Probing molecular motions within macromolecular systems: An insight into their mechanical / rheological behavior

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Part of the mechanical / rheological properties displayed by macromolecular materials are strongly related to the molecular motions developed by the corresponding polymer chains. Understanding the relationships between this macroscopic behavior and the polymer chemical structure require detailed investigations of these polymer motions. From an experimental point of view, solid-state NMR offers a well-suited approach to determine the characteristic motional frequencies as well as the geometry of the various kinds of movements developed over several time- / length-scales. In this presentation, two illustrative examples will be shown: in each case, solid-state NMR was used to probe molecular motions occurring within polymer materials and these information on the dynamical behavior led to a better understanding of their mechanical / rheological properties.

The first example will concern the origin, at the molecular length scale, of relaxation processes observed for amorphous polymers ***in the glassy state***. The ***localized*** molecular motions underlying these secondary relaxations will be investigated by ^{13}C solid-state NMR (exchange experiments) and their influence on the viscoelastic behavior of these glassy polymers will be described. The second part will be dedicated to more extended motions, the ***segmental*** motions. In that case, ^{2}H solid-state NMR approaches (double-quantum coherence build-up curves) will be used to probe the segmental dynamics of amorphous polymer chains, considered ***in the molten state***. More precisely, the molecular motions displayed by such a polymer component within the lamellar mesophase of a diblock copolymer will be investigated and a peculiar attention will be paid to the dynamics of the free chain end.