Self-Assembly of Polystyrene with Pendant Hydrophilic Gold Nanoparticles: The Influence of the Hydrophilicity of the Hybrid Polymers

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Fig. S1 shows photographs of citrate-stabilized AuNPs in aqueous solution (vial a) and toluene/water emulsion stabilized by amphiphilic AuNPs monomers (vial b). It can be found that AuNPs are well dispersed in water, and upon addition of MUMA and toluene, an emulsion was obtained under ultrasonication.

Fig. S1 Photogragh showing the aqueous dispersion of AuNPs (vial a) and emulsion of toluene and water stabilized by AuNPs monomer (vial b)

Fig. S2 $^1$H NMR spectrum of PVP prepared by RAFT polymerization.
Synthesis of PS-coated Fe₃O₄ nanoparticles

FeCl₃·6H₂O (2.16 g, 7.99 mmol) and FeCl₂·4H₂O (0.835 g, 4.20 mmol) were added into 6.50 mL of deoxidized HCl solution (0.411 M) under an argon atmosphere at stirring. The resulted solution was added dropwise into 82.5 mL of NaOH solution (1.50 M) under rigorous stirring. The solution was stirred for 30 min, and then centrifuged at 8000 rpm for 2 min. Dark Fe₃O₄ nanoparticles powder was filtered, washed by deoxidized doubly-distilled water, and dried in vacuum.

Fe₃O₄ nanoparticles coated with 4,4-azo-bis (4-cyanopentanoic acid) (ABCPA):
An acetone solution (20 ml) with Fe₃O₄ nanoparticles (1 g) was combined with ABCPA (1.3 g, 4.64 mmol) under argon atmosphere. The Fe₃O₄ nanoparticles were dispersed under ultrasonication at room temperature for 1.5 h. The solution was centrifuged at 8000 rpm for 5 min, and the dark-brown Fe₃O₄ nanoparticles were filtered, washed by CH₂Cl₂, and dried in vacuum.

Fe₃O₄ nanoparticles coated with polystyrene: Fe₃O₄ nanoparticles coated with ABCPA (8 mg) were dispersed in toluene (2 mL) under ultrasonic, and then styrene (2 mL) was added. The solution was bubbled with argon for 30 min, and the polymerization was conducted at 80 ºC for 12 h. The PS-coated Fe₃O₄ nanoparticles were precipitated in methanol and centrifuged at 8000 rpm for 5 min. In order to remove free polystyrene, the hybrid nanoparticles were redispersed in 5 mL of chloroform and centrifugated, and the hybrid nanoparticles at the bottom of vials were collected. The TEM specimen was prepared by dipping copper grids into the THF dispersion of the PS-coated Fe₃O₄ nanoparticles and dried in air. The average size of
PS-coated Fe₃O₄ nanoparticles determined by TEM was about 8 nm (Fig. S3).

**Fig. S3** A TEM image of PS-coated Fe₃O₄ nanoparticles in THF.

The number-average molecular weight and molecular weight distribution of PS were 161K and 2.48, respectively. TGA measurements (Fig. S4) for ABCPA modified Fe₃O₄ nanoparticles (curve a) and PS-coated Fe₃O₄ nanoparticles (curve b) were found to have 17 wt% and 28 wt% volatile materials, so the weight percentage of PS on Fe₃O₄ nanoparticles was about 11 wt%.

**Fig. S4** TGA curves of ABCPA free-radical initiator modified Fe₃O₄ nanoparticles (curve a) and PS-coated Fe₃O₄ nanoparticles (curve b).