Observing Apparent Nonuniform Sensitivity Enhancements in Dynamic Nuclear Polarization Solid-State NMR Spectra of Polymers

Giulia Mollica,[†] Dao Le,[†] Fabio Ziarelli,[‡] Gilles Casano,[†] Olivier Ouari,[†] Trang N. T. Phan,[†] Fabien Aussenac,[§] Pierre Thureau,[†] Didier Gigmes,[†] Paul Tordo,[†] and Stéphane Viel*,[†]

[†]Aix Marseille Université, CNRS, ICR UMR 7273, 13397 Marseille, France

[‡]Aix Marseille Université, Centrale Marseille, CNRS, Fédération des Sciences Chimiques de Marseille FR 1739, 13397 Marseille, France

[§]Bruker Biospin SAS, 67160 Wissembourg, France

ⓢ *Supporting Information*

ABSTRACT: High-field dynamic nuclear polarization (DNP) may enhance the sensitivity of solid-state NMR experiments on a wide range of systems, including synthetic polymers, owing to the transfer of electron spin polarization from radicals to nuclei upon microwave irradiation (usually at cryogenic temperatures). Provided that the radicals are homogeneously dispersed in the sample, a uniform DNP enhancement is expected for all the signals in the ^{13}C cross-polarization magic angle spinning (CPMAS) spectrum. Here, we show that, in the case of methyl group containing polymers, a change in the cross-polarization (CP) dynamics induced by the moderate increase in sample temperature due to microwave irradiation may lead to the observation of apparent nonuniform enhancements in the DNP-enhanced ^{13}C CPMAS spectra. This peculiar behavior should be accounted for when measuring ^{13}C CP DNP enhancements on polymer materials, especially for heterogeneous polymer samples (for which truly nonuniform DNP enhancements could potentially be detected), or when quantitative results are sought.

Temperature change due to μW irradiation *vs* Cross-polarization dynamics in DNP NMR
With DNP (**110 K**)
Without DNP (**100 K**)
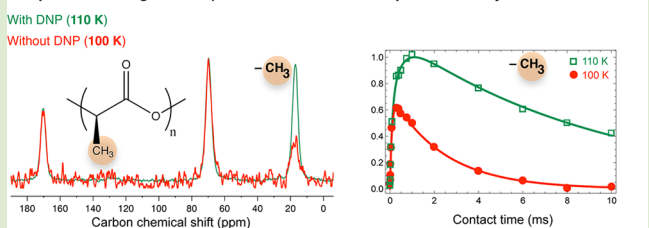
High-field dynamic nuclear polarization (DNP) low-temperature magic angle spinning (MAS) solid-state NMR (SSNMR) has recently emerged as a powerful technique for improving the characterization of a wide range of systems in the solid state,[1] such as biomolecules,[2] materials,[3] and polymers.[4,5] DNP is based on the microwave-driven polarization transfer (usually at cryogenic temperatures) of the electron spin polarization to nuclei,[6] yielding a maximum increase in NMR signal strength equal to the ratio of the electron to nuclear magnetogyric ratios (~660 for ^{1}H). As a result, overall sensitivity enhancements of about 1 to 2 orders of magnitude can now be obtained. All DNP investigations require the presence of unpaired electrons used as a source of electron polarization, which may imply doping the samples with exogenous paramagnets, such as mono- or biradicals. Typically, DNP-enhanced SSNMR experiments that involve cross-polarization (CP) from abundant spins (usually ^{1}H) to rare spins X (e.g., ^{13}C, ^{15}N···) can be thought of as a two-step process. First, spin polarization gets transferred upon microwave irradiation from the unpaired electrons of the radicals (the so-called DNP polarizing agents) to the nearby protons of the matrix. Second, this enhanced proton magnetization spreads out through the medium by ^{1}H−^{1}H spin diffusion, eventually reaching the vicinity of the investigated solute (or material surface) where it is transferred to a heteronucleus of interest by conventional CP techniques. In this context, when DNP polarizing agents are

homogeneously distributed (either in a glassy matrix or in a polymer film), ^{1}H−^{1}H spin diffusion is expected to result in a *uniform* CP DNP enhancement ($\varepsilon_{X,CP}$) for all the X signals in the cross-polarization magic angle spinning (CPMAS) spectrum, where $\varepsilon_{X,CP}$ is defined as the ratio of the intensity of the X resonances measured with (I_{ON}) and without (I_{OFF}) microwaves ($\varepsilon_{X,CP} = I_{ON}/I_{OFF}$). Recently, however, in connection with an ongoing project directed toward the development of high-field DNP SSNMR for the analysis of polymer materials,[4,7] we have observed instances of *nonuniform* $\varepsilon_{X,CP}$ values when analyzing polymer samples containing methyl groups, such as polylactide (PLLA or PDLLA) and poly(methyl methacrylate) (PMMA), regardless of the method used for preparing the DNP samples, being either film casting (FC) or glass forming (GF). Here, we show that these apparent nonuniform enhancements are not related to the DNP process itself but have to do with a change in the CP dynamics. Precisely, we show that, in the range of cryogenic temperatures used for current high-field DNP-enhanced SSNMR (~90−110 K), switching on the microwave field typically induces a temperature increase of the sample that is sufficient to impact the

