Diffusion processes in soft matter studied by field-cycling proton NMR relaxometry

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With the availability of commercial (electronic) field-cycling (FC) relaxometers together with recent progress of home-built instruments, NMR relaxometry has gained new momentum investigating the dynamics in liquids, polymers, and plastic crystals [1-3]. The method provides the frequency dependence (dispersion) of the spin-lattice relaxation rate $R_1(\omega)$. Commercial machines cover a frequency range of 10 kHz – 30 MHz, home-built ones may achieve 100 Hz – 40 MHz [2]. Most of the studies employ protons. Here, the relaxation is caused by fluctuations of the magnetic dipole-dipole interaction, and one has to distinguish intra- and intermolecular relaxation pathways. The intermolecular relaxation caused by translational diffusion dominates at low frequencies whereas rotational dynamics at high frequencies, i.e., rotational and translational relaxation contributions are more or less separated in $R_1(\omega)$. The latter displays a universal low-frequencies dispersion law which allows determining the diffusion coefficient $D(T)$ without taking recourse to isotope dilution experiments. This is demonstrated for simple liquids and polymer melts in comparison to results from field gradient (FG) NMR. Sub-diffusive translation found in polymers caused by Rouse and entanglement dynamics is accessed by singling out the full intermolecular relaxation rate $R_1^{inter}(\omega)$ via isotope dilution experiments. By Fourier transformation, the segmental mean square displacement (msd) as a function of time is revealed [4], thus competing with neutron scattering (NS) experiments [5]. Complementing the msd data by that from FG NMR, nine decades in time are covered and all four diffusion regimes forecast by the tube reptation (TR) model are revealed (cf. Figure 1) [4].
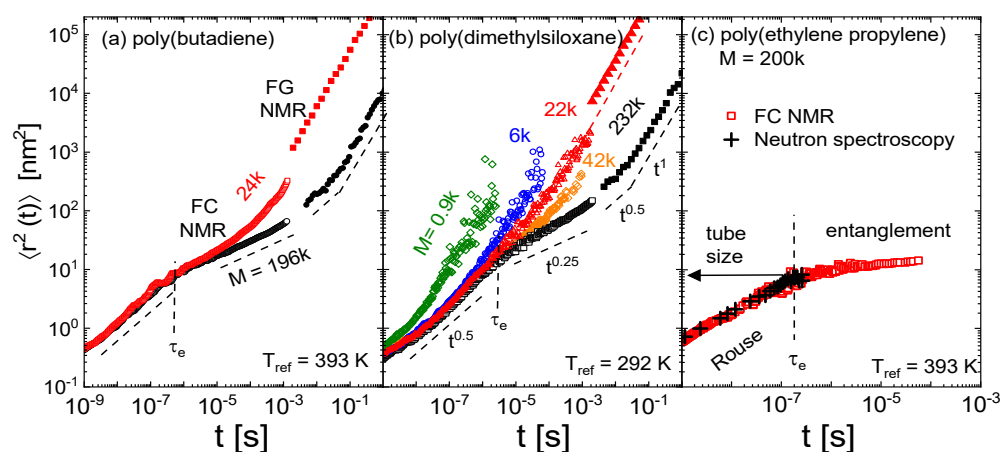

Figure 1: Segmental msd $\langle r^2(t)\rangle$ of different polymer melts as revealed by FC ^{1}H NMR relaxometry: Concerning PB and PDMS, the FC data (open symbols) of selected M was complemented toward long times by FG ^{1}H NMR (closed symbols). For high M the power-law regimes (I-IV) of the TR model are indicated (dashed lines). Concerning PEP, NS data is included (Wischnewski et al. PRL **90**, 058302, 2003).

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