

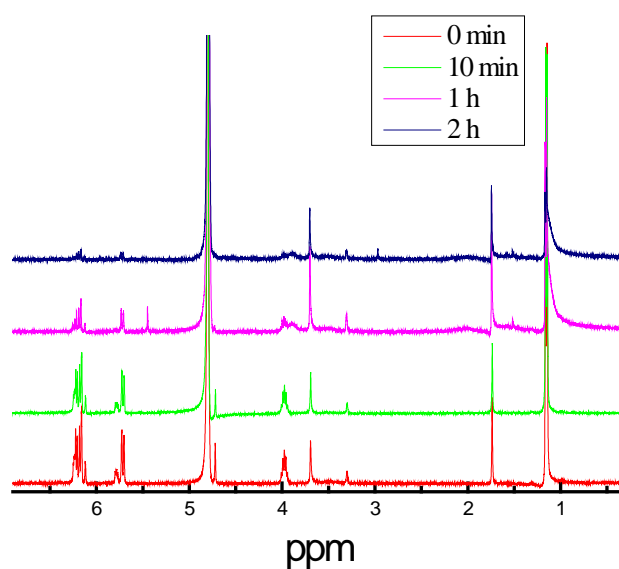
Support Information

**Linear Coupling of Spherical Block Copolymer Micelles Induced by Gradually Depositing an Insoluble Component onto the Core-Shell Interface**

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S1. Evidence for the polymerization of MBA and NIPAM at 65 °C:

