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Segmental Dynamics of Entangled Poly(ethylene oxide) Melts: Deviations from the Tube-Reptation Model

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Abstract

© 2018 American Chemical Society. The dynamics of entangled polymer melts not only is of fundamental theoretical interest but also has wide-reaching consequences for developing a theoretical foundation for investigating biological macromolecules and complex systems relevant to material sciences. Despite several decades of intensive experimental and theoretical research in this field, open questions remain regarding segmental dynamics over the wide range of time scales from local to global motion. This work employs a novel approach based on nuclear magnetic relaxation to scrutinize the character of dipolar interactions in entangled polymer melts, thereby accessing unique information about segmental diffusion and rotation. The main focus is set on the separate consideration of intra- and intermolecular contributions to the proton dipolar interactions, which have been previously shown to possess a different, nontrivial time dependence. A combination of well-established field-cycling T1 relaxometry and recently developed methods based on spin echo is utilized to investigate dipolar couplings in entangled poly(ethylene oxide) melts of various molecular weights. Isolation of the intermolecular contributions to the corresponding experimental quantities provides a means to observe segmental translations taking place during more than 6 orders of magnitude in time. Time dependences of the mean-square displacement obtained in this way revealed apparent exponents of the power laws significantly deviating from predictions of the widely used tube-reptation model of polymer dynamics in the regime of entangled motion. In addition to that, the relative ratio of intermolecular dipolar interactions over the intramolecular counterpart is probed through their corresponding contributions to the transverse relaxation rate. A strong deviation from the tube-reptation model predictions for the evolution of this quantity is observed in the whole range probed experimentally. The obtained data do not reflect the restricted character of segmental motion anticipated in the corresponding time regime. It is emphasized that similar results, both in amplitude and in qualitative behavior, have been previously demonstrated in polybutadiene and polyethylene-alt-propylene, thereby allowing to discuss the universality of the observed deviation.

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