Supporting Information

Design of Chemosensors and Dynamic Anticounterfeiting Inks based on Colloidal Nanoprecipitated Polymers

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1. Synthesis of the polymer and copolymers

Briefly, a typical batch of polymerization was run at 80 °C with the molar ratio of 200:0.5:1:1 for [M]:[CVA]:[CuBr₂]:[PMDETA] to reach a theoretical degree of polymerization of 200. THF as a solvent was added in a dry glass tube, and then, activated CuBr₂ was added under N₂ purging to remove oxygen. The resulting mixture was stirred for 10 min and sonicated to disperse CuBr₂ in THF. Afterward, the ligand (PMDETA) was added to the reaction mixture and stirred for 20 min to form the metal complex, which could be recognized by forming a green mixture. In the following, MMA monomer or MMA monomer and functional comonomers (with a molar ratio of 1:0.25, respectively) were added to the reaction vessel and stirred for 1 h.^{1–5} The solution of CVA in 4 mL THF was added to the reaction medium, and the temperature was raised to 80 °C to initiate the polymerization. After 24 h, the polymerization was terminated and the resulting product was passed through a basic aluminum oxide several times to remove CuBr₂ and dried at 25 °C for 6 h.

2. Preparation of the fluorescent polymer and copolymers by nanoprecipitation

The sample P_1 was used to reach the smallest nanoparticles by optimizing the concentration of the polymer solution and the ratio of solvent to nonsolvent in the nanoprecipitation method. The other samples were precipitated at the same condition. Two different concentrations of polymer solutions (6 and 8 wt.%) for sample P_1 were added via a syringe pump to the tube containing water as a nonsolvent with two different ratios of solvent to nonsolvent (0.2 and 0.1). The evaluation of the particle size of the four polymeric nanoparticles prepared from the P1 sample shows that the smallest nanoparticles were obtained at the concentration of 6 wt.% and solvent-to-nonsolvent ratio of 0.1. Therefore, all the fluorescent samples with a concentration of 6 wt.% were nanoprecipitated in solvent to nonsolvent ratio of 0.1 at seven different pH values (1, 3, 5, 7, 9, 11, and 13) to evaluate the pH-responsivity of the light-responsive colloidal polymer nanoparticles. The rate of syringe pumping of nonsolvent and stirring speed during the addition of the polymer solution was selected as 0.1 mL/h and 800 rpm, respectively.

3. Characterization

Using a Bruker DPX 400 MHz apparatus, characterization of the chemical structure and molecular weight of the telechelic polymers and copolymers and also the chemical structure of fluorescein was carried out by proton nuclear magnetic resonance (¹H NMR) spectroscopy in CDCL₃. The average molecular weights and molecular weight distribution of the samples were studied by the size exclusion chromatography (SEC) technique. A Waters 2000 ALLIANCE with a set of three columns of pore sizes of 10 000, 1000, and 500 Å was utilized to determine polymer average molecular weight and polydispersity index (PDI). THF was used as the eluent at a flow rate of 1.0 mL.min⁻¹, and the calibration was carried out using low polydispersity polystyrene standards. For the SEC measurements, catalyst particles were removed by passing the polymer solutions through a neutral aluminum oxide column. By diluting the nanoparticles to a concentration of 0.2 mg/mL in deionized (DI) water, ZETASIZER NANO ZSP dynamic light scattering (DLS, Malvern, United Kingdom)

was used to measure the size and distribution of nanoparticles at 25 and 45 °C. TEM observations for the size and morphology of the nanoparticles were performed by using LEO 906 instrument (Zeiss, Oberkochen, Germany) with an accelerating voltage of 100 kV. The specimens for TEM analysis were prepared by deposition of the polymer solutions with a concentration of about 0.2 mg.mL⁻¹ on the carbon-coated copper grids and drying in vacuum at 25 °C. In addition, by using a Tescan Mira III (Czech Republic), field-emission scanning electron microscopy (FE-SEM) micrographs were recorded. After placing a drop of samples colloidal dispersions with a concentration of about 0.06 mg/mL and drying it in a vacuum at 25 °C, a Tescan Mira III (Czech Republic) was used to record the FE-SEM micrographs. An EMITECH K450x sputter-coating system (England) was used to place the samples in a vacuum and evacuate and also deposit a layer of gold under flushing with argon. UV-vis analysis was used to evaluate UV adsorption properties of the nanoparticle by using Jenway 6705 UV/Visible scanning spectrophotometer (United Kingdom). A JASCO FP-750 spectrofluorometer (Japan) was used to observe fluorescence emission of the colloidal samples. Excitation was done by a UV lamp (365 nm, 6 W/m², CAMAG 12VDC/VAC (50/60 Hz, 14VA, Switzerland)).

4. Study of the polymer structure and measurement of molecular weights

To confirm the successful synthesis of PMMA, poly(MMA-*r*-HEMA), poly(MMA-*r*-AAm), and poly(MMA-*r*-DMAEMA), the chemical structure and molecular weight of these polymers were studied by ¹H NMR in CDCl₃ solvent. The theoretical degree of polymerization (DP) for PMMA is 200, where the experimental DP is obtained about 94 based on the ¹H NMR results, as shown for Table 1. In the copolymer samples (poly(MMA-*r*-HEMA), poly(MMA-*r*-AAm), and poly(MMA-*r*-DMAEMA)), the experimental DP for PMMA, PAAM, PDMAEMA, and PHEMA

blocks is measured close to their theoretical values. This indicates the successful synthesis of the telechelic polymers and copolymers by RATRP method.

