

Polymers under Multiple Constraints

Polymer- & Soft-Matter-Seminar

Monday, 22nd October 2018

at: 5.15pm

VDP4 1.27, Von-Danckelmann-Platz 4, 06120 Halle

Prof. Siegfried Stapf

(Technische Universität Ilmenau, Dept. Technical Physics II, Ilmenau, Germany)

"Relaxation and diffusion in polymer melts and solutions: new experimental approaches to probe molecular dynamics in homopolymers and copolymers"

The time-dependence of the rms displacements of chain segments in polymer melts has been a cornerstone of experimental tests of various chain motion models. Rouse and Reptation dynamics (below and above the entanglement limits for chain lengths, respectively) are described by characteristic power-laws. Neutron spin echo and gradient NMR studies have tested and confirmed these power-laws, but have also found discrepancies in some cases. The wide time gap between these two techniques is partially covered by NMR relaxometry. Again, relaxometry finds power-law relationships between NMR relaxation times and Larmor frequency, but both the dependence on frequency and molecular weight were shown to deviate substantially from tube-reptation predictions. In recent years, intra- and intermolecular spin interactions were found to possess quite different frequency dependences which makes them distinguishable. In principle, the mean-squared displacement can be obtained with the help of partial deuteration of the polymer.

More complex structures, such as branched polymers or block-copolymers, have only rarely been the subject of relaxometry studies because of difficulties to separate individual species: in particular field-cycling relaxometers to not possess the spectral resolution to allow such identification. Recently, we have demonstrated that two- or three-component systems can be studied with much improved reliability if their separation in the T2-domain can be achieved by TE-ARDROPS. A different approach, both improving the signal-to-noise ratio and introducing specificity of chemical interaction, requires the use of DNP in solution; the additional relaxivity brought about by the dissolved radicals is eliminated by measurements of at least two radical concentrations (FIVE-AND-DIME), recovering the true relaxation dispersion of the polymer protons. Experiments on block-copolymers revealed the distinct dynamics of both blocks, dominated by bulk-like Rouse mode behaviour but modified in dependence of concentration and macrophase ordering.







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