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COMMUNICATION

Frozen Acrylamide Gels as Dynamic Nuclear Polarization Matrices.

Jasmine Viger-Gravel, ‡ [a] Pierrick Berruyer, ‡[b] David Gajan, [b] Jean-Marie Basset,[c] Anne Lesage, [b] Paul Tordo, [d] Olivier Ouari, [d] and Lyndon Emsley*[a]

[a] Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne CH-1015, Switzerland.
[b] Université de Lyon, Institut des Sciences Analytiques (UMR 5280 CNRS/UCBL/ENS Lyon), Centre de RMN à Très Hauts Champs, Villeurbanne 69100, France.
[c] King Abdullah University of Science and Technology (KAUST), KAUST Catalysis Center (KCC), Thuwal, 23955-6900, Saudi Arabia.
[d] Aix Marseille Uni, CNRS, ICR UMR 7273, 13397 Marseille, France.

Abstract: We show that aqueous acrylamide gels can be used to provide dynamic nuclear polarization (DNP) NMR signal enhancements of around 200 at 9.4 T and 100 K. The enhancements are shown to increase with cross linker concentration and low concentrations of the AMUPol biradical. We show that this DNP matrix can be used in situations where conventional incipient wetness methods fail, such as to obtain DNP surface enhanced NMR spectra from inorganic nanoparticles. In particular, we obtain ^{113}Cd spectra from CdTe-COOH NPs in minutes. The spectra clearly indicate a highly-disordered cadmium rich surface.

Dynamic nuclear polarization (DNP) is a rapidly expanding method that can provide an increase in solid-state NMR signal intensity by 2 orders of magnitude,[1] enabling atomic-level characterization of systems that were previously completely inaccessible.[1a, 1c, 2] DNP works by transferring polarization from unpaired electrons to nearby nuclei. This is enabled in diamagnetic samples by doping with a stable radical as a polarization source. Additionally, a medium is required to transfer polarization by spin diffusion from the source to the nuclei of interest and to distribute the polarizing agents homogeneously. This typically leads to formulations of frozen solutions of organic nitroxide based biradicals (TEKPol,[3] AMUPol,[4] TOTAPOL[5]…) in glass forming mixtures which can either be aqueous water/glycerol or water/DMSO, or a range of organic solvents from 1,1,2,2-tetrachloroethane[6] to *!"#$!*-terphenyl.[7] Substrates are either directly dissolved in the solution,[8] or for materials samples impregnated with the polarizing solution.[9] Glass formation has proven to be an essential requirement to avoid separation or precipitation effects upon freezing leading to poor DNP performance.[3, 10]

However, there is still today essentially only one water based formulation. The most popular DNP matrix is glycerol-‰$_8$/D_2O/H_2O in a ratio of (6/3/1 v/v) which has been empirically optimized to give the best enhancements (typically around 200 at 9.4 T and 100 K), and which is often referred to as “DNP Juice.” Even the organic solvents, which have a broad range of properties and are compatible with many substrates, encounter problems in systems prone to aggregation, with semiconductor nanoparticles a prime example, not so far amenable to study in ordinary solvents.[11]

The importance of these limitations is demonstrated if we consider the work that has been done to find alternatives. De Paëpe and others have used so-called matrix-free DNP methods to characterize liposomes,[12] small proteins[13] or membrane proteins.[14] Matrices are not actually needed for some special samples, such as silicon nanoparticles since the radical is intrinsic to the material.[15] To prevent aggregation of colloidal solutions of nanoparticles (NPs) at cryogenic temperatures, they have been dispersed in mesoporous silicas.[11] Ordinary incipient wetness impregnation of NPs has so far only been shown for the case of CeO_2.[16] Pure water has been polarized in hybrid solids.[17] In the case of reactive surface organometallic complexes, methods were developed to avoid contact between free radical and reactive site (using materials with small pores or bigger radicals) so as to prevent reaction.[18] Others have separated the radical from the substrate by creating dendrimers around the polarizing source.[18b] Micelle or supramolecular based systems have also been considered.[19] These methods are often not trivial to implement, and they all lead to significant reductions in DNP efficiency as compared to ordinary DNP Juice.

