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Supporting Information

pH-Responsive Self-Assembly of Fluorophore-Ended Homopolymers

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1. Materials

2-[(*tert*-Butoxycarbonyl) amino] ethyl methacrylate (Boc-AEMA) was prepared according to previous reports.[1] 2-Butanone (Sinopharm, 99%) were purified by vacuum distillation before use. 4,4'-di-*tert*-Butyl-2,2'-bipyridine (DTB-bipy, Aldrich, 98%) and copper (I) bromide (CuBr, Alfa Aesar, 99.999%) were used without further purification. The buffer solutions were prepared by 0.1 M Tris and 0.1 M HCl. PMI-labeled initiator was synthesized as described before.[2] Other reagents were purchased from Alfa Aesar without further purification.

2. Instruments

2.1 Nuclear magnetic resonance (NMR), Gel Permeation Chromatography (GPC), Fourier transform infrared (FTIR), et al.

Nuclear magnetic resonance (NMR) spectra were recorded on Bruker 400 (400 MHz ^{1}H) spectrometer using $CDCl_3$, MeOD and D_2O as solvent at room temperature. The gel permeation chromatography (GPC) setup comprised two Polymer Laboratories PL gel 5 μm Mixed-C columns maintained at 60°C in series with a Varian 390 LC refractive index detector. The flow rate was 1.0 mL/min, and the mobile phase contained 10 mmol LiBr. A total of 10 near-monodisperse PMMA standards (M_p = 600 to 618000 g/mol) were used for calibration. The pH measurements were carried out using a pH meter (Mettler Toledo S40K), which was calibrated with pH 4 and pH 7 buffers before use. UV-visible spectra were obtained on a spectrometer (Cintra 20, GBC, Australia). The corrected fluorescence spectroscopic studies were performed on a fluorescence spectrophotometer (Horiba Jobin Yvon FluoroMax-4 NIR, NJ, USA) at room temperature. Fourier transform infrared (FTIR) spectra (KBr pellets) were collected on a NEXUS 670 FTIR spectrometer (Nicolet, US).

2.2 Scanning Electron Microscope (SEM)

Samples for SEM observation were prepared at various pH values on the surface of silica. HITACHI S-4700 (Japan) scanning electron microscope (SEM) operated at an accelerating voltage of 10 kV. Samples for SEM observation were vacuum sputtered with Pt.

2.3 Laser light scattering (LLS)

Laser light scattering experiments were performed on a commercial LS instrument (ALV SP-86) equipped with a Spectra Physics 2011-s Kr ion laser (637.2 nm wavelength, 500 mW output power) and an ALV-5000 correlator. The dispersions used in LLS experiments were clarified by a 0.80 μm Millipore filter. All the measurements were carried out at 25±0.1 °C.

The dynamic light scattering (DLS) was used to determine the hydrodynamic radius (R_h) and polydispersity of colloidal spheres formed in aqueous media. The scattering angle used for the DLS measurement was 60°. For a system of polydispersed particles in suspension, the first-order electric field correlation function $g(1)(t)$ is related to the linewidth distribution function $G(\Gamma)$ by

$$g^{(1)}(t) = \int_0^{\infty} G(\Gamma) e^{-\Gamma t} dt \qquad (1)$$

where t denotes the delay time. Two methods (the cumulant analysis and the CONTIN analysis) are used for data processing. The cumulant analysis (Eq. 2) was used to describe logarithm of the first-order electric field correlation function $(g(1)(t))$ as a series expansion of time (t), where the first cumulant ($<\Gamma>$, the decay rate of the process) yields the z-averaged diffusion coefficient and the second cumulant (μ_2) is related to the second moment of the distribution of relaxation times.[3]

$$\ln[g^{(1)}(t)] = -<\Gamma>t + \left(\frac{\mu_2}{2}\right)t^2 - \left(\frac{\mu_3}{6}\right)t^3 + \cdots \quad (2)$$

$$\mu_2 = \int_0^\infty G(\Gamma)(\Gamma - <\Gamma>)^2 d\Gamma \quad (3)$$

where G(Γ) is a linewidth distribution function and Γ is given by

$$\Gamma = Dq^2 \quad (4)$$

where D is the translation diffusion coefficient, and q [$=(4\pi n/\lambda_0)\sin(\theta/2)$] is the scattering vector, θ is the scattering angle, n is the refractive index of the solvent, and λ_0 is the wavelength of the incident light. The average hydrodynamic radius ($<R_h>$) was obtained from the particle diffusion coefficient based on the Stokes-Einstein equation.[4]