Sample	CVA (g)	CuBr ₂ (g)	PMDETA (g)	MMA (g)	HEMA (g)	AAM (g)	DMAEM A (g)	Theoretical DP		Experimental DP*	
~								РММА	copolymer	PMMA	copolymer
P ₁	0.014	0.022	0.0173	2	-	-	-	200	-	196	-
P ₂	0.014	0.022	0.0173	1.6	0.52	-	-	160	40	157	36
P ₃	0.014	0.022	0.0173	1.6	-	0.284	-	160	40	152	32
P ₄	0.014	0.022	0.0173	1.6	-	-	0.64	160	40	155	34

Table S1. Typical procedures used for the synthesis of PMMA and its copolymers by RATRP

* Measured by ¹H NMR spectroscopy

¹HNMR spectra (400 MHZ, CDCl₃):

PMMA: (x, δ=1.35 (CNCH₂C-CH₃) 1 (COO(CH₂)₂C-CH₃), 1.85 (CH₃CNCH₂C-CH₂-COOCH₃CH₂), (m, 3.65 (O-CH₃))

poly(MMA-*r*-DMAEMA): (x, δ= 1.37 (CNCH₂C-CH₃), 1 (COO (CH₂)₂C-CH₃), 1.24 (COO(CH₂)₂C-CH₃), 1.85 (CH₃CNCH₂C-CH₂)

CH₂-COOCH₃CH₂), (d, 2.25 (N-(CH₃)₂)), 3.65 (O-CH₃), 4 (O-CH₂-CH₂);

poly(MMA-*r*-HEMA): (x, δ= 1.35 (CNCH₂C-CH₃), 1 (COO(CH₂)₂C-CH₃), 1.27 (COO (CH₂)₂C-CH₃), 1.85 (CH₃CNCH₂C-CH₂-

COOCH₃CH₂), 3.65 (O-CH₃), 3.90 (CH₂-CH₂-OH), (h, 4.1 (O-CH₂-CH₂))

poly(MMA-*r*-AAm): (x, δ= 1.36 (CNCH2C-CH3), 1 (COO(CH₂)₂C-CH₃), 1.85 (CH₃CNCH₂C-CH₂-COOCH₃CH₂), (m, 3.65 (O-CH₃) (a, 6.9 (NH₂) and 2.40 ((NH₂)CO-CH)).



Figure S1. ¹H NMR spectra of (A) P₁, (B) P₂, (C) P₃, and (D) P₄ in CDCl₃

The chemical structure of polymers was evaluated by the characteristic peaks of monomers (m, h, d, and a). Also, the peaks of x are attributed to the chain end group of the initiator (CVA). The characteristic peaks of the chain end groups were used to measure molecular weight, according to the Equations 1-3 presented for MMA, DMAEMA, HEMA, and AAM, respectively.

$DP_{MMA} = (m/3)/(x/3)$	(Equation 1)
$DP_{HEMA} = (h/2)/(x/3)$	(Equation 2)
$DP_{DMAEMA} = (d/6)/(x/3)$	(Equation 3)

 $DP_{AAM} = (a/2)/(x/3)$

(Equation

4)

5. Size of the polymer nanoparticles



Figure S2. SEC traces for P₁, P₂, P₃, and P₄



Figure S3. DLS curves of P₁ in different conditions: A) low solvent-to-nonsolvent ratio low polymer concentration, B) low solvent-to-nonsolvent ratio and high polymer concentration, C) high solvent-to-nonsolvent ratio and low polymer concentration, and D) high solvent-to-nonsolvent ratio and polymer

concentration



Figure S4. DLS curves of the fluorescein-containing nanoparticles prepared from nanoprecipitation of A) P₁, B) P₂, C) P₃, and D) P₄ in aqueous media

6. Morphology of the copolymer particles



Figure S5. TEM images of the A) P1, B) P2, C) P3, and D) P4 nanoparticles

7. Optical properties of the light-responsive polymer nanoparticles





P₁, B) P₂, C) P₃, and D) P₄ in aqueous media



Figure S7. UV-vis spectra of the fluorescein-containing nanoparticles at pH 7 before and after coagulation for A) P1, B) P2, C) P3, and D) P4

Sample	P ₁	P ₂	P ₃	P ₄
pH of max emission	13	13	13	13
pH of max absorbance	13	13	13	13
pH of min emission	1	1	1	1
pH of min absorbance	1	1	1	1
Max emission at pH 13	-	-	-	\checkmark
Max absorbance at pH 13	-	-	-	\checkmark
Min emission at pH 13	\checkmark	-	-	\checkmark
Min absorbance at pH 13	\checkmark	-	-	\checkmark
Range of sensitivity	1-14	1-14	1-14	1-14
Selected sample	-	-	-	\checkmark
Effect of CO ₂ bubbling on				
the emission and	-	-	-	Decrease
absorbance of P_4				
Increasing CO ₂ bubbling				
time on emission and	-	-	-	Decrease
absorbance of P_4				

Table S2. Summary of fluorescence and UV-vis spectra results

8. Calibration curve for pH detection



Figure S8. I/I_{max} values against pH as the calibration curve for the P₄ sample to estimate pH of an unknown sample

9. References

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