

Supporting Information for

PNIPAM-based Heteroarm Star-Graft Quarterpolymers: Synthesis, Characterization and pH-Dependent Thermoresponsiveness in Aqueous Media

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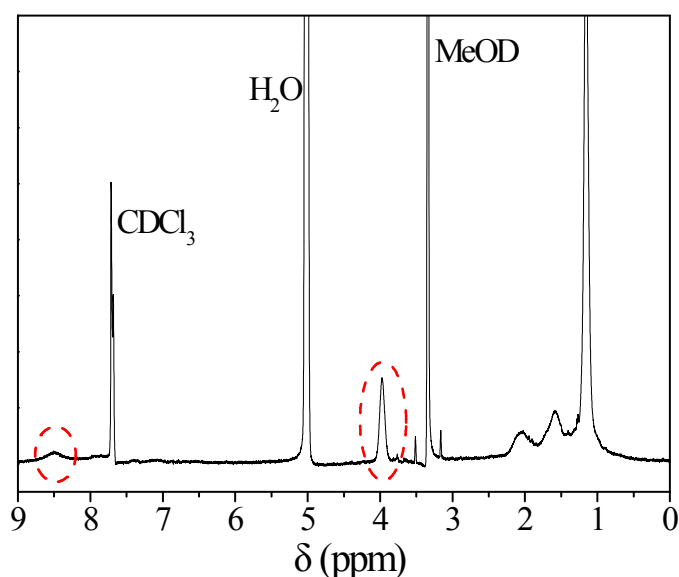


Fig. S1. ¹H-NMR spectrum of S₃₄₂₂(V_{136-b}-A_{119-g}-N₄₈₄)₂₂.

The grafting density of the star-graft quarterpolymers, expressed as the average number of PNIPAM chains per PAA arms (equal to P2VP arms), was determined by ¹H-NMR in a mixture of deuterated solvents MeOD/CDCl₃ (3/2 v/v). The calculation of the grafting density was performed using the intensity ratio of the -CH- unit of the isopropylene group of PNIPAM (with a resonance at δ ~ 3.8–4.1 ppm) and the proton atom in the 3-position of the pyridine ring (with a resonance at δ ~ 8.3–8.7 ppm) in the following equation:

$$\text{grafting density} = \frac{\text{intensity ratio} * DP_{P2VP}}{DP_{PNIPAM}}$$

where DP_{P2VP} and DP_{PNIPAM} are the degrees of polymerization of P2VP and PNIPAM, respectively.

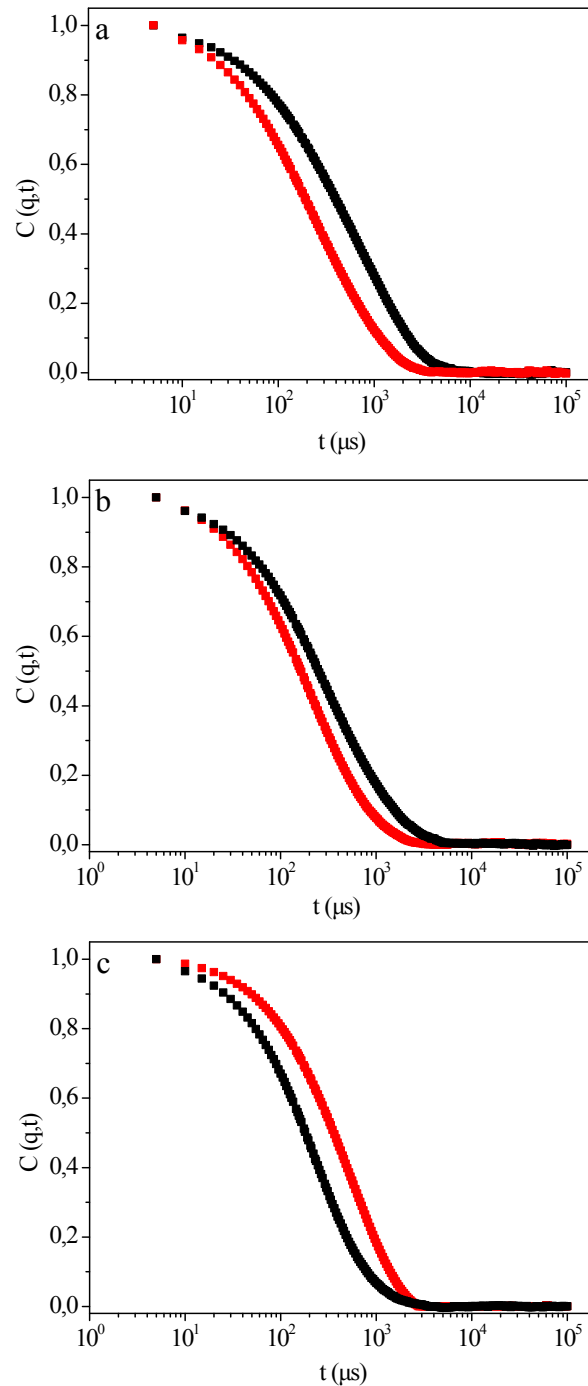


Fig. S2. Autocorrelation functions of 0.2 wt% $S_{339}(V_{126-b-A69-g-N48_{3,4}})_9$ (a), $S_{339}(V_{126-b-A69-g-N48_{4,5}})_9$ (b) and $S_{339}(V_{126-b-A69-g-N48_{11}})_9$ (c) aqueous solutions measured at pH 8 and at 25°C (black color) or 45°C (red color).

