Electronic Supplementary Information (ESI†)

pH-Responsive Physical Gels Based on Poly(meth)acrylic Acid-Containing Crosslinked Particles. Structure - Mechanical Properties Relationship.

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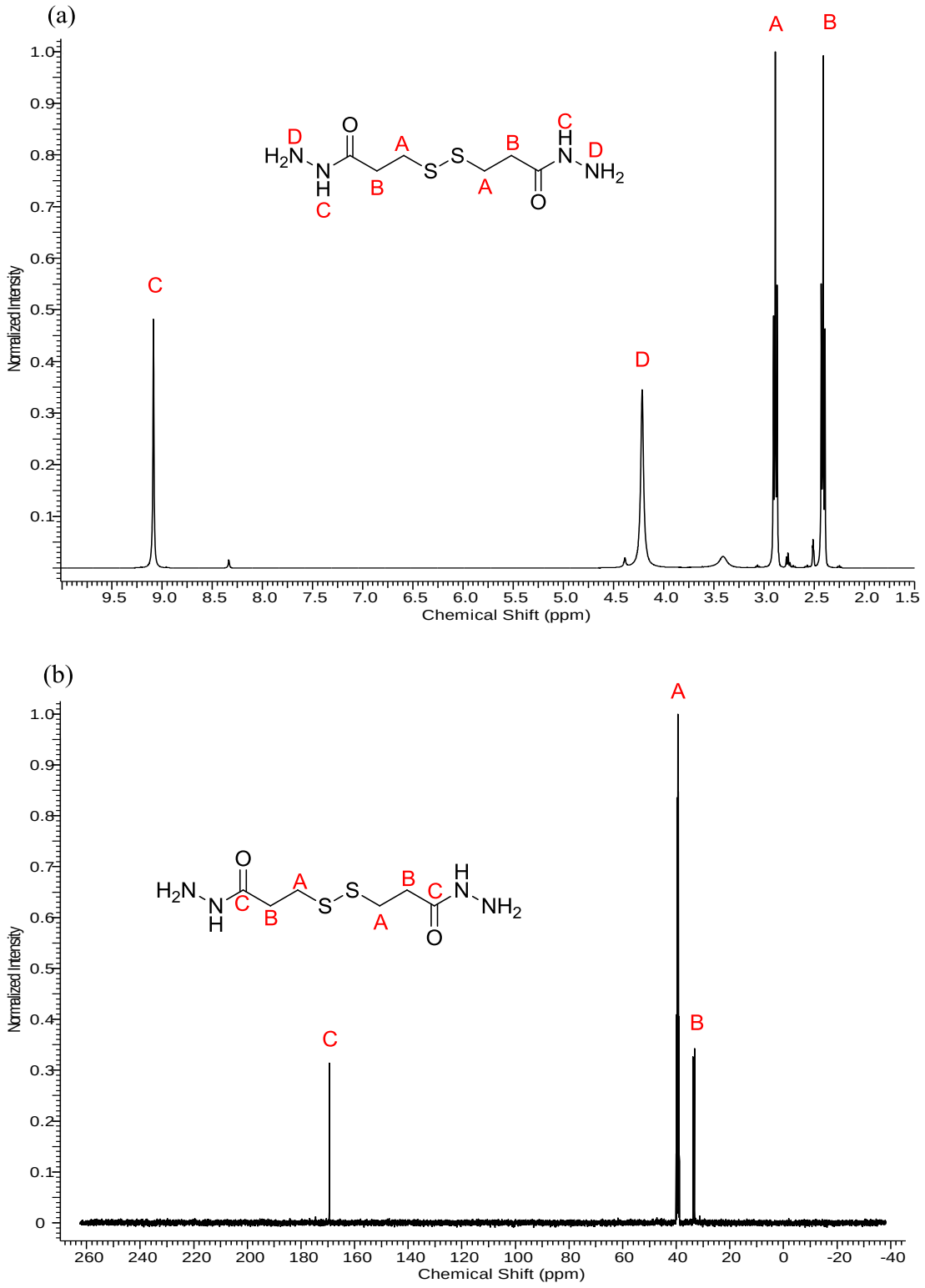

Fig. S1. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of DTP in DMSO-d_6.

