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(V136-b-A119-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 \( \delta \sim 3.8–4.1 \) ppm) and the proton atom in the 3-position of the pyridine ring (with a resonance at \( \delta \sim 8.3–8.7 \) ppm) in the following equation:
\[
\text{grafting density} = \frac{\text{intensity ratio} \times DP_{\text{P2VP}}}{DP_{\text{PNIPAM}}}
\]

where \(DP_{\text{P2VP}}\) and \(DP_{\text{PNIPAM}}\) are the degrees of polymerization of P2VP and PNIPAM, respectively.

**Fig. S2.** Autocorrelation functions of 0.2 wt% \(S_{33g}(V_{126-b-A69-g-N48}_{3,4})_9\) (a), \(S_{33g}(V_{126-b-A69-g-N48}_{4,3})_9\) (b) and \(S_{33g}(V_{126-b-A69-g-N48}_{11})_9\) (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% $S_{339}(V_{126-b-A_{69-g-N_{48-}}})_9$ 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 $S_{3422}(V_{136-b-A_{119-g-N_{48}}})_{22}$ (C$_p$=3 wt%).