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Thiolated cationic poly(aspartamides) with side group dependent gelation properties for the delivery of anionic polyelectrolytes

Supplementary information

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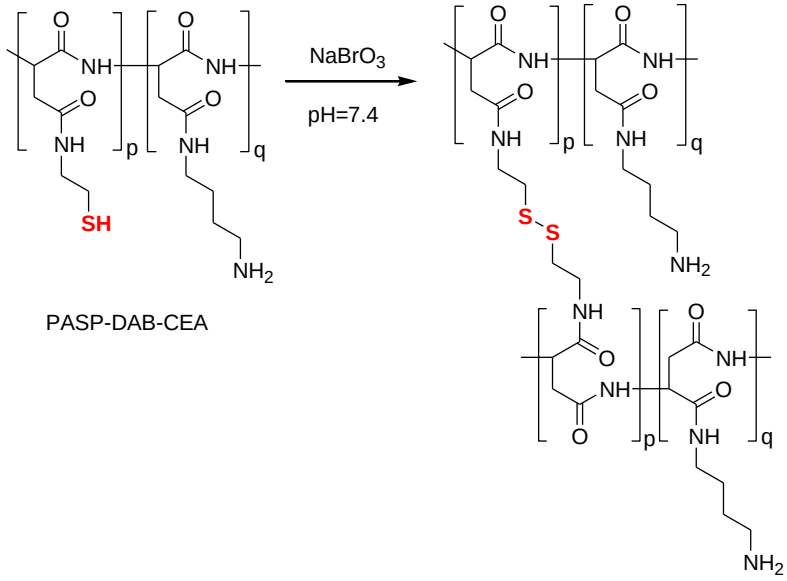

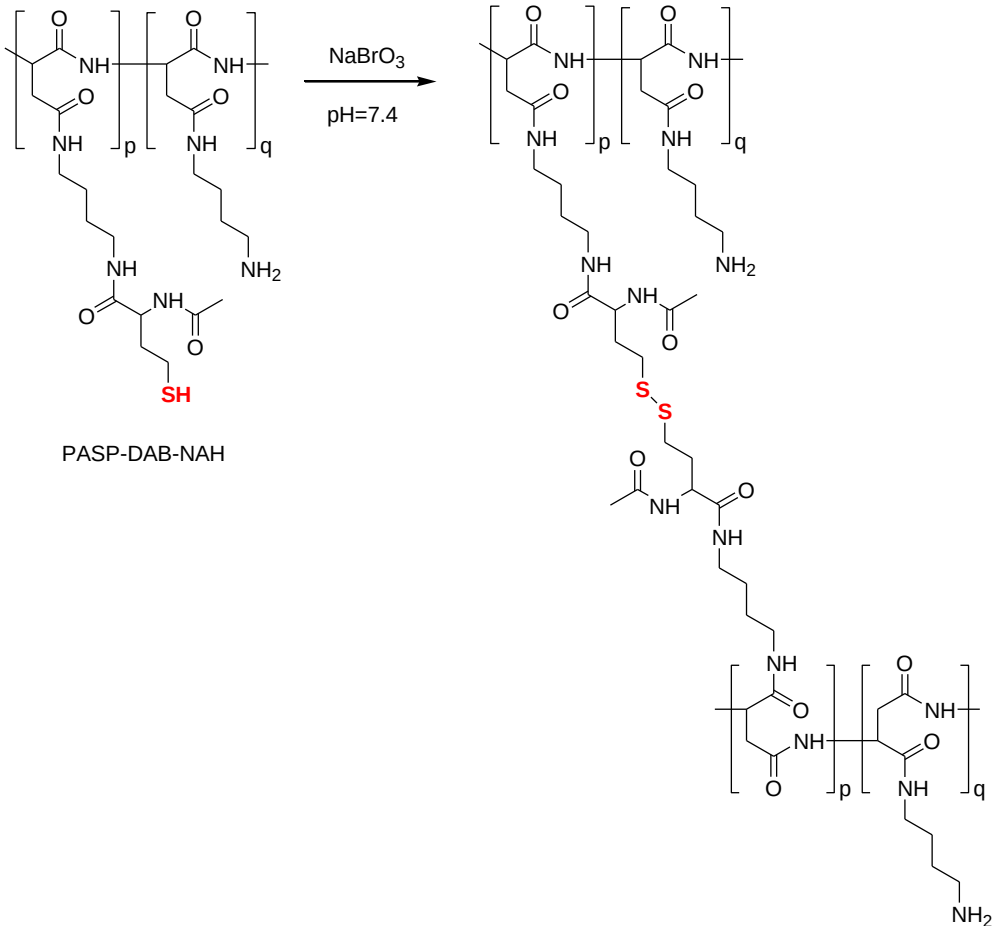

Scheme S1. Mechanism of oxidation-induced gelation of thiolated polyaspartamides.

