

Recent advances in the study of high molecular mass polymer melts diffusion by proton NMR

N. Fatkullin^{1*}, E.A. Roessler², M. Hofmann², A. Lozovoi³, C. Mattea³, S. Stapf³

¹ Institute of Physics, Kazan Federal University, Kazan, 420008, Tatarstan, Russia

² University of Bayreuth, Dept. Experimentalphysik II, 95440 Bayreuth, Germany

³ Technische Universität Ilmenau, Dept. Technical Physics II, 98684 Ilmenau, Germany

* nail.fatkullin@kpfu.ru

In high molecular mass polymer melts due to the linear structure of macromolecules and their mutual uncrossability a region of anomalous diffusion cover a very broad space/time interval. It extends up to the terminal relaxation time of a macromolecule $\tau_1 \propto \tau_s N^{3,4}$, where τ_s is the segmental relaxation time and N is a number of Kuhn segments per chain. During the time τ_1 polymer segments are displaced due to the thermal motions on a length scale on the order of a polymer chain linear size $R_f = bN^{1/2}$, where b is the Kuhn segment length. Proton spin relaxation, i.e. longitudinal (spin-lattice) and transverse (spin-spin) relaxation, is mainly determined by the magnetic dipole-dipole interactions between different protons, which can be both intermolecular and intramolecular. During many decades it was assumed analogously to the solid state NMR that proton spin relaxation in polymer melts is mainly determined by an interaction between the nearest protons from the same macromolecule, and magnetic dipole-dipole intermolecular contribution to different NMR phenomena connected with spin relaxation were completely ignored. Recent progress in theory and experiments devoted to the proton spin relaxation in polymer melts shows that due to the strongly anomalous nature of polymer segments diffusion on a very long time scale, $t \leq \tau_1$, relative contributions from the intermolecular magnetic dipole-dipole interactions in NMR phenomena like spin-lattice relaxation, different types of proton spin echoes, double quantum resonance etc. are essentially different. The mentioned contributions are directly connected with the relative mean-squared displacement of polymer segments from different polymer chains, which opens new possibilities for experimental investigations of anomalous diffusion in polymer melts on the length-scale of $10 - 200 \text{ \AA}$,



corresponding at temperatures high enough above the glass transition temperature to times on the order of $10^{-9} - 10^{-2} s$.

References

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