methyl group dynamics, which results in a modified CP efficiency that may contribute to *artificially* enhance (or reduce) the I_{ON} with respect to I_{OFF} signal intensity of all carbon nuclei in the sample, hereby leading to apparent nonuniform CP DNP enhancements.

Observation of nonuniform $\varepsilon_{X,CP}$ values is illustrated in Figure 1 for methyl groups, both for a PDLLA and a PMMA

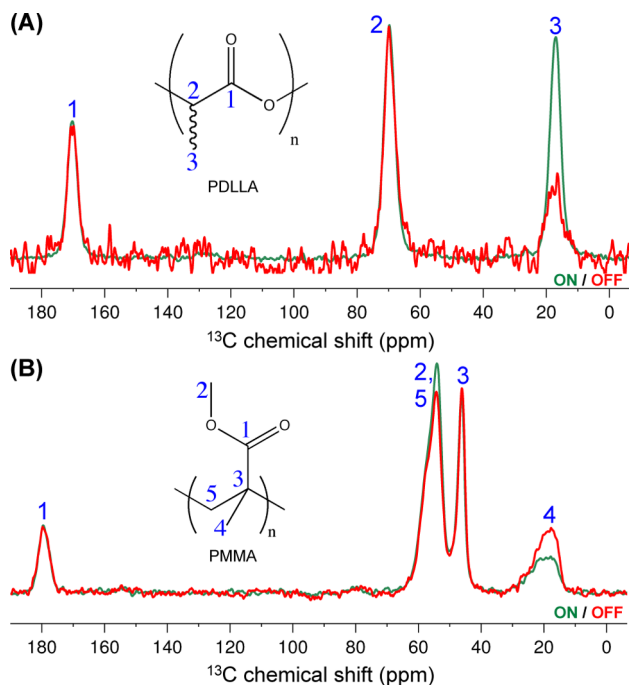**Figure 1.** DNP-enhanced ^{13}C CPMAS spectra (contact time: 1 ms) obtained on (A) a PDLLA sample (M_n ~5 kg mol^{-1}) and (B) a PMMA sample (M_n ~100 kg mol^{-1}) prepared by film casting with TEKPol as a polarizing agent (11 μmol g^{-1}). The traces in red and green were obtained with the microwave field *off* and *on*, respectively, and they are normalized in each case to match the intensity of the carbonyl signals. This reveals the apparent nonuniform DNP enhancement of the methyl groups because the intensity of the C3 signal due to PDLLA or that of the C4 signal due to PMMA seem enhanced and reduced, respectively. Likewise, the intensity of the C2 signal due to PMMA seems slightly enhanced.

sample prepared by FC. Similar results were obtained when using GF with 1,1,2,2-tetrachloroethane (TCE) as the solvent. However, in this case, the ^{13}C signal due to TCE (at ~76 ppm) partially overlapped with the resonance due to carbon C2 in PDLLA (Figure 1A), and hence FC data were preferred. More specifically, Figure 1 compares the ^{13}C CPMAS spectra recorded with the microwave field *on* and *off* on PDLLA (Figure 1A) and PMMA (Figure 1B) by normalizing in each case the intensity of the resonances due to the carbonyls. In other words, if $\varepsilon_{X,CP}$ were the same for all the signals, the *on* and *off* spectral traces should fully overlap. As seen in Figure 1, this is not the case for carbons C3 and C4 for PDLLA and PMMA, respectively (the former is largely enhanced, whereas the latter is significantly reduced). Note that PLLA and PDLLA samples, which are semicrystalline and amorphous polymers, respectively, yielded similar results (data not shown). Importantly, it will be shown later that this observation, which applied independently of the sample molecular weight, is not a specific feature of the ^{13}C signals due to methyl groups, as Figure 1

could suggest, even though it does arise from the presence of methyl groups in the sample (*vide infra*).