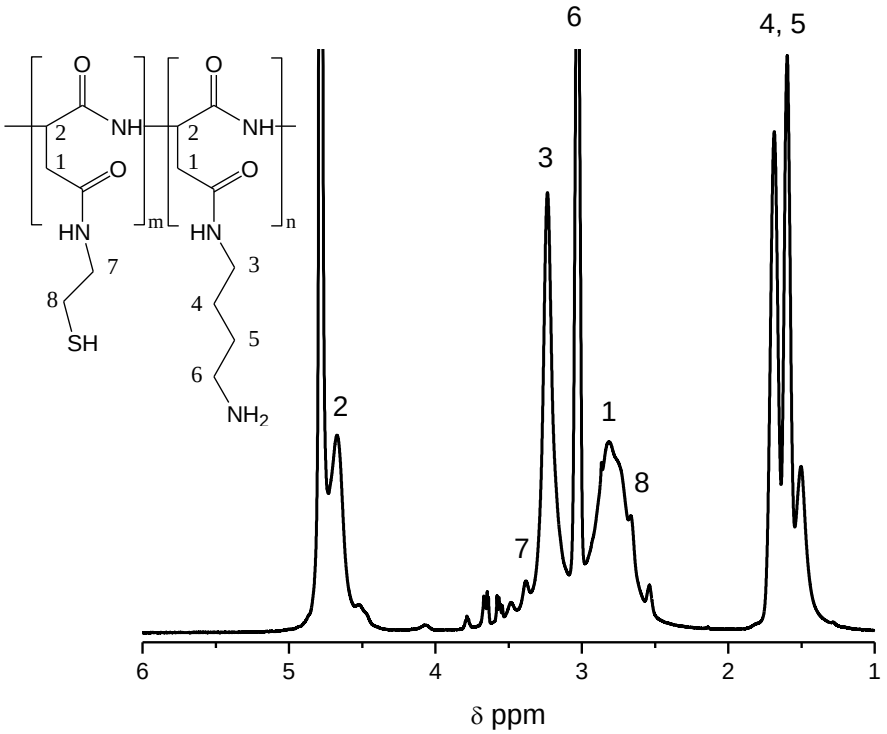

Figure S1. ^{1}H NMR spectrum of PASP-DAB-CEA10 in D_2O

^{1}H NMR, D_2O, δ(ppm): 4.67 ppm (1H of methine group in the backbone (2)), 3.44-3.38 ppm ((half peak) 2H of CEA in α position to amide group (7)), 3.35-3.10 ppm (2H of DAB δ position to amide group (6)), 3.10-2.98 ppm (2H of DAB in α position to amide group (3)), 2.81 ppm (2H of methylene group in the backbone (1)), 2.66-2.57 ((half peak) ppm 2H of CEA in β position to amide group (8)), 1.75-1.64 ppm (2H of DAB in γ position to amide group (5)), 1.64-1.54 ppm (2H of DAB in β position to amide group (4)). CEA content was calculated from the peak area between 2.66-2.57 ppm and 3.35-3.10 ppm.

