Triply-responsive OEG-based microgels and hydrogels: Regulation of swelling ratio, volume phase transition temperatures and mechanical properties

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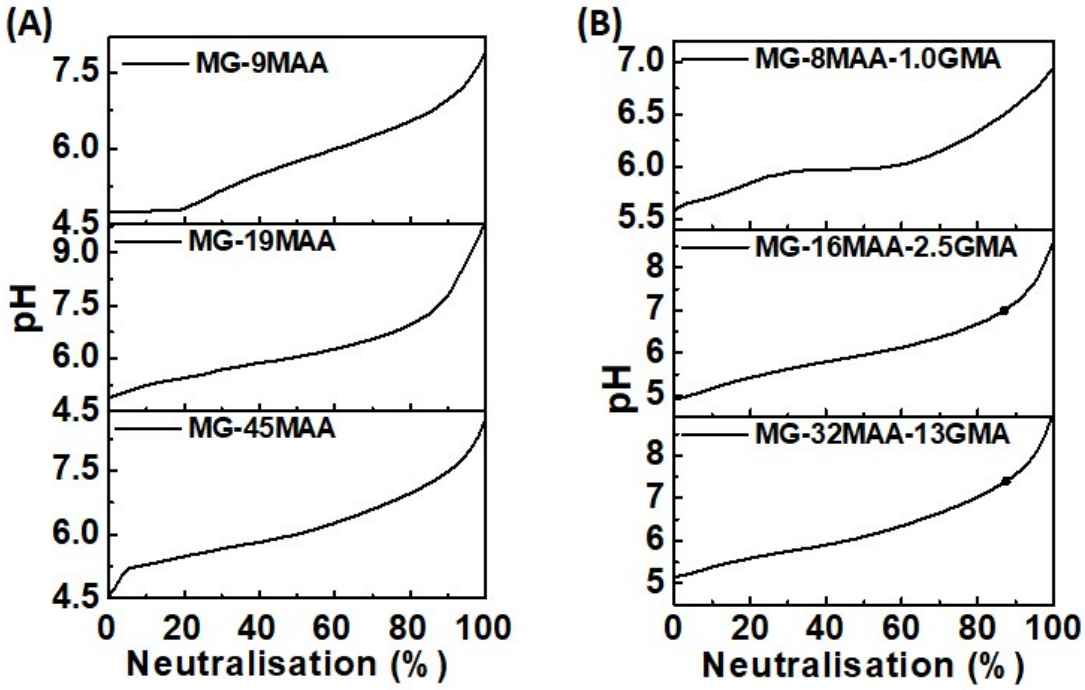

Figure S1. Potentiometric titration data for the MG-*x*MAA and functionalised MG-*x*MAA-*y*GMA dispersions. The apparent pK_a values were obtained from the pH corresponding to 50% neutralisation.

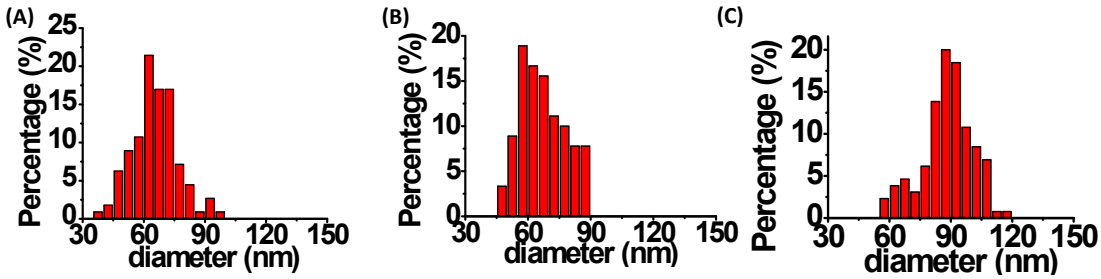

Figure S2. The size distributions of TEM for MG-9MAA **(A)**, MG-19MAA **(B)**, MG-45MAA **(C)**.

