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Signature of reptation in the long-time behavior of the deuteron NMR Free Induction Decay in high molecular mass polymer melts☆

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ABSTRACT

The classical tube-reptation (TR) model is based on the assumption, that in entangled polymer melts diffusion takes place inside the effective tubes having a conformation of ideal chains and being stable on the time scale of the terminal relaxation time τ_t, the latter being strongly molar mass (M) dependent. We argue, that this assumption leads for high M to a characteristic, strongly non-exponential time dependence of the deuteron Free Induction Decay, or likewise of the Hahn Echo amplitude. This holds for times t satisfying the condition $\tau_e \ll T_2 < t \ll \tau_t$, where $T_2$is an effective spin-spin relaxation time andτ_e is the entanglement time.

1. Introduction

Regarding the investigation of the dynamics in polymer systems, NMR methods based on spin relaxation are well established [1–17]. In general, one distinguishes two different types of spin relaxation, longitudinal relaxation and transverse relaxation. The longitudinal or spin-lattice relaxation describes the thermal equilibration of the z-component of the total spin magnetization, which is aligned parallel to the direction of the external magnetic field H_0. Its characteristic time is given by the frequency dependent spin-lattice relaxation time $T_1(\omega)$. For high-M polymer melts, $T_1(\omega)$ shows a pronounced frequency dependence in the range $\omega/2\pi = 10^3 \div 10^9 Hz$ [5,8,9,18–20] and changes of its magnitude in the range $10^{-3} \div 1s$. The transverse or spin-spin relaxation denotes the decay of the x and y components of the total spin magnetization. The corresponding relaxation time $T_2(\omega)$ depends rather weakly on frequency in the mentioned high-frequency region and its magnitude is on the order $T_2(\omega) = 10^{-4} - 10^{-3}s$ for high M and well above the glass transition temperature [4,10–13,21–23]. Usually $T_1(\omega) \geq T_2(\omega)$, and at sufficiently low frequencies both relaxation times become the same in isotropic systems.

The spin-lattice relaxation is caused by the non-secular part of the spin-lattice interaction Hamiltonian, which does not commute with the z-component of the total spin operator $\hat{I}_z^{tot}$. In contrast, the spin-spin relaxation is caused by the full Hamiltonian, i.e. by both the secular and non-secular part (see, for example [24–28]). The latter circumstance makes the theory of spin-spin relaxation in viscous liquids and polymer melts more complex in comparison with the theory of the spin-lattice relaxation. The non-secular part of the Hamiltonian induces transitions between different stationary states of spins in the external magnetic field and oscillates in the rotating frame with frequencies proportional to the Larmor frequency $\omega_0 = \gamma H_0$, $\gamma$is the gyromagnetic ratio of the spin bearing nucleus. In a typical experimental situation $\omega_0 T_1 > 1$, the so called Redfield limit applies. This allows to describe the spin-lattice relaxation using the short-correlation time approximation in terms of spectral densities. The latter represent Fourier transforms of binary dynamical correlation functions constructed from the lattice factors of the Hamiltonian, and they are probed at frequencies of multiples of ω_0. For a situation of identical spins or of fast flip-flop processes establishing a common spin temperature, the longitudinal relaxation is exponential yielding the time constant T_1.

The spin-spin relaxation, as already mentioned, can be induced by the secular part of the Hamiltonian, resulting in dephasing processes, which do not oscillate in the rotating frame. In the case of viscous liquids, the secular dominates over the non-secular contribution. Due to this, the condition for the Redfield limit has to be re-formulated: $T_2 > \tau_t$, where $\tau_t$is the terminal relaxation time

☆ In memoriam of Yulii Yakovlevich Gotlib.

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