$$<R_h> = {k_BT}/{6\pi\eta D} \quad (5)$$

where k_B is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the solvent. The cumulant methods can result in $<\Gamma>$ and μ_2 directly, which is most reliable for a variance $\mu_2/ <\Gamma>^2 \leq 0.3$. The hydrodynamic radius distribution $f(R_h)$ was obtained by the CONTIN program in the correlator.[5] The Laplace inversion (CONTIN analysis) of the measured electric field correlation function $g_{(1)}(t)$ can result in a linewidth distribution function $G(\Gamma)$. For a diffusive relaxation, Γ is related to the translational diffusion coefficient by $\Gamma=Dq^2$. Therefore, $G(\Gamma)$ can be converted to a hydrodynamic radius distribution $f(R_h)$ according to the Stokes- Einstein equation.

The static light scattering (SLS) was employed to determine the weight-average molar mass of the colloidal spheres ($M_{w,sphere}$), the radius of gyration (R_g), and the second virial coefficient (A_2).[4] The particles scatter light according to the following relation:

$$\frac{Kc}{R_{vv}(\theta)} = \frac{1}{M_W}(1 + \frac{1}{3}q^2 < R_g^2 > +A_2c \quad (6)$$

where K [$=4\pi^2n^2 (dn/dC)^2/(\lambda_0{}^4N_A)$] is the contrast factor, q [$=(4\pi n/\lambda_0)\sin(\theta/2)$] is the scattering vector, c is the concentration, θ is the scattering angle, $R(\theta)_{vv}$ is the

Rayleigh ratio at the angle of measurement, n is the refractive index of the solvent, dn/dc is the specific refractive index increment, λ_0 is the wavelength of the incident light, N_A is the Avogadro number, and A_2 is the second virial coefficient. The parameters could be estimated through the Zimm plot analysis. The extrapolations regarding to c and θ yield $M_{w,sphere}$ from the intercept on the ordinate as well as A_2 and $<R_g^2>$ from the slope of the corresponding curves. In this study, the colloidal dispersion was so dilute that the extrapolation of c to zero was not necessary.

3. Synthesis and characterizations

3.1 ATRP polymerization of poly(BOC-AEMA)

The monomer BOC-AEMA and the initiator was placed in a Schlenk flask and dissolved in the 2-butanone. CuBr was then added, and the mixture was degassed by three freeze–pump–thaw cycles. The ligand DTB-bipy was added under argon, and then the solution was stirred at 25 °C for 10 min. Finally, the flask was sealed and placed in a thermostatted oil bath at 70 °C to start the reaction. The polymerizations were stopped by cooling with liquid nitrogen after a defined reaction time. The monomer conversion was determined by ^{1}H NMR spectroscopy. The reaction mixture was diluted and eluted through a column filled with neutral alumina to remove the copper complex. The solvent was removed under vacuum, and the polymer was isolated by precipitation into methanol/water (1:1) mixture and drying under vacuum to constant weight.

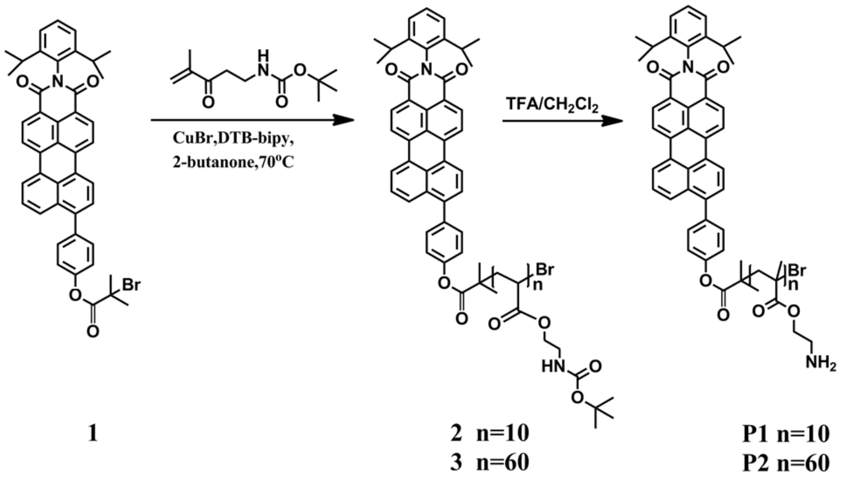
Table S1. Homopolymers by ATRP Process

Homopolymer	**DP** [a]	**$M_{n,GPC}$(Da)**[b]	**$M_{w,GPC}$(Da)**[b]	**M_w/M_n**[b]	**$M_{n,NMR}$ (Da)**[c]	**convn[d] (%)**
P1	10	2500	4000	1.64	5314	10
P2	60	16000	22000	1.42	13474	60

[a] Theoretical degree of polymerization assuming 100% monomer conversion;
[b] M_n, M_w and M_w/M_n were determined by GPC in THF;
[c] Calculated M_n by ^{1}H NMR, corresponding to the real composition in the first column;
[d] Conversion of monomer.