Here, we introduce a new water-based matrix for DNP using acrylamide based gels. Polyacrylamide gels, which are easy to make and widely used, for example in electrophoresis,[20] are made of a cross-linked network formed of polymer chains which provides interstitial spaces filled with water.[21] Notably they can undergo large deformations such as significant reversible swelling or collapsing to accommodate substrates.[21a, 22] We show that polyacrylamide gels can be used to achieve enhancements of over 200 at 9.4 T and 100 K. We also demonstrate that hydrophilic carboxylic acid capped CdTe (CdTe-COOH) quantum dots can be characterized with DNP using this matrix.

&"!'() +,"-.+/‰(* 1(.2* 3!"* 456* ()$+),(%* 578 29(,#"!2,!9-:**Scheme 1 shows the chemical structures used to form the polyacrylamide gel. The monomer, acrylamide (acryl), is copolymerized in D_2O with the crosslinker, *5*, *5*’- methylene bisacrylamide (bisacryl), using ammonium persulfate (APS) as the initiator and tetramethylethyldiamine (TEMED) as a redox activator. We investigated three different acryl:bisacryl ratios: 37.5:1 (2.7 % crosslinker), 29:1 (3.3 % crosslinker) and 19:1 (5 % crosslinker) which we refer to as gels **A**, **B** and **C** respectively. Varying the monomer to cross linker ratio has the known effect of varying the interstitial space in the gel, which can be thought of in terms of a pore size.[23] In order to remove excess initiators (that can react with the polarizing agents) and residual monomers, the gel is then purified using the breathing technique of Willner and

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coworkers (see SI),[24] initially developed to uniformly distribute gold NPs in the gel matrix.[22d, 24-25]

Scheme 1. (a) Polyacrylamide components: monomer acrylamide; cross-linker N,N'- methylene bisacrylamide; initiator ammonium persulfate and accelerator tetramethylethyldiamine. (b) DNP Jelly.

Here we first add acetone to the gel, which collapses and turns as a white soft solid (see Figure S2 (b)) as the water containing APS and TEMED is expulsed. The soft solidl is then immersed in an excess of D_2O, in which it swells back to its initial state, regaining a translucent gel aspect (see Figure S2 (c)). This breathing cycle is repeated four times. Once the gel is pure, it is immersed in a 1:1 w/v solution of varying concentrations of AMUPol in D_2O for one hour (Scheme 1 (b)), allowing diffusion of the free radical into the gel, leading to a polarizing gel that can be used for DNP experiments, and that we refer to as DNP Jelly. (Refer to SI for a more complete description of the method.)

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Figure 1(a) shows the ε_H, $\varepsilon_{C=O,\ CP}$, and $\varepsilon_{alkyl,\ CP}$ factors obtained for gels **A**, **B**, and **C**. They were obtained by comparing integration of the resonances of interest for the gel spectra acquired with and without microwave irradiation and correspond to the carbonyl and alkyl functionalities of the propionamide units. The ^{13}C CPMAS NMR spectra of the gels are shown in Figure S3. ε increases as the acryl:bisacryl ratio decreases for gels **A**, **B** and **C** respectively: from 119(35) to 192(59) (for the carbonyls), and 75(11), to 131(26) (for the alkyls) and from 54 to 75 for ^1H. The ratio between monomer and cross-linker is known to have an influence on the pore size in the gel, larger pore sizes are found for low crosslinker concentrations. Here the pore size decreases from gel **A**>**B**>**C,** and varies between 41 to 10 nm, respectively, as estimated using the approach of Holmes et al.).[23] Thus we can hypothesise that smaller pores improve either the homogeneous dispersion of the free radical in the gel, or the quality of the glass formed upon cooling, and leads to better DNP enhancements.[26]

