Facile synthesis of thermo-responsive Au-polymer hybrid microgels through temperature-induced co-aggregation and self-crosslinking

1. Materials

Hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O, 99%), trisodium citrate dihydrate (99%), silver nitrate (AgNO₃, 99%) and 4-nitrophenol (4-NP, 98%) were purchased from Shanghai Chem. Co. and used as received. 2-(2-Methoxyethoxy)ethyl methacrylate (MEO₂MA, 95%; Aldrich) and oligo(ethylene glycol)methyl ether methacrylate (OEGMA, $M_n = 475$ g/mol; Aldrich) were purified by passing through a neutral aluminum oxide column to remove inhibitor. 3-(Trimethoxysilyl)propyl methacrylate (TMSPMA, 95%; Aldrich) was purified by distillation under reduced pressure. Azobisisobutyronitrile (AIBN, 98%; Aldrich) was recrystallized from ethanol prior to use. Tetrahydrofuran (THF) was purified by standard procedures. 4-(4-Cyanopentanoic acid) dithiobenzoate (CPADB) was synthesized according to reference.¹

2. Characterization

¹H NMR measurements were conducted on a BrukerAV300 NMR spectrometer instrument with D₂O as solvent and tetramethylsilane (TMS) as internal reference.

Molecular weight and molecular weight distribution were determined on a Waters 515 GPC instrument equipped with three microstyragel columns (500, 10³ and 10⁴ Å) and a refractory index detector (RI 2414). The measurements were conducted at 35 °C, monodispersed polystyrene standards were used in the calibration of M_n , M_w and M_w/M_n , and THF was used as eluent at a flow rate of 1.0 mL/min.

UV-vis measurements were performed on a Unico UV-vis 2802PCS spectrophotometer. Besides, a thermostatically controlled cuvette was used in the LCST determination, the heating rate was 0.2 °C/min.

Transmission electron microscope (TEM) observations were performed on a Hitachi H-7650 transmission electron microscope at an accelerating voltage of 100 kV. To prepare the TEM samples, a drop of the dispersion was dripped on a copper grid and then dried at room temperature until the solvent was evaporated thoroughly.

Dynamic light scattering (DLS) measurements were conducted on a DynaPro Light Scattering instrument (DynaPro-99E) at 25 °C with 824.3 nm laser.

3. Synthesis of P(MEO₂MA-co-OEGMA-co-TMSPMA)

In a typical process, MEO₂MA (1.20 g, 6.3 mmol), OEGMA (0.337 g, 0.7 mmol), TMSPMA (0.174 g, 0.7 mmol), AIBN (0.836 mg, 5.1×10^{-3} mmol), CPADB (14.3 mg, 0.051 mmol) and THF (3 mL) were added into a 10-mL polymerization tube. The mixture was degassed through three freeze-pump-thaw cycles, and the tube was then sealed under vacuum. The sealed tube was immersed into an oil bath thermostated at 70 °C. After 8 h, the tube was cooled to room temperature rapidly and then the reaction mixture was precipitated into an excess of n-hexane. The obtained product was dried under high vacuum for 30 min, and then stored in a vial filled with dry N₂.

4. Preparation of Au nanoparticles.

Monodispersed quasi-spherical gold nanoparticles (GNPs) were prepared according to

reference.² Briefly, 10 mL of aqueous solution of HAuCl₄·3H₂O (10 mM) and 0.34 mg of AgNO₃ were added to 10 mL of aqueous solution of sodium citrate (35.5 mM) under stirring. This mixture was incubated for 5 min. About 230 mL of water in a 500 mL round bottom flask was heated under reflux condition. After the water continuously boiled for 10 min, the HAuCl₄-AgNO₃-sodium citrate mixture was quickly injected into the boiling water under vigorous stirring. The color of the solution quickly changed from colorless to grayish blue, to purple, and then to ruby red in less than 2 min. The reaction was allowed to proceed under reflux for another 1 h and then cooled to ambient temperature. The obtained GNP solution was preserved in room temperature and used directly in the preparation of Au-polymer hybrid microgels.

5. Preparation of hybrid microgels.

In a typical process, 5 mg of $P(MEO_2MA$ -co-OEGMA-co-TMSPMA) and 2 mL of the GNP solution was added into a tube. The tube was then immersed statically in an oil bath of 70 °C for at least 4 h.

