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Improved Structural Elucidation of Synthetic Polymers by Dynamic Nuclear Polarization Solid-State NMR Spectroscopy

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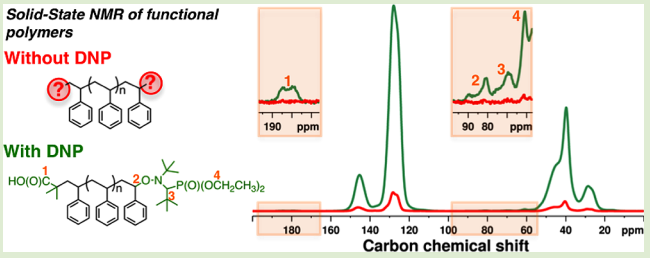
Supporting Information

ABSTRACT: Dynamic nuclear polarization (DNP) is shown to greatly improve the solid-state nuclear magnetic resonance (SSNMR) analysis of synthetic polymers by allowing structural assignment of intrinsically diluted NMR signals, which are typically not detected in conventional SSNMR. Specifically, SSNMR and DNP SSNMR were comparatively used to study functional polymers for which precise structural elucidation of chain ends is essential to control their reactivity and to eventually obtain advanced polymeric materials of complex architecture. Results show that the polymer chain-end signals, while hardly observable in conventional SSNMR, could be clearly identified in the DNP SSNMR spectrum owing to the increase in sensitivity afforded by the DNP setup (a factor ∼10 was achieved here), hence providing access to detailed structural characterization within realistic experimental times. This sizable gain in sensitivity opens new avenues for the characterization of "smart" functional polymeric materials and new analytical perspectives in polymer science.



Development of controlled radical polymerization techniques and "click chemistry" strategies has led over the last two decades to a large number of investigations dedicated to the synthesis, analysis, and application of increasingly sophisticated polymer architectures and compositions. Thanks to this spectacular takeoff of the so-called macromolecular engineering, advanced polymeric materials are about to play critical roles in areas of major importance for society, such as energy, health, environment, and advanced technologies.[1] Traditionally, nuclear magnetic resonance (NMR) is regarded as a technique of choice for studying polymeric materials, especially in the solid state where they are predominantly used,[2] because of its ability to yield highly informative spectra in a nondestructive way. Overall, this has contributed to enhance the description of microstructure/properties relationships in polymeric materials, which are essential to clarify their macroscopic behavior. However, NMR is still currently limited by its intrinsically low sensitivity, which precludes the elucidation of subtle structural information in polymers, especially for large molecular weight species. As a result, structural features, such as chain ends or junctions in linear, block, cross-linked, star, hyperbranched, or grafted (co)-polymers, which impact the reactivity of the macromolecular assemblies and their nanostructuration properties, may not be thoroughly characterized. Several methods have been proposed in the literature to boost the NMR sensitivity, including dynamic nuclear polarization (DNP).[3] DNP exploits the microwave-driven transfer of polarization from the electron spins of a paramagnetic center (i.e., polarizing agent) to surrounding nuclei. The maximum theoretical enhancement achievable is given by the ratio of the electron and nuclear magnetogyric ratios (∼660 for ^{1}H). Although DNP is hardly a new technique,[4] it has recently received renewed attention owing to substantial technological and theoretical developments. On the one hand, state-of-the-art DNP equipment nowadays allows DNP solid-state nuclear magnetic resonance (SSNMR) investigations to be conducted at high magnetic fields (>9 T) and low temperatures (∼100 K),[5] while maintaining adequate instrumental stability to achieve large signal averaging, which is classically required for analyzing NMR spectra with a low signal-to-noise ratio (S/N). On the other hand, novel polarizing agents have been developed that yield significant DNP signal enhancements even at high magnetic fields.[6,7] This progress has recently led to remarkable advances in high-resolution SSNMR, from the analysis of highly relevant biomolecular samples to the characterization of surfaces and materials,[7−13] which would have been completely unfeasible without DNP. Surprisingly, however, the potential of high-field DNP SSNMR for the analysis of synthetic polymers, while already acknowledged,[7,14] has been largely ignored. Indeed, most DNP NMR investigations reported on polymers

