



Fast-field-cycling relaxometry enhanced by Dynamic Nuclear Polarization



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ABSTRACT

Fast-field-cycling (FFC) NMR relaxometry experiments enhanced by in-situ Dynamic Nuclear Polarization (DNP) were performed for ¹H and ¹³C nuclear spins with a setup based on a commercial electronically switching FFC relaxometer and a recently-built Alderman–Grant type microwave resonator for 2 GHz. DNP-enhanced ¹H relaxation dispersion profiles were compared to reference measurements and literature data in order to prove the reliability of DNP-enhanced relaxometry data. The method was then used to investigate the paramagnetic nuclear spin relaxation of ¹³C in a benzene-¹³C₆D₆ solution of nitroxide radicals. Dispersion profiles of good quality were obtained within 2 h of measurement time from a comparatively small sample of 60 μl. As a prospect for future applications, DNP experiments with a high-molecular weight Poly(butadiene-1,4) melt and BDPA radical were carried out at 2 GHz and 9.7 GHz microwave frequency, showing solid effect DNP enhancements. In-situ hyperpolarization by DNP may provide extended possibilities for FFC relaxometry, e.g. by allowing enhanced detection of dilute or insensitive nuclear spins, additional selectivity or faster measurements of small samples.

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1. Introduction

Dynamic Nuclear Polarization (DNP) is a versatile technique for the hyperpolarization of nuclear spins, based on the transfer of electron spin thermal equilibrium polarization to nuclear spins via concomitant electron–nuclear spin flips. Different effects enable polarization transfer in solid and liquid samples, respectively. Solid state DNP effects [1–5] are based on static dipolar couplings between electron spins and nuclear spins. Herein, microwave irradiation with a frequency offset from the electron spin Larmor frequency of about the nuclear spin Larmor frequency is used to drive spin transitions involving two or more electron and nuclear spins. In non-viscous liquid samples, polarization transfer is based on the Overhauser effect [6], i.e. on relaxation processes due to electron–nuclear spin couplings and the saturation of electron spin transitions by on-resonant microwave irradiation.

In the last decade, major improvements in hardware and methods have driven the development of various applications of DNP in both the liquid and solid state. For example, the development of the dissolution DNP method [7] has enabled sensitive detection of ¹³C in magnetic resonance imaging (MRI) and led to metabolic

imaging applications [8] based on hyperpolarized metabolites. Hardware improvements, such as high frequency gyrotron microwave sources and low-temperature magic angle spinning probes that allow for in-situ microwave irradiation have brought up DNP applications for solid state NMR [9]. Recent developments for liquid state DNP involve the minimization of sample heating effects as well as the theoretical description and reliable measurement of DNP saturation [10–12] and coupling [13–15] factors. Moreover, DNP polarization at moderate magnetic field strengths and high-field NMR detection were combined using shuttling techniques [16], which aim at hyperpolarized high-resolution liquid-state NMR. However, fewer attempts were made to explore applications of DNP for NMR experiments operating at magnetic fields below 1 T, such as fast-field-cycling (FFC) NMR [17,18]. FFC is a well-established technique that allows one to measure the nuclear spin relaxation rate over a broad range of magnetic fields, providing an access to the spectral density of the randomly fluctuating couplings that cause nuclear spin relaxation. Therefore, FFC NMR relaxometry is suitable to study the molecular dynamic processes that cause such fluctuations, covering dynamics on the time scale from 10 ns up to hundreds of microseconds. Furthermore, it provides a method for the measurement of DNP coupling factors [11,19,20]. However, due to the low magnetic fields, which result in small thermal nuclear spin polarization, this technique makes use of relatively large sample amounts to obtain appreciable signal

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intensity. While the sensitivity can be as large as to permit the detection of millimolar protein concentrations in D₂O [21], hyperpolarization may for example enable detection of considerably smaller sample amounts or facilitate the detection of insensitive heteronuclei.

In this contribution, the implementation of a DNP setup for FFC NMR relaxometry is demonstrated by combining a commercial FFC relaxometer (Spinmaster FFC2000, Stelar s.r.l., Pavia, Italy), a recently-built 2 GHz Alderman-Grant-type microwave resonator [22] and inexpensive S-Band microwave devices. A simple and well-characterized sample, consisting of an aqueous solution of the free nitroxide radical TEMPOL, was used to evaluate the obtainable gain in sensitivity by DNP and to test the reliability of DNP-enhanced FFC relaxometry data by comparison with standard, non-enhanced measurements and literature data. We show a first application, which uses the enhanced sensitivity to study the paramagnetic nuclear spin relaxation of ¹³C and to obtain the ¹³C DNP coupling factor for a sample of benzene-¹³C₆,D₆ with TEMPO radical. In order to test the possibility of DNP-enhanced measurements in viscous systems, ¹H DNP experiments were performed with a sample of BDPA radical dissolved in high-molecular weight Poly(butadiene-1,4) (PB), measuring magnetic field-dependent DNP enhancements at microwave frequencies of 2 GHz and 9.7 GHz (DNP spectra). These experiments provide a proof of principle for DNP-enhanced NMR measurements in viscous systems demonstrating the applicability of our approach to one of the most important applications of FFC. In future applications, ¹H relaxometry studies of partially deuterated polymers could be facilitated due to the increased sensitivity offered by DNP or covalently attached radicals may be used in DNP-enhanced FFC for selective measurements of domains in block-copolymers. A detailed analysis of DNP effects in polymer melts will be given in a forthcoming publication.

