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# Dynamical behavior of heterogeneous polymeric materials: What can we learn from NMR relaxation times ?

## Résumé

Polymers are giant molecules in which  $N$  repeat units ( $N \approx 100-1000$ ) are connected together by covalent bonds to form long chains. Their typical size stands in the range 5-15 nm and as a result, their dynamical behavior involves various kinds of dynamical processes, ranging from the local scale motions of a given bond (librations, conformational jumps) to the global motions of the chains (diffusion). The macroscopic behavior of bulk polymeric materials, especially their mechanical / rheological properties, strongly depends on the molecular motions displayed by the polymer chains at the molecular length scale. In this context, the design of new polymer architectures to get materials with specific macroscopic properties requires a detailed description of the dynamical behavior of the corresponding chains.

NMR spectroscopy offers a good avenue to probe these molecular motions. Among the possible approaches, the various NMR relaxation times that may be measured ( $T_1$ ,  $T_{1\rho}$  and  $T_2$ ) and their temperature dependence allow different kinds of molecular motions to be captured over complementary frequency ranges (a few tens of kHz up to a few hundreds of MHz, typically). Based on the analysis of these relaxation data with models of polymer dynamics, a detailed description of both characteristic correlation times and motional geometries may be obtained. Some examples of such approaches to polymers, mostly based on  $^1\text{H}$  and  $^{13}\text{C}$  NMR measurements, will be presented.

In the case of polymer materials in the solid-state (amorphous polymers in the glassy state, semi-crystalline polymers),  $^1\text{H}$ -driven spin diffusion may influence some of the measured relaxation times and care should be taken in the interpretation of these relaxation times in terms of molecular dynamics. From another point of view, these spin diffusion effects may be fruitfully used to probe the local organization of heterogeneous polymer materials in the bulk state, at various length scales. Such structural information may provide key features to help understanding the mechanical performances of polymer-based materials. Some examples of this second type of applications of NMR relaxation times will be shown.