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so far have been constrained to low magnetic fields (1.4 T).[15,16] To the best of our knowledge, the sole exceptions are the works conducted at moderate fields (5 T) by R. Griffin's and F. Horii's research groups,[17,18] where a polystyrene (PS) sample and submicrometer poly(methyl methacrylate) particles, respectively, were analyzed using monoradicals as polarizing agents. More recently and in a different context, dissolution DNP has been used to analyze living chain ends of growing polymers in the liquid state.[19] However, while of interest, these studies did not reveal the potential of high-field DNP for the structural elucidation of synthetic polymers, which constitutes the purpose of the present investigation. Specifically, we focus here on the analysis of functional polymers (*living* polymers and macromonomers) whose chain end(s) can be subsequently involved in further reactions, including polymerization reactions and chemical transformations. Living polymers are primarily obtained by controlled radical polymerization techniques, such as atom transfer radical polymerization, reversible addition−fragmentation chain transfer, or nitroxide-mediated polymerization (NMP).[20] In particular, NMP is based on the reversible equilibrium between macroalkoxyamine and radical species, which results from the thermally labile C−ON bond (Figure S1, Supporting Information). Successful polymerization of polymeric architectures through these techniques demands a detailed structural elucidation of the polymer chain ends to evidence the quality of the control and further exploit their reactivity. The analytical challenge comes from the inherent dilution of chain ends with respect to the polymer backbone. This results in intrinsically weak NMR signals that can only be unequivocally detected if optimal sensitivity is achieved, while maintaining realistic experimental times. This difficulty could in principle be circumvented by using the so-called melt-state NMR approach,[21] where the NMR analysis is carried out in the melt state under moderate spinning speed, hence affording very narrow peaks with good S/N. However, although very appealing, this method is unsuitable for analyzing thermally reactive polymers. As a matter of fact, it is inappropriate for the living polymers described herein since an increase in temperature would irremediably lead to the modification of the polymer chain ends. More precisely, the functional polymer models analyzed here were living PS and poly(ethylene oxide) (PEO) samples obtained via NMP and 1,2-intermolecular radical addition, respectively, in the presence of the MAMA-SG1 initiator (Figure 1a−c and Figure S2, Supporting Information).

The key to successful DNP SSNMR analysis is sample preparation. While a few methods have already been proposed in the literature (film casting,[15,17] incipient wetness impregnation,[11] glass forming,[8] spin labeling,[14] matrix free[12,13]), no general protocol is available for synthetic polymers. Basically, these methods can be grouped into two categories depending on whether the sample is analyzed in the presence of additional components (e.g., solvent, cryoprotectant, nonsolvent, ...). Both the glass-forming and the incipient wetness impregnation methods commonly require the use of such components (albeit in distinct respective amounts), which may give NMR signals that interfere with those of the sample (especially for natural isotopic abundance samples). In addition, in the glass-forming method, the presence of a large amount of solvent in the frozen solution induces conformational line broadening, leading to a concomitant loss of spectral resolution and sensitivity. In contrast, spin-labeling[14] and matrix-free[12,13] methods eliminate these shortcomings while optimizing experimental sensitivity because the NMR rotor only contains the sample (without extra component). Matrix-free appears even more promising than spin-labeling because no synthesis (hence sample modification) is required. However, the extent to which these methods yield a uniform and reproducible dispersion of the radicals within the polymer matrix remains to be assessed (a point of significance if quantitative results are to be obtained).

As a result and to avoid the previously mentioned drawbacks, the film casting sample preparation method was selected in this work. Samples were solubilized in an appropriate solvent (here, dichloromethane), and then radicals were added to the polymer solution prior to solvent evaporation. Note that this method clearly resembles that proposed by Takahashi et al.,[12] with the distinction that macromolecules are here solvated rather than suspended. We used bCTbK dinitroxide as a polarizing agent (Figure 1d) because it gives optimal DNP enhancements (ε_{DNP}) in organic media.[7] The amount of bCTbK was optimized to obtain the highest S/N per unit of square time, hereafter referred to as $(S/N)_{t1/2}$, while maintaining an adequate spectral resolution. ^{13}C cross-polarization magic angle spinning (CPMAS) experiments were recorded on PS samples (M_n = 5500 g mol^{-1}) prepared using the film casting method with a bCTbK weight fraction ranging from 0.2% to 1.5% (see Supporting Information). Results reported in Figure 2a indicate that bCTbK weight fractions higher than 0.5% give

