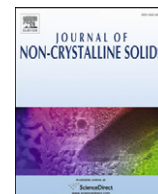


Contents lists available at [ScienceDirect](http://ScienceDirect.com)

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Proton spin dynamics in polymer melts: New perspectives for experimental investigations of polymer dynamics



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ARTICLE INFO

Article history:

Received 2 May 2014

Received in revised form 3 July 2014

Available online 24 July 2014

Keywords:

polymer dynamics;

proton NMR;

spin-relaxation;

polymer melts

ABSTRACT

The proton spin dynamics in polymer melts is determined by intramolecular and intermolecular magnetic dipole-dipole interactions among the proton spins. During many decades it was postulated that the main contribution is a result of intramolecular magnetic dipole-dipole interactions of protons belonging to the same polymer segment. This postulate is far from reality. The relative weights of intra- and intermolecular contributions are time (or frequency) dependent and sensitive to details of polymer chain dynamics. It is shown that for isotropic models of polymer dynamics, in which already at short times the segmental displacements are not correlated with the polymer chain's initial conformation, the influence of the intermolecular dipole-dipole interactions becomes stronger with increasing evolution time (i.e. decreasing frequency) than the corresponding influence of the intramolecular counterpart. On the other hand, an inverted situation is predicted by the tube-reptation model: here the influence of the intramolecular dipole-dipole interactions increases faster with time than the contribution from intermolecular interactions. This opens a new perspective for experimental investigations of polymer dynamics by proton NMR, and first results are reported.

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1. Introduction

Proton NMR is a powerful method for experimental investigations of structure and dynamics in different fields of condensed matter in general, and polymer physics in particular [1–13]. This favorable situation is determined at least by the two following facts. First, protons are ubiquitous and are present in the majority of soft matter of interest. Second, the dynamics of the proton spin, as of any another spin nucleus, in an external magnetic field is simple and exactly solvable using rather elementary mathematics. In the absence of other interactions the nuclear spin performs precession around the Z axis along which the magnetic field is aligned with the Larmor frequency given by the simple relation:

$$\omega = -\gamma_H B_0, \quad (1)$$

where B_0 is the experimentally controlled external magnetic field, γ_H is the gyromagnetic ratio of the proton. Interactions of protons with each other as well as other degrees of freedom disturb the simple picture. A quantitative description of these various influences is the main subject

of NMR theory in condensed matter. Additional interactions induce a shift of the proton frequency and create relaxation processes. Shifts of the resonance frequency, the most important of which is the chemical shift generated by electronic shielding, are the main subject of NMR spectroscopy [1–3] and form a basis for studying the microscopic structure of polymers based on the experimentally observed NMR spectra. The dynamics of the investigated systems is mainly reflected through characteristic features of nuclear spin relaxations. Important findings of recent years [7,11–30], affecting the understanding of the proton spin dynamics in polymer melts are the subject of the discussion of this paper.

One has to distinguish relaxation parallel and perpendicular to the quantization (Z) axis, which is defined by the direction of the external magnetic field. The longitudinal relaxation, i.e. the spin relaxation along Z direction, is characterized by the spin-lattice relaxation time $T_1(\omega)$. The transverse relaxation, i.e., the spin relaxation in the XY plane is given by the spin-spin relaxation time $T_2(\omega)$. For polymer systems with large molecular masses, $T_1(\omega)$ possesses a non-trivial frequency dispersion covering an extremely broad frequency range which nowadays can be measured most easily by field cycling techniques (FC) in a range of 100 Hz – 40 MHz when earth field compensation is included [24,25,30,32]. The relaxation time $T_2(\omega)$ has weaker frequency dependence and is usually investigated at fixed resonance frequency. As a rule, $T_1(\omega) \geq T_2(\omega)$.

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