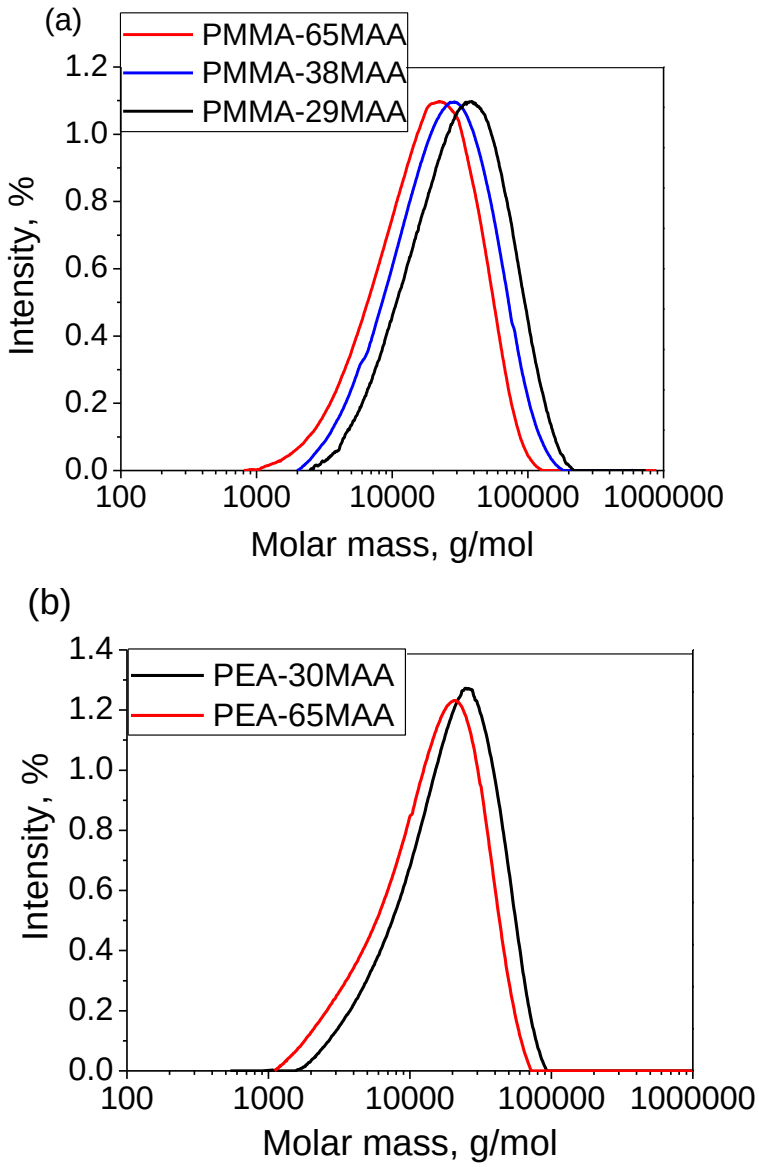

Fig. S2. GPC traces of (a) PMMA-MAA copolymers; (b) PEA-MAA copolymers.