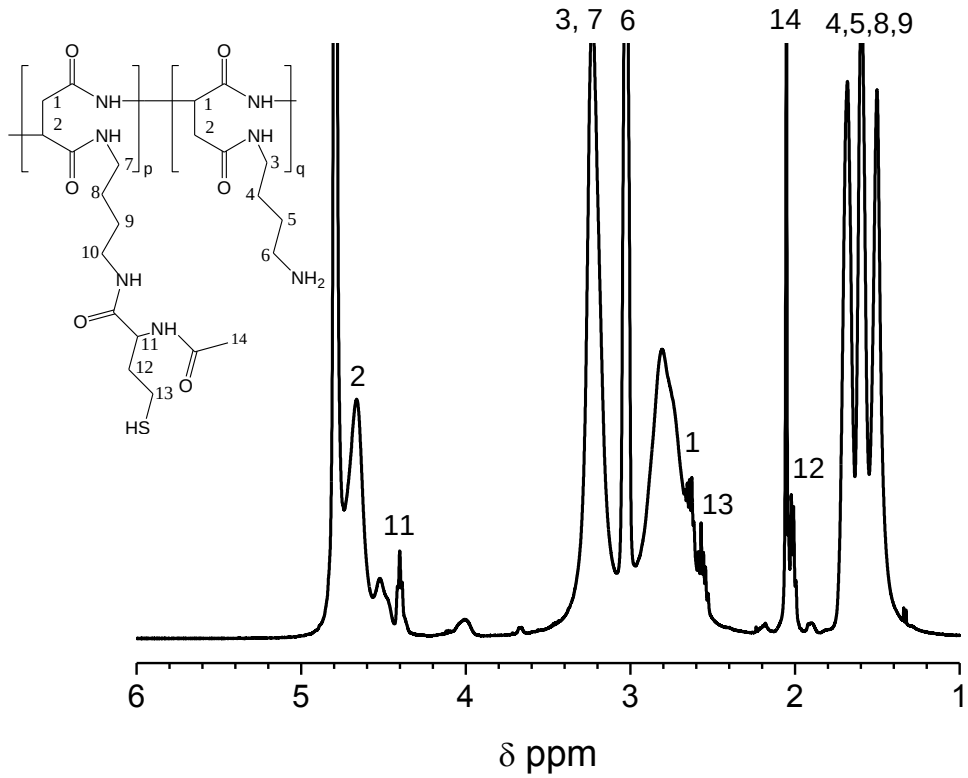

Figure S2. ^{1}H NMR spectrum of PASP-DAB-NAH10 in D_2O

^{1}H NMR, D_2O, δ(ppm): 4.67 ppm (1H of methine group in the backbone (2)), 4,40 ppm (1H of NAH (11), 3.4-3.00 ppm (2H of DAB α position to amide group (3, 7)), 3.00-2.96 ppm (2H of DAB in δ position to amide group (6)), 2.64 ppm (2H of methylene group in the backbone (1)), 2.56 ppm (2H of NAH (13)), 2.05 ppm (3H of NAH (14)), 2.00 ppm (2H of NAH (12)), 1.68 ppm, 1.59 ppm, 1.50 ppm (2H of DAB in β and γ position to amide group (4, 5, 8, 9)). NAH content was calculated from the peak area between 3.00-2.96 ppm and 2.00 ppm.

Table S1. The degree of thiolation (X_{SH}) of polymers in mol% to repeating units from ^{1}H NMR spectra (experimental error of determination is approximated as ± 2%).

Composition	X_{SH}
PASP-DAB-CEA2	3.0
PASP-DAB-CEA4	5.0
PASP-DAB-CEA6	6.9
PASP-DAB-CEA8	8.1
PASP-DAB-CEA10	7.0
PASP-DAB-NAH2	2.5
PASP-DAB-NAH4	5.5
PASP-DAB-NAH6	5.8
PASP-DAB-NAH8	12.7
PASP-DAB-NAH10	11.5