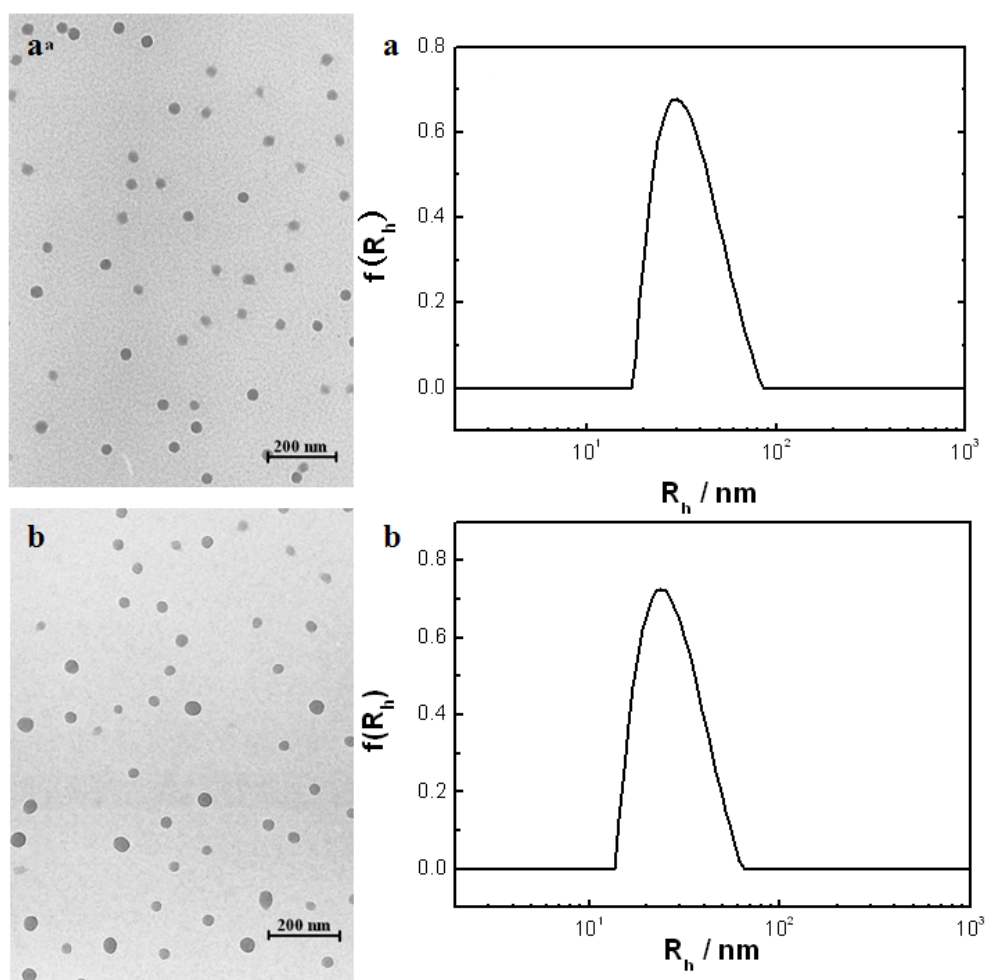


**Fig. S1** <sup>1</sup>H-NMR spectra of the samples at different polymerization times (0 min, 10 min, 1 h and 2 h) in the deuterated mixture solvent.

<sup>1</sup>H-NMR spectra show that the relative intensity of the signal of carbon-carbon double bonds of NIPAM (5.7 ppm) and that of MBA (6.2 ppm) decreases as the

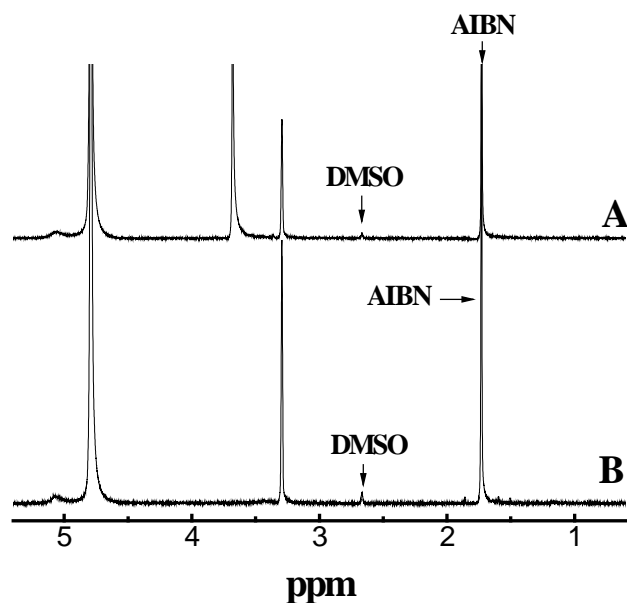
reaction proceeds, indicating the occurrence of the polymerization of NIPAM and MBA.

S2. TEM and DLS measurements of the particles formed in control experiments 1 and 2:



**Fig. S2** TEM images and hydrodynamic radius distributions  $f(R_h)$  of nanoparticles formed in the control experiments 1 (a) and 2 (b).

S3. Determination of weight ratio of AIBN located in the core of the polymeric micelles:



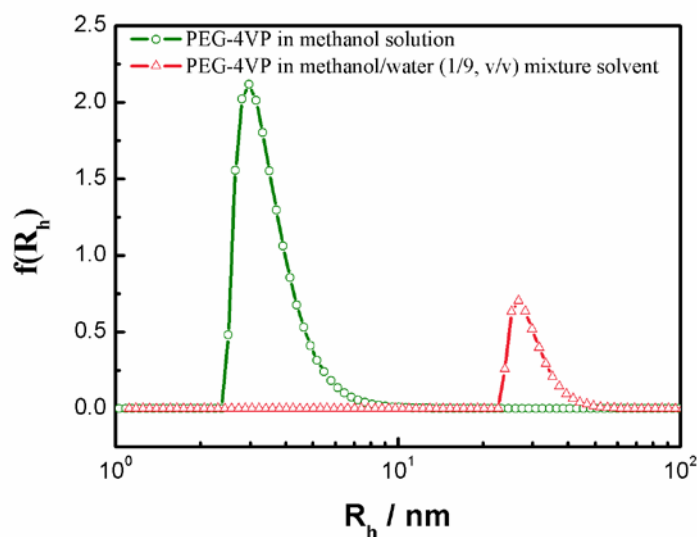
**Fig. S3**  $^1\text{H}$ -NMR spectra of sample A: 5 mg PEG-*b*-P4VP + 0.8 mg AIBN + 50  $\mu\text{L}$  *d*-DMSO (as the internal standard) + 0.5 ml  $\text{CD}_3\text{OD}$  + 4.5 mL  $\text{D}_2\text{O}$ ; and sample B: 0.8 mg AIBN + 50  $\mu\text{L}$  *d*-DMSO + 0.5 mL  $\text{CD}_3\text{OD}$  + 4.5 mL  $\text{D}_2\text{O}$ .