6. Reduction of 4-NP.

At 25 °C, aqueous solutions of 4-NP (0.1 mL, 1.5 mM), NaBH₄ (0.5 mL, 0.3 M) and deionized water (2 mL) were added into a quartz cuvette and the mixture was incubated for 5 min. The hybrid microgels ([Au] = 10 mM, D_h = 835 nm, 0.2 mL) was then added into the reaction solution, and UV-vis spectra of the solution were recorded at regular intervals during the reaction.



Scheme S1. Synthesis of P(MEO₂MA-co-OEGMA-co-TMSPMA) via RAFT polymerization.

ruble ST. feff i Copolymerization of MEO2/MIC, ODOMIT and TMOTIMIT						
Samples	$[M]_0/[O]_0/[T]_0^b$	Conv. ^c	DP^{d}	$M_{n,NMR}$	M _{n, GPC}	PDI
		(%)		(g/mol)	(g/mol)	
PMOT1	90:10:10	59	90	20040	14200	1.09
PMOT2	85:15:10	52	85	20050	15900	1.08
PMOT3	80:20:10	49	81	20170	19600	1.09

Table S1. RAFT copolymerization of MEO₂MA, OEGMA and TMSPMA^a

^a [CPADB]₀/[AIBN]₀ = 10:1, T = 70 °C, Time = 8 h, solvent: THF, 3 mL.

^b [M]₀/[O]₀/[T]₀ represents the feed molar ratio of MEO₂MA, OEGMA and TMSPMA.

^c Calculated by gravimetry.

^d DP represents the degree of polymerization, calculated on the basis of integral ratio of signals at $\delta = 4.03$ ppm (f) and $\delta = 7.4-8.0$ ppm (a, b, c) on ¹H NMR spectra.



Fig. S1 GPC traces of P(MEO₂MA-co-OEGMA-co-TMSPMA).



Fig. S2 ¹H NMR spectra of PMOT1 (A) and the obtained microgels (B) recorded in D₂O.



Fig. S3 The temperature dependence of the transmittance for the aqueous solution of P(MEO₂MAco-OEGMA-co-TMSPMA), measured of UV-Vis spectroscopy at $\lambda = 600$ nm and concentration of 3 mg/mL.



Fig. S4 Digital photos of the aqueous solution of PMOT1 (2.5 mg/mL) before (left) and after (right) being heated at 70 °C for 4 h.



Fig. S5 TEM image of the microgels assembled from PMOT1 (2.5 mg/mL) in pure water.



Fig. S6 TEM image of GNPs combined with P(MEO₂MA-co-OEGMA-co-TMSPMA).



Fig. S7 Digital photos of the aqueous solution of GNPs combined with P(MEO₂MA-co-OEGMA -co-TMSPMA) before (left) and after (right) being heated at 70 °C.





Fig. S8 TEM images of GNPs combined with $P(MEO_2MA-co-OEGMA-co-TMSPMA)$ after being heated at 70 °C.



Fig. S9 Temperature dependence of hydrodynamic diameters of the hybrid microgels assembled from $P(MEO_2MA\text{-}co\text{-}OEGMA\text{-}co\text{-}TMSPMA)$ (0.75 mg/mL) of different LCSTs in the GNP solution: (A) PMOT1, LCST = 36 °C, (B) PMOT2, LCST = 41 °C and (C) PMOT3, LCST = 46 °C.



Fig. S10 Color changes of the reaction solution of 4-NP and NaBH₄ when the hybrid microgels (A) or naked gold nanoparticles (B) are used as catalysts.



Fig. S11 TEM images of the hybrid microgels (A) and naked gold nanoparticles (B) after catalyzing the reduction of 4-NP.



Fig. S12 Plots of C_t/C_0 to reaction time in three courses of the reduction of 4-NP using the hybrid microgels (a) or naked GNPs (B) as catalysts, C_t and C_0 represent the concentration of 4-NP at time *t* and at the beginning of the reaction, respectively.

References

- 1 Q. Zheng and C.-Y. Pan, *Macromolecules*, 2005, **38**, 6841.
- 2 B. Zhang, T. Cai, S. Li, X. Zhang, Y. Chen, K.-G. Neoh, E.-T. Kang and C. Wang, *J. Mater. Chem. C*, 2014, **2**, 5189.