2. Experimental

A commercial electronically switching FFC NMR relaxometer (Spinmaster FFC2000, Stelar s.r.l., Pavia, Italy) was equipped with an S-Band DNP setup, a block diagram of which is given in the [Supplementary information](#). An S-Band resonator with a transverse microwave magnetic field was used for microwave irradiation, providing DNP polarization for comparatively large sample volumes and minimized sample heating effects. Technical details of the resonator are given in Ref. [22]. A saddle coil was used for NMR detection at 18.7 MHz and 3.5 MHz for ¹H and ¹³C nuclear spins, respectively. The microwave resonator was critically coupled

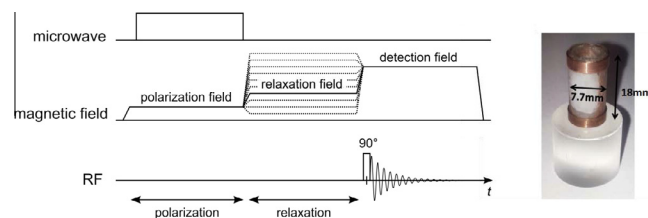


Fig. 1. Pulse sequence used for DNP enhanced FFC relaxometry (left) and a photograph of the resonator (right).

and a TTL port of the FFC relaxometer was used to control a microwave relay switching the microwave signal input to the amplifier. A temperature-controlled nitrogen gas flow was applied in all experiments to regulate the sample and resonator temperature. For DNP-enhanced relaxation measurements a pre-polarization sequence was modified in order to incorporate microwave irradiation during the polarization period of the field cycle at a field strength of 73 mT (Fig. 1). The polarization time was set to at least five times the spin-lattice relaxation time of the measured nuclear spins at 73 mT. ¹H and ¹³C NMR detection was done at detection fields of 0.44 T and 0.33 T, respectively. The relaxation field step was omitted for the measurements shown in Fig. 2a. Reference measurements of the ¹H Nuclear Magnetic Relaxation Dispersion (NMRD) profile without DNP enhancement were done using the standard probe and standard settings of the instrument. The aqueous sample was prepared by dissolving TEMPOL (4-Hydroxy-TEMPO) in 60 μ l of purified water to obtain a 20 mM solution and was subsequently flame sealed. The benzene sample was prepared by dissolving TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) in 60 μ l of benzene-¹³C₆,D₆ (99 atom% ¹³C, 99 atom% D) to obtain a 160 mM solution, degassed by four freeze-pump-thaw cycles and flame-sealed. Unless stated otherwise, all DNP-enhanced FFC experiments used a microwave power of 5.7 W. All samples were contained in thin-walled, 3 mm outer diameter glass tubes.

DNP experiments with Poly(butadiene-1,4) (PB) samples were done at 9.7 GHz microwave frequency and a constant magnetic field of about 0.35 T, using an electromagnet. The technical details of the corresponding DNP setup are given in Ref. [23]. Additionally, field-cycled DNP measurements with PB were performed at 2 GHz microwave frequency using the above-mentioned FFC relaxometer. PB was obtained from PSS (Polymer Standards Service GmbH, Mainz, Germany) with a weight-averaged molecular weight of 23.6 kg/mol and a polydispersity of 1.01. The PB samples were prepared by adding BDPA (α,γ -bis(diphenylene)- β -phenylallyl) and sonicating at +40 °C for around 20 h. The use of small amounts of

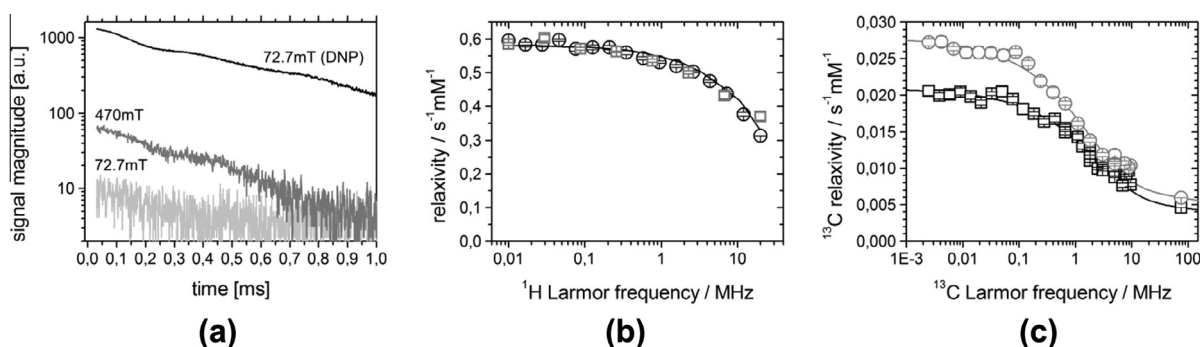


Fig. 2. (a) Single scan ¹H FID signals obtained from 20 mM TEMPOL in H₂O for thermal polarization at 72.7 mT and 470 mT and from DNP polarization at 72.7 mT. Reprinted from Ref. [22] with permission from Elsevier. (b) ¹H NMRD profiles of 20 mM TEMPOL in H₂O at 22 °C with DNP polarization (circles) and thermal polarization at 470 mT (squares) and literature data for 5 mM TEMPOL in H₂O at 25 °C from Ref. [24] (solid line). (c) DNP-enhanced ¹³C NMRD profiles of 160 mM TEMPO in benzene-¹³C₆,D₆ at +22 °C (squares) and +6.5 °C (circles) together with best fits according to Eq. (1). The fit parameters are given in Table 1.

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