For preparation of sample A, 0.8 mg AIBN and 5 mg PEG-P4VP was dissolved in 0.5 mL  $\text{CD}_3\text{OD}$ , followed by addition of 4.5 mL  $\text{D}_2\text{O}$ . Sample B was prepared by mixing 0.8 mg AIBN with 0.5 ml  $\text{CD}_3\text{OD}$  and then with 4.5 mL  $\text{D}_2\text{O}$ . 50  $\mu\text{L}$  DMSO was used as the internal standard.

In spectra A and B, the intensity ratios of the signal at 1.7 ppm (the signal of AIBN) to that at 2.8 ppm (the signal of DMSO) are 20.9 and 54.1, respectively. This indicates that in the suspension of the micelles, 61%  $((54.1-20.9)/54.1=61\%)$  AIBN is

located in the core of the micelles and thus loses its mobility and becomes undetectable by  $^1\text{H-NMR}$ .

S4. The number-averaged DLS curves of the PEG-*b*-P4VP in pure methanol and methanol/water (1/9) mixture solvent:

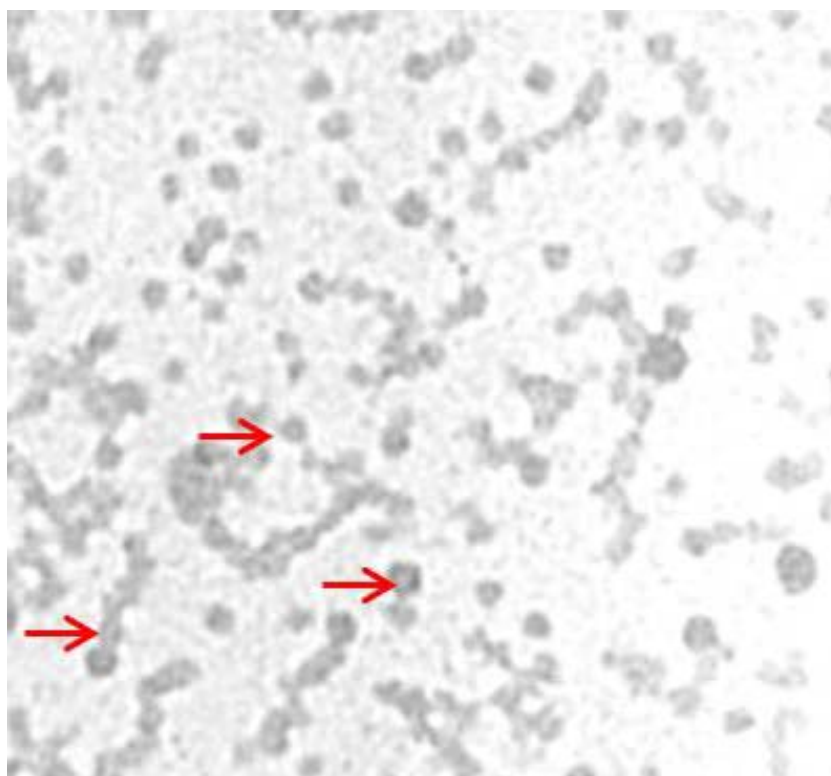


**Fig. S4** Number-averaged hydrodynamic radius distribution  $f(R_h)$  of the PEG-*b*-P4VP (circles) in methanol and that in methanol/water (1/9, v/v) mixture solvent (triangles).