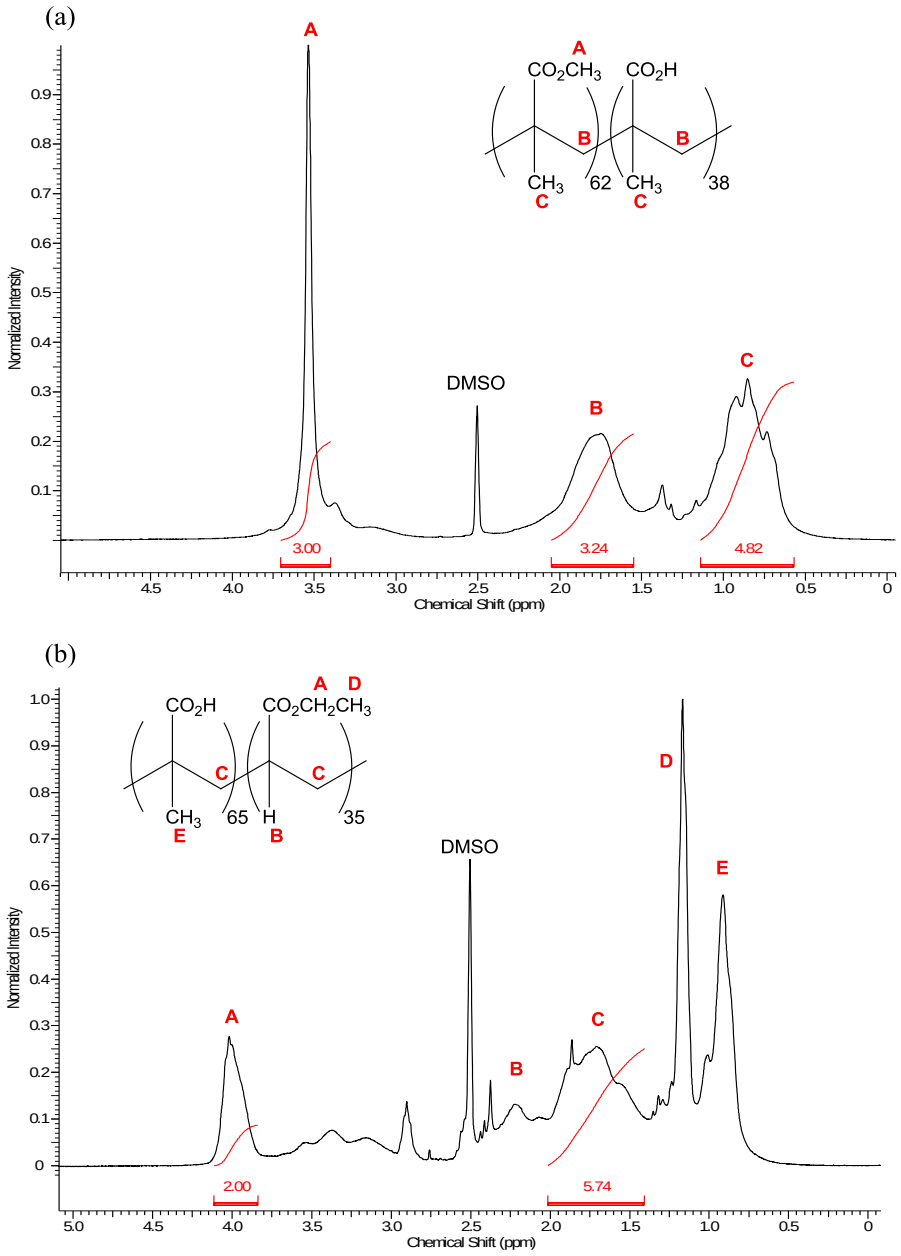

Fig. S3. ^{1}H NMR spectra of (a) PMMA-38MAA and (b) PEA-65MAA in DMSO-d_6.

To determine the percentage MAA content in PMMA-38MAA the intensity of **A** was set to 3H. It follows that

$$\% \text{ MAA} = \{(\mathbf{B} - 2)/\mathbf{B}\} \times 100$$

or

$$\% \text{ MAA} = \{(\mathbf{C} - 3)/\mathbf{C}\} \times 100$$

To determine the percentage MAA content in PEA-65MAA the intensity of **A** was set to 2H. It follows that

