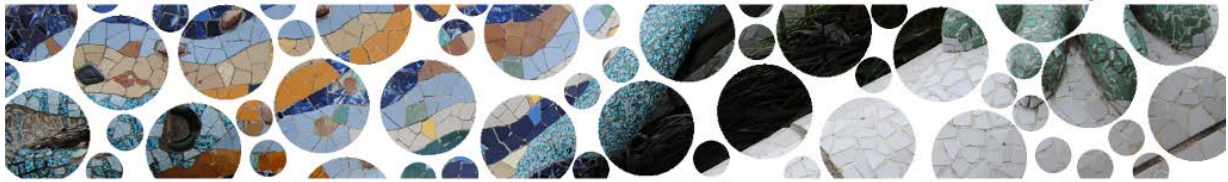


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Universitat Politècnica de Catalunya
Barcelona, Catalonia (Spain)
Sunday, July 21st - Friday, July 26th, 2013

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Equilibrium versus out-of-equilibrium dynamics in polymers under confinement**Cangialosi San Sebastian, Daniele¹**

(1) CSIC

The spontaneous evolution toward equilibrium of glasses, the so-called physical aging, is known to be one-to-one related to the glass intrinsic molecular mobility. This relation is generally found to hold in bulk glasses. In this talk we address this issue in polystyrene (PS) under confinement. To do so, we probe the segmental mobility, the glass transition temperature (T_g) and physical aging of thin PS films [1,2]. The former is investigated by alternating current (AC) calorimetry and broadband dielectric spectroscopy (BDS). The T_g , underlying the equilibrium to out-of-equilibrium crossover from the supercooled liquid to the glass, and physical aging are studied by differential scanning calorimetry (DSC) and capacitive dilatometry (CD). We show that the intrinsic molecular mobility of PS is thickness independent, whereas the T_g decreases and the physical aging accelerates with decreasing film thickness. Analogy with results in different confining geometries, in particular polymer nanocomposites [3] and nanospheres [4], is discussed. The key implication of these results is that the notion that segmental mobility and the out-of-equilibrium dynamics are fully interrelated must be questioned in confinement. In this case, the molecular mobility and out-of-equilibrium dynamics are affected differently by geometric factors [2-4].

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Influence of confinement to nanostructured matrices on the molecular mobility and phase transformations of several glass formers

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Motivated by the knowledge that molecular mobility and phase transformations can be significantly altered when a glass-former is confined into the nanoscale, several molecular guests impregnated in mesoporous silica matrixes were investigated. When the dimensions of the pore matrix interfere with the length scale of molecular motions it can influence the dynamic glass transition and enhance molecular mobility. By other side for rather low pore sizes, the guest molecules can undergo specific interactions with the pore wall, and the molecular dynamics can slow down. Therefore both confinement and surface effects can influence the molecular mobility of the guest hosts being possible to find conditions where both effects manifest simultaneously. This was shown by dielectric relaxation spectroscopy for confined Ibuprofen drug [1] and the nematic E7 [2]. Additionally, nanoconfinement can be used as a strategy to avoid crystallization allowing producing usable amorphous materials stabilized in highly disordered forms as found for a surfactant and an ionic liquid.

Acknowledgements: The authors thank Fundação para a Ciência e Tecnologia by the financial support through contract PEst-C/EQB/LA0006/2011 and projects PTDC/CTM/098979/2008 and PTDC/CTM/103664/2008. M.T.V. thanks F.C.T. by the postdoctoral fellowship SFRH/BPD/39691/2007.

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