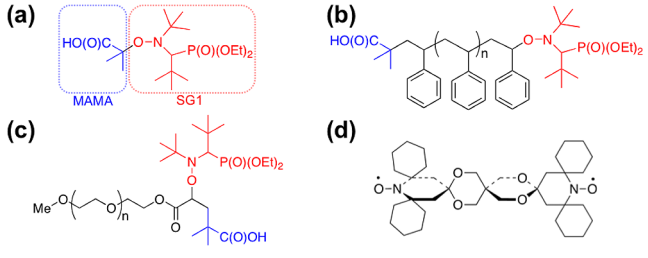

Figure 1. Structures of (a) MAMA-SG1, (b) living PS, (c) living PEO, and (d) bCTbK (see also Figures S1 and S2, Supporting Information).

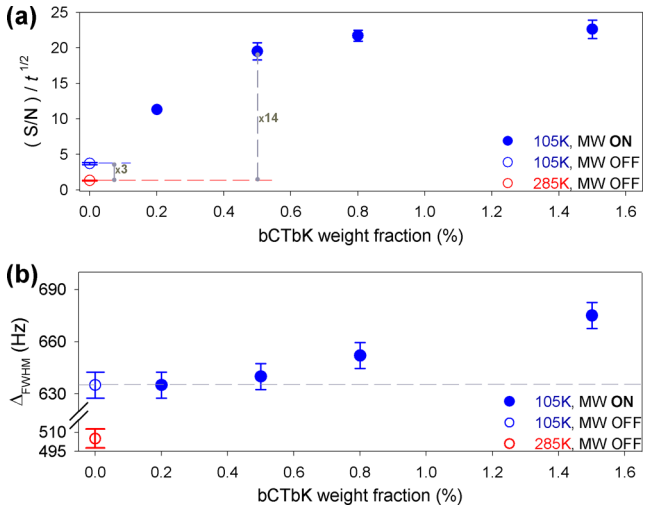

Figure 2. Evolution as a function of the bCTbK weight fraction of (a) the signal-to-noise ratio per unit of square time $(S/N)_{t1/2}$ and (b) the signal full width at half-maximum Δ_{fwhm} (the signal at 128 ppm was considered in both cases), for a series of ^{13}C CPMAS spectra recorded on a living PS sample (M_n = 5500 g mol^{-1}) without or with DNP, i.e., with microwave (MW) irradiation *off* or *on*, respectively.

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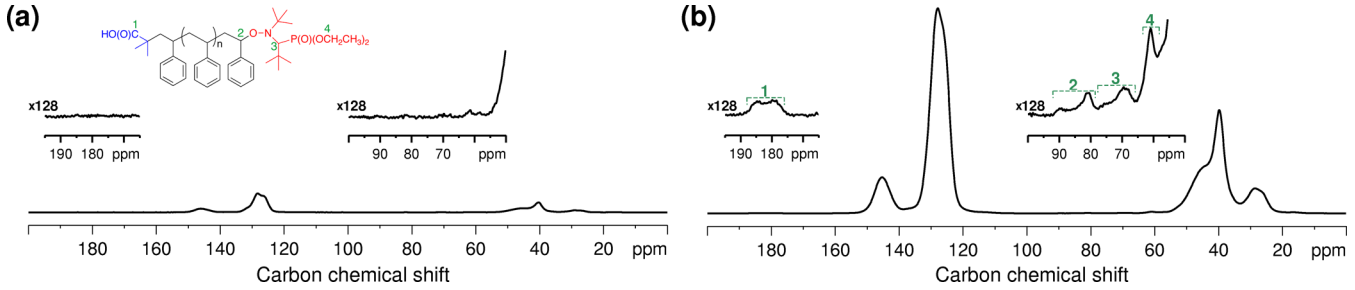

Figure 3. ^{13}C CPMAS SSNMR spectra of a living PS sample (M_n = 13 500 g mol^{-1}) obtained (a) without or (b) with DNP (at 285 and 105 K, respectively). The sample in (b) was doped with 0.5 wt % bCTbK. In both cases 26 624 scans were used (~15 h), and intensity scales are identical.