$$\% \text{ MAA} = \{(\mathbf{C} - 2)/\mathbf{C}\} \times 100$$

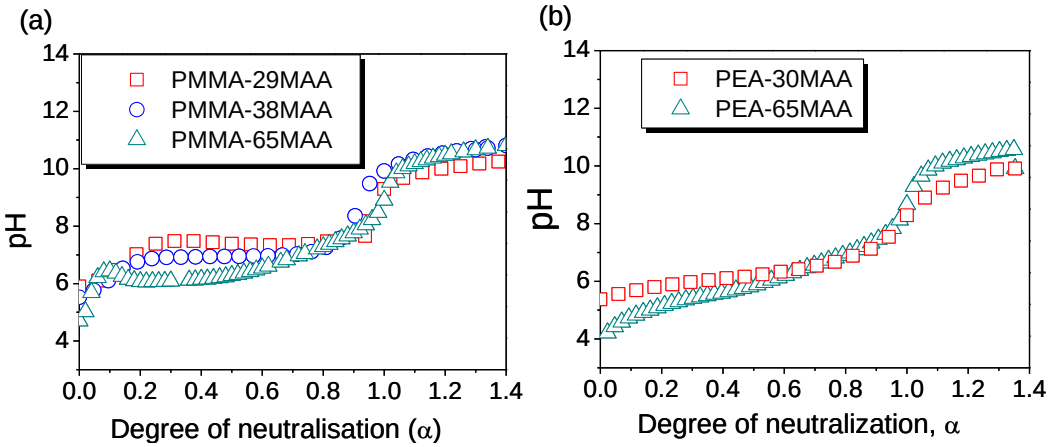

Fig. S4. Potentiometric titration data for non-crosslinked PMMA-MAA and PEA-MAA particles.

Table S1. Variation of the Hydrodynamic Diameter (D_h, in nm) with pH for non-crosslinked and crosslinked particles

Entry	pH / Particle composition	5.4	6.0	6.5	7.0	7.5	8.0
		D_h (nm)					
1	PMMA-29MAA	-	1928	1830	1650	1245	45
2	PMMA-20MAA/9CYS	-	1355	2250 [a]4.6	2455 [a]5.9	1865 [a]2.6	905 [a]0.1
3	PMMA-25MAA/4DTP	-	1386	2236 [a]4.2	3124 [a]11.4	1800 [a]2.2	1005 [a]0.4
4	PMMA-38MAA	-	[b] 1826[59],370[41]	[b] 1027[88], 211[12]	778	574	68
5	PMMA-24MAA/14CYS	-	1485	1923 [a]2.3	2235 [a]3.4	1828 [a]1.9	535 [a]0.1
6	PMMA-36MAA/2DTP	-	1490	2543 [a]4.9	3400 [a]11.9	3125 [a]9.1	620 [a]0.1
7	PMMA-65MAA	2215	151	160	161	101	67
8	PMMA-45MAA/20DTP	2049	2158 [a]1.2	3414 [a]4.7	3052 [a]3.3	2898 [a]2.8	1586 [a]0.5
9	PEA-30MAA	1845	1730	1600	435	205	60
10	PEA-20MAA/10CYS	[b] 307[7], 1986[93]	[c] 185[26],990[10], 4340[64] [d]10.4	[c] 191[19],1095[23], 4505[58] [d]11.5	[b] 200[24], 2855[66] [d]2.9	1540 [a]0.5	395 [a]0.01
11	PEA-10MAA/20DTP	[c] 47[15], 232[30], 2400[55]	[c] 146[11],830[37], 4302[52] [d]5.8	[c] 210[18],1210[41], 4886[41] [d]8.4	[c] 207[31],770[7], 4525[61] [d]6.7	[b] 264[45], 2797[55] [d]1.6	[b] 67[15], 210[85] [d]0.0007
12	PEA-65MAA	3909	3062	[b] 1322[81], 170[19]	1257	725	210
13	PEA-59MAA/6DTP	[c] 230[16], 1032[29], 4350[55]	[c] 270[12], 1179[25], 4543[63]	[c] 370[22], 1592[18] 4560[60]	[b] 1274[92], 188[8]	1114	963

[a] The swelling ratios calculated from the ratio of the volume of the swelled particles at given pH to the volume of the non-swelled particles at the lowest pH tested. [b] Bimodal distribution. [c] Trimodal distribution. [d] Swelling ratios calculated for the slow modes. [e] The intensities of the different modes as percentages are presented as superscript on the particles' D_h. The swelling ratios of the PEA-59MAA/6DTP particles are not presented as the particles were already swollen at the pH of 5.4.

