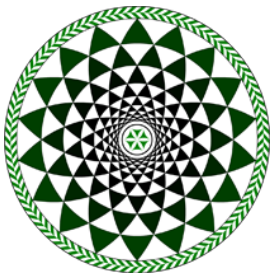

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Dielectric spectroscopy in bulk and at nanoscale

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Glass-forming systems are characterized by complex relaxation dynamics involving a wide range of time and length scales. Broadband Dielectric Spectroscopy (BDS) is able to study the orientational response of molecular dipoles to external electric fields, covering more than 16 decades (0.1 mHz - 1 THz) [1]. Thus it is a suitable method to study the relaxation processes in glass-forming systems since, in contrast with proper frequencies of resonant phenomena, their timescales are highly temperature-dependent, varying over 13-15 orders of magnitude between the glass temperature and the normal melting temperature. Polymers, in particular, show a rich scenario originating at short times from local motions and from side chain groups (β-type), followed by segmental (α-) cooperative relaxation related to the glass transition, and by chain motions (i.e. sub-Rouse and Rouse type) at larger time and length scales. In the present study we will show recent results on the dynamics polymeric systems (polyethers and derivatives of polylactic acids) where chain, segmental and secondary relaxations can be revealed by BDS. In particular, it can be shown that normal-mode process can be used as a "molecular ruler"to investigate the length scale of the glass transition.

The length scale over which dynamical processes are active is of paramount importance for nano-confined systems, such as ultrathin polymer films (thicknesses < 200 nm) or close to interfaces, like in polymer nanocomposites or at the free interface. When the physical dimension of a film or the spacing between nanoparticles in a composite is comparable to the characteristic length scale of a physical process, such as the characteristic length scale of relaxation processes, the related properties can be truly different with respect to the bulk behavior. A comprehension of the intriguing phenomena connected to these changes is required in order to design polymeric nanodevices. An increasing number of experimental works based on BDS have recently dealt with the influence of the substrate interactions on the properties of the polymer layers at the very interface with it [2, 3] or in extreme nano-confinement [4].Actually, quite rare in literature are studies enabling an assessment of the dielectric relaxation properties at the nanoscale with a high spatial resolution, that is of strong interest in the study of nanostructured materials or polymer blends. To answer to this challenge, local dielectric spectroscopy (LDS) has been recently implemented [5, 6]:by measuring electric force between a polarized tip and a conducting substrate supporting a thin polymeric film, the dielectric relaxation dynamics of a small volume ofmaterial can be investigated over a size of tens nanometer, releasing the need of continuous and uniform ultrathin polymer films to avoiding short circuits between the substrate and the upper electrode. A strong effect at the interface of polymers with embedded nanoparticles will be shown, as well as a recent technical development [7], allowing LDS to span more than 7 decades.

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