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Chain confinement and anomalous diffusion in polymer melt.

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Dynamics of polymer melts is multiscale, extending from the local monomer motion to diffusion over the distances beyond the size of the whole chain. For relatively short chains (M<Mc, Me), where the inter-chain interactions are not pronounced, the Rouse model provides a good description with physically realistic parameters of the chain dynamics. Dynamics of long or strongly entangled chains can be successfully described by the reptation model. The intermediate range of polymer chain lengths is less understood. By neutron spin echo (NSE) and pulsed field gradient (PFG) NMR we study the dynamics of a polyethylene-oxide melt (PEO) with molecular weight in the transition regime between Rouse and reptation dynamics. We analyze the data with a Rouse mode analysis allowing for reduced long wavelength Rouse modes amplitudes including sub-diffusive center of mass motion . This approach captures the NSE data well and provides accurate information on the topological constraints in a chain length regime, where the tube model is inapplicable. As predicted by reptation for the polymer center of mass mean square displacement, we found a sub-diffusive regime with an exponent close to 0.5, which, however, crosses over to Fickian diffusion not at the Rouse time, but at a later time, when the mean squared displacement has covered a distance related to the tube diameter.

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