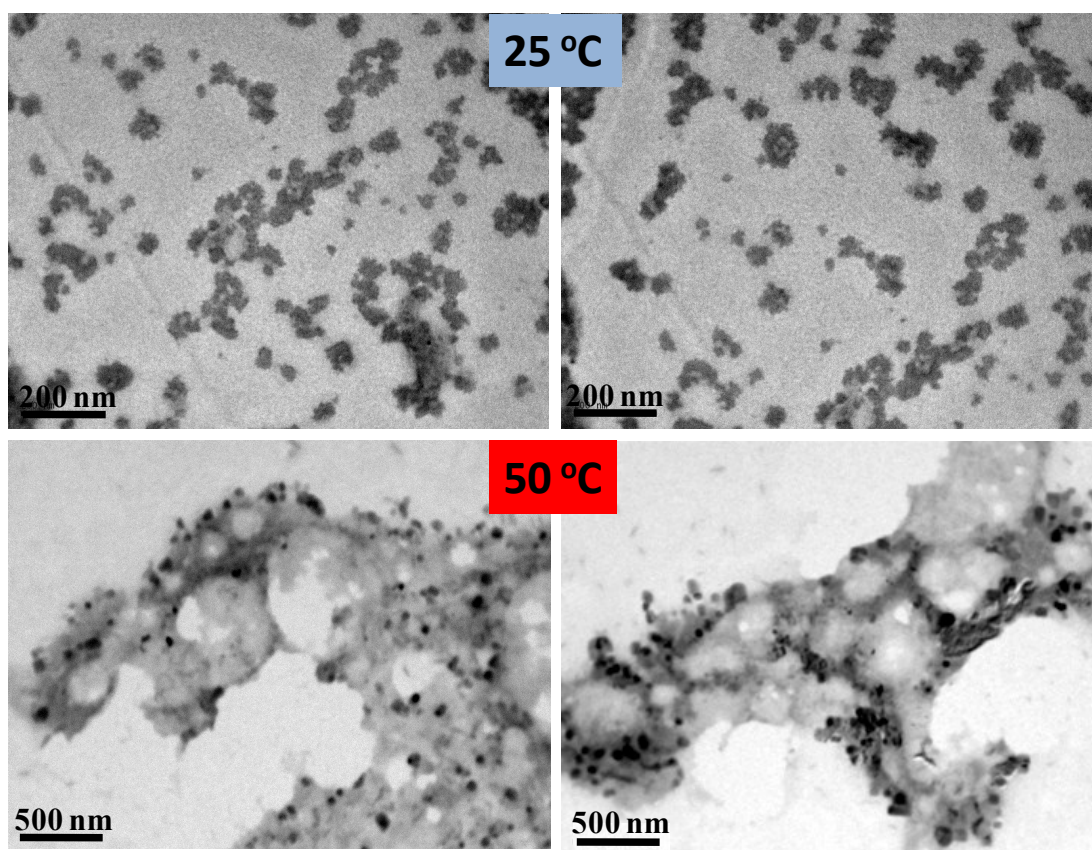


Fig. S3. TEM images of 0.006 wt% S₃₃₉(V₁₂₆-*b*-A₆₉-*g*-N_{484.5})₉ aqueous solutions of pH 2.4 at 25 and 50°C.

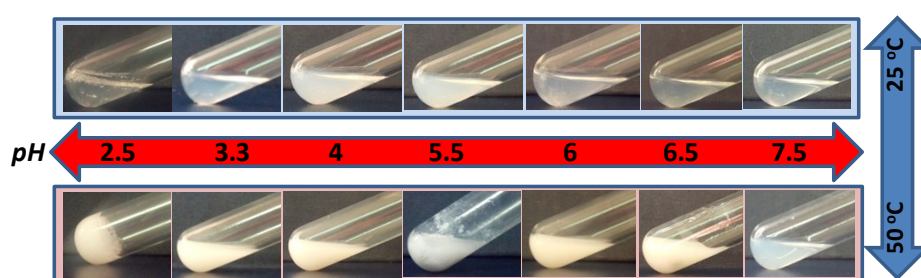


Fig. S4. Sol-gel phase behavior upon heating from 25°C (upper line) to 50°C (lower line) at various pH of S₃₄₂₂(V₁₃₆-*b*-A₁₁₉-*g*-N₄₈₄)₂₂ ($C_p=3$ wt%).