

## All Polymer Diffusion Regimes Covered by Combining Field-Cycling and Field-Gradient $^1\text{H}$ NMR

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### Abstract

© 2015 American Chemical Society. Field-cycling and field-gradient  $^1\text{H}$  NMR experiments were combined to reveal the segmental mean-square displacement as a function of time for polydimethylsiloxane (PDMS) and polybutadiene (PB). Together, more than 10 decades in time are covered, and all four power-law regimes of the tube-reptation (TR) model are identified with exponents rather close to the predicted ones. Characteristic polymer properties like the tube diameter  $a_0$ , the Kuhn length  $b$ , the mean-square end-to-end distance  $\langle r^2 \rangle$ , the segmental correlation time  $\tau_s(T)$ , the entanglement time  $\tau_e(T)$ , and the disengagement time  $\tau_d(T)$  are estimated from the measurements and compared to results from literature. Concerning  $\tau_d(T)$ , fair agreement is found. In the case of  $\tau_e$ , agreement with rheological data is achieved when the time constant is extracted from the minimum in the shear modulus  $G''(\omega)$ . Concerning the TR predictions the molar mass ( $M$ ) dependence of  $\tau_d$  is essentially reproduced. Yet, calculating  $\tau_e$  from  $\tau_d$  for PDMS yields agreement with experimental data while for PB it gets by 2 orders of magnitude too short. In no case  $\tau_e$  is correctly reproduced from  $\tau_s(T)$ . Segmental and shortest Rouse times appear to coincide for PB, while in the case of PDMS the latter turns out to be longer by 1 decade.

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