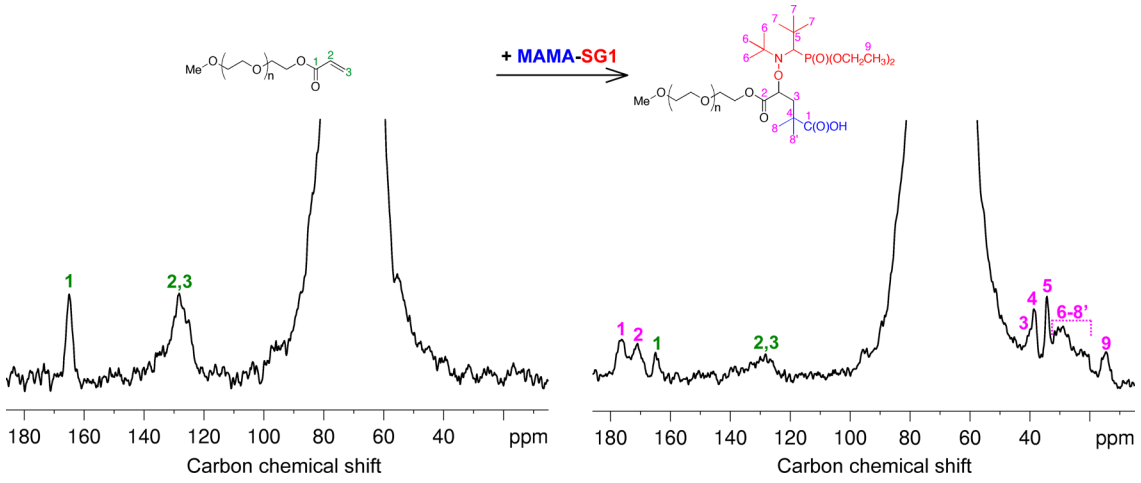

Figure 4. ^{13}C DNP CPMAS SSNMR spectra of an acrylate-terminated PEO sample (M_n = 35 000 g mol^{-1}) obtained before (left) and after (right) the 1,2 intermolecular radical addition with MAMA-SG1. In both cases 0.5 wt % bCTbK and 1600 scans were used (~13 h). On the right, NMR signals due to both the acrylate PEO and the living PEO samples can be observed, implying that the reaction was not complete.

the highest $(S/N)_{t1/2}$ but at the expense of an increase in the apparent signal line width (Figure 2b). Optimizing both sensitivity and spectral resolution thus requires a compromise (0.5 wt % was here selected as appropriate). Interestingly, the variation in the apparent signal line width observed in Figure 2b predominantly arises from the temperature decrease, whereas the effect of adding paramagnetic radicals to the sample appears relatively moderate. Moreover, as seen in Figure 2a, the origin of the sensitivity enhancement in DNP SSNMR is not exclusively due to the DNP effect (e.g., $\varepsilon_{DNP} \sim 6$ for the 0.5 wt % bCTbK sample) because there is also a contribution from the temperature at which these experiments are conducted (105 K). With respect to NMR experiments recorded at room temperature, a factor of ~3 increase in sensitivity is thus expected for the DNP SSNMR spectrum because thermal nuclear magnetization is inversely proportional to temperature (thermal noise variations are here neglected for simplicity).

