Electronic Supporting Information

## Autonomous Fluorescence Regulation in Responsive Polymer Systems Driven by a Chemical Oscillating Reaction **

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# Part Ⅰ  Experimental details

## 1  Materials

2-Dodecylsulfanylthiocarbonylsulfanyl-2-methylpropionic acid (DMP) chain transfer agent (CTA) was prepared as previously reported. [1] 4-Carboxyphenylboronic acid (PBA), Alizarin Red S (ARS), N,N-dimethylacrylamide (DMA, 98%), 2,2'-Azobisisobutyronitrile (AIBN, 98%) and hydrogen peroxide ($H_2O_2$) (30 wt. %) were purchased from *J&K* chemicals (Beijing, China). N-(2-hydroxy-ethyl) acrylamide and dioxane were obtained from TCI (Shanghai, China). 4-(Dimethylamino)pyridine (DMAP) and N,N'-dicyclohexyl carbodiimide (DCC) were purchased from Adamas Reagent Co., Ltd (Shanghai, China). DMA was passed through a small column of basic alumina for catalyst removal prior to polymerization. AIBN was recrystallized from ethanol. Sodium dithionite ($Na_2S_2O_4$) was purchased from Aladdin Co., Ltd (Shanghai, China). The water used in this study was distilled and further purified using a filtration system. All other reagents were commercial chemicals and they   were used without further purification.

## 2  Characterizations

^{1}H NMR spectra were recorded on a 300 MHz Bruker Avance-300 NMR spectrometer. Chemical shifts were reported in parts per million (ppm) with reference to the residual protons of the deuterated solvents. GPC was conducted in DMF at 40 ℃ with a flow rate of 0.4 mL/min (HLC-8320 GPC; Column: TSK gel Super AWM-H; Standard sample: PMMA). The transmittance was detected by UV-Vis spectrophotometer (TU-1810). A PHSJ-3F pH meter (Shanghai REX, China) was used to record the pH-time curve using the REX DC1.0 data collection software package (Shanghai REX, China). The reactor for the pH oscillating system was fed by a Longer Dispensing Peristaltic Pump (BT100-1F, China). Movies and pictures were obtained by a Nikon COOLPIX S3000 digital camera.

## 3  Synthesis of monomers and copolymers

### 3.1  Synthesis of 4-((2-acrylamidoethoxy)carbonyl)phenylboronic acid monomer (APBA)

N,N'-dicyclohexyl carbodiimide (DCC) (6.98 g, 33.5 mmol) in $CH_2Cl_2$ (50 mL) were added dropwise to a suspension of 4-carboxybenzeneboronic acid (5.01 g, 30.2 mmol), N-(2-hydroxyethyl)acrylamide (4.18 g, 36.3 mmol) and 4-(dimethylamino)pyridine (DMAP) (379 mg, 3.07 mmol) in $CH_2Cl_2$ (100 mL) over 3 h. After 24 h, the reaction solution was filtered and purified via flash chromatography (gradient 30:1 DCM:MeOH). A white solid was obtained (2.38 g; yield: 31.9 %). ^{1}H NMR (δ, ppm) (300 MHz, $CD_3OD$) 7.98-8.01 (d, 2H, ArH), 7.72-

