

Combining Neutron Scattering and Molecular Dynamics Simulations to Unravel the Structure and Dynamics of Polymer Systems

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Polymers are rather complex systems displaying different structural and dynamical features depending on the length scale of observation. At large length scales (hundreds of Å) the macromolecular character of the structural units prevails and the processes associated to the chain dynamics (entropy-driven 'Rouse'-like dynamics, reptation, diffusion of the whole macromolecule) play the most relevant role. However, observing the system at length scales of ≈ 10 Å or smaller, chain connectivity is not so important anymore and the characteristics are those universal for glass-forming systems: some short range order in the amorphous material is the main structural feature, while the structural relaxation and other dynamics associated to the glassy state are the dominant processes from a dynamical point of view. In this talk, we will focus on aspects of polymers related to their glass-forming nature, i.e., properties at inter- and intramolecular length scales will be discussed.

The structure and dynamics of glass-forming polymers can be investigated at a molecular level by means of neutron scattering (NS). On fully deuterated samples, coherent scattering is addressed revealing the (static and dynamic) structure factor. Additional structural information can be obtained by considering different levels of deuteration and selecting thereby other partial correlation functions. Moreover, studies on protonated samples allow insight into the atomic self-motions through the incoherent scattering function of the hydrogens. Thus, NS provides a very powerful tool to investigate these materials at microscopic and mesoscopic level. However, NS techniques are limited (e.g., the information is always obtained in the reciprocal space, or it might be extremely difficult –or impossible– to isolate the signal of a given

kind of atom) and the results are sometimes difficult to interpret. In this direction, the combination with fully atomistic molecular dynamics (MD) simulations is essential. But a first necessary step is the validation of the MD-simulations by a critical and extensive direct comparison with experimental results. This is the approach we have been following during the last years in our investigations of polymer structure and dynamics. Once we have proven that our MD-simulations provide a good mimic of the real polymer, we take advantage of the simulations and calculate magnitudes that cannot be (or at least easily) accessed by the experiments.

We will consider some examples of this combined approach including dynamic and structural aspects: (i) the origin of the non-Gaussian effects in the α -relaxation¹⁻³; (ii) the role of local processes involved in the β -process of an archetypal polymer, polybutadiene,⁴ and (iii) the short-range order of poly(methyl methacrylate).⁵

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