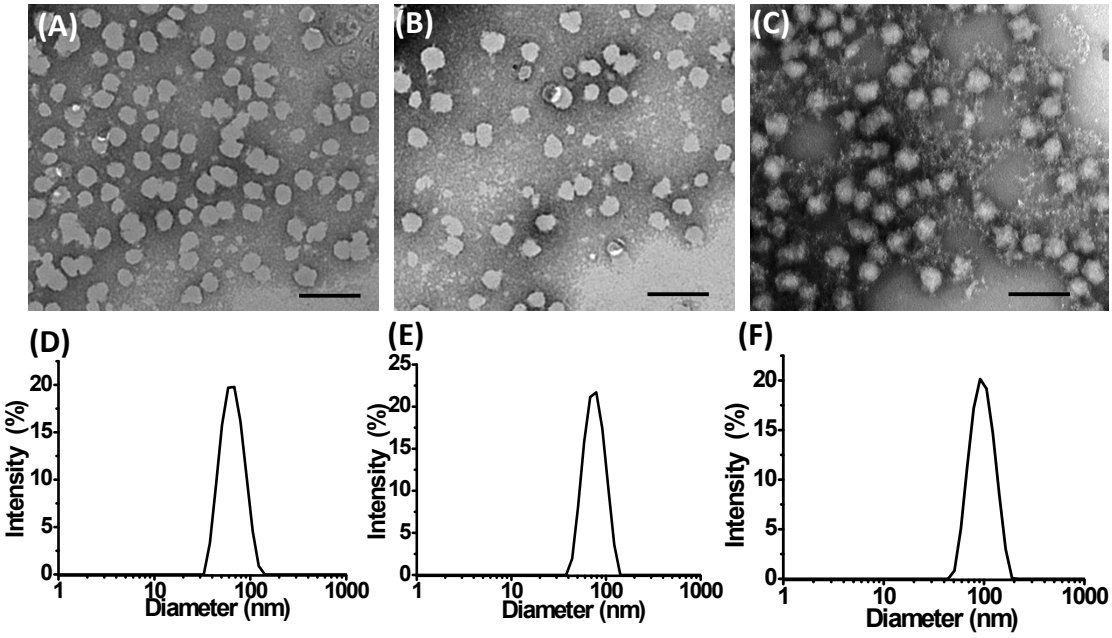

Figure S3. TEM images for **(A)** MG-8MAA-1.0GMA, **(B)** MG-16MAA-2.5GMA and **(C)** MG-32MAA-13GMA. DLS size distributions for **(D)** MG-8MAA-1.0GMA, **(E)** MG-16MAA-2.5GMA and **(E)** MG-32MAA-13GMA. The dispersion used in (D) - (F) had a pH 5.4 and the temperature was 60 °C.

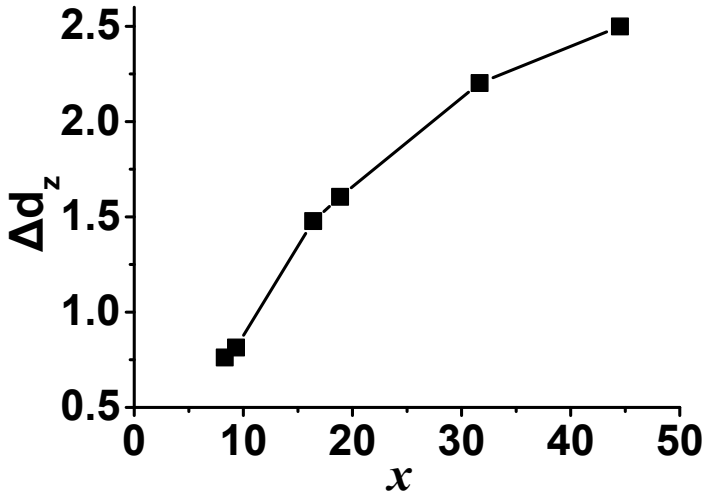

Figure S4. The change ratio of d_z (Δd_z) *vs.* MAA content of all MGs. $\Delta d_z = (d_{z\,(\text{pH } 7.4)} - d_{z\,(\text{pH } 5.0)}) / d_{z\,(\text{pH } 5.0)}$.