7.83 (d, 2H, ArH), 6.23-6.26 (dd, 2H, CH2CH), 5.64-5.68 (t, 1H, CH2CH), 4.38-4.42 (t, 2H, CH2O), 3.64-3.67 (t, 2H, CH2NH).
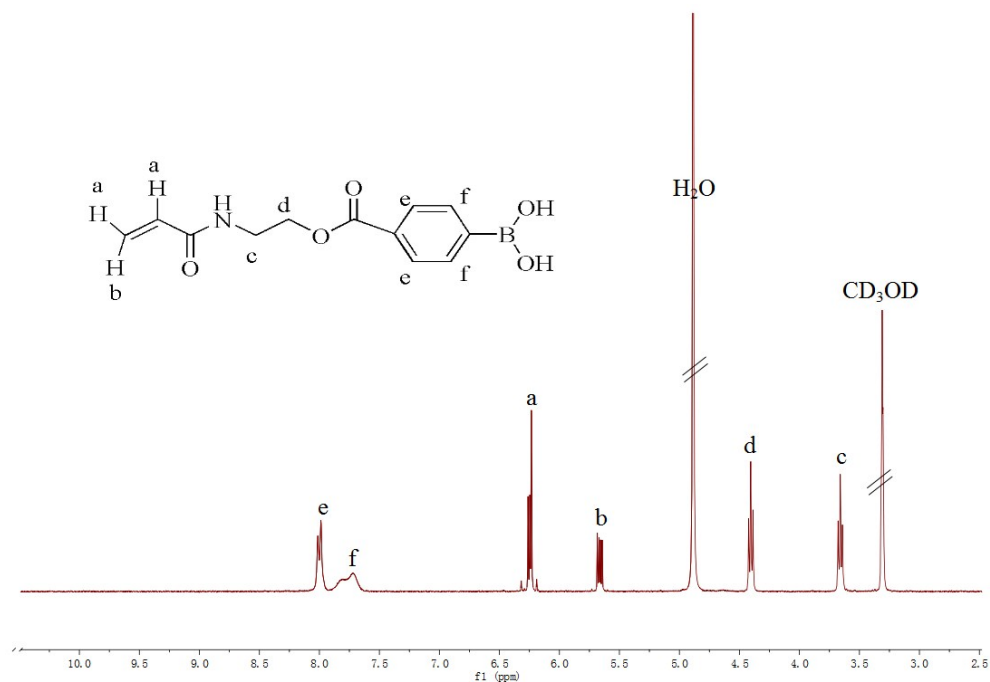


Figure S1 $^1$H NMR spectrum of APBA

## 3.2  RAFT homopolymerizations of DMA (PDMA)

An example RAFT polymerization of DMA was as follows. DMA (8.77 g, 88.5 mmol), DMP (0.315 g, 0.885 mmol), and AIBN (29 mg, 0.182 mmol) were dissolved in dioxane (30 mL) in a sealed 50 ml vial. The sealed vial was deoxygenated with nitrogen for approximately 30 min and then placed in a preheated reaction block at 70 ℃. Samples were removed periodically by syringe to determine molecular weight, polydispersity index (PDI), and momomer conversion by GPC (Figure S4) and $^1$H NMR spectroscopy (Figure S2). CDCl$_3$ was used as the solvent for $^1$H NMR spectroscopy. The result PDMA was isolated by precipitating into diethyl ether, filtering, and drying under vacuum.
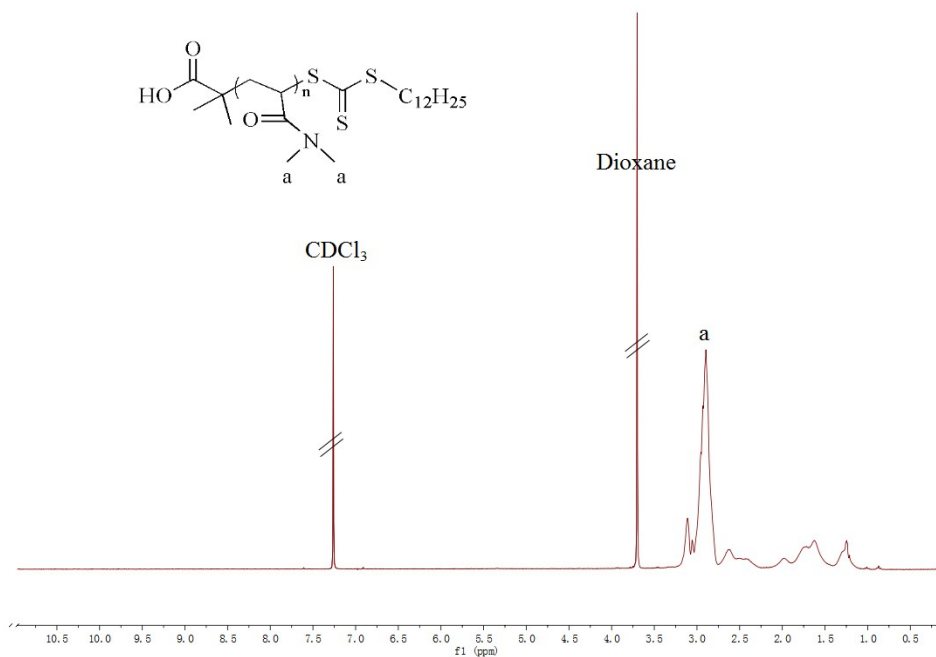
Figure S2 $^1$H NMR spectrum of PDMA

