

Dynamic Nuclear Polarization with a Cyclotron Resonance Maser at 5 T

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DNP (dynamic nuclear polarization) experiments at 5 T are reported, in which a cyclotron resonance maser (gyrotron) is utilized as a 20 W, 140 GHz microwave source to perform the polarization. MAS (magic angle spinning) NMR spectroscopy with DNP has been performed on samples of polystyrene doped with the free radical BDPA (α, γ -bisdiphenylene- β -phenylallyl) at room temperature. Maximal DNP enhancements of ~ 10 for ^1H and ~ 40 for ^{13}C are observed and are considerably larger than expected. The DNP and spin relaxation mechanisms that lead to these enhancements at 5 T are discussed.

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DNP (dynamic nuclear polarization) is a magnetic resonance technique utilized to enhance the polarization of nuclei in samples containing paramagnetic centers [1,2] through irradiation of the electron spins with microwaves in the neighborhood of their Larmor frequency. In studies on solids, this technique has been primarily employed to produce polarized targets for neutron scattering experiments, and to explore magnetic ordering at μK temperatures [1].

More recently, DNP has been utilized in high-resolution solid-state NMR (nuclear magnetic resonance) experiments. In MAS (magic angle spinning) NMR spectra, signal enhancements of greater than an order of magnitude have been regularly obtained at room temperature [3–5]. Moreover, with high efficiency microwave cavities and with small static samples, enhancements of 50–200 have been achieved [6]. Such enhancements clearly enable significant reductions in the amount of sample or the acquisition time needed to perform an NMR experiment and are therefore of great interest.

The utility of these experiments has, however, been limited to date, since they have been performed only at a relatively low field—specifically 1.4 T, corresponding to Larmor frequencies for ^1H and electron of $\omega_{\text{H}}/2\pi \approx 60$ MHz and $\omega_e/2\pi \approx 40$ GHz, respectively. Consequently, the inherent sensitivity and spectral resolution routinely available in high field NMR has not been accessed in DNP-NMR experiments. The restriction to low fields arises mainly from the difficulty in procuring adequate high-power, high-frequency microwave sources. The primary millimeter wave sources, such as the EIO (extended interaction oscillator) or BWO (backward wave oscillator), rely on fragile slow-wave structures to generate microwave radiation, and thus at the high power levels required for DNP experiments have limited operating lifetimes.

In the experiments described here, we have surmounted this problem by introducing a cyclotron resonance maser, or gyrotron, as the microwave source. Gyrotrons are

presently employed extensively in plasma physics [7]. In the gyrotron, a continuous magnetic field replaces the slow wave structure, and the device is thus capable of generating high microwave powers over a lifetime that is considerably longer than that of an EIO or BWO [8]. The microwave frequency of a gyrotron is determined by the applied magnetic field strength and accelerating voltage: gyrotron operation has been demonstrated from 8–600 GHz [8], and could therefore be utilized in DNP/NMR experiments in the 12–900 MHz (^1H) NMR regime, thus considerably expanding the range of DNP/NMR experiments.

In the results described below, we have achieved surprisingly large enhancements at 5 T fields (210 MHz for ^1H and 140 GHz for electron resonance, respectively). For PS (polystyrene) doped with the free radical BDPA (α, γ -bisdiphenylene- β -phenylallyl) [9], we have observed maximal enhancements of ~ 10 for ^1H and ~ 40 for ^{13}C , corresponding to reductions in signal averaging times of 100 and 1600, respectively.

In Fig. 1, we show ^{13}C MAS NMR spectra obtained with these samples. The spectra in Fig. 1 were acquired with ^1H - ^{13}C cross polarization and with the external field adjusted such that the microwave frequency was applied at $\omega_e - \omega_{\text{H}}$ (top). In the bottom trace we show a spectrum recorded without microwave irradiation and a comparison with the top trace clearly illustrates the enhanced signal intensity; the ^{13}C spectra acquired in this manner thus provide an indirect method of probing ^1H polarization enhancements. We also directly detected the ^1H NMR spectrum, which consists of an 80 kHz wide featureless line, obtaining similar results. The spectra in Fig. 2 were acquired with microwave irradiation at $\omega_e + \omega_{\text{C}}$, ω_e , and $\omega_e - \omega_{\text{C}}$, but without cross polarization, and thus provide a direct measure of ^{13}C polarization enhancements. In the ^{13}C spectra, the peaks at 125 and 40 ppm correspond to the polystyrene aromatic and aliphatic carbons, respectively; the remaining lines are the sidebands associated with MAS at rates of 2–5 kHz. The

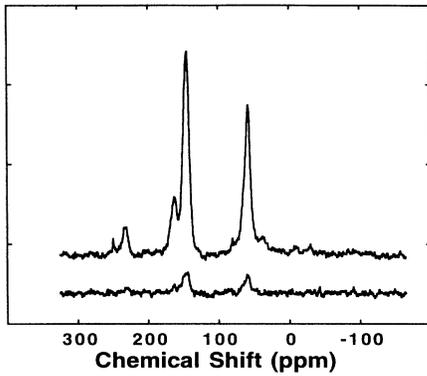


FIG. 1. ^{13}C cross-polarization MAS spectrum of (2%) BDPA/PS at 5 T and room temperature. The sample was alternatively irradiated with 139.6 GHz microwaves at $\omega_e - \omega_H$ for 8 s before acquisition of the DNP enhanced spectrum (top), or not subject to microwave irradiation (bottom).