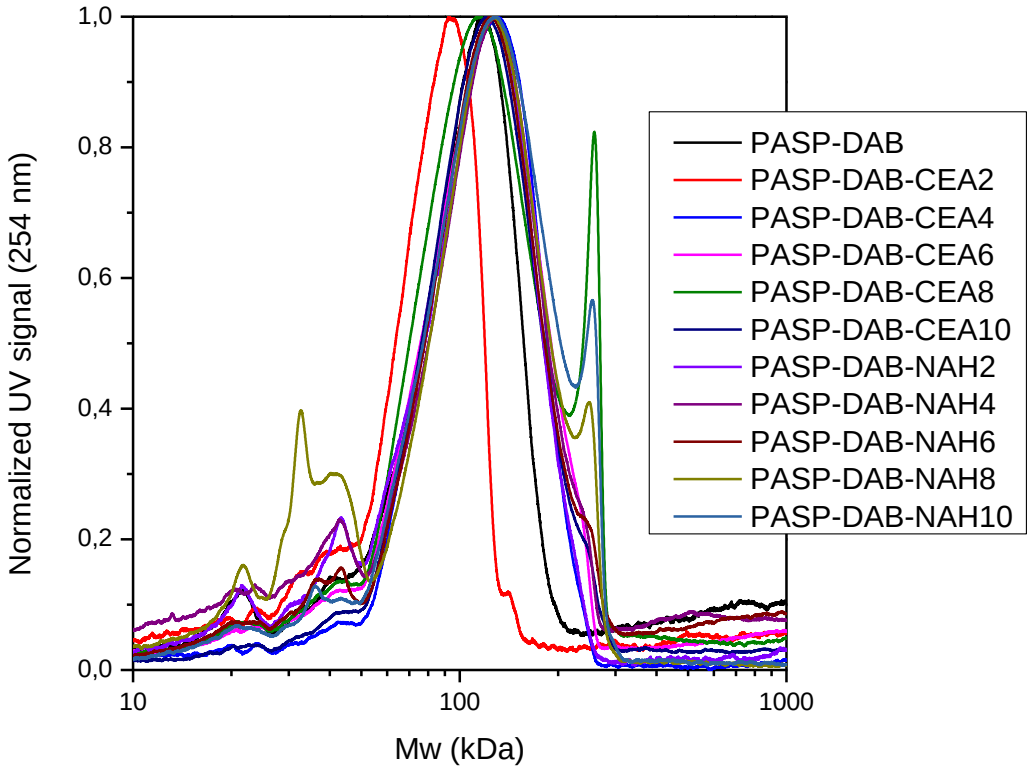

Figure S3. SEC profiles of thiolated polyaspartamides.

