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Polymer chain dynamics and NMR

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Abstract

The universal features of polymer dynamics are specifically represented by laws for (anomalous) segment diffusion and chain relaxation modes. Nuclear magnetic resonance (NMR)-based techniques provide direct access to these phenomena. This in particular refers to NMR relaxation and diffusion studies. Methods suitable for this purpose are described in detail. Three basic classes of polymer dynamics models, namely the Rouse model, the tube/reptation model, and the renormalized Rouse models are outlined and discussed with respect to predictions for NMR measurands. A wealth of experimental NMR data are reviewed and compared with predictions of the model theories. It is shown that characteristic features of all three types of models can be verified in great detail provided that the model premisses are suitably mimicked in the experiments. Rouse dynamics is shown to be relevant for polymer melts with molecular weights below the critical value and for solutions of diminished entanglement effect. Features specific for the renormalized Rouse model reveal themselves in the form of high- and low-mod--number limits of the spin-lattice relaxation dispersion. These results are considered to mirror the analytical structure of the Generalized Langevin Equation. Finally, anomalous-diffusion and relaxation laws characteristic for the tube/reptation model can be perfectly reproduced in experiment if the polymer chains are confined in a nanoporous, solid matrix whereas bulk melts are not in accord with these predictions. The dynamics of chains confined in artificial tubes can be treated analytically assuming a harmonic radial potential for the polymer/wall interaction. These results derived for a real tube closely render the characteristic features of the original Doi/Edwards model predicted for a fictitious tube.

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Keywords

Diffusion, NMR, Relaxation, Renormalized Rouse model, Reptation, Rouse model