In the ^{13}C CPMAS spectra shown in Figure 1, the microwave field was turned *on* and *off*, and the polymer samples contained biradicals. To simplify the system under study, we analyzed the same samples but without radicals. Switching on the microwave field in this case gave results that were essentially comparable to those depicted in Figure 1, obviously without the signal enhancement due to DNP, which was no longer observed owing to the absence of radicals in the sample. Specifically, upon switching on the microwave field, the intensity of the CO and CH resonances remained constant, whereas the intensity of the CH$_3$ resonance increased, in a similar fashion to that evidenced in Figure 1A (the same observations were made for PMMA but with an opposite trend, in agreement with Figure 1B). At this point, considering that turning on the microwave field is known to induce a change in sample temperature,[8] three distinct ^{13}C CPMAS spectra were recorded on a PLLA sample without radicals and with the microwave field *off*, using three distinct sample temperatures: 100, 105, and 110 K. This range of temperatures was selected because it corresponds to the actual temperature increase that is experienced by the sample when turning on the microwave field in the framework of a typical DNP-enhanced SSNMR experiment. This point was experimentally verified by using the KBr thermometer proposed by Thurber and Tycko.[9] The corresponding data are reported in Figure 2. As seen in Figure 2, and similarly to
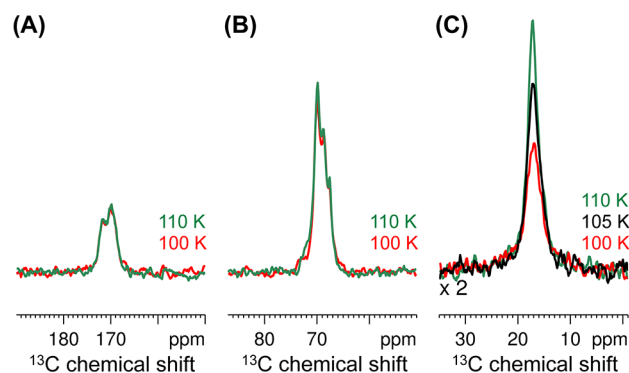

Figure 2. Expanded regions of the ^{13}C CPMAS spectra (contact time: 1 ms) recorded on a PLLA sample (M_n 5 kg mol^{-1}) without radicals and with the microwave field *off* at different temperatures, showing the resonances due to (A) CO, (B) CH, and (C) CH$_3$. In (C), the absolute intensity of the spectra has been increased by a factor of 2 with respect to (A) and (B). Note that, in (A) and (B), the trace at 105 K overlapped with those at 100 and 110 K, and hence it was not displayed to ease the comparison.

Figure 1, the intensity of the CO and CH resonances remains constant as the temperature increases from 100 to 110 K, whereas the intensity of the methyl group is clearly increased.

To better understand these observations, variable contact time (ct) ^{13}C CPMAS experiments were recorded on the PDLLA and PMMA samples without DNP polarizing agents, with the microwave field *off* and *on* (corresponding to an effective sample temperature of 100 and 110 K, respectively). The results are reported in Figure 3, where the data related to the CO, CH, and CH$_3$ resonances for PDLLA and to the CO, C, and CH$_3$ resonances for PMMA are compared. For short ct values (<0.1 ms), data obtained at both temperatures are roughly equivalent in all of the cases for both polymers. In
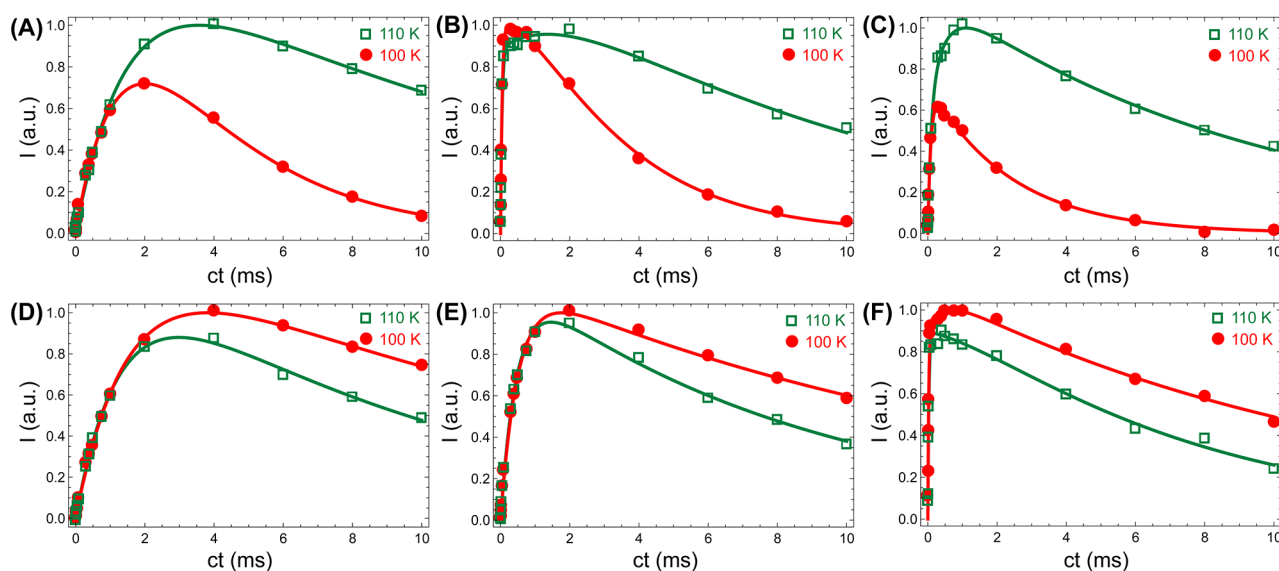
Figure 3. ^{13}C CPMAS build-up curves as a function of the CP contact time (ct) obtained on (A−C) a PDLLA sample ($M_n \sim 5$ kg mol^{-1}) and (D−F) a PMMA sample ($M_n \sim 100$ kg mol^{-1}) without a polarizing agent, showing the (A) CO, (B) CH, and (C) CH$_3$ resonances of PDLLA and the (D) CO, (E) C, and (F) CH$_3$ resonances of PMMA. The traces in red and green were obtained with the microwave field *off* and *on*, respectively, which corresponded to a sample temperature of 100 and 110 K, respectively.