3.2 Hydrolysis of poly(BOC-AEMA)

The PMI-Labeled homopolymer poly(BOC-AEMA) was dissolved by CH_2Cl_2 in a 100 mL round-bottomed flask, and trifluoroacetic acid (TFA) (1 M in CH_2Cl_2) was added and the mixture was stirred for 2 h at room temperature. The product was precipitated upon addition of abundant diethyl ether and dried under vacuum.



Scheme S1. Synthesize of **P1** and **P2**.

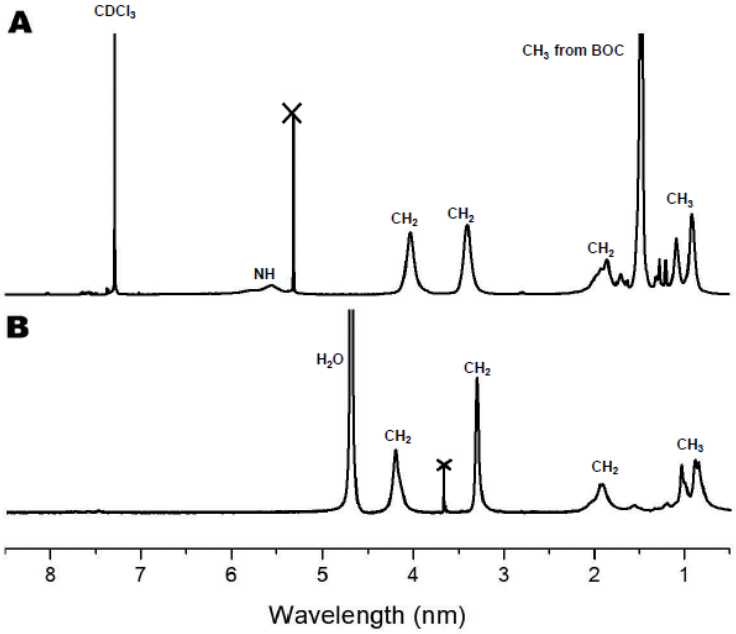


Fig. S1 ^{1}H-NMR spectra of product **2**,**3** (A in $CDCl_3$, 400 MHz, 298 K) and **P1**, **P2** (B in D_2O 400 MHz, 298K); Note: By comparing ^{1}H-NMR spectrum of PMI-P(Boc-AEMA) to that of PMI-PAEMA, one can clearly observe that the methyl groups from BOC protective groups have been completely removed.

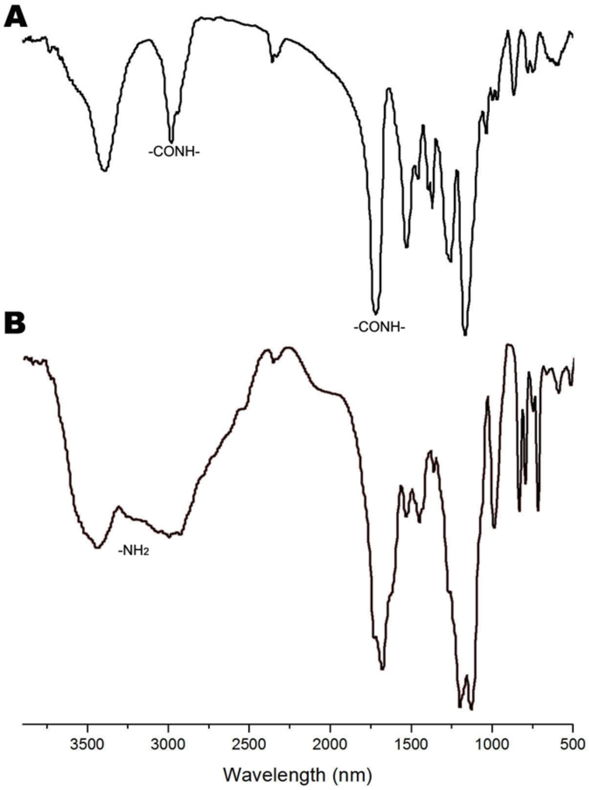


Fig. S2 FT-IR spectra of product **2**,**3** and **P1**,**P2**. Note: One can observe the typical peaks of –NH_2 groups in the region of 2500-3600 cm^{-1}.

