] A.F. Lopeandia, J. Rodriguez-Viejo, M. Chacon, M.T. Clavaguera-Mora, F.J. Muñoz, J. Micromech. Microeng. 16 (2006) 965–971.
[17] A.F. Lopeandía, F. Pi, J. Rodriguez-Viejo, Appl. Phys. Lett. 92 (2008) 122503.
[18] M.Yu. Efremov, E.A. Olson, M. Zhang, Z. Zhang, L.H. Allen, Phys. Rev. Lett. 91 (2003) 085703.
[19] M.Y. Efremov, E.A. Olson, M. Zhang, Z. Zhang, L.H. Allen, Macromolecules 37 (2004) 4607–4616.
[20] K. Takeda, O. Yamamuro, H. Suga, J. Phys. Chem. 99 (1995) 1602–1607.
[21] S.F. Swallen, K.L. Kearns, M.K. Mapes, Y.S. Kim, R.J. McMahon, M.D. Ediger, T. Wu, L. Yu, S. Satija, Science 315 (2007) 353–356.
[22] K. Ishii, H. Nakayama, S. Hirabayashi, R. Moriyama, Chem. Phys. Lett. 459 (2008) 109–112.
[23] E. Leon-Gutierrez, G. Garcia, A.F. Lopeandia, J. Fraxedas, M.T. Clavaguera-Mora, J. Rodriguez-Viejo, J. Chem. Phys. 129 (2008) 181101.
[24] C. Alba, L.E. Busse, D.J. List, C.A. Angell, J. Chem. Phys. 92 (1990) 617–624.
[25] P. Robyr, B.H. Meier, P. Fischer, R.R. Ernst, J. Am. Chem. Soc. 116 (1994) 5315–5323.
[26] G.P. Johari, J. Chem. Phys. 127 (2007) 157101.
[27] K.L. Kearns, S.F. Swallen, M.D. Ediger, T. Wu, L. Yu, J. Chem. Phys. 127 (2007) 154702.
[28] N. Giovambattista, C.A. Angell, F. Sciortino, H.E. Stanley, Phys. Rev. E 72 (2005) 011203.
[29] C.A. Angell, Y.Z. Yue, L.M. Wang, J.R.D. Copley, S. Borick, S. Mossa, J. Phys.: Condens. Matter 15 (2003) 51051.
[30] P. Scheidler, W. Kob, K. Binder, Europhys. Lett. 59 (2002) 701–707.