**3.3 RAFT block copolymerizations of APBA with a PDMA macro-chain transfer agent (macro CTA)**

An example RAFT block copolymerization was as follows. APBA (2.104 g, 8 mmol), PDMA-macro CTA ($M_n$=3622; $M_w/M_n$=1.5) (0.3622 g, 0.1 mmol), and AIBN (0.8 mg, 0.005mmol) were dissolved in 95/5 DMF/water (15 mL) in a sealed 50 mL vial. The sealed vial was deoxygenated with nitrogen for approximately 30 min and then placed in a preheated reaction block at 70 ℃. The polymerization was quenched after 20 h by removing the polymerization vial from the heating block and exposing the reaction solution to air. The resulting PDMA-b-PAPBA (block composition calculated by GPC: PDMA=70%, and PAPBA=30%; $M_n$=7302; $M_w/M_n$=1.631) was isolated by precipitating into diethyl ether, filtering, and drying under vacuum. Methanol-$d_4$ was used as the solvent for $^1$H NMR spectroscopy (Figure S4).
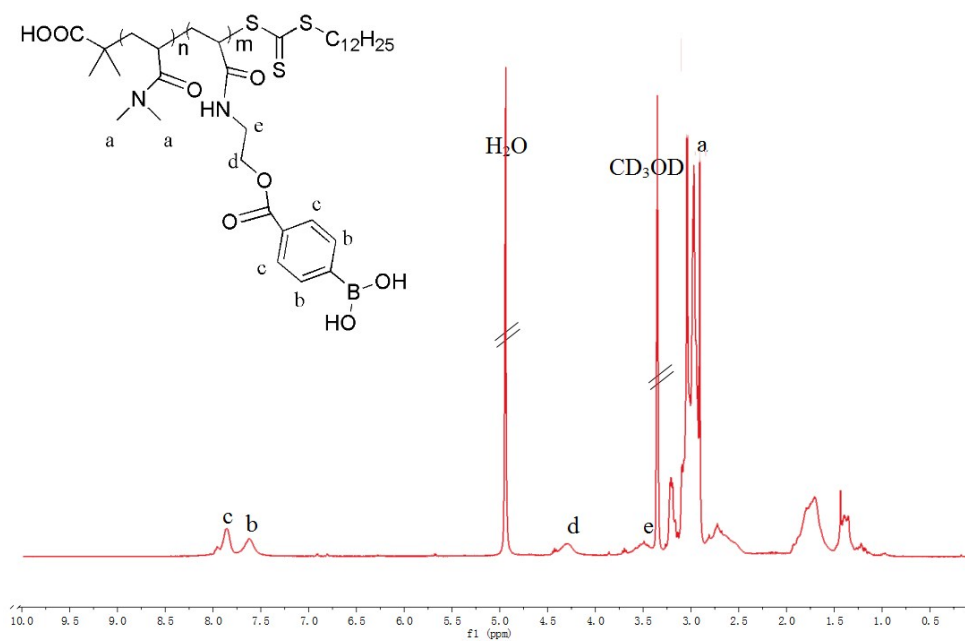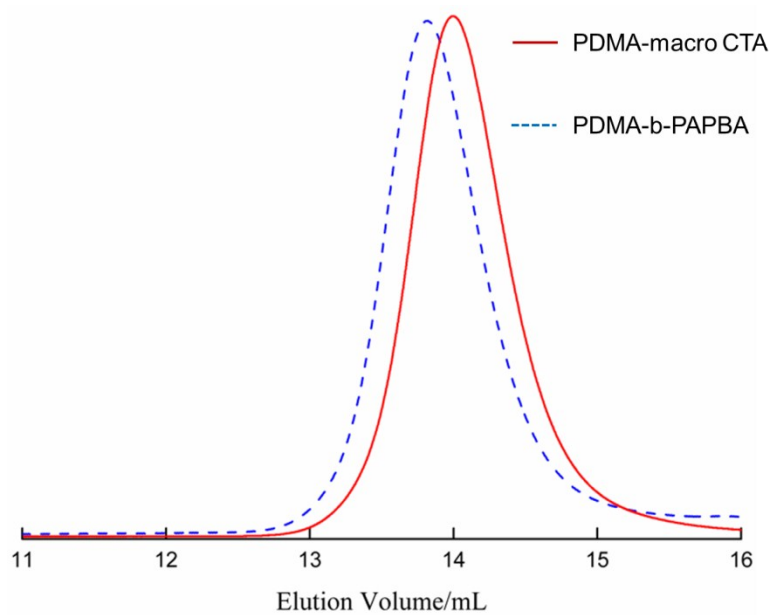
Figure S3 $^1$H NMR spectrum of PDMA-b-PAPBA



