Supporting Information

In situ synthesis and self-enhancement of polymeric composite hydrogel based on particulate macro-RAFT agents

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Part I. The $^1$H NMR spectrum of DMP

**Figure S1.** The $^1$H NMR spectrum of 2-dodecylsulfanyltiocarbonylsulfanyl-2-methyl propionic acid in CDCl$_3$. 
Part II. The $^1$H NMR spectrum of PAA-DMP

![NMR Spectrum](image)

**Figure S2.** The $^1$H NMR spectrum of PAA-DMP in DMSO-d$_6$. 
Part III. The $^1$H NMR spectra of PAA-\textit{b}-PS copolymer

**Figure S3.** The $^1$H NMR spectra of PAA-\textit{b}-PS with different lengths of PS block in CDCl$_3$/DMSO-d$_6$ = 1/1 (v/v).
Part IV. The stability of PAA-\textit{b}-PS nanoparticles in water

The appearances of the initial aqueous dispersion of $\text{PAA}_{60}\text{-b-PS}_{127}$, $\text{PAA}_{60}\text{-b-PS}_{150}$, and $\text{PAA}_{60}\text{-b-PS}_{180}$ was recorded by the digital camera as shown in Figure S4, compared with those after standing for 30 d.

![0 days vs. After 30 days](image)

\textbf{Figure S4.} The digital photos of the appearance of the aqueous solution of PAA-\textit{b}-PS nanoparticles standing at different time. (1: $\text{PAA}_{60}\text{-b-PS}_{150}$, 2: $\text{PAA}_{60}\text{-b-PS}_{127}$, and 3: $\text{PAA}_{60}\text{-b-PS}_{180}$)
Part V. The swelling of PAA-b-PS vesicles by EGDMA in water.

The optical image and DLS analysis of the mixture of EGDMA and vesicle dispersion to confirm the swelling of the vesicles by EGDMA as shown in Figure S5. It can be seen that when EGDMA was dispersed in pure water, large oil droplets can be observed in water under optical microscope (Fig. S5-A). But if EGDMA was dispersed in the aqueous dispersion containing PAA-b-PS vesicles, no large oil droplets could be observed (Fig. S5-B), indicating most of EGDMA will be distributed in the vesicles. At the same time, the size of the vesicles increases obviously after the addition of EGDMA, as detected by DLS.

![A and B images](image)

**Figure S5.** The optical micrographs of 28.5 μL of EGDMA dispersed in 6 mL of different solvent: (A) pure water, (B) water containing PAA-b-PS vesicles (2×10⁻⁴ g/mL) after stirring 6 h. (C) The size of the vesicles in water (2×10⁻⁴ g/mL) before and after the addition of EGDMA (5%) measured by DLS.
Part VI. The compressive stress-strain curves of PNR-HG.

**Figure S6.** The compressive stress-strain curves of PNR-HG with 20% of AM, 5% of EGDMA, and $1.6 \times 10^{-4}$ g/mL $\text{PAA}_{60-} - b - \text{PS}_{150}$ nanoparticles.