Supporting Information to

Zero-valent Iron (Fe(0)) mediated RAFT Miniemulsion Polymerization: A Facile Approach for Fabrication of Fe(0)-Encapsulated Polymeric Nanoparticles

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Experimental part:

Materials

Methyl methacrylate (MMA, 99%, Shanghai Chemical Reagents Co.) was freshly distilled under reduced pressure. Ethylene glycol dimethacrylate (EGDMA, 98%, Alfa Aesar) was de-inhibited by passing through a column of activated basic alumina. 2,2'-Azobisisobutyronitrile (AIBN, 99%, Shanghai Chemical Reagents Co.) was recrystallized three times from ethanol before being used. Brij 98 (Acros), hexadecane (HD, 99%, Alfa Aesar), iron(II) chloride (FeCl₂, 99.99%, Aladdin), lithium triethylborohydride-tetrahydrofuran (1.0 mol/L) (superhydride-THF, J&K Chemical) were used as received without further treatment. 2-Cyanoprop-2-yl 1-dithionaphthalate (CPDN) was synthesized according to the method reported elsewhere.¹ All other chemicals were obtained from Shanghai Chemical Reagents and used as received unless mentioned.

Characterization

The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the synthesized polymer was determined by a Waters 1515 size exclusion chromatography (SEC) equipped with a refractive index

detector (Waters 2414), using a HR 1 (pore size: 100 Å, 100-5000 Da), HR 2 (pore size: 500 Å, 500-20 000 Da) and HR 4 (pore size 10 000 Å, 50-100 000 Da) columns (7.8×300 mm, 5 µm beads size) with molecular weights ranging from $10^2 - 5 \times 10^5$ g mol⁻¹. THF was used as the eluent at a flow rate of 1.0 mL min⁻¹ and 30 °C. SEC samples were injected using a Waters 717 plus autosampler and calibrated with PMMA standards purchased from Waters. 1H NMR spectrum of the precipitated polymer was recorded on an INOVA 400 MHz nuclear magnetic resonance instrument using CDCl₃ as the solvent. Matrixassisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry measurement was performed using a Bruker autoflex(III) TOF/TOF mass spectrometer mass spectrometer (Bruker Daltonics, Inc., Billerica) equipped with a Nd:YAG laser (355 nm). All spectra were measured in positive reflection mode. Dynamic light scattering measurements were conducted using a Malvern Zetasizer Nano ZS instrument equipped with a 4 mW He-Ne laser operating at $\lambda = 633$ nm and with an avalanche photodiode detector with high quantum efficiency. The miniemulsions were analyzed after a 1:50 dilution. The measurements were conducted at 25 °C and the data were analyzed by Malvern Dispersion Technology Software 3.0. A vibrating sample magnetometer (VSM-7407, Lake Shore, USA) was used at room temperature to measure the magnetic properties of PMMA nanoparticles. The morphologies of aggregates were observed by a FEI TECNAI G² 20 transmission electron microscopy (TEM) instrument operating at 200 kV. A drop of a 1:50 dilution miniemulsion was deposited onto the carbon-coated copper grid and allowed to evaporate at room temperature before measurement. Thermo gravimetric analysis (TGA) was carried out using a SDT 2960 (TA instruments, New Castle) with a heating rate of 10 °C min⁻¹ from room temperature to 550 °C under a nitrogen atmosphere. Inductively coupled plasma-optical emission spectrometer (ICP-OES, Vista-MPX Varian) was used to measure iron content in crosslinked PMMA nanoparticles.

Synthesis of pre-prepared PMMA Coated Zero-valent Iron

The synthetic route was according to the procedure described by Guo *et al.*.² MMA (4.0 mL, 37.7 mmol) and AIBN (0.0077 g, 0.0464 mmol) were added to an ampule. The reaction was stabilized at 70 °C for 2 h to obtain original PMMA. A mixture of superhydride-THF (22 mL) and dry THF (50 mL) was added

dropwise to a mixture of FeCl₂ (1.20 g) and PMMA (2.30 g) in THF (50 mL) within half an hour and reacted for one additional hour under ultrasonic stirring condition. The reaction mixture was precipitated in 500 mL of ethanol. The supernatant was discarded and the remaining black paste was dissolved in THF. The precipitation and dissolution were repeated three times to remove by-products soluble in ethanol. The black product was dried under vacuum at a period of 24 h and stored under nitrogen.