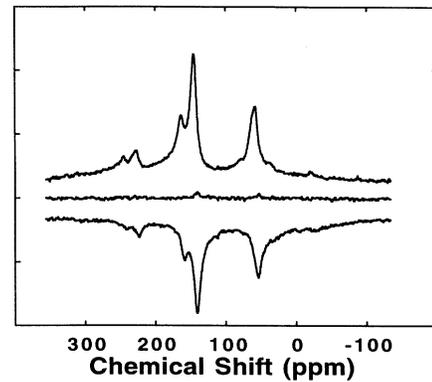


FIG. 2. ^{13}C MAS spectrum of (2%) BDPA/PS at 5 T and room temperature. The external field strength was adjusted such that the 139.6 GHz microwave irradiation (20 s) alternatively corresponds to (top) $\omega_e - \omega_c$; (middle) ω_e ; (bottom) $\omega_e + \omega_c$.

peaks in Fig. 2 are clearly broader than those of Fig. 1. This situation stems from the distinct methods of polarizing the ^{13}C : when indirectly polarized, spin diffusion among the abundant ^1H nuclei distributes the polarization enhancements over extended polymer domains; when directly polarized, the ^{13}C nuclei that are located near the paramagnetic centers, and which therefore experience some electron-nuclear dipolar broadening, are selectively enhanced.

The detailed dependences of the ^1H and ^{13}C polarization enhancements on electron spin resonance offset are illustrated in Figs. 3 and 4. Specifically, we show the enhancement as a function of the difference between the applied field and the center of the BDPA EPR line. For the protons, the depicted behavior epitomizes the well-resolved solid effect [1]. To date, the maximal enhancements obtained amount to 10, and are similar to those obtained for PS/BDPA at 1.4 T under otherwise similar conditions. Such enhancements are considerably smaller than the theoretical maximum of γ_e/γ_n , and thus imply substantial "leakage" of the nuclear polarization.

Leakage should generally be negligible, when the spin-lattice relaxation of a set of nuclei (undergoing of rapid spin diffusion) is governed by their interaction with isolated paramagnetic centers. In this situation,

$$T_{1n}^{-1} \approx \frac{N_e}{N_n} \frac{\gamma_e}{\gamma_n} \left(\frac{\Delta B_n}{B_0} \right)^2 T_{1e}^{-1}, \quad (1)$$

in which N_n and N_e are the nuclear and electronic spin concentrations ($\sim 3 \times 10^{25} \text{e}^-/\text{m}^3$ and $5 \times 10^{28} \text{H}/\text{m}^3$ in our sample), ΔB_n is the nuclear resonance linewidth and B_0 is the external field strength. This relation ensures that after a forbidden transition is driven, an electron spin can relax before the N_n/N_e nuclei in its field of influence return to thermal equilibrium as $T_{1e}^{-1} \gg T_{1n}^{-1} N_n/N_e$.

Although the incorporation of BDPA into PS leads to a substantial reduction of the proton T_{1n} —from 7 s for the neat material to 1.6 s in the presence of BDPA—the relation between T_{1n} and T_{1e} expressed in Eq. (1) does not apply. Measurements of T_{1e} at 4–18 GHz and 95 GHz suggest that under our experimental conditions, $T_{1e} \approx 0.5$ ms [10], thus implying a T_{1n} of ~ 5600 s. The gross disparity in the calculated and observed values of T_{1n} indicates that the nuclear relaxation in the radical-doped sample originates in processes other than electron spin-lattice relaxation. Following Ref. [1], we define the leakage coefficient f as the ratio of the calculated and observed values of T_{1n} , whence $f \approx 3500$. In such a case of strong leakage, the maximum enhancement for the resolved solid effect is given by ε :

$$\varepsilon = \left(\frac{\gamma_e}{\gamma_n} \right) \frac{1}{1 + \alpha f + f/s}, \quad (2)$$

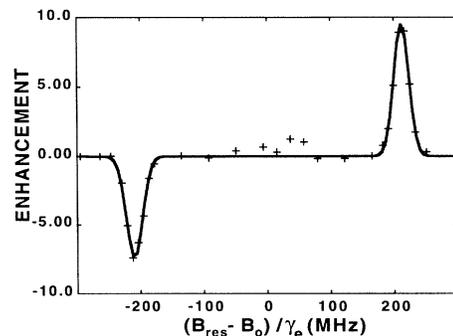


FIG. 3. DNP enhancement profile for (2%) BDPA/PS at 5 T and room temperature. The enhancement is plotted versus the offset of the external magnetic field (B_0) from the center of the BDPA EPR line (B_{res}) for ^1H DNP.

