Supporting information to the manuscript:

Multi-stage freezing of HEUR polymer network with magnetite nanoparticles

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1. Differential Scanning Calorimetry measurements of the nanocomposites

The DSC heating curves of the HEUR hydrogels with 0.46 wt% MNP and 0.8 wt% MNP are shown in Fig. S1. Three main phase transitions are observed: the glass transition (T_g) of the PEO portion of the HEUR polymer at ~ -80°C, the cold crystallization of water at -48°C and the melting of deuterated water at -4°C. Besides the slight decrease of the glass transition of few degrees for the nanocomposite with 0.8 wt% MNPs (T_g = -83 °C), there are no significant differences between the DSC curves of the pure HEUR gel and of the nanocomposites.

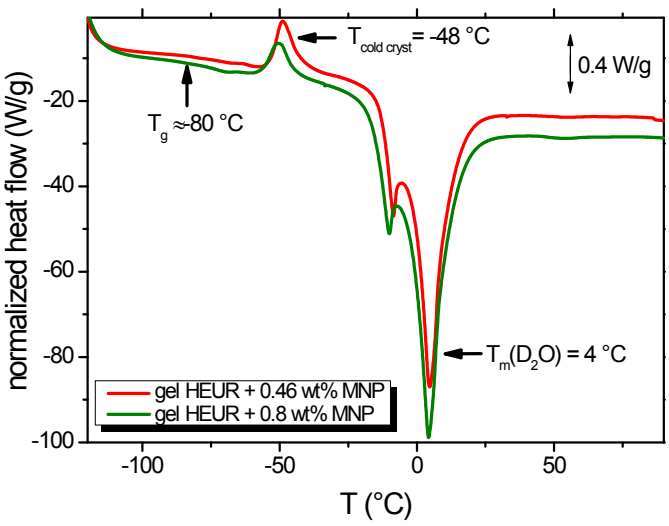

Figure S1 DSC heating curves of the nanocomposite hydrogels. The glass transition T_g, the cold crystallization temperature of D_2O, and the melting point of D_2O are highlighted by arrows.

2. Dielectric Relaxation Spectroscopy measurements: isochronal plot

The isochronal plot of the pure HEUR hydrogel 25 wt% (aq) showing the real part of the permittivity, ε', at the same frequency as the ones shown in Fig.4 in the main text are shown in **Fig. S2**. The red dashed line shows the step visible also in **Fig. 4**, indicating the phase transition, i.e. melting of D_2O, in the samples. The red arrow highlights the high value of the permittivity at low frequencies (~10^6 Hz) which indicates the occurrence of the electrode polarization process [1].

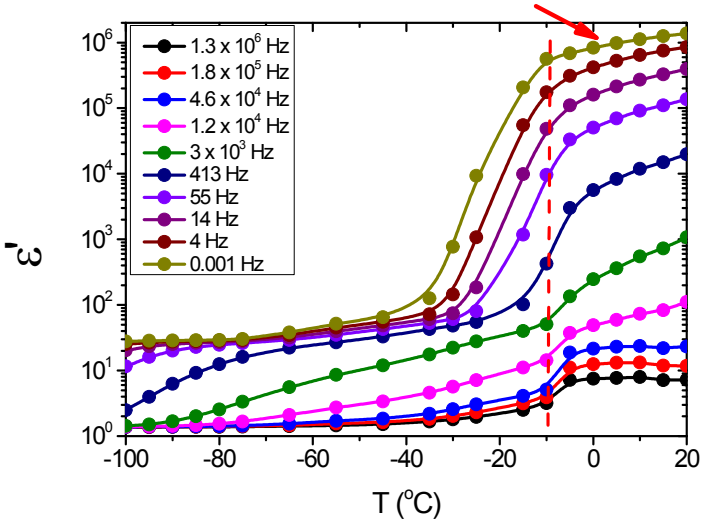

Figure S1 Real part of the permittivity ε' as a function of the temperature at selected frequencies. The dashed line shows the step due to the melting of D_2O and the red arrow indicates the high value of the plateau at 0.001 Hz.

3. Neutron Spin Echo measurements on the nanocomposites

The intermediate scattering functions of the nanocomposite hydrogels with 0.46 wt% and 0.80 wt% MNPs are shown in **Fig. S3 a) and b)**. The time decays of the scattering function for the nanocomposites present the same features as the one of the pure HEUR gel 25 wt % (aq) shown in **Fig. 10** in the main text. The data were fitted with equation 13 explained in the main text.

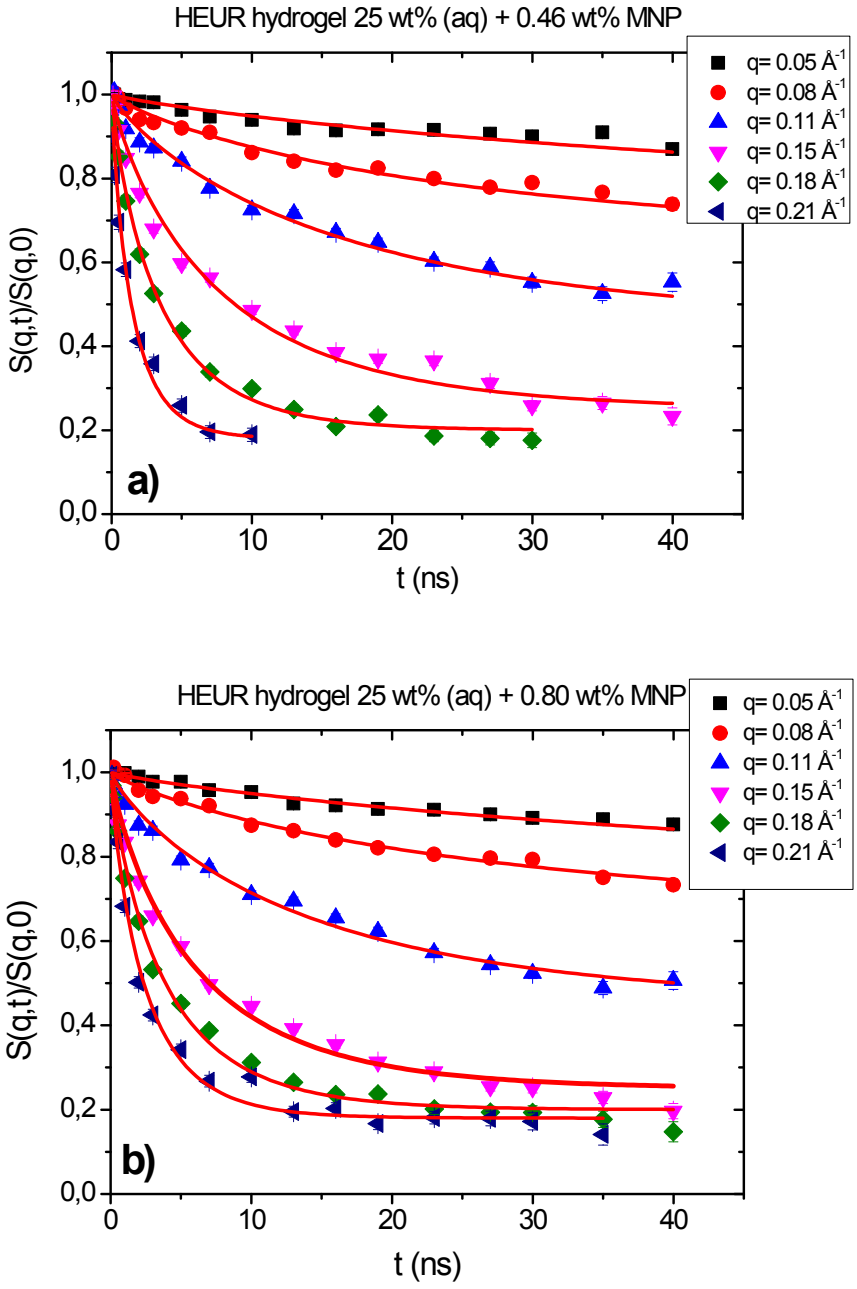

Figure S3 Intermediate scattering functions of the nanocomposite hydrogels containing a) 0.46 wt% MNP and b) 0.80 wt% MNP. The red lines are fits with equation 13 reported in the main text.

References

[1] A. Serghei, M. Tress, J. R. Sangoro, F. Kremer, Phys. Rev., 2009, B 80, 184301