

Electronic Supplementary information for:

Preparation of polymer nanoparticle-based complex coacervate hydrogels using polymerisation-induced self- assembly derived nanogels

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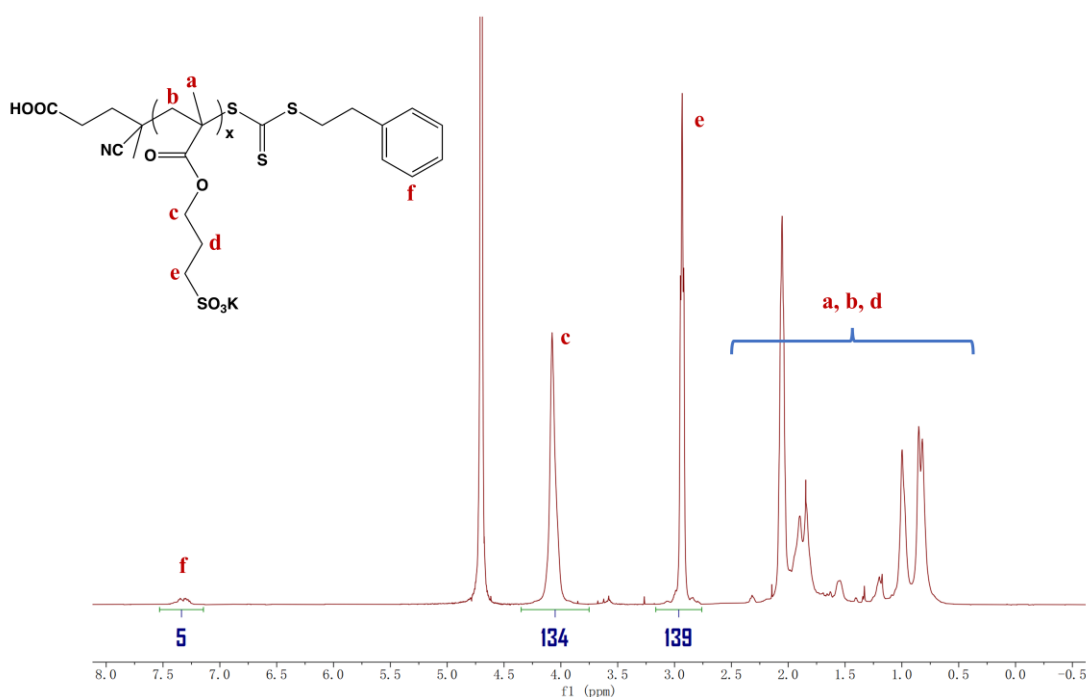


Figure S1: ¹H NMR spectra of a purified and freeze-dried PKSPMA₆₈ macro-CTA. The sample was dissolved in D₂O prior to analysis. The degree of polymerisation for this macro-CTA was calculated by comparing the integrated proton signals corresponding to the methacrylic polymer backbone at 2.75-3.25 ppm and 3.75-4.3 ppm with that corresponding to the aromatic protons of the chain end at 7.2-7.4 ppm.