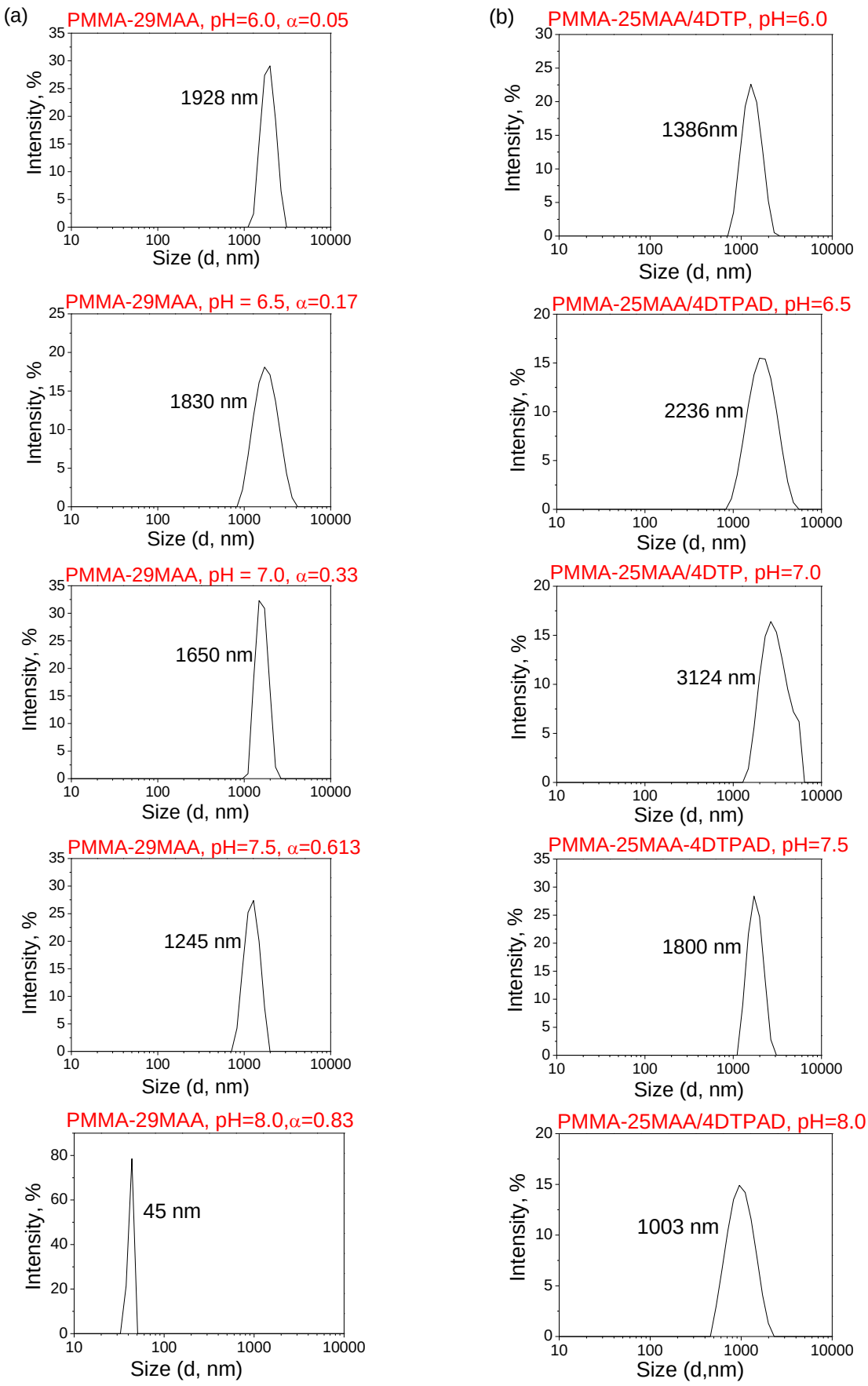

Fig. S5. Size distribution functions for (a) non-crosslinked PMMA-29MAA and (b) crosslinked PMMA-25MAA/4DTP particles taken at various pH values.

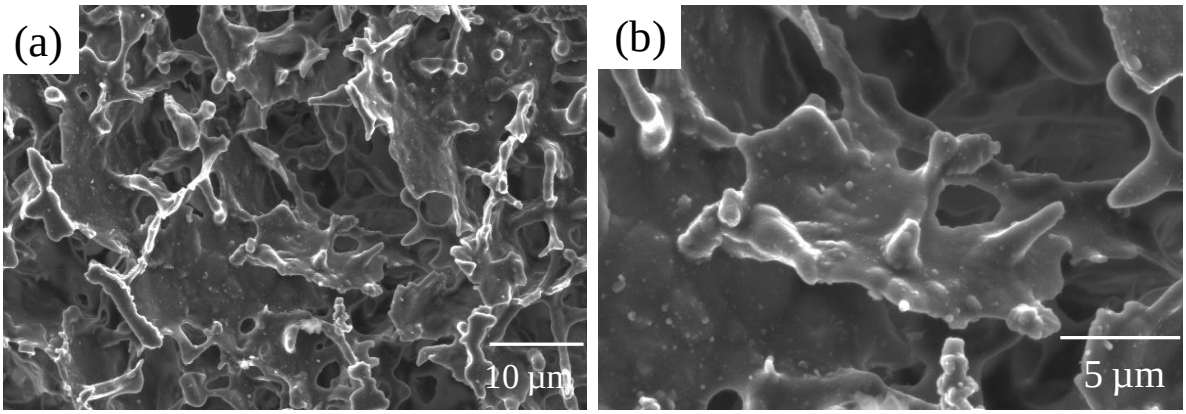

