Local dielectric spectroscopy for nanoscale mapping of amorphous/ crystalline phase in semicrystalline and nanostructured polymers

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The issue of determination of crystal size, typology and distribution into the amorphous matrix in semicrystalline polymers becomes challenging when the crystal size reduces to the nanometric scale. Spatially resolved diffraction techniques, like electron diffraction in transmission electron microscopy, demand high crystalline order, that often is not present in polymers, where crystalline structures can be rather disordered. Furthermore, functional properties of crystals in contrast to those of the surrounding amorphous material can be of interest, for instance the dielectric constant, and the role in establishing Maxwell-Wagner-Sillars or interfacial polarization that is at the base of nanodielectrics [1]. Another relevant issue is how the properties of the polymer are perturbed at the interface with inclusions in nanocomposites. Measurement methods to access directly to these properties, at least at the outer surface of specimens, are represented by scanning probes with sensitivity to electrical properties. Notably, Local Dielectric Spectroscopy (LDS) [2,3] allows to obtain local dielectric spectra with the same spatial resolution than electrostatic force microscopy, that is, a few nanometers [4], with a frequency range up to 8 decades [5], not far from that of Broadband Dielectric Spectroscopy (BDS). In this work, we illustrate progress in the application of LDS to discriminate crystalline regions from surrounding amorphous ones in semicrystalline polymers like PVDF-HFP or PLLA, and to characterize interfaces in nanostructured polymers, like self-assembled block copolymer thin films of PS/PMMA [6]. On materials with specific spectral features that can be derived from studies of the bulk, discrimination of different phases can be possible for instance by exploring the dependence on temperature of such spectral features, related e.g. to the amorphous or the crystalline phase.

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