Abstract Submitted for the MAR12 Meeting of The American Physical Society

NMR-based Molecular Rheology of Entangled Polymers in Bulk and in Nanoscopic Confinement¹ KAY SAALWACHTER, MARIE-LUISE TRUTSCHEL, FABIAN VACA CHAVEZ², Martin-Luther-Univ. Halle-Wittenberg — We demonstrate the use of simple proton low-field NMR to probe the validity of the tube model of polymer dynamics. The method yields a time-domain measure of the segmental orientation autocorrelation function C(t), which in turn is directly related to the stress relaxation modulus G(t), thus providing a true molecular measure of rheologically relevant quantities. The fixed-tube model does not describe actual data well, and current work focuses on deuteron labeling schemes to investigate the relevance of contour-length fluctuation (CLF) or constraint release (CR) effects. As first results, we found that unexpectedly, CR processes are responsible for modified chain modes faster than actual reptation [1], and also that the dynamics is inhomogeneous along a given chain, stressing also the significance of CLF. We also present recent results for melt dynamics in nanoscopic confinement of long cylindrical channels of 20-400 nm diameter [2]. We consistently observe a fraction of chains whose dynamics is less isotropic on long time scales, i.e., in the Doi-Edwards regimes III (reptation) and IV (disentangled dynamics)

F. Vaca Chávez, K. Saalwächter, *Phys. Rev. Lett.* **104**, 198305 (2010), [2] S. Ok et al., *Macromolecules* **43**, 4429 (2010)

¹Funding from the DFG (grants no. SA982/3-2 and 4-2) is gratefully acknowledged. Kay Saalwachter

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Date submitted: 24 Oct 2011

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