Figure S4 The GPC curves of PDMA-macro CTA and PDMA-b-PAPBA

## 4 Determination of CMC of PDMA-b-PAPBA

The CMC was measured through turbid metrical determination. The transmittance was used on behalf of the turbidity.
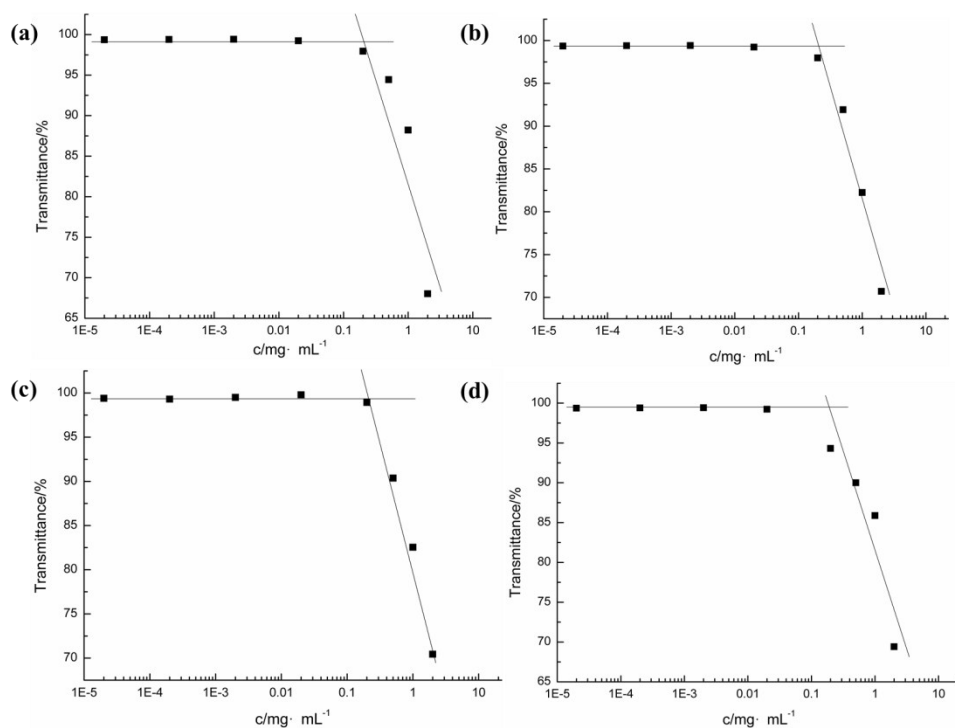
Figure S5 The CMCs of PDMA-b-PAPBA in the pH range of 3-7 of phosphate buffers. (a) pH 3.68; (b) pH 5.29; (c) pH 6.24; (d) pH 7.17