Figure 1. (a) DNP $\varepsilon_{C=O,\ CP}$, $\varepsilon_{alkyl,\ CP}$ and ε_H factors of the gels as a function of acryl: bisacryl ratio for polyacrylamide gel in 10 mM AMUPol/D_2O. (b) A_B acquired with μwave off as a function of the AMUPol concentration in *456%(..-***C**. (c) Plot of the ^{13}C and ^1H DNP enhancement as a function of the effective AMUPol concentration in gel C (acryl:bisacryl 19:1 ratio).

In Figure 1 (a), we note a significant difference between the proton enhancements measured directly (ε_H) or measured through cross polarization ($\varepsilon_{C,\ CP}$) for all three gels. We believe that the higher factor observed with CP indicates that the AMUPol has an affinity for the polymer, and thus higher hyperpolarization is obtained for protons which are inside the gel network. The lower ε for the total ^1H content reflects an average between ^1H enhancements of the gel network and those of excess water outside the network where the local AMUPol concentration would then be lower and DNP less efficient. We note that the opaque white color of the sample might correspond to micro-domains of crystalline excess water (see SI, Figure S5).

Figure 1b and c show ^1H build-up times (A_B) and ε_H, $\varepsilon_{C=O,\ CP}$, $\varepsilon_{alkyl,\ CP}$ for gel **C** as a function of the free radical concentration. $A_{B,\ off}$ decreases with increasing radical concentration in line with expectations.[4, 27] The maximum DNP enhancement is obtained at lower radical concentrations than for conventional glycerol-%8/D_2O/H_2O formulations. The concentration of AMUPol in the gel

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sample (gel type C) after diffusion has been estimated by measuring the concentration of remaining AMUPol in the supernatant with quantitative liquid-state NMR (see SI for the complete procedure). The concentration curve is broader than those previously reported for other nitroxide biradicals.[6, 28] The best formulation found here for gel **C** with 3.8 mM AMUPol in D_2O yields ε_C of around 200, which compares favourably to the gold standard 10 mM AMUPol glycerol-‰/D_2O/H_2O (6/3/1 v/v) that provides a typical ε of 250 under the same conditions (see Figure S4) at 9.4 T. Note that if we assume no proton/deuterium exchange for the alkyl chains, then the ^1H concentration in DNP Jelly is the same (15 M) as glycerol-‰/D_2O/H_2O (6/3/1 v/v).[29]

CCD ;% 456* !3* CdTe-COOH* 56:* As discussed above, and reported in the literature,[11] spectra of the surface of quantum dots (QDs) are particularly challenging to acquire using conventional NMR due to low concentrations. The application of DNP surface Enhanced NMR Spectroscopy (SENS)[9] is hindered by aggregation of NPs upon freezing of colloidal solutions at 100 K.[11] The capacity of polyacrylamide gels as soft matter to adapt to a range of impregnated substrates by breathing properties makes them potentially very well suited for DNP SENS of NPs. Here hydrophilic CdTe-COOH core-type QDs (λ_{em}= 520 nm) were therefore dispersed into a formulation of DNP Jelly with the breathing technique[22d] (see SI for method). ^1H-^{113}Cd CP DNP SENS experiments where then performed to obtain surface selective spectra, while direct excitation experiments permit the entire NP to be analysed.

Figure 2. ^{113}Cd DNP CP-CPMG (black) and CPMG (dashed), as well as isotropic projection of 2D CP-PASS (orange) spectrum of CdTe-COOH NP dispersed in gel **C**. Spinning sidebands can be depicted (MAS of 10 kHz) in the (CP-)CPMG experiments. (The full 2D PASS spectrum is shown in figure S8).