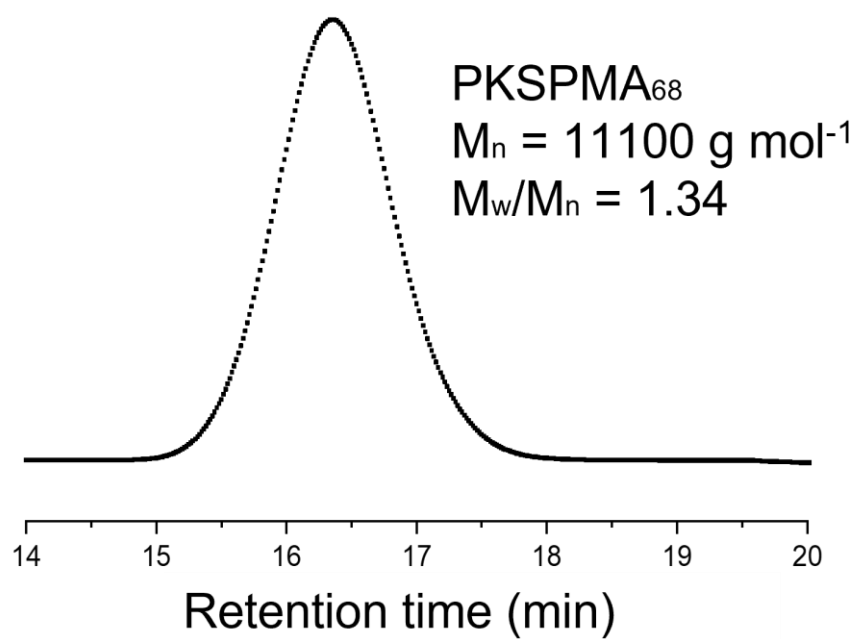


Figure S2: Aqueous gel permeation chromatography chromatograms obtained for PKSPMA₆₈ macro-CTA. A relatively narrow molecular weight distribution was achieved, suggesting successful RAFT polymerisation.

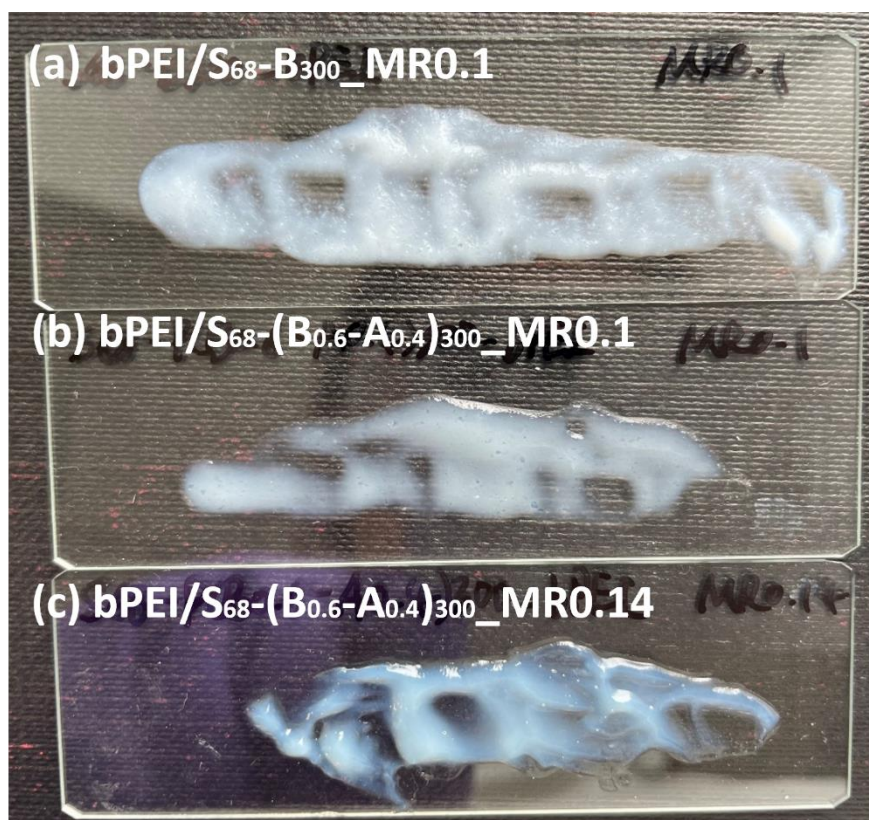


Figure S3: Images obtained for mixtures of branched polyethyleneimine and copolymer nanoparticles at different bPEI-to-NP mass ratios: (a) bPEI with $\text{S}_{68}\text{-B}_{300}$ nanoparticles at MR 0.1; (b) bPEI with $\text{S}_{68}\text{-P(B}_{0.6}\text{-A}_{0.4})_{300}$ nanoparticles at MR 0.1; (c) bPEI with $\text{S}_{68}\text{-P(B}_{0.6}\text{-A}_{0.4})_{300}$ nanoparticles at MR 0.14.