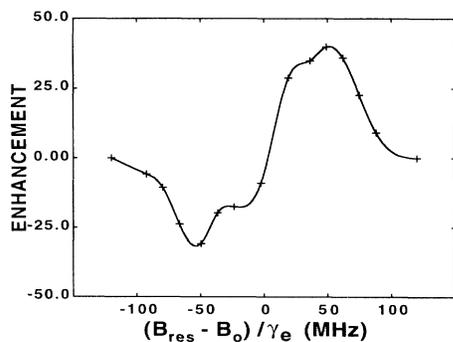


FIG. 4. DNP enhancement profile for (2%) BDPA/PS at 5 T and room temperature. The enhancement is plotted versus the offset of the external magnetic field (B_0) from the center of the BDPA EPR line (B_{res}) for ^{13}C DNP.

in which a is $\gamma_e/\gamma_n (\Delta B_n/B_0)^2$, s , the saturation factor, is $\pi(\gamma_e B_1)^2 g(\omega=0) T_{1e}$, and $g(\omega)$ is the normalized EPR lineshape function, centered at $\omega=0$. Assuming that the microwave field in the sample is approximately the same as inside the waveguide, namely ≈ 1 G, we estimate that $s \approx 70$, and the enhancement, according to Eq. (2), is ~ 15 , in reasonable agreement with the observed value of 10.

The inadequacy of Eq. (1) for predicting T_{1n} is attributable to the large value of N_e . The paramagnetic centers are not isolated, but sustain significant electron spin-spin interactions, and engage in electron spin flip-flop processes at a rate that can be approximated, very roughly [11], as $T_{ee}^{-1} \approx \Delta\omega_d (\Delta\omega_d/\Delta\omega) \approx 1$ MHz, in which $\Delta\omega_d$ is the mean electron dipolar coupling, $\Delta\omega$ is the EPR linewidth, and the parenthetical factor accounts for the inhibition of flip-flops by detuning. The observed nuclear relaxation rate can be rationalized by identifying the electron flip-flop time, rather than T_{1e} , as the relevant correlation time for the fluctuations of the electron-nuclear interaction, and thus replacing T_{1e} with T_{ee} in Eq. (1). (See Refs. [1,12] for further discussion.) Notably, since the recovery of the electron spin polarization remains governed by T_{1e} , while the nuclear relaxation is governed by the much smaller T_{ee} , the guarantee of negligible leakage, implicit in Eq. (1), is no longer applicable.

In many systems with significant electron-electron spin interactions, DNP occurs via thermal mixing. This DNP process involves the energy conservative coupling of the electron-electron flip-flop process to the flip of a nuclear spin. Its efficacy varies with the value $f(\omega_n)$ of a lineshape function $f(\omega)$, which gives the probability that an electron spin pair changes its energy by ω upon execution of a flip-flop [1,12]. If we assume that $f(\omega)$ is Lorentzian [1] with the width roughly equivalent to the observed EPR linewidth, then we would expect the thermal mixing enhancement to decrease with increasing Zeeman field, all other quantities remaining equal. In particular, comparing experiments at 1.4 [3] and 5 T, we

would expect a decrease of ~ 4 for ^{13}C enhancements and ~ 10 for ^1H enhancements. On the basis of the results of Wind and co-workers at 1.4 T [3,6], we thus expect enhancements of 40 and 0.6 for ^{13}C and ^1H , respectively at 5 T. Consistent with this expectation, no clear indication of any ^1H thermal mixing is apparent in the DNP profile of Fig. 3. In addition the ^{13}C profile (Fig. 4) shows thermal mixing enhancements of ~ 15 . The solid effect gives rise to slightly greater ^{13}C DNP and amounts to roughly $\gamma\text{H}/\gamma\text{C}$ times the ^1H solid-effect DNP enhancement.

Our results demonstrate the feasibility of performing DNP-NMR at higher magnetic field strengths than has been previously attempted. By utilizing a gyrotron as the microwave source, we have obtained substantial solid-effect DNP enhancements at 5 T, which are equivalent to those obtained under analogous conditions at 1.4 T, notwithstanding the significantly decreased moments of the driven EPR transitions. By contrast, we find that the thermal mixing effects are significantly reduced at the higher field. This reduction, gauged by $f(\omega)$, reflects the decreasing likelihood of an energy conserving electron-electron-nucleus spin flip as the nuclear Larmor frequency is increased; thermal-mixing DNP enhancements need not necessarily decline sharply at higher fields, but can vary in behavior, depending on the spectral properties of the electron spin system employed for DNP.

Finally, since gyrotrons can be operated at higher microwave frequencies, it should be possible to extend these and other experiments involving DNP to even higher magnetic fields.

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