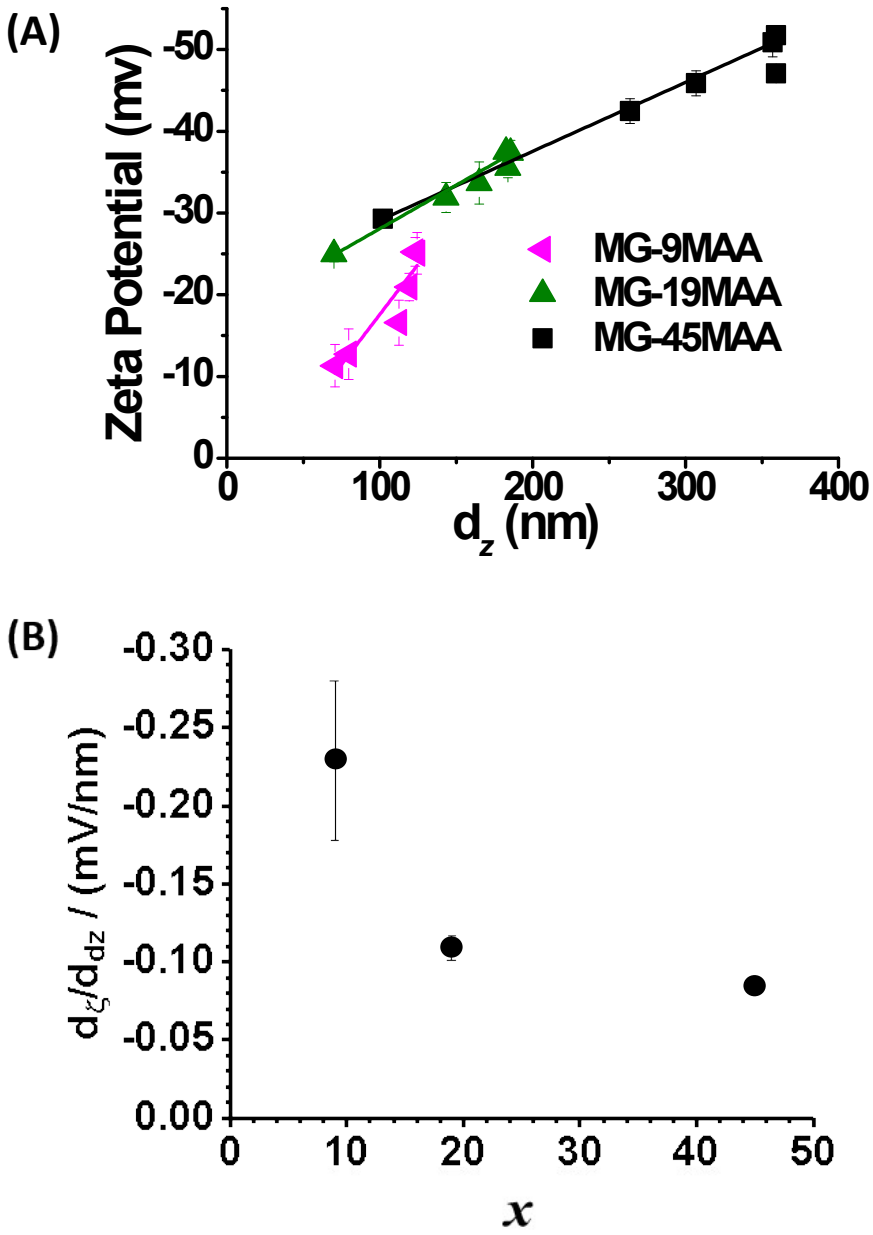

Figure S5. (A) Zeta potential (ζ) plotted as a function of z-average diameter (d_z) from the data shown in Figures 2A and 2B. **(B)** Variation of the gradients of the lines of best fit from (A) with MAA content of the MGs.