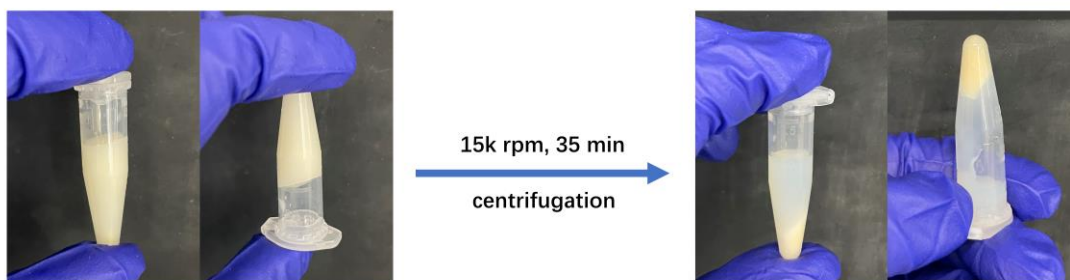


Figure S4: bPEI/S₆₈-P(B_{0.6}-A_{0.4})₃₀₀_MR 0.14 mixture before and after centrifugation (15k rpm for 35 min). Liquid-liquid phase separation occurs, with water being expelled from the gel, indicating complex coacervate formation.

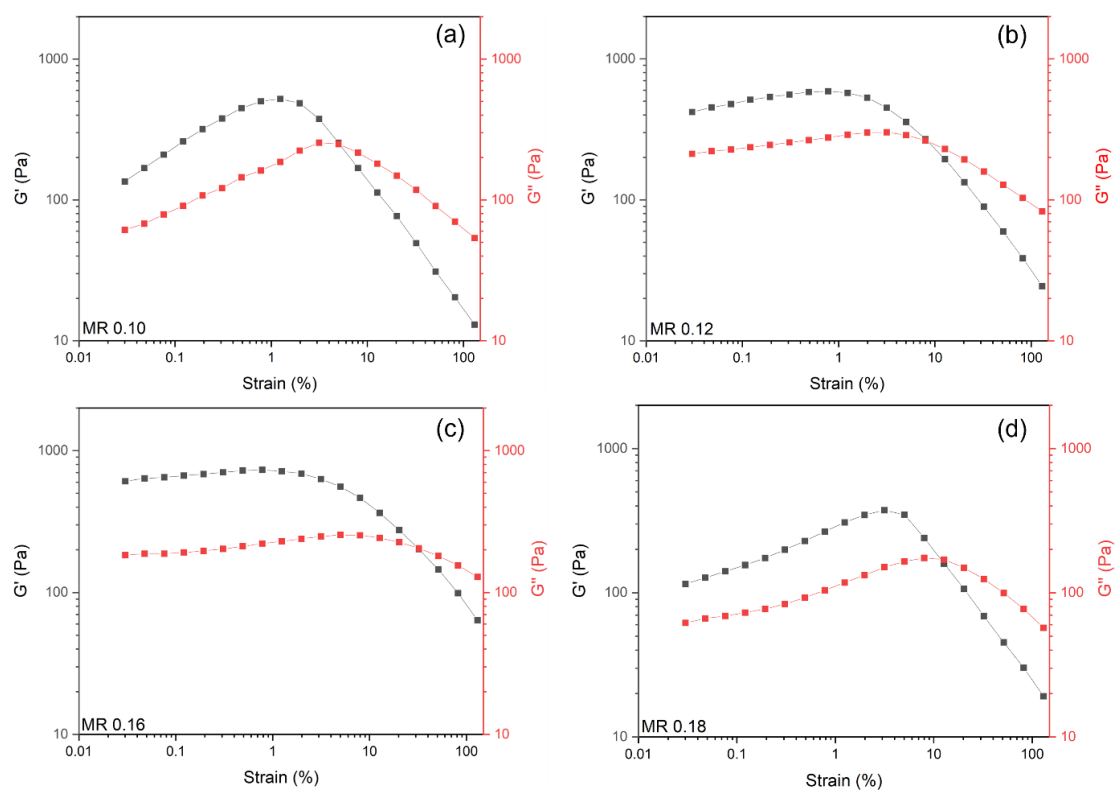


Figure S5: Strain-dependent oscillatory rheology measurements ($\omega = 