Fig. S6. SEM images of freeze-dried PMMA-25MAA/4DTP gels formed at pH 7.0

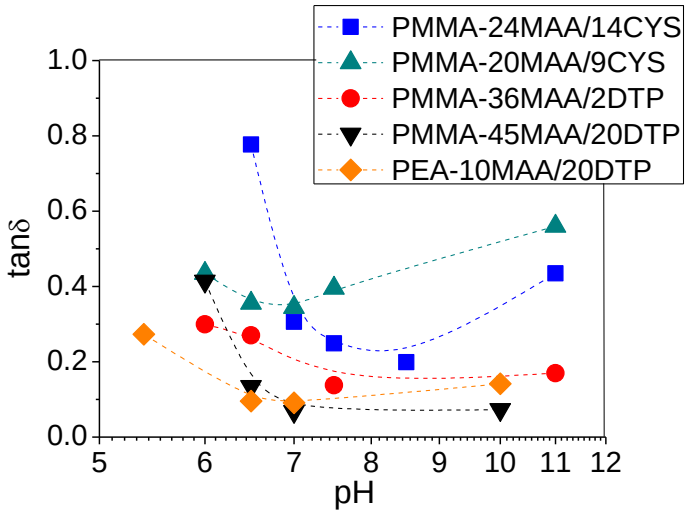

Fig. S7. Variation of tanδ with pH for PMMA-MAA and PEA-MAA-based crosslinked particles

