Electronic Supplementary Information

Photoinduced Controlled Radical Polymerization of Methacrylates with Benzaldehyde Derivatives as Organic Catalysts

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Reaction setup

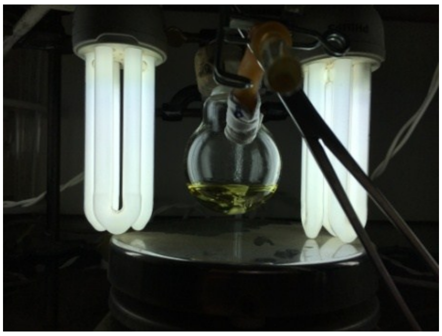

Fig. S1 The apparatus for the photo-induced reactions under 23 W CFL bulbs irradiation.

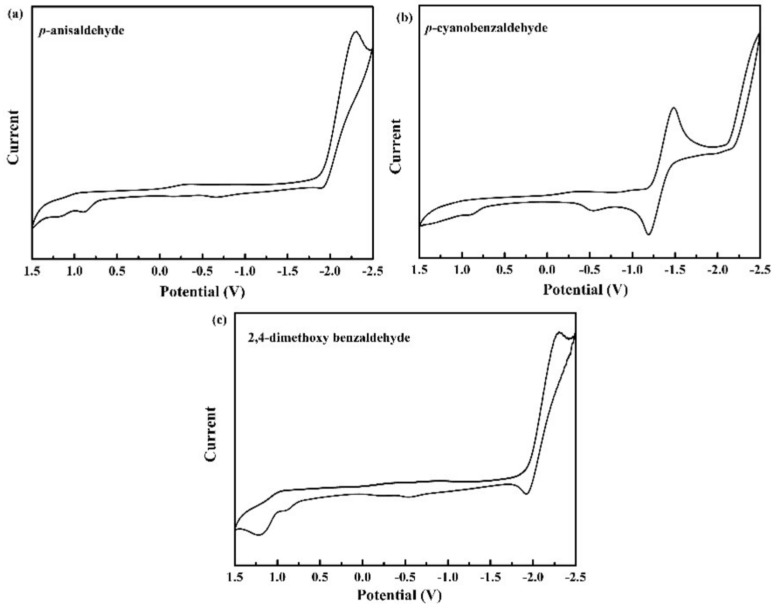

Fig. S2 Cyclic voltammogram of (a) *p*-anisaldehyde, (b) *p*-cyanobenzaldehyde, and (c) 2,4-dimethoxy benzaldehyde in DMF at room temperature, respectively. Scan rates: 100 mV s^{-1}.

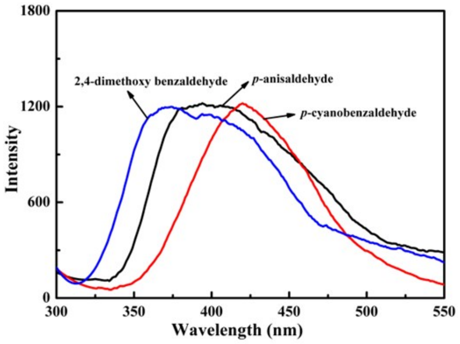

Fig. S3 Excitation spectra of *p*-anisaldehyde (20 mM), *p*-cyanobenzaldehyde (10 mM), and 2,4-dimethoxy benzaldehyde (10 mM) in DMF solution.

Recipes for homopolymerizations of methacrylic monomers:

Photopolymerization of MMA with *p*-anisaldehyde as an organocatalyst

The concentration of MMA in DMF (6.0 g) was set to be about 24 wt%. Specifically, the molar ratio of reagents [MMA]/[$CF_3(CF_2)_5$-I]/[*p*-anisaldehyde]/[DMA] was 100/2/-/5, 100/2/5/5, 100/2/10/5, 100/1/5/5, and 100/-/5/5, respectively.

Influence of different initiator on the polymerization of MMA

When using EBPA as the initiator, the concentration of MMA in DMF (6.0 g) was set to be about 24 wt%. Specifically, the molar ratio of reagents [MMA]/[EBPA]/[*p*-anisaldehyde]/[DMA] was 100/2/5/- and 100/2/5/5. The recipe for initiator EBiB was slightly different from the EBPA. The molar ratio of reagents [MMA]/[EBiB]/[*p*-anisaldehyde]/[DMA] was 100/2/5/5 and the concentration of MMA in DMF (6.0 g) was set to be about 25 wt%.

