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Glassy dynamics of polymers in geometrical confinement: From nanometric layers to single condensed isolated coils

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The (dynamic) glass transition of polymers in nanometer thin layers is both a prevailing but as well a highly controversial topic. In the current review the literature for the most studied case of polystyrene (as freestanding films or as deposited and suspended layers) will be discussed. Based on this, the extraordinary impact of sample preparation is immediately evident and outlined in detail. Recent results are presented on nanometric thin ($\geq$5 nm) layers of polystyrene (PS) having widely varying molecular weights and polymethylmethacrylate (PMMA) deposited on different substrates. For the dielectric measurements two sample geometries are employed: the conventional technique using evaporated electrodes and a recently developed approach taking advantage of silica nanostructures as spacers. *All* applied methods deliver the concurring result that deviations from glassy dynamics and from the glass transition of the bulk never exceed margins of $\pm$3 K *independent* of the layer thickness, the molecular weight of the polymer under study and the underlying substrate. Novel experiments are described on thin layers of polyisoprene, a type A polymer, having relaxation processes on two different length scales, the segmental and the normal mode. A further exciting perspective is the measurement of the dynamics of isolated polymer coils, for which first results will be presented.

The question of how the *dimensionality of geometrical confinement* influences the molecular dynamics is up to now unexplored; 1-dimensional (1-D) confinement is realized in nanometer thin layers or films, while 2-D constraints take place for molecules contained in nanopores. Experimental results of poly-*cis*-1,4-isoprene (PI) in thin layers down to 6 nm thickness prepared as part of a nanostructured capacitor arrangement and when deposited in unidirectional nanopores having pore diameters down to 4 nm will be presented. Due to the fact that PI is a type – A polymer having two dielectrically active relaxation processes; one corresponding to the fluctuations of 2–3 polymer segments and the other being assigned to that of the end-to-end vector of the chain, it is possible to sense the dynamics at two well separated length scales. First results will be presented and compared to studies on the dynamics of low molecular weight glass formers and liquid-crystals confined in 2-D contraints of nanopores.

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