contrast, for larger ct values, the situation becomes highly polymer- and signal-dependent. Indeed, for PDLLA, the intensity of all 110 K curves is systematically (much) higher than that of the 100 K curves, whereas the opposite (albeit in a lesser extent) is observed for PMMA, independently of the type of carbon. These curves allow us to clarify the observations made in Figures 1 and 2. In these cases, ct had been optimized to 1 ms. As seen in Figure 3, for both polymers, this ct value lies in a peculiar range where the *off* and *on* CP build-up curves (red and green curves, respectively) of all the signals are still overlapping, except for the CH$_3$ groups. Data in Figure 3 also show that, while initially illustrated for CH$_3$ groups (as seen in Figures 1 and 2), nonuniform $\varepsilon_{X,CP}$ values could well be obtained for all types of ^{13}C signals, depending upon the ct value that is selected to record the ^{13}C CPMAS spectrum (e.g., a 2 ms ct value for PDLLA would yield different $\varepsilon_{X,CP}$ values for all ^{13}C signals). Still, even in the (unlikely) case where the intensity of all signals was to be enhanced (or reduced) to a similar extent upon switching on the microwave field (not as a result of DNP but due to the temperature increase only), this interference would still be detrimental because it would yield wrong $\varepsilon_{X,CP}$ values (being either over- or underestimated, respectively). While the detailed analysis of the data reported in Figure 3 clearly lies outside the scope of this work (and will be the subject of a future publication), Figure 3 strongly suggests that the change in sample temperature modifies the dynamics of the system under study. This is in agreement with ^1H spin−lattice relaxation time ($T_1(^1H)$) measurements. Specifically, upon increasing the temperature from 100 to 110 K, $T_1(^1H)$ for PDLLA went from 3.2 to 1.2 s (and from 3.4 to 1.3 s for PLLA), whereas $T_1(^1H)$ for PMMA remained constant to 0.4 s. In this range of cryogenic temperatures (~ 100 K), the motion of methyl groups remains one of the most significant relaxation sinks.[10] In particular, for PLLA, literature data even indicate that there is a strong variation in the second moment of the ^1H line shape between 90 and 130 K.[11] Modification of spin−lattice relaxation times in the rotating frame is also very much likely, which could partly explain the trends observed in Figure

3. Overall, this suggests that polymers that contain methyl groups are most probably to be affected by the interference illustrated here. As a matter of fact, the CP build-up curves recorded on a polystyrene sample in these conditions fully overlapped (see Supporting Information (SI)).

In summary, this work has shown that, when measuring $\varepsilon_{X,CP}$ on synthetic polymers, especially those carrying methyl groups, low ct values should preferentially be used. Alternatively, the whole build-up curves should be recorded, both with the microwave field *off* and *on*, so as to pinpoint possible changes in sample dynamics that could possibly modify the CP efficiency, hence altering the measurement of $\varepsilon_{X,CP}$. This is especially important in order to interpret correctly the DNP enhancements obtained when analyzing heterogeneous polymer samples[12] (such as block copolymers grafted onto inorganic substrates), where nonuniform DNP enhancements could potentially be detected, or when quantitative results must be obtained.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental methods. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: s.viel@univ-amu.fr.

Notes

The authors declare no competing financial interest.

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