This talk deals with segmental orientation correlations, as arising from constraints to the polymer chains such as crosslinks and entanglements in elastomers (networks far above T_g). They are reflected in NMR observables such as the apparent proton residual dipolar coupling constant (RDCC), and based on a suitable, robust low-field NMR experiment [1], we can extract important information on the crosslink density and possible inhomogeneities on a molecular level in different types of networks, and for instance evaluate the effect of filler particles [2-4]. A particularly promising approach is the comparison between results from NMR and equilibrium-swelling experiments [4], which reveals the nature of elastomer-filler interactions.

It is further shown that the RDCC is sensitive to the thermodynamic state of a swollen network [5,6]. It is proportional to a dynamic tensor order parameter of the network chain, which depends upon the fluctuation statistics of a network chain subject to swelling-induced stretching and excluded-volume interactions. The correlation of its value at swelling equilibrium with the corresponding degree of swelling for different networks directly reflects the value of the thermodynamic interaction parameter. A description of the phenomenon based on scaling theory allows for conclusions on the limited validity of the classical Flory–Rehner (FR) model for the good-solvent case [6]. The failure of the FR model for the good-solvent case is rationalized in terms of the ratio of the network correlation length and the thermal blob size.

References: