

## Supporting Information for:

# Synthesis of polyacid nanogels: pH-responsive sub-100 nm particles for functionalisation and fluorescent hydrogel assembly

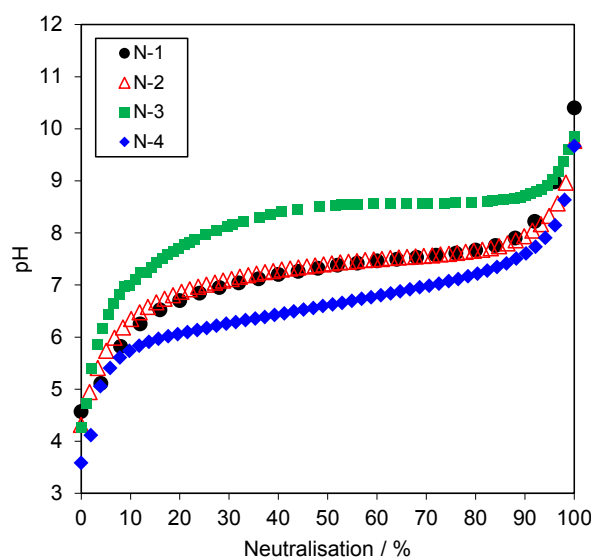
Amir H. Milani<sup>a\*</sup>, Jennifer M. Saunders<sup>a</sup>, Nam T. Nguyen<sup>a</sup>, Liam P. D. Ratcliffe<sup>b</sup>, Steven P. Armes<sup>b</sup>, Daman J. Adlam<sup>c</sup>, Anthony J. Freemont<sup>c</sup>, Judith A. Hoyland<sup>c,d</sup> and Brian R. Saunders<sup>a,\*</sup>

<sup>a</sup>School of Materials, University of Manchester, Manchester, M13 9PL, U.K.

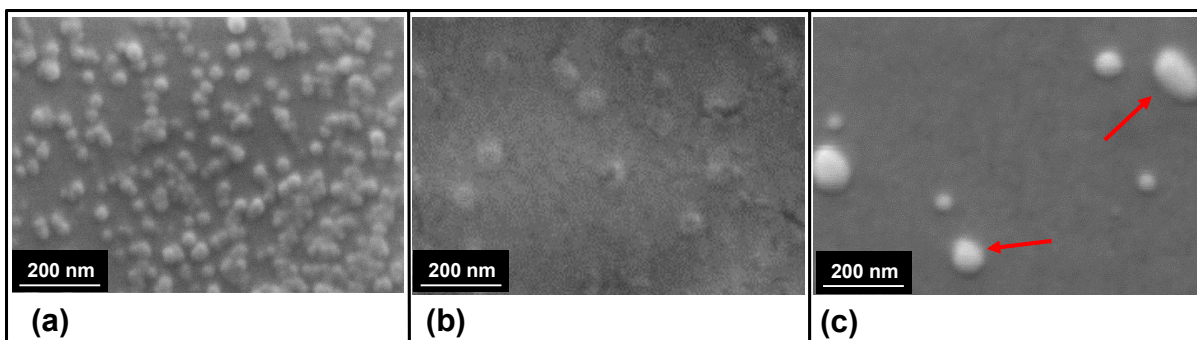
<sup>b</sup>Department of Chemistry, The University of Sheffield, Dainton Building, Brook Hill, Sheffield, South Yorkshire, S3 7HF, U.K.

<sup>c</sup>Division of Cell Matrix Biology and Regenerative Medicine, Faculty of Biology, Medicine and Health, University of Manchester, Oxford Road, Manchester, M13 9PL, U.K.

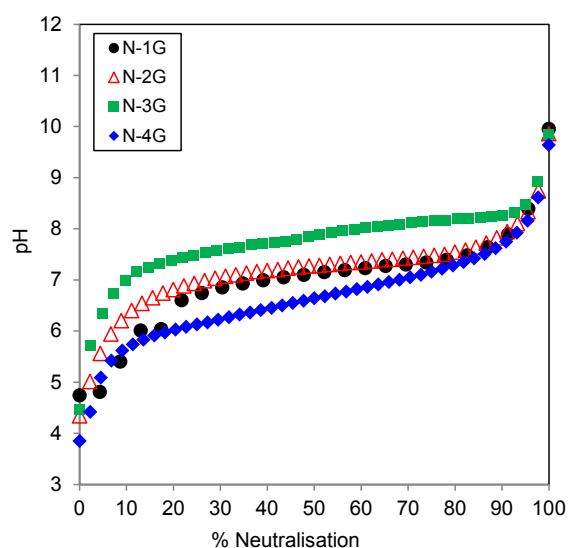
<sup>d</sup>NIHR Manchester Musculoskeletal Biomedical Research Unit, Manchester Academic Health Science Centre, Manchester, U.K.



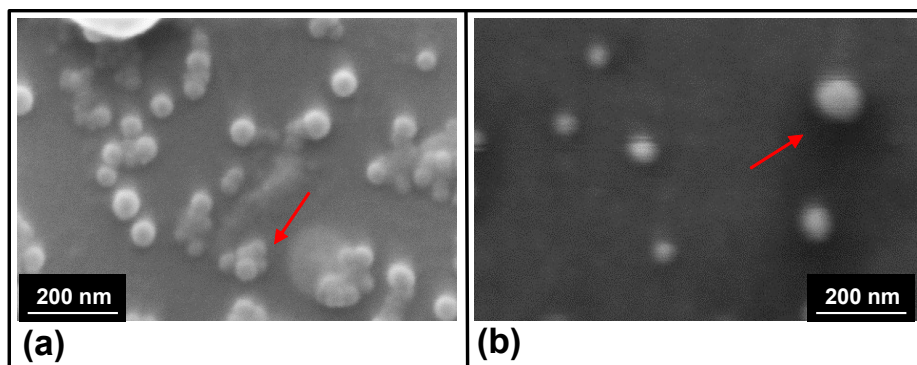
**Figure S1.** Potentiometric titration data for the non-functionalised nanogel dispersions. The apparent  $pK_a$  values were obtained from the pH corresponding to 50% neutralisation.



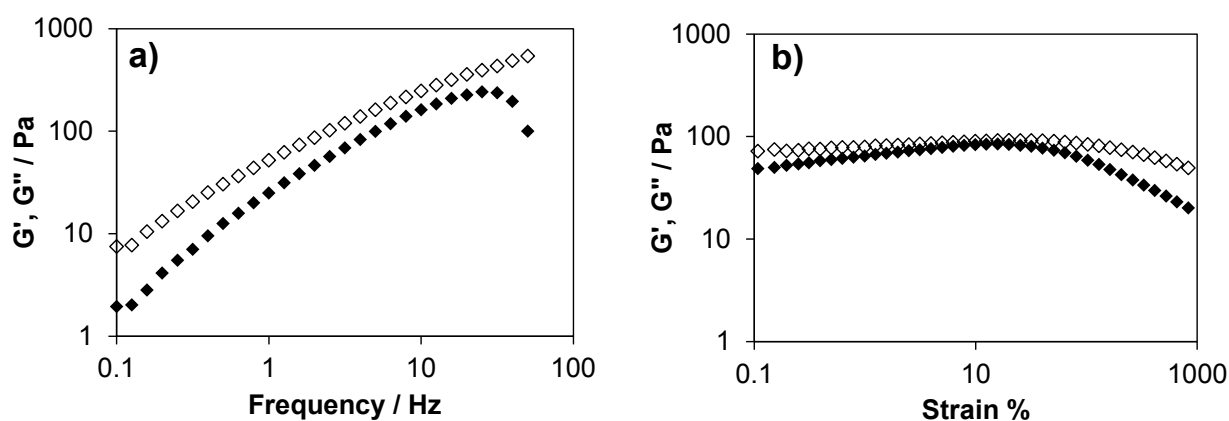
**Figure S2.** Representative SEM images for (a) N-2, (b) N-3 and (c) N-4. The N-4 particles had a tendency to coalesce during sample drying (due to their low glass transition temperature,  $T_g$ ) and some examples of this are indicated by the red arrows. (The  $T_g$  of poly(ethyl acrylate) is  $-22\text{ }^\circ\text{C}^1$ .) Only the isolated nanoparticles were used for calculating the average particle size.



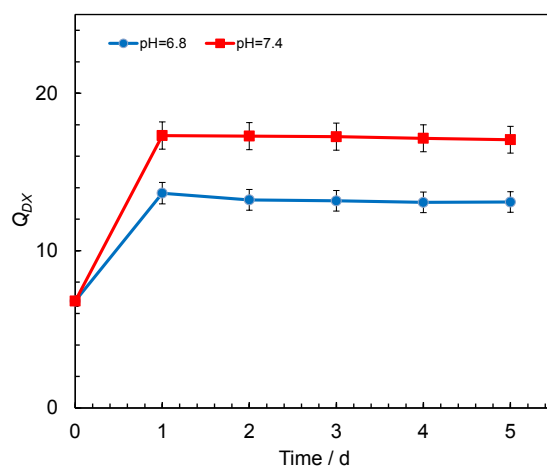
**Figure S3.** Potentiometric titration data for GMA-functionalised nanogels.



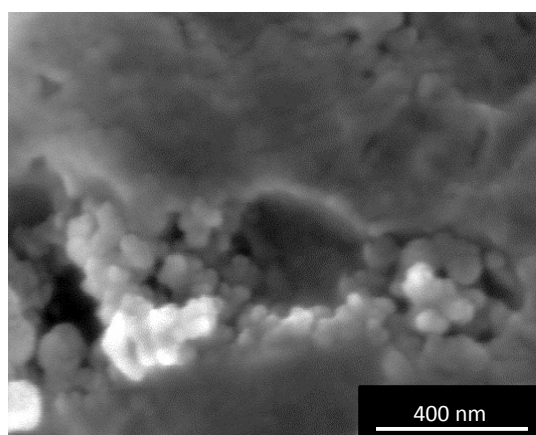
**Figure S4.** Representative SEM images for (a) N-2G and (b) N-4G. The red arrows highlight (a) aggregates and (b) coalesced nanoparticles that formed during sample drying. The N-2G nanoparticles were based on poly(methyl methacrylate) which has a  $T_g$  of 114 °C<sup>2</sup>. The latter glassy nanoparticles did not coalesce during SEM sample preparation.



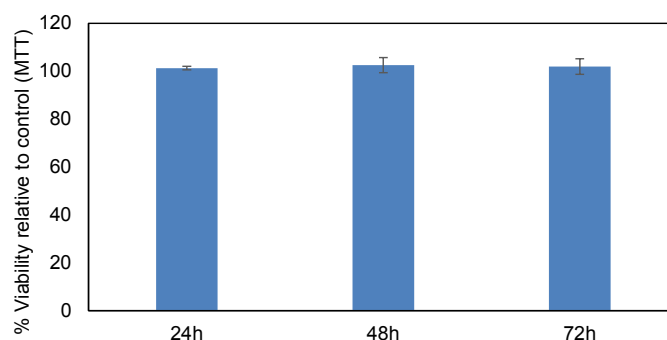
**Figure S5.** Frequency-sweep (a) and strain-sweep (b) rheology data for N-1G dispersion with a concentration of 12 wt% and pH of 7.4.  $G'$  (storage modulus) and  $G''$  (loss modulus) data are shown by the closed and open symbols, respectively.



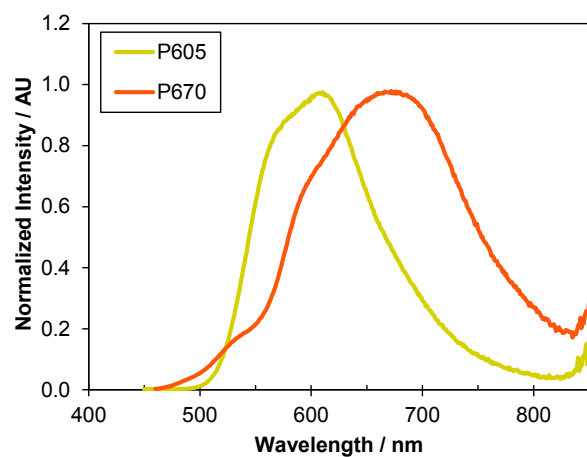
**Figure S6.** Variation of the volume-swelling ratio for DX N-1G with time. Phosphate buffer solutions were used (0.1 M). There was an initial “breathing in” due to the DX NGs being placed in a large volume of aqueous solution. The DX N-1G gel swelled more at pH 7.4 which was expected from the pH-triggered swelling of the parent N-1G (See Fig. 2b).



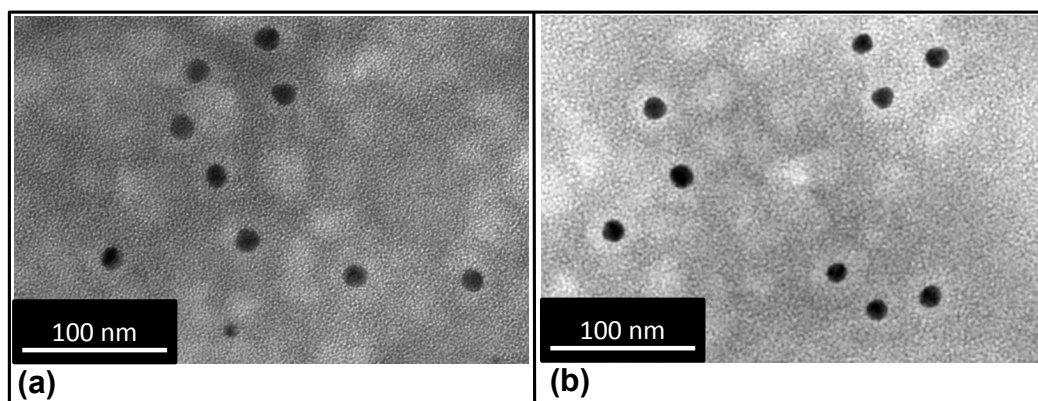
**Figure S7.** SEM micrograph of freeze dried DX N-1G



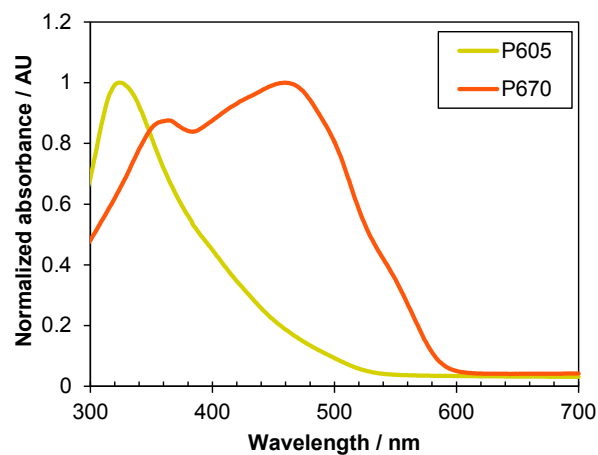
**Figure S8.** Relative MTT assay data for nucleus pulposus cells exposed to DX N-1G for 24, 48 and 72 hours. The data are shown relative to control samples which were empty inserts.



**Figure S9.** PL spectra for P605 and P670 PDs dispersed in water. The excitation wavelengths used were 380 and 450 nm, respectively. The structures for P605 and P670 are shown in Fig. 3a.



**Figure S10.** TEM images for (a) P605 and (b) P670 polymer dots.



**Figure S11.** UV-visible spectra for P605 and P670 PD dispersions. The dispersion concentrations were 0.1 wt.%.

## References

1. L. H. Sperling, D. W. Taylor, M. L. Kirkpatrick, H. F. George and D. R. Bardman, *J. Appl. Polym. Sci.*, 1970, **14**, 73-78.
2. Y. Grohens, M. Brogly, C. Labbe, M.-O. David and J. Schultz, *Langmuir*, 1998, **14**, 2929-2932.