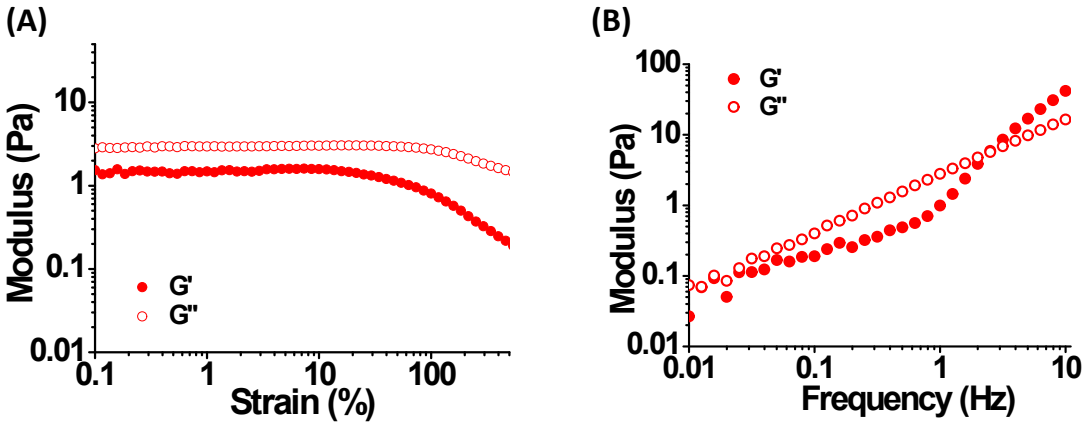

Figure S6. Strain-sweep **(A)** and frequency-sweep **(B)** rheology data for the concentrated MG-8MAA-1.0GMA. The frequency used in (A) is 1.0 H_Z and the strain used in (B) is 1.0%. The MG concentration and pH were 14% and 7.4, respectively.

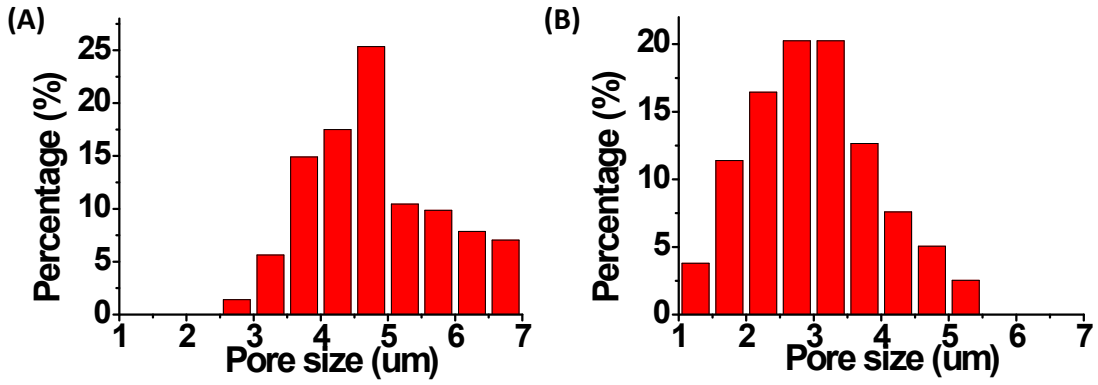

Figure S7. Pore size distributions for DX MG-16MAA-2.5GMA **(A)** and DX MG-32MAA-13GMA **(B)** from Figure 5A and Figure 5B, respectively.

