Supporting information

Novel azobenzene-based amphiphilic copolymers: synthesis, self-assembly Behavior and its multiple-stimuli-responsive properties

Yiting Xu, Jie Cao, Qi Li, Jilu Li, Kaiwei He, TongShen, Xinyu Liu,
Conghui Yuan, Birong Zeng, Lizong Dai

*Corresponding authors

*aFujian Provincial Key Laboratory of Fire Retardant Materials, Xiamen University, Xiamen 361005, People’s Republic of China.

E-mail: xyting@xmu.edu.cn

Tel:+8618750256597
Synthesis copolymers of P(AZOMA-co-DMAEMA), P(POSSMA-co-DMAEMA), P((POSSMA-co-AZOMA)-b-DMAEMA) and P(POSSMA-co-AZOMA-co-DMAEMA) as control samples

Azobenzene-based random copolymer of P(AZOMA-co-DMAEMA) was synthesized with monomers of AZOMA and DMAEMA via RAFT polymerization as shown in Scheme S1. The RAFT polymerization was followed: AZOMA (0.6748 g, 2.0 mmol), DMAEMA (0.6288 g, 4.0 mmol), CDB (0.0109 g, 0.04 mmol), and AIBN (0.0013 g, 0.008 mmol) were added into the Schlenk tube with 3.0 mL of THF. The polymerization ampoule was degassed with five freeze–pump–thaw cycles. Then the Schlenk tube was filled with argon and placed in an oil bath at 65°C for 48h. The reaction was stopped into liquid nitrogen. Then the product was precipitated in excess hexane, and washed with hexane three times. The resulting red powder was dried overnight under vacuum at room temperature.

Scheme S1 Synthesis of copolymer of P(AZOMA-co-DMAEMA).

Random copolymer of P(POSSMA-co-DMAEMA) was synthesized with monomers of POSSMA and DMAEMA via RAFT polymerization as shown in Scheme S2. The RAFT polymerization was followed: POSSMA (0.4526 g, 0.48 mmol), DMAEMA (0.6288 g, 4.0 mmol), CDB (0.0109 g, 0.04 mmol), and AIBN (0.0013 g, 0.008 mmol) were added into the Schlenk tube with 3.0 mL of THF. The polymerization ampoule was degassed with five freeze–pump–thaw cycles. Then the Schlenk tube was filled with argon and placed in an oil bath at 65°C for 48h. The reaction was stopped into liquid nitrogen. Then the product was precipitated in excess...
methanol, and washed with methanol three times. The resulting pink powder was dried overnight under vacuum at room temperature.

Scheme S2 Synthesis of copolymer of P(POSSMA-co-DMAEMA).

Azobenzene-based copolymer of P((POSSMA-co-AZOMA)-b-DMAEMA) was synthesized via RAFT polymerization as shown in Scheme S3. First, macromolecular chain transfer agent of P(POSSMA-co-AZOMA) was synthesized with monomers of POSSMA and AZOMA via RAFT polymerization. The RAFT polymerization was followed: AZOMA (0.6748 g, 2.0 mmol), POSSMA (0.4526 g, 0.48 mmol), CDB (0.0109 g, 0.04 mmol), and AIBN (0.0013 g, 0.008 mmol) were added into the Schlenk tube with 3.0 mL of THF. The polymerization ampoule was degassed with five freeze–pump–thaw cycles. Then the Schlenk tube was filled with argon and placed in an oil bath at 65°C for 48h. The reaction was stopped into liquid nitrogen. Then the product was precipitated in excess methanol, and washed with methanol three times. The resulting red powder was dried overnight under vacuum at room temperature.

Then copolymer of P((POSSMA-co-AZOMA)-b-DMAEMA) was be synthesized with P(POSSMA-co-AZOMA) and DMAEMA via RAFT polymerization. The RAFT polymerization was followed: P(POSSMA-co-AZOMA) (0.42 g, 0.035 mmol), DMAEMA(0.5495 g, 3.5 mmol) and AIBN(0.0011 g, 0.007 mmol) were added into the Schlenk tube with 3.0 mL of THF. The polymerization ampoule was
degassed with five freeze–pump–thaw cycles. Then the Schlenk tube was filled with argon and placed in an oil bath at 65°C for 48h. The reaction was stopped into liquid nitrogen. Then the product was precipitated in excess hexane, and washed with hexane three times. The resulting red powder was dried overnight under vacuum at room temperature.

**Scheme S3** Synthesis of copolymer of P((POSSMA-co-DMAEMA)-b-P(DMAEMA)).

Azobenzene-based copolymer, P(POSSMA-co-AZOMA-co-DMAEMA), was synthesized with monomers of AZOMA, POSSMA and DMAEMA via conventional free radical polymerization as shown in Scheme S4. The free radical polymerization was followed: AZOMA (0.6748 g, 2.0 mmol), POSSMA (0.4526 g, 0.48 mmol), DMAEMA (0.6288 g, 4.0 mmol), and AIBN (0.0013 g, 0.008 mmol), were added into the Schlenk tube with 3.0 mL of THF. The polymerization ampoule was degassed with five freeze–pump–thaw cycles. Then the Schlenk tube was filled with argon and placed in an oil bath at 65°C for 48h. The reaction was stopped into liquid nitrogen. Then the product was precipitated in excess hexane, and washed with hexane three times. The resulting red powder was dried overnight under vacuum at room temperature.
Scheme S4 Synthesis of copolymer of P(POSS-co-AZOMA-co-DMAEMA) by conventional free radical polymerization.

Figure S1 $^1$H NMR spectrum of HOAZO (d$_6$-DMSO).
Figure S2 Mass spectrum of HOAZO.

Figure S3 $^1$H NMR spectrum of AZOMA (d$_1$-CDCl$_3$).

Figure S4 Mass spectrum of AZOMA.
Figure S5 FTIR spectra of HOAZO and AZOMA.

Figure S6 FTIR spectrum of RCP-2.
Figure S7 $^1$H NMR spectrum of RCP-2 ($d_1$-CDCl$_3$).
Figure S8 $^1$H NMR spectra of control samples.
**Figure S9** GPC of control samples, C-1: P(AZOMA-DMAEMA), C-2: (POSS-DMAEMA), C-3: (P(POSS-AZOMA)-b-P(DMAEMA)), C-4: P(POSSMA-AZOMA-DMAEMA) and macro-CTA for C-3: P(POSS-AZOMA).

**Figure S10** GPC of P(POSSMA-co-AZOMA-co-DMAEMA).
Figure S11 $^1$H NMR spectra of P(POSSMA-co-AZOMA-co-DMAEMA) with various molecular weights.

Figure S12 $^1$H NMR spectra of micelles in D$_2$O.
**Figure S13** Fluorescence emission spectra of Nile Red in the micellar solution and the relationship between $I_{620 \text{ nm}}$ and log c: (a) RCP-1, (b) RCP-2, (c) RCP-3.

**Figure S14** Fluorescence intensity dependence of Nile red concentration.