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SUPPORTING INFORMATION

Dynamic Nuclear Polarization of a glassy matrix prepared by solid state mechanochemical amorphization of crystalline substances.

Elena Elisei[1,2], Marta Filibian[3], Pietro Carretta[3], Sonia Colombo Serra[4], Fabio Tedoldi[4], Jean-François Willart[2], Marc Descamps[2], and Attilio Cesàro[1,5]*

[1] Department of Chemical and Pharmaceutical Sciences, University of Trieste, Via Giorgieri 1, 34127 Trieste, Italy,

[2] Université Lille Nord de France, F-59000 Lille, USTL, UMET (Unité Materiaux et Transformations), UMR CNRS, 8207 F-59650 Villeneuve d'Ascq, France,

[3] Department of Physics, University of Pavia-CNISM, 27100 Pavia, Italy,

[4] Bracco Research Center, Bracco Imaging S.p.A., via Ribes 5, 10010 Colleretto Giacosa (TO), Italy,

[5] Elettra Sincrotrone Trieste, Area Science Park, I-34149 Trieste, Italy.

Anhydrous crystalline trehalose (β polymorph) from Acros Organics was used as the primary component of the amorphous samples, and the radical TEMPO (2,2,6,6,-Tetramethyl-1-piperidinyloxy) from Sigma Aldrich, was used as the polarizing agent. The concentrations most widely investigated were 0.15, 0.34, 0.50, 0.64 and 0.81% (w/w), which are conventionally expressed, in the case of solutions, as 14.7, 33.7, 48.7, 62.9 and 79.4 mM respectively. The sample amorphization was performed through the use of a high energy planetary mill (Pulverisette 7 from Fritsch) at room temperature. Each sample was inserted in a ZrO_2 milling bowl (volume of about 45 cm^3) containing seven ZrO_2 balls (diameter 15 mm) and co-milled by setting the rotation frequency of the solar disk at 400 RPM (the corresponding acceleration of the balls is 5 g). The amorphization process lasted from 10 min to 16 h, with 5 min pauses each 15 min of milling, in order to avoid raising the process temperature: therefore the effective amorphization time ranged from 10 min to 12 h, the latter corresponding to a reasonable time for obtaining a sample in the fully amorphous state.[1]

The calorimetric measurements were performed by using a DSC Q200 (TA Instruments), a heating rate of 5 °C/min was chosen for all the scans and all the samples analyzed. Other calorimetric parameters were set under the conventional mode.

The diffractometric measurements were performed by using an Inel CPS 120 diffractometer (λCuK_α = 1.540Å) equipped with a 120° curved position sensitive detector coupled to a 4096 channel analyzer.

DNP measurements were performed on five samples with different concentrations of TEMPO (0.15, 0.34, 0.50, 0.64 and 0.81%). The samples were cooled in a bath cryostat between 1.7 K and 4.2 K, in a magnetic field of 3.46 T and were irradiated with a 30 mW microwave (MW) source operating in the 96÷98 GHz range. To determine the optimal MW frequency, a preliminary test was carried out on a 3 M reference Sodium Acetate solution in D_2O/CD_3CD_2OD (2/1, w/w) containing TEMPO with a concentration of 30 mM. The maximum value of ε obtained in this reference sample at 4.2 K was about 80, corresponding to P = 6.5%, at a nominal MW frequency of 96.93 GHz. This P value is very close to the one reported in the literature, around 8% at 3.35 T and 4.2 K.[2] The polarization build up was subsequently measured in all the trehalose samples upon switching on the MW at 96.93 GHz, by resorting to small angle acquisition schemes of the ^1H NMR signal.[3]

The enhancement ε and the polarization time constant T_{pol} were extracted from each polarization build-up curve using suitable fitting procedures that take into account the reduction of the ^1H signal amplitude induced by the small flip angle readout pulses.[4]

The build-up curves were fitted to the function

$$S(n\Delta t) = M_{\infty}[(1-\sum_{i=1}^{n}\cos\alpha^{i-1}(1-\cos\alpha)\exp(-\frac{i\Delta t}{T_{pol}})) - \exp(-\frac{n\Delta t}{T_{pol}})\cos\alpha^{n}]$$

that takes into account the artificial reduction of the signal introduced by the radiofrequency pulses. In this equation, the flip angle of the nuclear magnetization α induced by the pulses and the repetition time Δt are fixed parameters determined by the experimental conditions. The fit retrieves the steady state signal intensity S_∞ and the polarization time T_{pol} as free parameters. The enhancement ε, i.e. the ratio between the steady state signal intensity under MW irradiation and the signal intensity at thermal equilibrium at the same temperature, is expressed as

$$\epsilon = \frac{S_{\infty ON}\, RG_{OFF}}{S_{\infty OFF}\, RG_{ON}}$$

where the subscripts ON and OFF indicate that the microwaves are switched respectively ON and OFF and RG is the receiver gain of the spectrometer. The nuclear polarization is then obtained by multiplying the thermal equilibrium value by the enhancement according to

$$P\% = \epsilon\, tgh\left(\frac{\gamma\hbar H}{2k_B T}\right)$$

where γ is the nuclear gyromagnetic ratio, ħ is Planck's constant and H is the magnetic field.

