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

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Abstract

© 2015 American Chemical Society. Field-cycling and field-gradient ^{1}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 a0, the Kuhn length b, the mean-square end-to-end distance , 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 τe, 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 τd is essentially reproduced. Yet, calculating τe from τd for PDMS yields agreement with experimental data while for PB it gets by 2 orders of magnitude too short. In no case τe 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.