Supporting Information

In situ synthesis and self-enhancement of polymeric composite

hydrogel based on particulate macro-RAFT agents

Lanlan Li^a, Ruyi, Jiang^b, Jinxing Chen^a, Mozhen Wang^a*, Xuewu Ge^a*

^aCAS Key Laboratory of Soft Matter Chemistry, Department of Polymer

Science and Engineering, University of Science and Technology of China,

Hefei, Anhui 230026, PR China

^bPetroChina Company Limited, Beijing, 100007, PR China

*To whom the correspondence should be addressed. E-mail: pstwmz@ustc.edu.cn; xwge@ustc.edu.cn Tel: + 86-551-63600843





Figure S1. The ¹H NMR spectrum of 2-dodecylsulfanylthiocarbonylsulfanyl-2methyl propionic acid in CDCl₃.







Part III. The ¹H NMR spectra of PAA-*b*-PS copolymer

Figure S3. The ¹H NMR spectra of PAA-*b*-PS with different lengths of PS block in $CDCl_3/DMSO-d_6 = 1/1$ (v/v).

Part IV. The stability of PAA-b-PS nanoparticles in water

The appearances of the intitial aqueous dispersion of PAA_{60} -b- PS_{127} , PAA_{60} -b- PS_{150} , and PAA_{60} -b- PS_{180} was recorded by the digital camera as shown in Figure S4, compared with those after standing for 30 d.



Figure S4. The digital photos of the appearance of the aqueous solution of PAA-*b*-PS nanoparticles standing at different time. (1: PAA₆₀-*b*-PS₁₅₀, 2: PAA₆₀-*b*-PS₁₂₇, and 3: PAA₆₀-*b*-PS₁₈₀)

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.



Figure S5. The optical micrographs of 28.5 μ L 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 1.6×10^{-4} g/mL PAA₆₀-*b*-PS₁₅₀ nanoparticles.