Miniemulsion RAFT Polymerization of MMA

The Fe(0)-mediated RAFT miniemulsion polymerization was prepared as the following procedure: The pre-prepared PMMA coated Fe(0) was added and distributed in MMA. Immediately, the solution was mixed with hexadecane, CPDN and crosslinker (if used). This organic mixture was then added to the aqueous phase (water and Brij 98) under magnetic stirring for 15 min. After pre-emulsion, the mixture was homogenized by using a ultrasonic cell disruptor at 20% amplitude (Ningbo Xinzhi Co., LTD. China, JY98-3D, 2000W, Pulser with 3 s on and 1 s off) in an ice-water bath for 180 s. The miniemulsion was then transferred to a Schlenk tube, and nitrogen purged for 30 min. The polymerization was carried out at prescribed temperature under vigorous magnetic stirring.



Fig. S1 TGA thermograms of pre-prepared PMMA stabilized Fe(0) nanoparticles with different iron content, (a) 29.64%, (b) 16.95%.



Fig. S2 TEM images of pre-prepared PMMA coated Fe(0) sample a (iron content = 29.64%) in Figure S1.



Fig. S3 Kinetic investigation $(\ln([M]_0/[M]))$ versus time) of Fe(0)/CPDN mediated miniemulsion polymerization of MMA at different temperature. $[MMA]_0/[CPDN]_0/[Fe(0)]_0 = 200/1/1$, 10 wt % Brij 98 rel. MMA, 8 wt % HD rel. MMA, MMA = 1.0 mL, water = 4.0 mL. CPDN and HD refer to 2-cyanoprop-2-yl 1-dithionaphthalate and hexadecane, respectively. Brij 98 is a kind of polyethylene glycol monooleyl ether.





Fig. S4 (a) Number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of Fe(0)/CPDN mediated miniemulsion polymerization of MMA at 25 °C, 40 °C and 60 °C. Reaction conditions are the same as in Figure S2. (b-d) SEC curves of the miniemulsion polymerization of MMA at 25 °C, 40 °C and 60 °C, repectively. Theoretical molecular weight $(M_{n,th}) = ([MMA]_0/[CPDN]_0) \times M_{MMA} \times \text{conversion} + M_{CPDN}$, where M_{MMA} and M_{CPDN} represent the molecular weights of MMA and CPDN.



Fig. S5 Photographs of miniemulsion system with crosslinker added. Reaction conditions are the same as in Fig. 3.



Fig. S6 SEC curves of Fe(0)/CPDN mediated miniemulsion polymerization of MMA at 25 °C, 40 °C and 60 °C, repectively. $[MMA]_0/[CPDN]_0/[Fe(0)]_0 = 200/1/1$, 10 wt % Brij 98 rel. MMA, 8 wt % HD rel. MMA, MMA = 1.0 mL, water = 4.0 mL. Theoretical molecular weight $(M_{n,th}) = ([MMA]_0/[CPDN]_0) \times M_{MMA} \times \text{conversion} + M_{CPDN}$, where M_{MMA} and M_{CPDN} represent the molecular weights of MMA and CPDN.

PMMA obtained by RAFT miniemulsion



Fig. S7 Intact SEC curves of the miniemulsion polymerization of MMA at low conversion in Fig. S3 (a) and (b).

Magnetic property of PMMA nanoparticles

The magnetic properties of magnetic PMMA nanoparticles were analyzed with VSM as shown in Fig. S8. These crosslinked polymeric nanoparticles were obtained from pre-prepared PMMA with different iron content, respectively. The saturation magnetization of these microspheres is about 0.080 emu/g and 0.037 emu/g, and the magnetization curve displays a ferrimagnetism behavior with slender hysteresis.



Fig. S8 Magnetization curve of magnetic PMMA nanoparticles at room temperature, obtained from preprepared PMMA with different iron content in Fig. S1, respectively. a: magnetic PMMA nanoparticles obtained from pre-PMMA coated Fe(0) with 29.64 w/w% iron content; b: magnetic PMMA nanoparticles obtained from pre-PMMA coated Fe(0) with 16.95% w/w% iron content.

References

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- [2]. Z. Guo, L. L. Henry, V. Palshin, E. J. Podlaha, Journal of Materials Chemistry, 2006, 16, 1772.