

On the theory of the proton dipolar-correlation effect as a method for investigation of segmental displacement in polymer melts

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Abstract

© 2017 Author(s). A thorough theoretical description of the recently suggested method [A. Lozovoi et al. *J. Chem. Phys.* 144, 241101 (2016)] based on the proton NMR dipolar-correlation effect allowing for the investigation of segmental diffusion in polymer melts is presented. It is shown that the initial rise of the proton dipolar-correlation build-up function, constructed from Hahn Echo signals measured at times t and $t/2$, contains additive contributions from both inter- and intramolecular magnetic dipole-dipole interactions. The intermolecular contribution depends on the relative mean-squared displacement of polymer segments from different macromolecules, which provides an opportunity for an experimental study of segmental translational motions at the millisecond range that falls outside the typical range accessible by other methods, i.e., neutron scattering or NMR spin echo with the magnetic field gradients. A comparison with the other two proton NMR methods based on transverse spin relaxation phenomena, i.e., solid echo and double quantum resonance, shows that the initial rise of the build-up functions in all the discussed methods is essentially identical and differs only in numerical coefficients. In addition, it is argued that correlation functions constructed in the same manner as the dipolar-correlation build-up function can be applied for an experimental determination of a mean relaxation rate in the case of systems possessing multi-exponential magnetization decay.

<http://dx.doi.org/10.1063/1.4998184>

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