



Contents lists available at ScienceDirect

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 xxxx

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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The main interaction controlling proton spin relaxation is the magnetic dipole-dipole interaction between different protons in the system, the Hamiltonian of which is as follows [1]:

$$\hat{H}_{dd} = \sum_{i < j} \frac{\mu_0 \gamma_H^2 \hbar^2}{4\pi r_{ij}^3} \left\{ \hat{I}_i \cdot \hat{I}_j - 3(\hat{I}_i \cdot \vec{e}_{ij})(\hat{I}_j \cdot \vec{e}_{ij}) \right\}, \quad (2)$$

where r_{ij} is the internuclear distance, $\vec{e}_{ij} = \vec{r}_{ij}/r_{ij}$, \hat{I}_i is the spin vector operator of spin number i , and μ_0 is the magnetic field constant. Summation in the expression (2) is to be taken over all pairs of spins. To be more specific, summation is performed over both spins belonging to the same macromolecule, which constitutes the intramolecular contribution, and spins from different macromolecules representing the intermolecular contribution.

The dynamics of spin relaxation is determined by second order corrections arising from the Hamiltonian (2). More precisely, the initial part of the spin relaxation at times $t \leq T_1(\omega)$, $T_2(\omega)$ is fully determined by the following time dependent dipolar correlation functions:

$$A_p(t) = \frac{1}{N_s} \sum_{k \neq m} \left\langle \frac{Y_{2p}(\vec{e}_{km}(t))}{r_{km}^3(t)} \frac{Y_{2p}^*(\vec{e}_{km}(0))}{r_{km}^3(0)} \right\rangle, \quad (3)$$

where $Y_{lp}(\vec{e}_{ij})$ is the component p of the spherical harmonics of rank l , N_s is the number of spins in the system, and $\vec{e}_{km}(t) = \frac{\vec{r}_{km}(t)}{r_{km}(t)}$, here $\vec{r}_{km}(t)$ are the internuclear vectors. In isotropic systems like polymer melts, the correlation function $A_p(t)$ does not depend on p , and all components are equal, i.e. $A_0(t) = A_1(t) = A_2(t)$. To illustrate the connection of the correlation function $A_p(t)$ with experimentally measurable quantities let us briefly discuss its connection with the free induction decay (FID), the spin-lattice relaxation rate and the normalized double quantum proton kinetic build up curve.

The free induction decay (FID) is conceptually the simplest NMR experiment. It is generated after applying to the equilibrium spin system in a magnetic field a radiofrequency pulse which rotates spins about an angle $\pi/2$ around an axis perpendicular to Z . In the framework of the Anderson-Weiss approximation the FID can be expressed through $A_0(t)$ [1,29], in the following way:

$$g(t) = \exp \left\{ -\left(\frac{\mu_0}{4\pi}\right)^2 \frac{9\pi}{5} \gamma_H^4 \hbar^2 \int_0^t d\tau (t-\tau) A_0(\tau) \right\}. \quad (4)$$

Recently using a modified Anderson-Weiss approximation, taking into account spin diffusion, i.e., transfer of longitudinal magnetization from one spin to another, it was shown that approximation (4) gives an error smaller than 10%, for times $t \leq 2T_2$ [22].

The spin-lattice relaxation rate is a linear combination of Fourier transforms of $A_p(t)$ at the resonance and the double resonance frequencies [1–6,11]:

$$\frac{1}{T_1(\omega)} = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{6\pi}{5} \gamma_H^4 \hbar^2 \int_0^\infty \left\{ \cos(\omega t) A_1(t) + 4 \cos(2\omega t) A_2(t) \right\} dt. \quad (5)$$

Note this expression is correct when the so-called short correlation time approximation, or Redfield limit, is satisfied, i.e. $T_1(\omega) \gg \min\{\omega^{-1}, \tau_1\}$, where τ_1 is the terminal relaxation time, i.e., the longest relaxation time in a polymer melt.

Double quantum proton NMR (DQ NMR) can be characterized as a response of the spin system to the particular DQ pulse sequence [8,22, 30,33–35] which effectively transforms the Hamiltonian of the dipole-

dipole interactions in the rotating frame to the DQ Hamiltonian which induces only even spin transitions, among which at times $t \leq 2T_2$ the two-spin transitions dominate. Experimentally measured data employing this method can be expressed through the so-called normalized DQ build-up curve. This DQ signal is, again in the framework of the Anderson-Weiss approximation, also fully determined by the correlation function $A_0(t)$ [29]:

$$I_{nDQ}(\tau_{DQ}) = \frac{1}{2} \left(1 - \exp \left\{ -\left(\frac{\mu_0}{4\pi}\right)^2 \frac{8\pi}{5} \gamma_H^4 \hbar^2 \int_0^{\tau_{DQ}} d\tau (\tau_{DQ} - \tau) (A_0(\tau_{DQ} + \tau) + A_0(\tau_{DQ} - \tau)) \right\} \right), \quad (6)$$

where τ_{DQ} is the experimentally controlled DQ excitation time. In the following chapters spin-lattice relaxation is discussed in more detail.

2. Main features of the total time-dependent dipole-dipole correlation decay in polymer melts

In polymer melts, protons are mobile. At short times $t < \tau_s$, where τ_s is the polymer segment relaxation time, relative displacements of protons are much smaller than their initial relative distances. At this situation just like in the solid state, the main contribution to the correlation function $A_p(t)$ stems from nearest intramolecular protons belonging to the same Kuhn segment. At longer times, the situation is qualitatively different, because intra- and intermolecular contributions to $A_p(t)$ decay in different ways, which depend on the detail of polymer dynamics at times $\tau_s < t < \tau_1$. Note that in entangled polymer melts, the terminal relaxation τ_1 time strongly increases with polymer chain length (or molecular mass), explicitly $\tau_1 \propto \tau_s N^{3.4}$, where N is the number of Kuhn segments per chain; values on the order of seconds or more are found for long chains.

The total dipolar correlation function can be represented as a sum of inter- and intramolecular components:

$$A_p(t) = A_p^{inter}(t) + A_p^{intra}(t). \quad (7)$$

We will address the two contributions separately.

2.1. Intermolecular relaxation contribution

Let us begin by discussing the intermolecular part $A_p^{inter}(t)$, which for times $t \gg \tau_s$ has a universal form valid for all dynamic models of polymer melts [16]:

$$A_p^{inter}(t) = \frac{4\pi}{9} n_s \widetilde{W}(0; t), \quad (8)$$

where n_s is the concentration of proton spins, and $\widetilde{W}(\vec{r}', \vec{r}; t) = \widetilde{W}(\vec{r}' - \vec{r}; t)$ is the propagator of relative displacements between two spins on different macromolecules, i.e., the density of probability for two spins separated initially by a vector \vec{r} to be separated by a vector \vec{r}' after an interval t . In fact, the intermolecular relaxation contribution for times $t \gg \tau_s$ is proportional to the probability density to recover after an interval t their initial spatial separation, i.e., the vector \vec{r} , which is not necessarily small and can be arbitrary. The derivation of expression (8) does not use specific details of polymer dynamics and can be used, in principle, for any liquid [16,21].

The next step of analysis of (8) is the approximation of the propagator by a Gaussian distribution [16,21]:

$$\widetilde{W}(r; t) = \frac{1}{((2\pi/3)\langle \tilde{r}^2(t) \rangle)^{3/2}} \exp \left\{ -\frac{3}{2} \frac{r^2}{\langle \tilde{r}^2(t) \rangle} \right\}, \quad (9)$$

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