10 \text{ rad s}^{-1}$, 25°C) of PEI/S₆₈-P(B_{0.6}-A_{0.4})₃₀₀ at different PEI-to-NP mass ratios; MR = (a) 0.10, (b) 0.12, (c) 0.16, (d) 0.18.

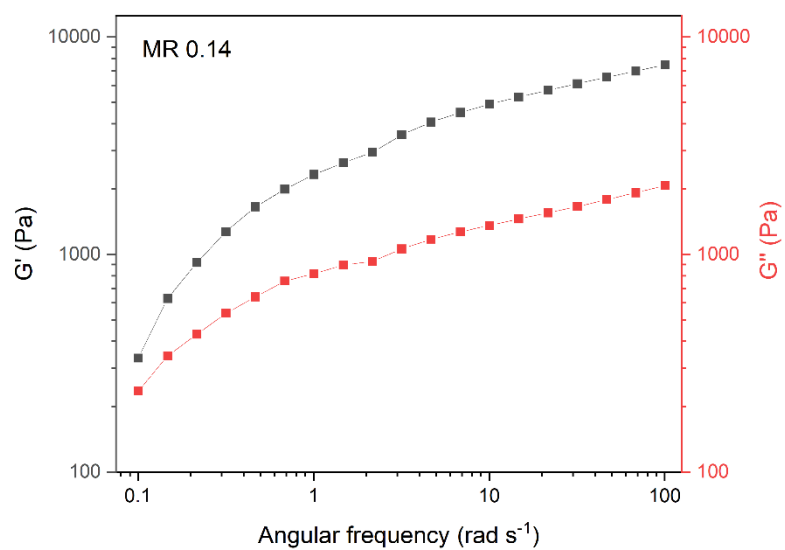


Figure S6: Angular frequency-dependent oscillatory rheology measurement ($\epsilon = 0.2\%$, $25\text{ }^{\circ}\text{C}$) of PEI/ S_{68} - $P(B_{0.6}-A_{0.4})_{300}$ at a PEI-to-NP mass ratio of 0.14.