## 5    The construction of an HPD pH oscillation reaction

### 5.1 Reactor

The pH-oscillating system used in our studies was based on the sulfur oscillatory mechanism under a continuously stirred tank reactor (CSTR). [2] The CSTR is a cylindrical-shaped glass reactor with a liquid volume of 20 mL with two input tubes and two output tubes, as shown in Figure S6(b). The reactor was closed with a silicon cap. A combination pH meter and a thermometer connected to a computer were led through the cap. The batch experiments were performed in a cylindrical-shaped thermostatic glass vessel with a liquid volume of 50 mL.
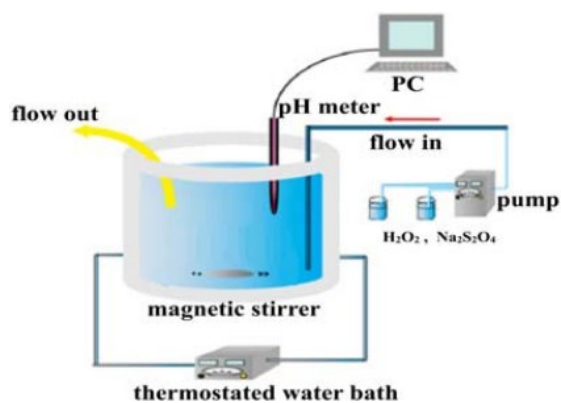


(a)                                                                                       (b)

Figure S6 The experimental setup (a) and the CSTR of the HPD pH oscillation reaction

**5.2 Procedures**

Sodium dithionite (7.5 mmol/L) ($Na_2S_2O_4$) with pH 12 and hydrogen peroxide (23 mmol/L) ($H_2O_2$) solutions were prepared separately using deionized water in 250 mL volumetric flasks. Throughout the experiments, the solution of sodium dithionite in its reservoir was bubbled with nitrogen gas to prevent autoxidation. The experimental setup for the pH oscillator was shown in Figure S6(a). The oscillating reactions were carried out at 22 °C in the CSTR. Reactant solutions were pumped into the reactor through the inlet tubes by means of a peristaltic pump (DESAGA). The excess reaction mixture was removed with the same pump through two outlet tubes. A magnetic stirrer at a constant stirring rate was used to ensure uniform mixing. The maximum pumping rate was used to fill the reactor, and then the rate was gradually lowered to the desired value. The reactions in the batch system were initiated by the addition of the $H_2O_2$ solution. The pH-time data was monitored by a pH meter connected to a computer using a REXDC 1.0 data collection software package. [3]

**6    References**

1 J. T. Lai, D. Filla and R. Shea, Macromolecules, 2002, 35, 6754-6756.

2 K. M. Kovács and G. Rábai, *J. Phys. Chem. A,* 2001, **105**, 9183–9187.

3 E. X. Liang, H. W. Zhou, X. B. Ding, Z. H. Zheng and Y. X. Peng, *Chem. Commun.,* 2013, **49**, 5384-5386.

# PartⅡ Other supporting materials



Video S1 This video showed the regulation between bright and dark states was completely controlled by the system itself without any on-off switching of external stimuli. The playback speed is set as 20× for more intuitive observation.