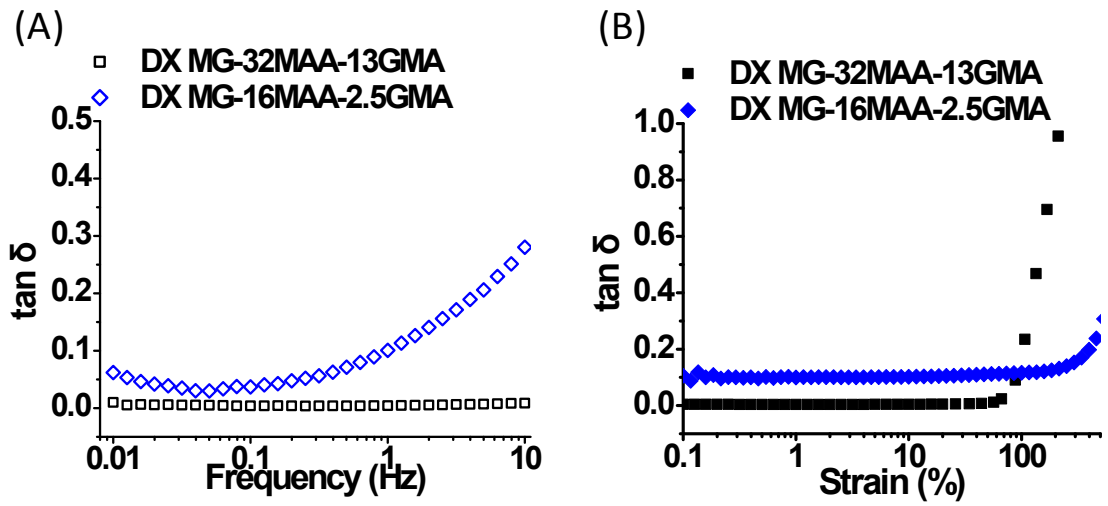

Figure S8. tan δ *vs.* frequency **(A)** and tan δ *vs.* strain **(B)** for DX MGs. tan δ = G″/ G′. The strain used in (A) is 1.0% and the frequency used in (B) is 1.0 H_Z.

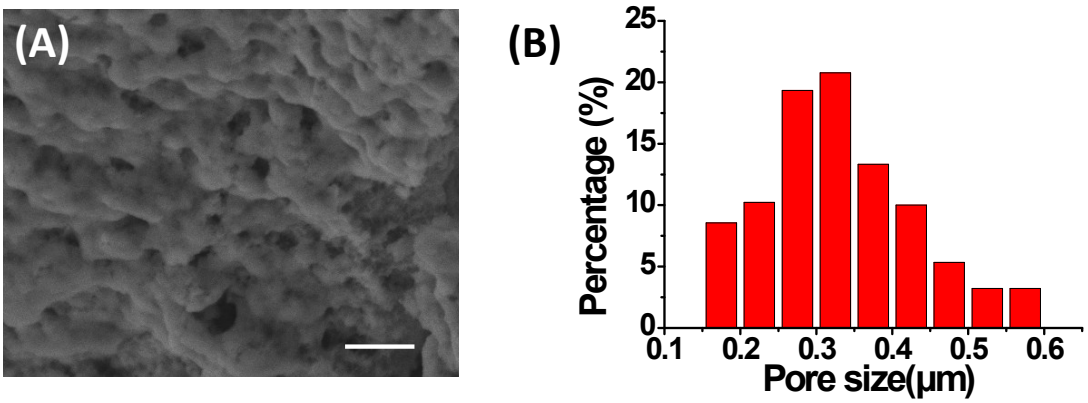

Figure S9. (A) SEM image of DX MG-32MAA-13GMA/Fe^{3+}. The scale bar is 2 μm and the average pore size is 0.31 μm. **(B)** Pore size distribution for the gel.