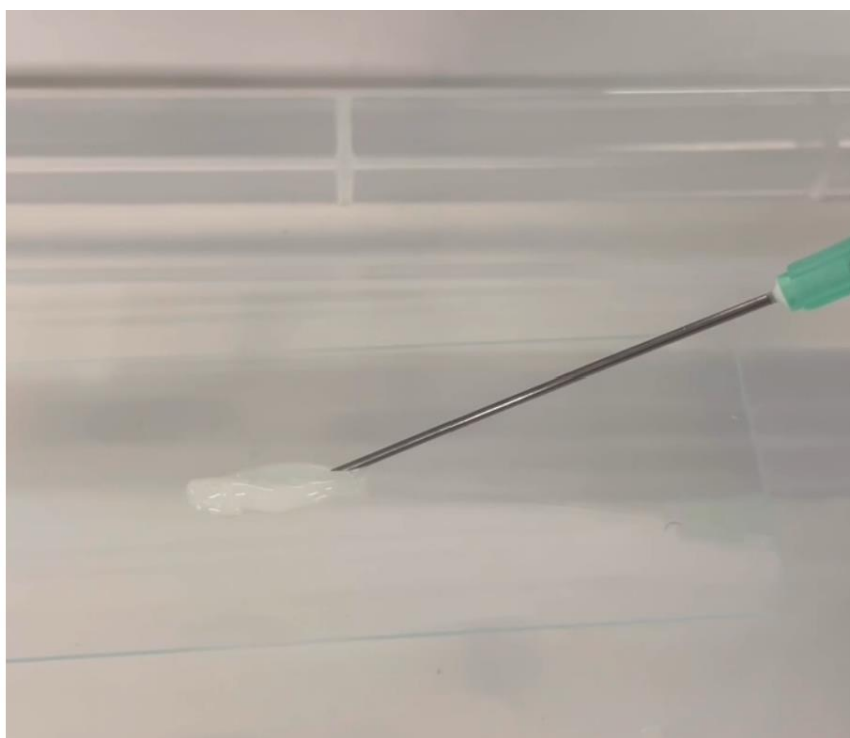


Figure S7: Photograph showing injectability of $b\text{PEI}/S_{68}\text{-}P(B_{0.6}\text{-}A_{0.4})_{68_MR0.14}$ hydrogel at room temperature.

Table S1: Particle diameters of S₆₈-P(B_m-A_{1-m})₃₀₀ nanoparticles at low pH and high pH. Particle diameters were measured by DLS and polydispersity index values are indicated in brackets.

Nanoparticle composition	Diameter at pH 2 / nm	Diameter at pH 10 / nm
S ₆₈ -B ₃₀₀	54 (0.245)	51 (0.176)
S ₆₈ -P(B _{0.8} -A _{0.2}) ₃₀₀	53 (0.0994)	63 (0.0821)
S ₆₈ -P(B _{0.6} -A _{0.4}) ₃₀₀	51 (0.106)	84 (0.194)
S ₆₈ -P(B _{0.4} -A _{0.6}) ₃₀₀	111 (0.27)	112 (0.199)
S ₆₈ -P(B _{0.2} -A _{0.8}) ₃₀₀	256 (0.336)	150 (0.41)

Synthesis of poly(potassium 3-sulfopropyl methacrylate) *via* RAFT solution polymerisation

KSPMA monomer (15.0 g, 60.9 mmol), PETTC RAFT agent (414 mg, ~1.2 mmol, dissolved in dioxane), ACVA (68 mg, 0.2 mmol, PETTC/ACVA molar ratio = 5), and pH 5.5 acetate buffer (65.5 g, final buffer/dioxane ratio = 3) were weighed into a round-bottomed flask, which was then sealed and purged with N₂ for 30 min. The sealed flask was placed in a preheated water bath at 70 °C for 90 min. The reaction was quenched by immersing the flask in an ice bath and opening it to air. The resulting PKSPMA macro-CTA (90.8 % conversion) was purified by dialysis against 10:1 water/methanol overnight. Then the purified solution was further dried under vacuum at 30 °C to evaporate volatiles and yield a yellow product (64.4 % yield). The degree of polymerisation (DP) was 68, as determined by ¹H-NMR using D₂O (Figure S1). This value was higher than the theoretical DP of ~45. This difference can potentially be attributed to RAFT agent inefficiency and/or moisture present in this particular batch of in-house prepared PETTC. Nevertheless, aqueous GPC analysis indicated an M_n of 11,100 g mol⁻¹ and an M_w/M_n of 1.34 (Figure S2).

Procedure for determining (co)monomer conversion by gravimetry:

Monomer conversions were determined *via* gravimetry by drying approximately 0.1 g of the final dispersion at 120 °C until constant weight using a Kern DBS 60-3 Moisture Analyser. Conversions were calculated based on the measured solids content and the theoretical solids content at full monomer conversion using

$$\text{Conversion (\%)} = \left[\frac{\text{Measured solids content (\%)}}{\text{Theoretical solids content at 100 \% monomer conversion (\%)}} \right] \times 100\%$$

$$\text{Theoretical solids content at 100 \% monomer conversion (\%)}$$

$$= \left[\frac{\text{Total mass of reagents (g)}}{\text{Total mass of reagents and solvent (g)}} \right] \times 100\%$$