

NMR Spin Probes in Liquid Crystalline Elastomers

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NMR spin probes are widely used to investigate orientational order in liquid crystalline systems (1). Of particular interest in this regard is the determination of biaxial ordering, as NMR is one of the most reliable methods to determine biaxiality at present. We present ^2H -NMR studies of two liquid crystalline side-chain elastomers that potentially exhibit a biaxial nematic and a biaxial smectic-A phase, respectively. NMR experiments using benzene- d_6 and HMB- d_{18} as spin probes, give a clear indication that both of the systems form biaxial mesophases. However, the observed biaxiality parameters for HMB and benzene differ, suggesting that the biaxiality of the spin probe only partly reflects the biaxiality of the investigated system.

NMR spectra of spin probes often reflect averaging processes arising from translational diffusion induced reorientation of the probe molecules. It is of essential importance for the interpretation of the static spectra to have a reasonable estimate of the typical domain size covered in this averaging process. This is most straightforward approached by measuring probe self-diffusion by PFG (pulsed field gradient) NMR methods. From this the domain size of a polydomain elastomer can be estimated.

For smectic systems the anisotropy observed in the probe diffusion can provide information about defects in the lamellar structure. We synthesized mesogens carrying ethylene oxide moieties that are suited to coordinate Lithium ions. We performed temperature dependent ^7Li PFG NMR experiments to determine the Li diffusion parallel and perpendicular to the director in the liquid crystalline phase. As expected, the diffusion within the layers is significantly faster than perpendicular to the layers. For the elastomer the observed anisotropy is about an order of magnitude smaller than for the low molecular LC system, indicating that the lamellar structure is strongly distorted in the networks.

(1) (a) K. Severing, K. Saalwächter, *Phys. Rev. Lett.* **2004** 92 12 (b) A. Lebar, Z. Kutnjak, S. Zumer, H. Finkelmann, A. Sanchez-Ferrer, B. Zala, *Phys. Rev. Lett.* **2005** 94 197801 (c) J. R. Hughes, G. Kothe, G. R. Luckhurst, J. Malthéte, M. E. Neubert, I. Shenouda, B. A. Timini, M. Tittelbach, *J. Chem. Phys.* **1997** 107 21