



ELSEVIER

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

Solid State Nuclear Magnetic Resonance

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

Probing α -relaxation with Nuclear Magnetic Resonance echo decay and relaxation: A study on nitrile butadiene rubber

Simone Sturniolo^{a,*}, Marco Pieruccini^b, Maurizio Corti^a, Attilio Rigamonti^a

^a Dipartimento di Fisica "A. Volta", Università di Pavia, v. Bassi 6, 27100 Pavia, Italy

^b CNR, Istituto Nanoscienze, v. Campi 213/A, 41125 Modena, Italy

ARTICLE INFO

Article history:

Received 24 July 2012

Received in revised form

26 December 2012

Available online 8 January 2013

Keywords:

Magic Sandwich Echo

Polymers

NMR

Dipolar interaction

Glass transition

Alpha relaxation

ABSTRACT

One dimensional ^1H NMR measurements have been performed to probe slow molecular motions in nitrile butadiene rubber (NBR) around its calorimetric glass transition temperature T_g . The purpose is to show how software aided data analysis can extract meaningful dynamical data from these measurements. Spin–lattice relaxation time, free induction decay (FID) and magic sandwich echo (MSE) measurements have been carried out at different values of the static field, as a function of temperature. It has been evidenced how the efficiency of the MSE signal in reconstructing the original FID exhibits a sudden minimum at a given temperature, with a slight dependence from the measuring frequency. Computer simulations performed with the software SPINEVOLUTION have shown that the minimum in the efficiency reconstruction of the MSE signal corresponds to the average motional frequency taking a value around the inter-proton coupling. The FID signals have been fitted with a truncated form of a newly derived exact correlation function for the transverse magnetization of a dipolar interacting spin pair, which allows one to avoid the restriction of the stationary and Gaussian approximations. A direct estimate of the conformational dynamics on approaching the T_g is obtained, and the results are in agreement with the analysis performed via the MSE reconstruction efficiency.

The occurrence of a wide distribution of correlation frequencies for the chains motion, with a Vogel–Fulcher type temperature dependence, is addressed. A route for a fruitful study of the dynamics accompanying the glass transition by a variety of NMR measurements is thus proposed.

© 2013 Elsevier Inc. All rights reserved.

1. Introduction

The diffuse transition from an undercooled liquid phase to a rigid phase in glass-forming polymers is a complex and still not fully understood process. Even though both the behaviours of macroscopic properties [1] and of relaxation dynamics [2] at the transition have been characterized, the theoretical understanding of the phenomenon itself is still incomplete. The signature of the glass transition is a molecular relaxation process known as the α -relaxation, characterized by cooperativity of the motions and high dynamical heterogeneity, which leads to a broad distribution of relaxation times [3]. A variety of spectroscopic techniques has been used at that aim, in particular broadband dielectric spectroscopy [2,4,5], neutron inelastic scattering [6] and dynamical mechanical spectroscopy [7]. A fruitful approach to the study of the problem at a microscopic level is offered by Nuclear Magnetic Resonance experiments [8], thanks to its selectivity and versatility. Different NMR approaches are available, from spin–lattice

relaxation time measurements with use of Fast Field Cycling [9] to complex multidimensional techniques involving cross-polarization and Magic Angle Spinning [10,11]. However, exploring the range of slow relaxation processes (< 1 MHz) involved in glass transition is generally hard to carry out with ordinary ^1H NMR. This paper addresses the problems inherent to this kind of measurements and proposes a novel approach to probe quantitatively these motions, by exploiting some phenomena specifically related to dipole–dipole interaction between hydrogen nuclei, which for many organic molecules has the remarkable property of having characteristic frequencies in the range around ~ 100 kHz.

In this work, the analysis of free induction decay (FID) as well as of spin–lattice and spin–spin relaxation rates in industrial amorphous Nitrile Butadiene Rubber (NBR) is performed. NBR, a well known block copolymer of 2-propenenitrile and different butadiene monomers (1,2-butadiene and 1,3-butadiene) has been chosen as a model system because it is almost completely amorphous and has a convenient value of the glass transition temperature T_g , estimated to be around 250–260 K [12–14], with a wide range of possible values depending on the production process employed. In the presence of fast decaying FID ($T_2 \lesssim 10$ μs), as it is expected in particular in any glassy state,

* Corresponding author.

E-mail address: simonesturniolo@gmail.com (S. Sturniolo).

the signal at short times, crucial for a thorough analysis, is often lost because of experimental limitations related to the dead-time of the spectrometer and to incomplete wipe-out of the ringing. In this case, since in proton NMR in polymers the dominant term is the dipolar interaction, a nice method to reconstruct the full FID signal is offered by the Magic Sandwich Echo (MSE) [15].

In this paper FID decays (with and without MSE reconstruction) and spin–lattice relaxation data in the temperature range including the boundaries of the diffuse transition are thoroughly analyzed. In particular the efficiency parameter of the MSE reconstruction allowed us to infer the temperature dependence for the central frequency of the α -relaxation. Furthermore, information on the chain dynamics carried by the FID signals is extracted by direct fitting with an analytical expression of a $\frac{1}{2}$ spin pair transverse magnetization correlation function derived in an exact way, which avoids the stationarity and Gaussian assumptions used in the classical Anderson–Weiss approach [16]. Combining this derivation with a motional distribution function, spin–lattice relaxation data have been simulated and compared to the experimental data, achieving a successful agreement. Overall, the experimental and analytical techniques adopted demonstrated to be very promising for characterizing the α -relaxation, and slow molecular motions in general, at a microscopic level.