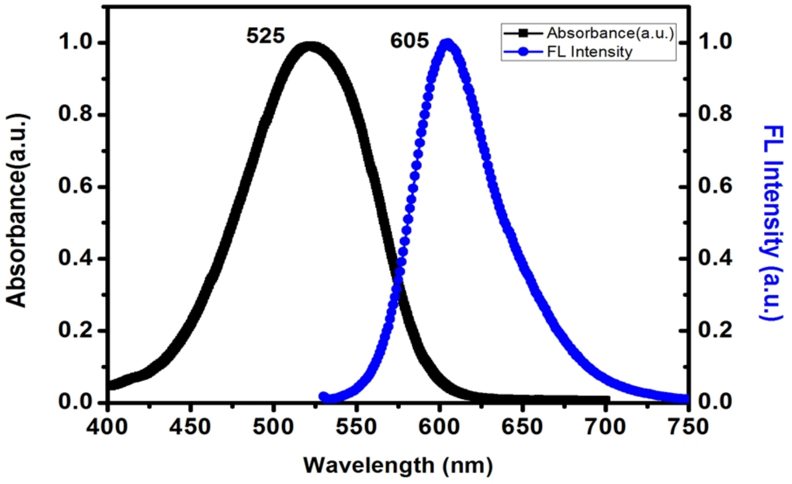


Fig. S3 Optical property of PMI-poly(AEMA) in water, the concentration is 0.125 mg/mL. The excited wavelength is 525 nm.

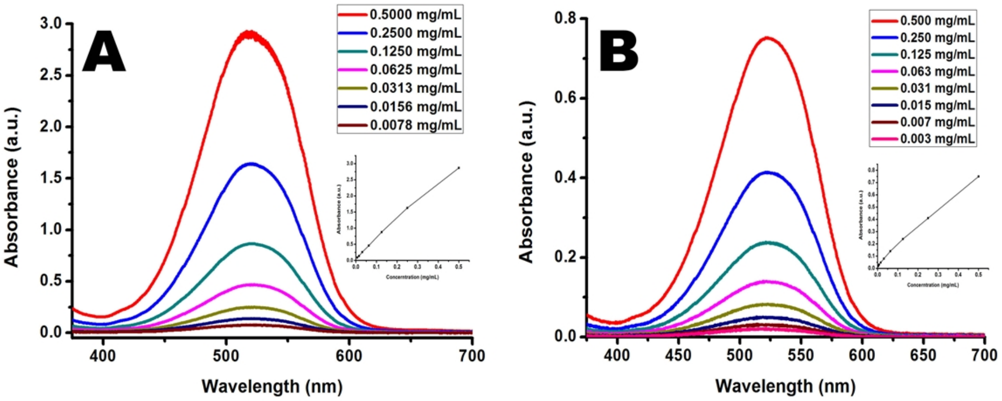


Fig. S4 Concentration-dependent absorbance spectra of (A) **P1** and (B) **P2** detected in aqueous solution. Inset: dependence of absorbance intensity (at λ_{max} of 525 nm) as a function of polymer concentration.

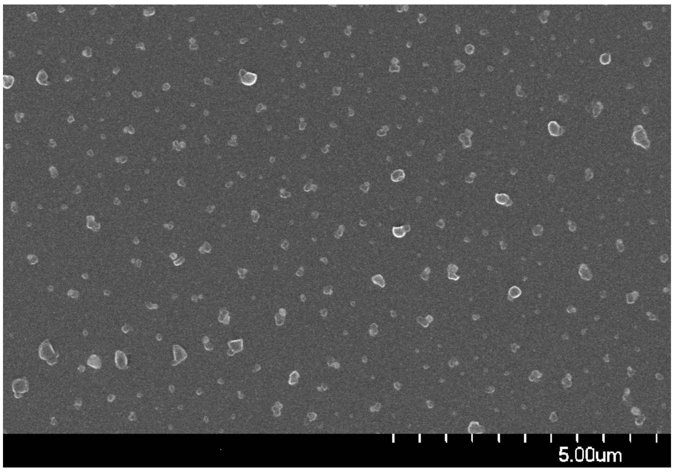


Fig. S5 SEM images of **P2** prepared under acid condition (from pH 2 to pH 4) at the concentration of 7.0×10^{-3} mg/mL. Note: The crystals are caused by pH-solution.