As shown in Figure 2, a ^{113}Cd CP-CPMG spectrum can be acquired in minutes with DNP, with an ε_{Cd} of 40 (see SI for the μwave off spectrum). The use of a CPMG experiment provides a further ε of 8 as compared to simple CP-echo experiment. The distribution of ^{113}Cd chemical shifts observed in Figure 2 in this way (δ) is very broad (δ(^{113}Cd) from 400 to -400 ppm) which signifies Cd atoms at the surface in a broad range of different disordered coordination environments.[30] Such broad Cd spectra have previously been observed for Cd-rich surfaces in CdS NPs (0 to -750 ppm).[30b] A two-dimensional sideband (PASS) experiment[31] of the NPs dispersed in the gel was acquired to obtain the isotropic spectrum devoid of spinning sidebands (Figure 2, orange trace), and is slightly narrower than the CP-CPMG spectrum, with the distribution of δ(^{113}Cd) concentrated towards low frequency range, as expected for surface atoms. When the direct excitation experiment (with CPMG) is compared to the surface CP spectrum, one can see a slight shift to higher frequencies, as expected since relatively more signal from the core atoms is enhanced, however the width of the spectrum remains broad. This suggests a Cd rich surface and Te rich core for the particles.

In conclusion, we have prepared a series of three polyacrylamide gels with different acryl: bisacryl ratios and studied their performance as a matrix for DNP experiments at 9.4 T, 100 K using the AMUPol biradical. We observed that high DNP ε (200) are obtained when higher cross linker concentration (acryl: bisacryl 19:1 ratio) is used to form the polymer matrix along with low concentration of radical (3.8 mM). A lower concentration of AMUPol (3.8 mM) is necessary in DNP Jelly to obtain a competitive ε compared to 10 mM of AMUPol in glycerol-‰/D_2O/H_2O (6/3/1 v/v). Finally, we have demonstrated these gels as a soft matter can be used as a medium to study material systems which could not be studied before using conventional NMR or conventional DNP formulations. We determine the structure of CdTe-COOH QDs to feature a disordered Cadmium rich surface with Cd atoms in a range of coordination environments using DNP Jelly, where the ^{113}Cd spectra were acquired in minutes.

Experimental

*578*EF9('!/()#2%* All DNP NMR experiments were acquired on a 263 GHz/400 MHz Bruker Avance I or III spectrometer equipped with a low temperature magic angle spinning probe operating at ^1H, ^{13}C, ^{113}Cd Larmor frequencies of 400 MHz, 125 MHz, and 88 MHz, respectively. Sample were packed in 3.2 mm o.d. sapphire rotors for experiments performed at low temperature (90-100K). Further details for acquisition parameters can be found in SI for CPMAS, (CP-)CPMG and PASS. *H(.*2-)#$(2%2%* Polyacrylamide reagents were from BioRad or Sigma Aldrich and used without further purification. Further details on gel preparation and cleaning can be found in SI. *;%A(*2+/9.(2%* CdTe core-type COOH capped QDs were bought from Aldrich and used without further purification. Details on the sample formulation with the gel can be found in SI.

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Keywords: Dynamic nuclear polarization, polyacrylamide gel, nanoparticles, quantum dots.

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Layout 1:

COMMUNICATION

Aqueous acrylamide gels can be used to provide dynamic nuclear polarization (DNP) NMR signal enhancements of around 200 at 9.4 T and 100 K. This new DNP matrix can be used when conventional methods fail, such as to obtain DNP SENS from CdTe-COOH NPs revealing a highly-disordered cadmium rich surface.

Jasmine Viger-Gravel, ‡ [a] Pierrick Berruyer, ‡[b] David Gajan, [b] Jean-Marie Basset,[c] Anne Lesage, [b] Paul Tordo, [d] Olivier Ouari, [d] and Lyndon Emsley*[a]

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Frozen Acrylamide Gels as Dynamic Nuclear Polarization Matrices.