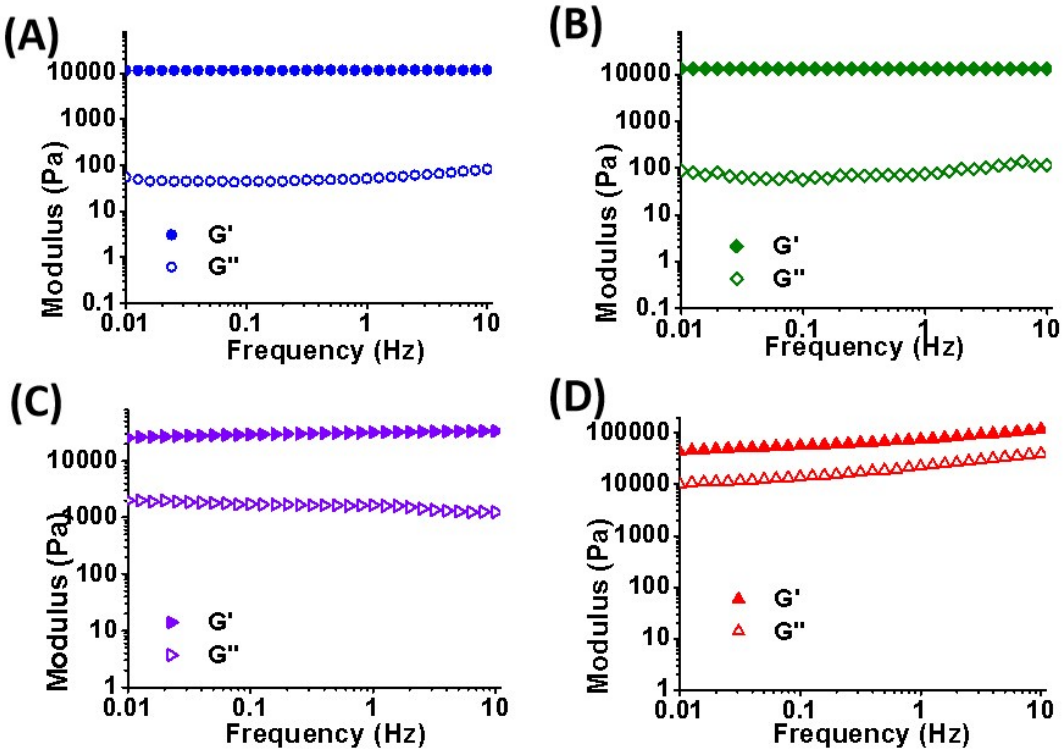

Figure S10. Frequency-sweep rheology data for the DX MG-32MAA-13GMA immersed into ionic solution of (A) NaCl, (B) $MgCl_2$, （C） $AlCl_3$, (D) $FeCl_3$. The strain used for all figure is 1.0%

Supplementary tables

Table S1 Comonomer formulations used to prepare the MGs[a]

MGs	MEO_2MA / wt.%	MAA / wt.%	EGD / wt.%
MG-9MAA	96.5	2.4	1.1
MG-19MAA	91.3	7.5	1.2
MG-45MAA	75.4	23.3	1.3

[a] The values given are with respect to monomer. Note that the amount of MAA given in the code for the MGs is mol.% based on the titration data from Table S2.

Table S2 Composition and properties of the MGs studied

MGs	MEO_2MA / mol%	MAA / mol% [a]	EGD/ mol%	GMA / mol% [b]	pK_a [c]	d_{TEM} /nm [d]	d_z /nm [e] (pH 5.4, 60°C)
MG-9MAA	89.8	9.3	1.0	-	5.7	66 (8)	73 (0.03)
MG-19MAA	80.0	18.9	1.0	-	6.0	67 (8)	70 (0.06)
MG-45MAA	54.5	44.5	1.0	-	6.0	88 (9)	102 (0.01)
MG-8MAA-1.0GMA	89.7	8.3	1.0	1.0	5.9	65 (7)	72 (0.07)
MG-16MAA-2.5GMA	80.1	16.4	1.0	2.5	6.0	67(6)	71 (0.05)
MG-32MAA-13GMA	54.4	31.7	1.0	12.9	6.1	82 (7)	91 (0.03)

[a] Determined from potentiometric titration data. [b] Calculated using the difference of the MAA content before and after functionalisation. [c]Apparent pK_a value determined from potentiometric titration data. [d] The numbers in brackets are the standard deviation. [e] The numbers in brackets are the PDI values.