On the other hand, this increase is partially offset by the loss of NMR signal in the doped sample (~25% for the 0.5 wt % bCTbK sample, see Supporting Information), which arises from a combination of paramagnetic effects due to the presence of radicals.[10] As a result, quantitatively deciphering the sensitivity gain afforded when using DNP is typically performed by invoking comprehensive factors, such as the global DNP enhancement factor,[14] the overall sensitivity enhancement factor,[10] or more recently, the absolute sensitivity ratio.[12] These strongly related factors represent formal elaborations of $(S/N)_{t1/2}$ and are very convenient because they decompose the whole sensitivity gain in a series of parameters that can be independently estimated. This provides a way of optimizing distinct experimental setups when required. Nonetheless, when experimental sensitivities must be globally compared, $(S/N)_{t1/2}$ remains the most meaningful indicator. In this respect, to demonstrate the gain in sensitivity available with DNP SSNMR, ^{13}C CPMAS SSNMR and DNP SSNMR experiments were recorded on another PS sample of higher molecular weight (M_n = 13 500 g mol^{-1}) at the same magnetic field (9.4 T) and in the same experimental time (Figure 3). Equivalent acquisition parameters were used in both cases (see Supporting Information) except for temperature and sample preparation, which remained identical to those typically used in each of these two distinct setups. Specifically, the DNP SSNMR spectrum was recorded at 105 K with a PS sample doped with bCTbK (0.5 wt %), whereas the SSNMR spectrum was obtained at 285 K on the same sample but without bCTbK. This procedure clearly illustrates the whole sensitivity gain that can be realistically achieved by using one setup in place of another. This gain can be most conveniently estimated by comparing the S/N of the two spectra reported in Figure 3 (700 and 9300 for the signal at 128 ppm in Figure 3a and 3b, respectively), leading to a gain in sensitivity of ~13. In other words, obtaining without DNP a SSNMR spectrum with a S/N equivalent to that of Figure 3b would have required a total experimental time of more than 100 days (instead of ca. 15 h). As a result of such large sensitivity enhancement, the signals of the polymer chain ends can be distinctly observed in the DNP SSNMR spectrum (Figure 3b), whereas they were not detected in the SSNMR spectrum (Figure 3a). Interestingly, although

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CPMAS data are not genuinely quantitative, the relative amount of living polymer chains could be roughly estimated (90%, see Supporting Information). The increase in sensitivity afforded by DNP SSNMR now allows chemical reactions to be monitored on relatively high molecular weight samples in the solid state at low temperature (i.e., in conditions that preserve the chain-end structure), as shown in Figure 4 on the PEO sample of Figure 1c. Precisely, the higher S/N of the DNP SSNMR spectrum (illustrated in Figure S4, Supporting Information) reveals the presence of characteristic resonances due not only to the expected living polymer chain ends (most of them assigned in Figure 4, except for those that overlap with the main PEO signal at ~65 ppm) but also to the acrylate PEO precursor, hence demonstrating that the reaction was not complete. Such information is critical to optimize the polymer functionalization and would have been virtually impossible to obtain by other means.

In conclusion, we have shown that the increase in sensitivity brought about by DNP allows polymer chain ends to be detected in high molecular weight functional polymers. Time-consuming two-dimensional correlation NMR experiments can now be envisioned, even for such intrinsically diluted NMR signals. While illustrated here for functional polymers, these results can easily be generalized, and DNP SSNMR should prove useful for the analysis of a large variety of polymer systems. Future developments can also be already anticipated. As such, use of improved sample preparation methods would enable the study of insoluble polymers, whereas analysis of NMR active nuclei other than ^{13}C (e.g., ^{2}H, ^{15}N, ^{17}O, ^{29}Si, ^{31}P), with and without ^{1}H cross-polarization, should eventually yield quantitative analytical protocols. Interestingly, the ϵ_{DNP} values obtained herein for bCTbK appear substantially lower than those that have been previously observed on other systems.[7,11] While several reasons could be invoked to explain this observation (partial aggregation of the polarizing agent during sample preparation, presence of a high proton density and/or low crystallinity of the analyzed polymer samples), additional investigations are clearly required at this stage to better ascertain this point. Overall, DNP SSNMR should prove attractive for other relevant applications in polymer science, such as analysis of additives in a polymer matrix, elucidation of undesired chemical modifications upon aging processes, and characterization of nanostructuration. Investigations along these lines are under way in our lab.

■ ASSOCIATED CONTENT

Supporting Information

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

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Notes

The authors declare no competing financial interest.

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