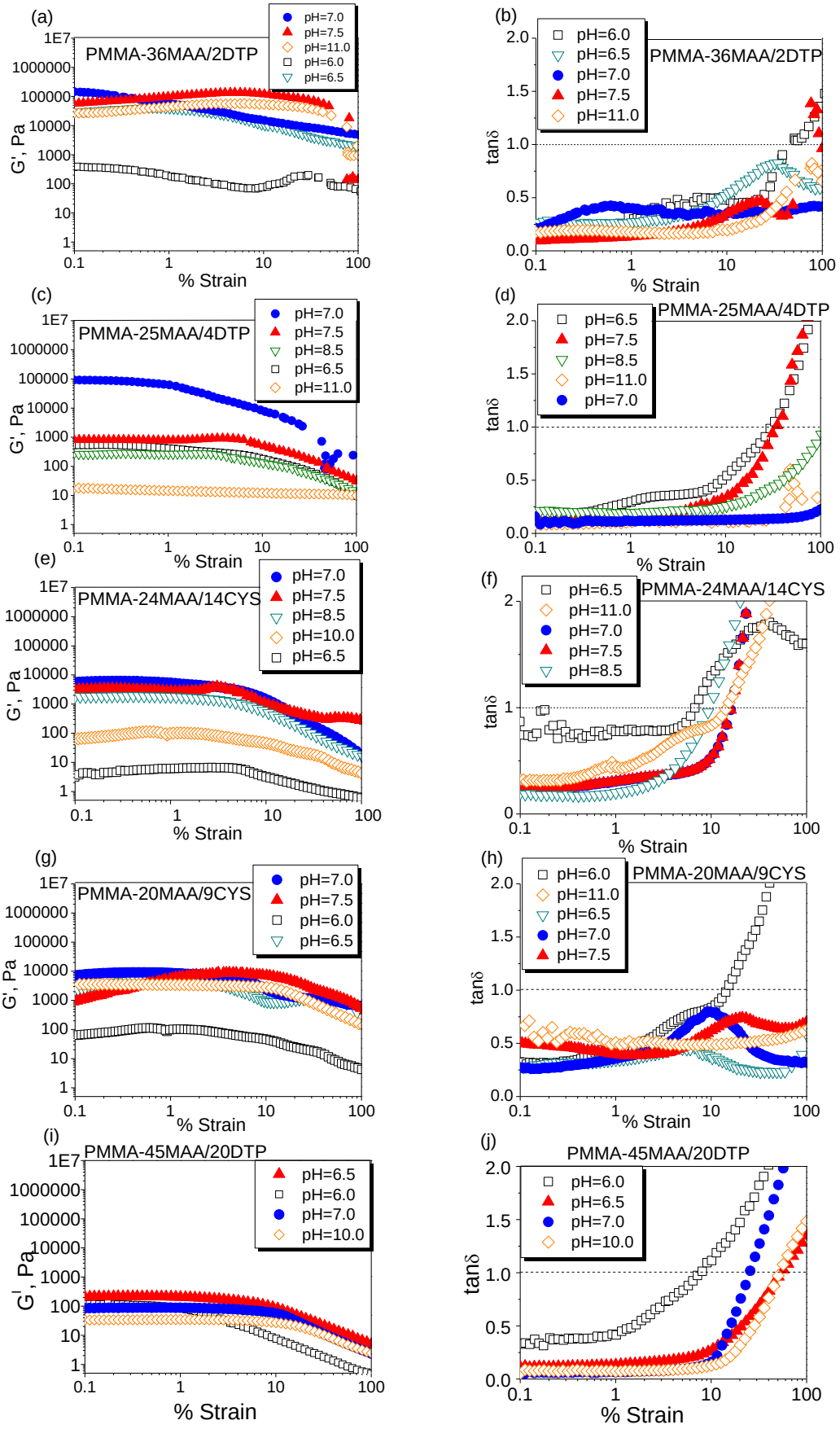

Fig. S8. The variation of *G'* and tanδ with the percentage strain for various PMMA-MAA-based crosslinked particle gels.