S5. Discussion on the mechanism for the core-core coupling:

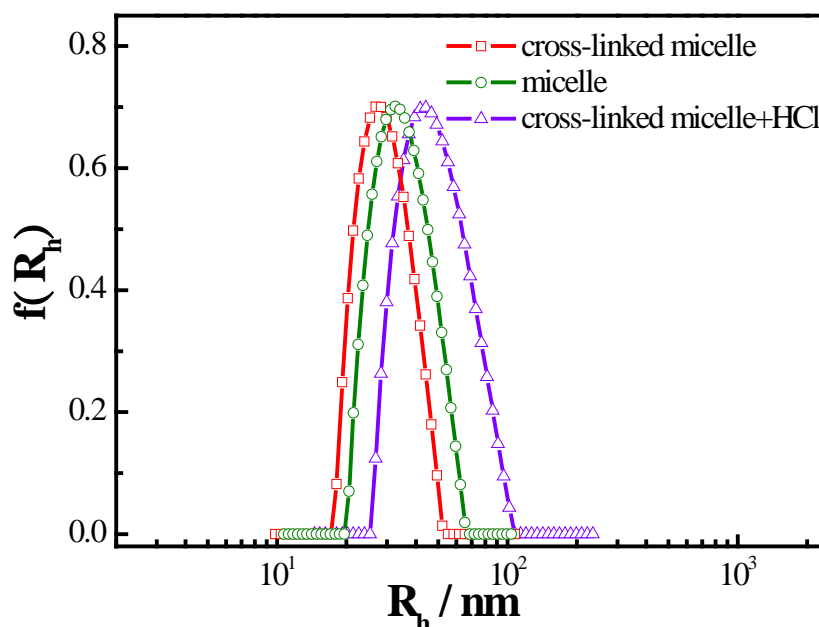
The coupling of the cores is mainly through the welding of the P4VP cores. As mentioned in the text, the insoluble and reactive copolymer of MBA and NIPAM deposited at the core-shell interface increased the size of the attractive cores, leading to the core-core coupling. In addition, in the final product, a large part of the

nanoparticles are nanofibers based on unbiased observation of the TEM images. After removing the PEO-b-P4VP micelles, a large part of the residual nanoparticles are hollow spheres (the spherical nanoparticles with a hole in the central area), as evidenced by TEM observations (Fig. S5). Although some residual nanoaggregates are with a linear structure, the average length is much less than that of the nanofibers before the removal of the micelles (Figure 3d in the main text). The fact that the nanofibers dissociated into the short linear nanoaggregates and even the hollow spheres after removing the micelles demonstrates that not all the micelles in a nanofiber are crosslinked together and the coupling is mainly through the welding.



**Fig. S5.** The TEM image of the residual nanoaggregates obtained after removing the micelles from the nanofibers.

S6. DLS characterizations of the PEO-P4VP micelles in methanol/water (1/9, v/v) mixture solvent, the micelles with the core being crosslinked in the medium, and the crosslinked micelles in the medium at pH of 2.0:



**Fig. S6** Hydrodynamic radius distributions  $f(R_h)$  of the PEG-4VP micelles (circles) in methanol/water (1/9, v/v) mixture solvent, the PEG-P4VP micelle with the core being crosslinked by 1, 4-dibromobutane (squares) in the same medium, and the core cross-linked micelle at pH of 2.0 by adding hydrochloric acid to the medium (triangles).

In Fig. S6, the signal of the uncross-linked micelles peaks at 32 nm. The core of micelle was cross-linked using 1, 4-dibromobutane. For the crosslinking reaction, 0.5  $\mu$ l 1, 4-dibromobutane was added into 15 ml micelle under strong stirring and the mixture solution was stirred for 48 h under ambient temperature to ensure the core was sufficiently cross-linked. After cross-linking the core by 1,4-dibromobutane, the peak shifts to a smaller  $\langle R_h \rangle$  (squares), indicating the intra-micellar crosslinking that

resulted in the collapse of the core and thus the decrease in  $\langle R_h \rangle$ . No other signals observed in the curve, which confirms that no inter-micellar cross-linking occurred. After the crosslinking reaction, when the pH of the medium was adjusted to 2.0, the  $\langle R_h \rangle$  apparently increases (triangles). This indicates that the core is cross-linked into an integrated network otherwise the micelles would dissociate into individual block copolymer chains at pH of 2.0 (as mentioned in the main text, the un-crosslinked micelles will dissociate at pH of 3.0). The increase in  $\langle R_h \rangle$  further demonstrates the formation of the integrated network, which is swollen in the acidic medium due to the protonation of the pyridine units.