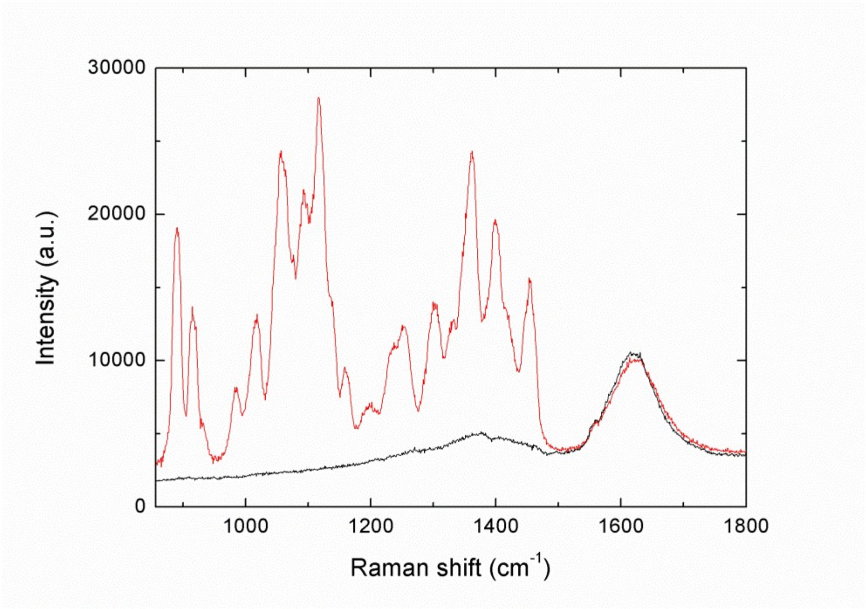

Figure S1. Raman spectra of crystalline trehalose (red) and trehalose milled for 12 h (black).

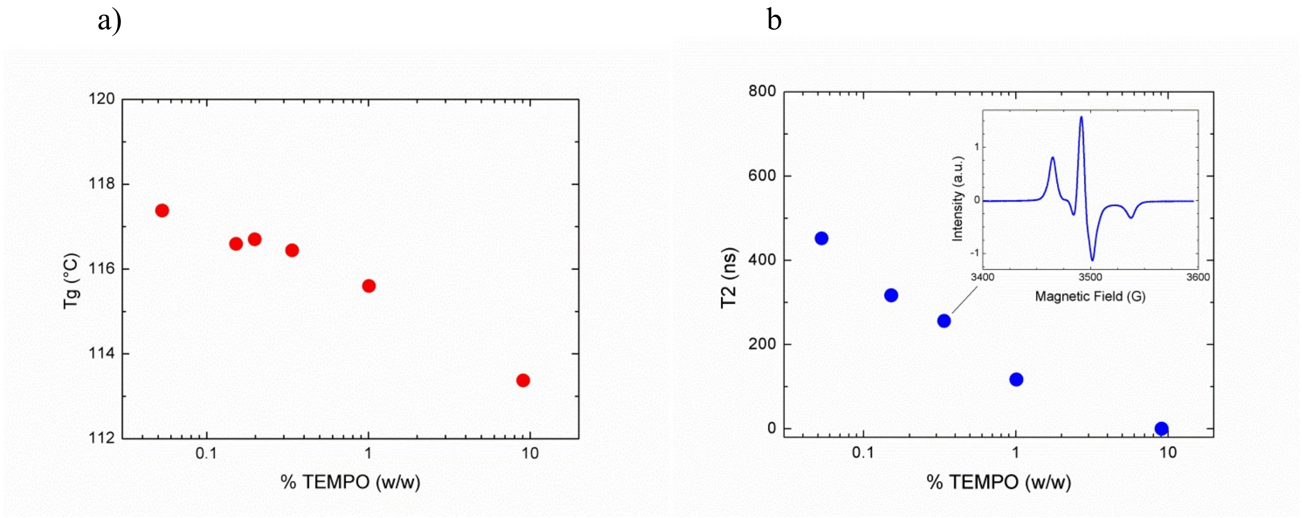

Figure S2. a) the glass transition temperature (taken as midpoint) and b) the electronic transverse relaxation time measured by ESR (frequency, 9.817 GHz; room temperature) as a function of the radical concentration for several samples milled for 12 h; the inset shows an example of the ESR spectrum (concentration = 0.34%).

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S.I. REFERENCES

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