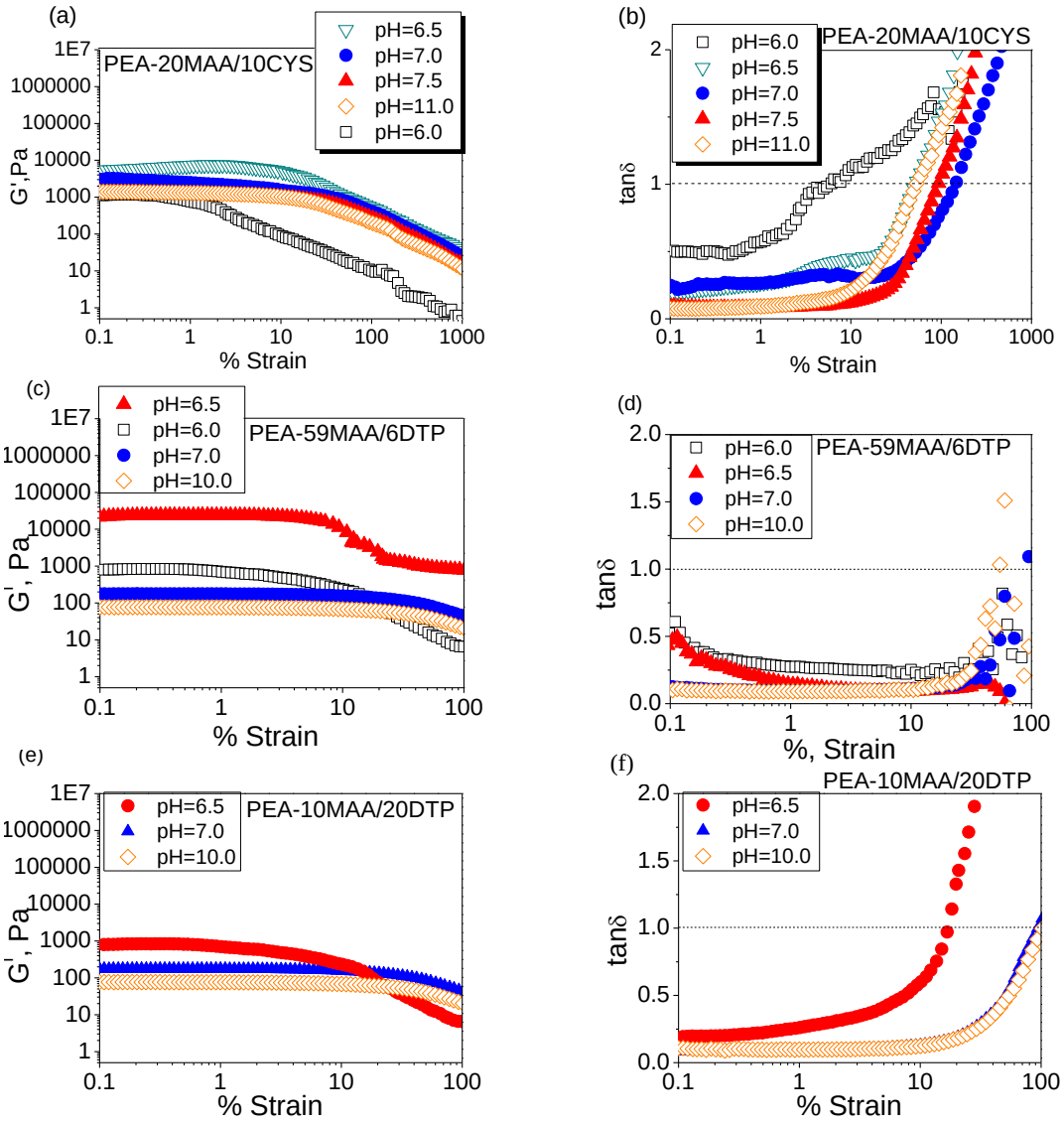

Fig. S9. The variation of (a) *G'* and (b) tanδ with the percentage strain for PEA-MAA-based crosslinked particle gels.