2. Experimental

The experiments have been carried out on a sample of NBR using a TecMag DoubleResonance Spectrometer based upon a tunable electromagnet, with a working range of 5–450 MHz and a minimum time resolution of 300 ns. The measurement chamber was insulated within a vacuum tube. Measurements were performed at three different values of the static magnetic field, corresponding to ^1H Larmor frequencies of 21, 41.8 and 60 MHz, and in the temperature range from 193 K to 333 K. The intensity of the RF field H_1 was typically 30 Oe and the MSE sequence we used was the version with a train of $\pi/2$ pulses replacing the long bursts described in [15]. The aim was to avoid the problems due to instrumental phase switching times between different pulses, while being substantially equivalent under the mathematical point of view. The phase switching time was of $3\ \mu\text{s}$ (doubled during the groups of four pulses along the X-axis constituting the core of the sequence), and the total length of the MSE sequence was set to $96\ \mu\text{s}$. The dead-time was around $5\ \mu\text{s}$, thus making it hard to interpret the direct FID signal at low temperatures but irrelevant when the MSE is used.

FID and MSE-reconstructed FID fittings were performed with a self made C++ software using Gnu Scientific Library.

SPINEVOLUTION simulations were carried out by introducing a simplified version of the effects due to molecular dynamics with the use of the “spin exchange” feature [17]. This consists in the possibility of switching in a random way certain groups of spins at a fixed rate. The model system adopted was a group of four proton pairs, all $1.8\ \text{\AA}$ apart (like ^1H belonging to a CH_2 unit in polymers) with four different orientations with respect to the field axis, homogeneously distributed along the solid angle. Dipolar couplings were turned on between spins belonging to the same pair and off between different pairs, making them effectively four separate systems. Using the spin permutation option in SPINEVOLUTION to simulate slow dynamic processes, the spins are cycled between pairs, thus creating the effect of an “isotropic rotation” of the same spin pair. The rate of this rotation is chosen to be a finite value ranging from 0.2 kHz to 5000 kHz.

T_1 calculations (see following Sections) were performed with a self made C++ software using a trapezoidal integration algorithm.

Another software written in C++ implementing a simplex algorithm was used for the fittings described in Section 4.3.

3. Results

Fig. 1(a, b, c) shows the FIDs acquired from NBR at three different temperatures and a Larmor frequency of 60 MHz. As already mentioned, because of the deadtime of the RF equipment, in the range of a few μs , and of the ringing noise (only partially removed by the standard phase sensitive cycles), the FID signal

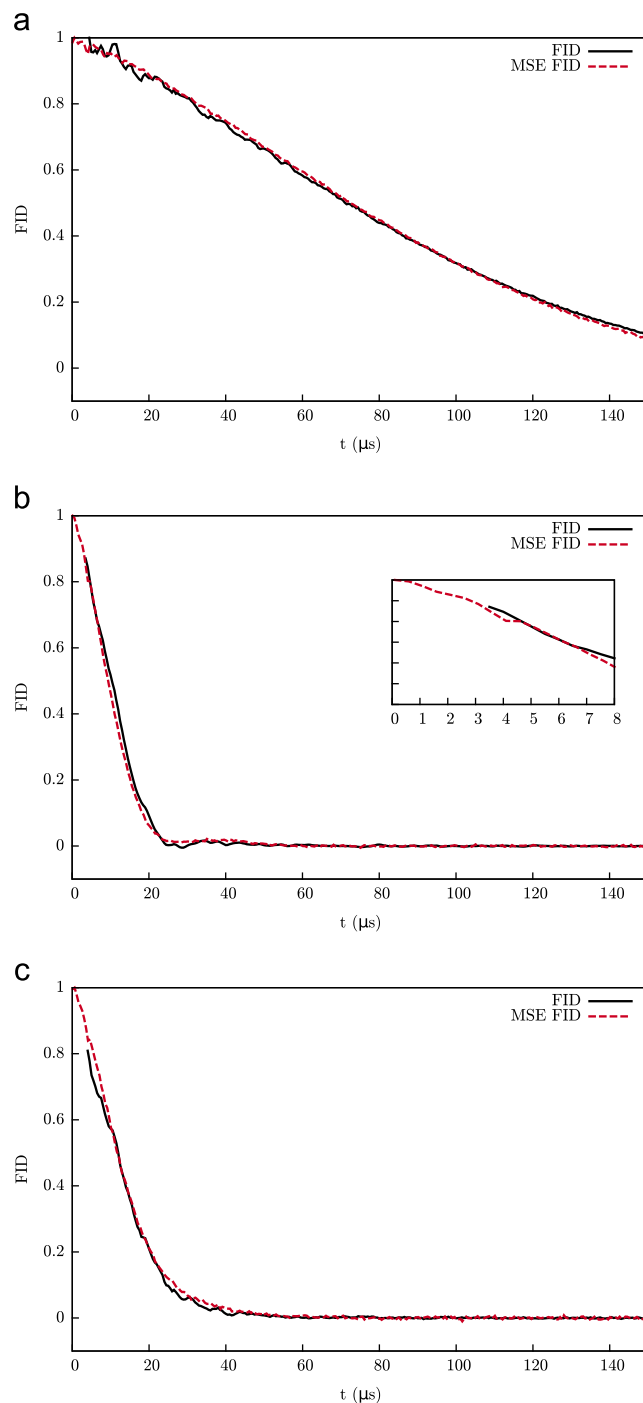


Fig. 1. FIDs and MSE reconstructed FIDs in NBR at three representative temperatures, in $H_0=1.5$ Tesla. (a) $T=293\ \text{K}$; (b) $T=203\ \text{K}$, in the inset the decay at short times is expanded; (c) $T=253\ \text{K}$. No dependence from the strength of the magnetic field H_0 was observed.

Download English Version:

<https://daneshyari.com/en/article/5420430>

Download Persian Version:

<https://daneshyari.com/article/5420430>

[Daneshyari.com](https://daneshyari.com)