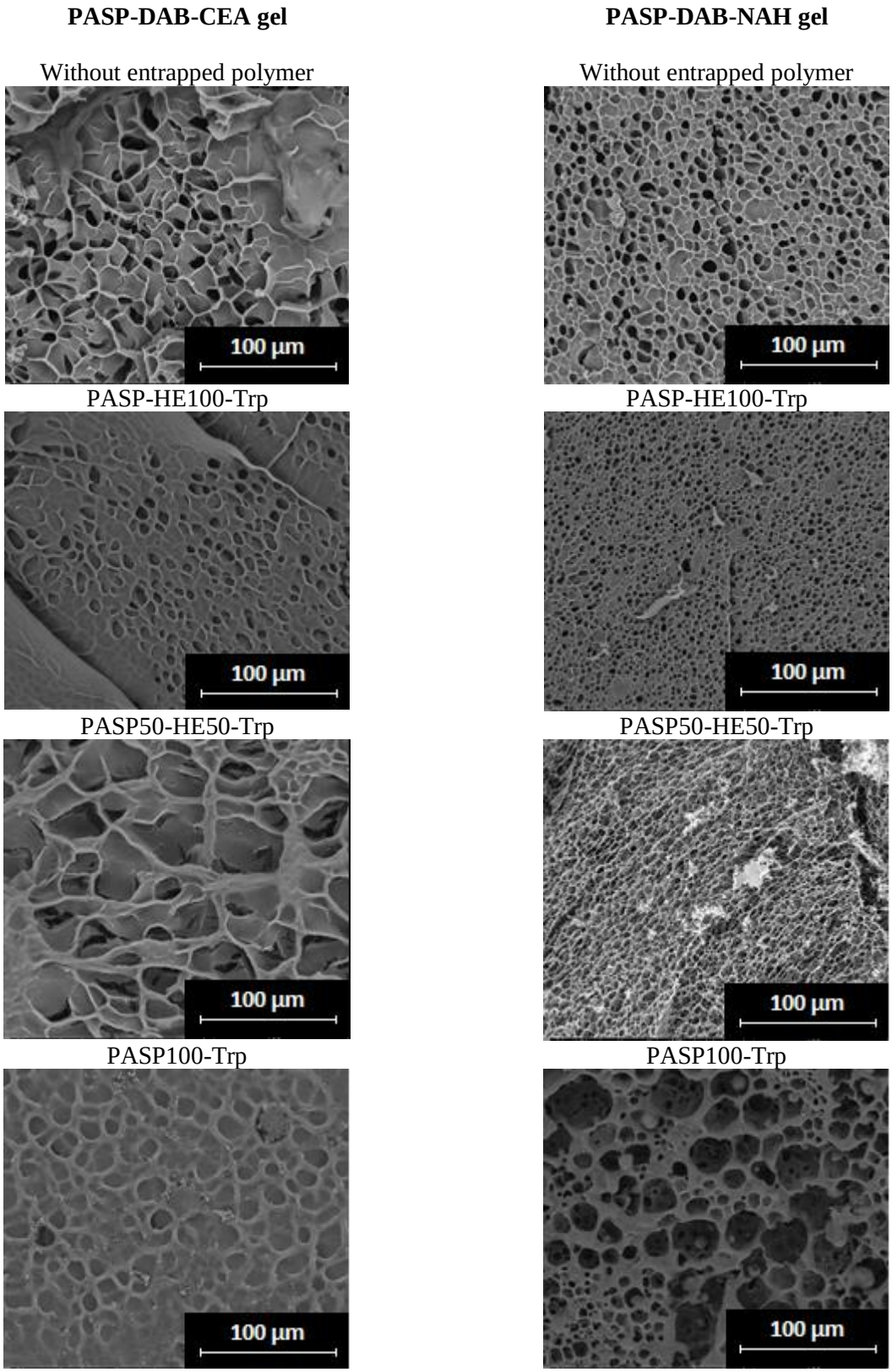

Figure S4. SEM images of thiolated polyaspartamides with different drug molecules.

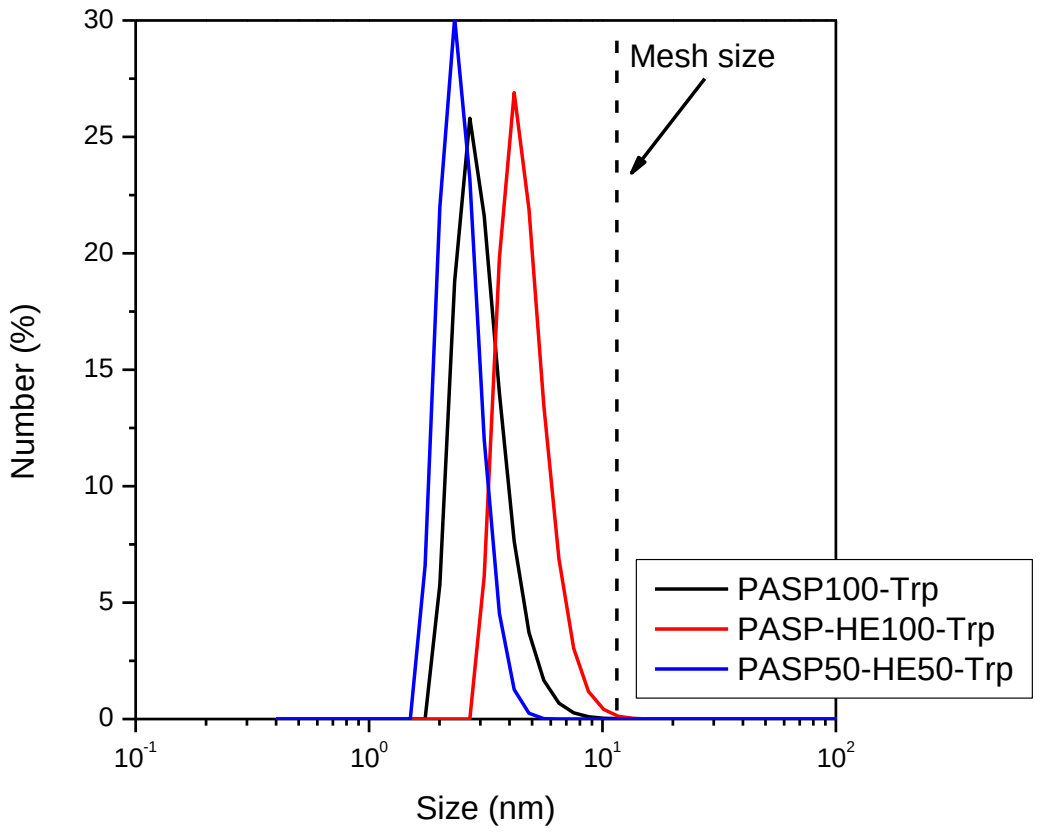

Figure S5. Particle size distribution of anionic (PASP100-Trp), neutral (PASP-HE100-Trp) and partially anionic (PASP50-HE50-Trp) fluorescent marked polymers. Dashed line shows the mesh size of thiolated cationic hydrogels.