Stable azlactone-functionalized nanoparticles prepared from thermoresponsive copolymers synthesized by RAFT polymerization

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Electronic Supporting Information

Synthesis and characterization of PNIPAM-CTA

The polymerization of NIPAM was performed under a nitrogen atmosphere at 70°C in DMF using the following conditions: $[NIPAM]_0 / [MTTCP]_0 / [AIBN]_0 = 74 / 1 / 0.1$. Conversion from monomer to polymer was determined by following the disappearance of the vinyl peaks of NIPAM using ¹H-NMR spectroscopy using DMF solvent as an internal standard (Fig. S1). After an initial induction period attributed to a pre-equilibrium, the first-order kinetic plot was linear, showing a constant concentration of active species in the polymerization (Fig. S2).



Fig. S1 NMR spectra of the raw polymerization with time for the RAFT polymerization of NIPAM using AIBN as initiator and mediated by MBTTCP in DMF at 70°C, $[NIPAM]_0 / [MTTCP]_0 / [AIBN]_0 = 74 / 1 / 0.1$. Polymerization performed at 30% solids.



Fig. S2 First-order kinetic plot for the RAFT polymerization of NIPAM using AIBN as initiator and mediated by MBTTCP in DMF at 70°C, $[NIPAM]_0 / [MTTCP]_0 / [AIBN]_0 = 74 / 1 / 0.1$. Polymerization performed at 30% solids.

Number-average molecular weights increased linearly with conversion and narrow PDIs were obtained (Fig. S3). The SEC chromatograms showed a shift towards higher molecular weight as the polymerization time increased. Moreover, symmetrical chromatograms were observed throughout the polymerization (Fig. S4).



Fig. S3 Plots of number-average molecular weight and polydispersity against conversion for the RAFT polymerization of NIPAM using AIBN as initiator and mediated by MBTTCP in DMF at 70°C, $[NIPAM]_0 / [MTTCP]_0 / [AIBN]_0 = 74 / 1 / 0.1$. Polymerization performed at 30% solids.



Fig. S4 Overlaid raw SEC chromatograms from the dRI detector for the RAFT polymerization of NIPAM using AIBN as initiator and mediated by MBTTCP in DMF at 70°C, $[NIPAM]_0 / [MTTCP]_0 / [AIBN]_0 = 74 / 1 / 0.1$. Polymerization performed at 30% solids.

Determination of LCST values by UV-Vis spectroscopy



Fig. S5 Measured transmittance at 500 nm at varying temperatures for aqueous solutions for a range of copolymers of the type PNIPAM-*b*-P(VDM-*co*-DMA) to determine the LCST of the copolymers.