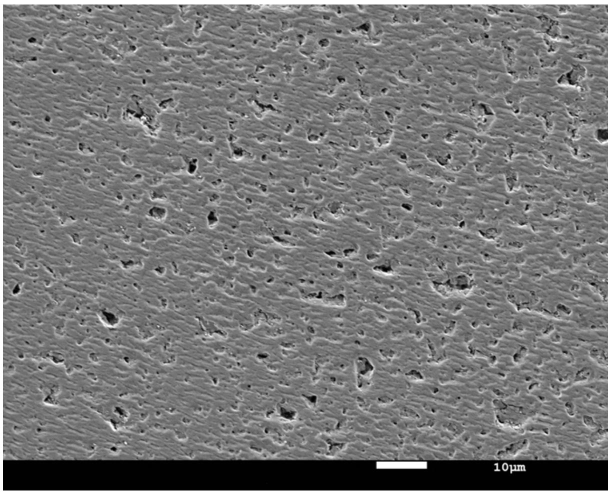


Fig. S6 SEM images of the homopolymer polyAEMA without PMI end-group carried out under the same condition at 7.0×10^{-3} mg/mL.

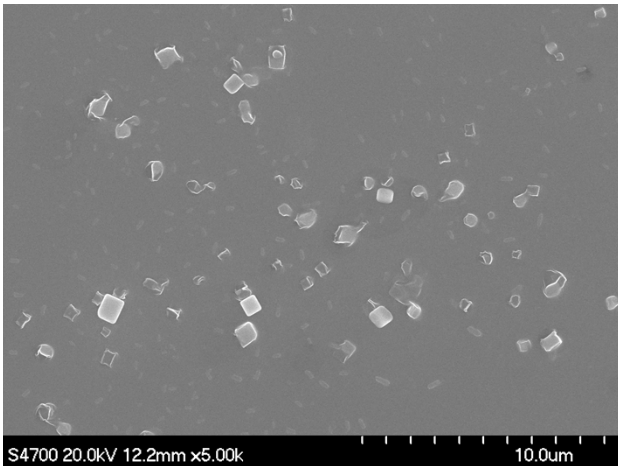


Figure S7. SEM images of the blank experiment prepared from HCl-NaOH solution.

Table S2. DLS results at different pH values

polymer[a]	pH[b]	diameter (nm)[c]	Polydispersity[d]
P1	2	58.7	0.138
	4	75.3	0.203
	8	103.8	0.127
	10	121.0	0.205
	12	169.1	0.105

[a] The concentration of homopolymer **P1** is 4.26×10^{-6} M.

[b] The samples was dissolved in HCl-NaOH solution .

[c,d] Z-averaged hydrodynamic diameter obtained by DLS.

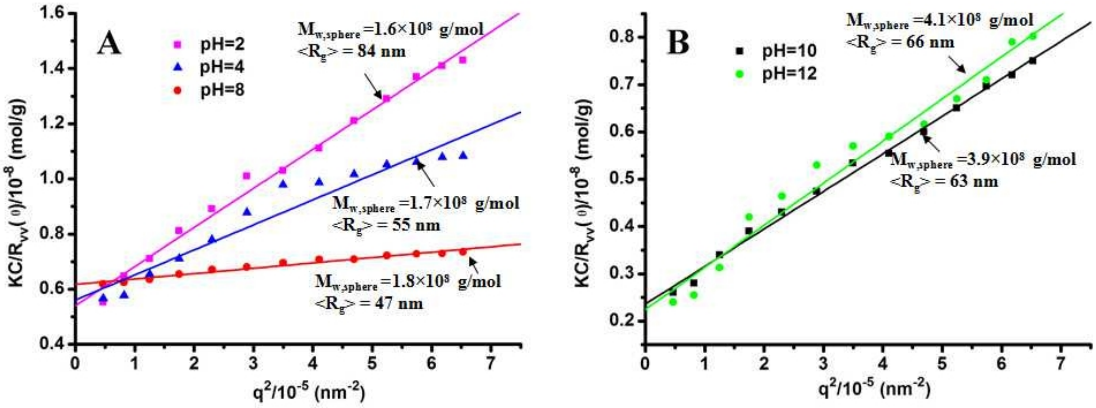


Fig. S8 Typical Zimm plot of **P2** dispersed in water for SLS analyses. The initial polymer concentration was 0.3 mg/mL. SLS experiments are performed at scattering angles between 30° and 150°, at 10° intervals. Note: pH=2 (pink line), pH=4 (blue line), pH=8 (red line), pH=10 (black line) and pH=12 (green line).

References

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