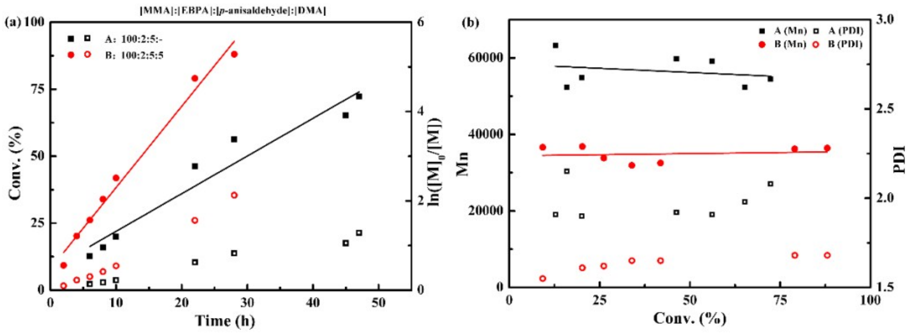

Fig. S4 (a) Monomer conversion (■, ●) and ln($[M]_0$/[M]) (□, ○) versus time and (b) evolution of M_n and PDI with monomer conversion of the polymerization of MMA using *p*-cyanobenzaldehyde as the organic catalyst irradiated with 23 W CFL bulbs. The molar ratio of [MMA]:[EBPA]:[*p*-cyanobenzaldehyde]:[DMA] was (A) 100:2:5:-, and (B) 100:2:5:5.

Photopolymerization of PEGMA with *p*-anisaldehyde as an organocatalyst

The concentration of PEGMA in DMF (5.0 g) was about 28wt%, and the ratio of [PEGMA]/[$CF_3(CF_2)_5$-I]/[*p*-anisaldehyde]/[DMA] was 42/2/5/5.

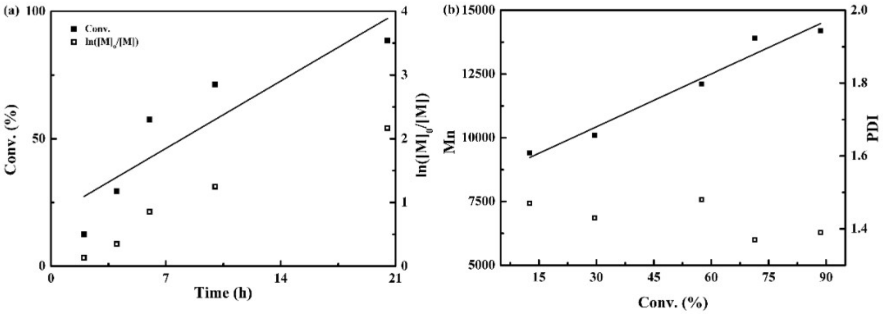

Fig. S5 (a) Monomer conversion (■) and ln([M]$_0$/[M]) (□) versus time and (b) evolution of M_n and PDI with conversion for the polymerization of PEGMA using *p*-anisaldehyde as the organic catalyst at ambient temperature irradiated with 23 W CFL. Reaction conducted with the molar ratio of [PEGMA]:[$CF_3(CF_2)_5$-I]:[*p*-anisaldehyde]:[DMA]=42:2:5:5.

Photopolymerization of MMA with *p*-cyanobenzaldehyde as an organocatalyst

In a typical run, a dry one-necked round-bottom flask was charged with MMA (2.06 g, 20 mmol), $CF_3(CF_2)_5$-I (0-0.18 g, 0-2 mol%), *p*-cyanobenzaldehyde (0.131-1.31 g, 1-10 mmol), DMA (0 or 0.121 g, 0 or 1mmol), and DMF (6.0 g). The reaction mixture was deoxygenated by three freeze-evacuate-thaw cycles and backfilled with argon.

Photopolymerization of BnMA with *p*-cyanobenzaldehyde as an organocatalyst

The process was the same as the general procedure of polymerization under 23 W CFL irradiation. The recipe was BnMA (2.05 g, 11 mmol), $CF_3(CF_2)_5$-I (0.085 g, 1.68 mol%), *p*-cyanobenzaldehyde (1.31 g, 10 mmol), DMA (0.072 g, 0.60 mmol), and DMF (5.0 g).

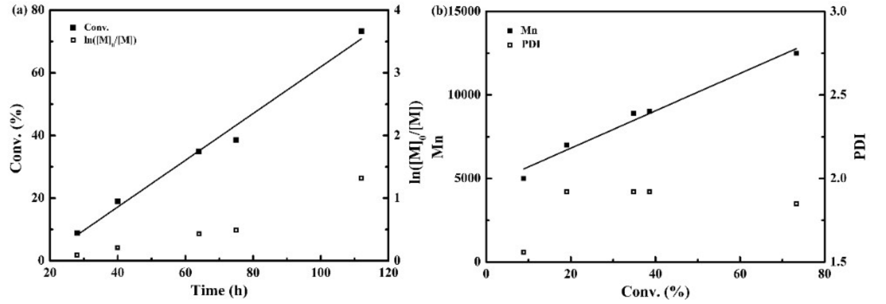

Fig. S6 (a) Monomer conversion (■) and ln([M]$_0$/[M]) (□) versus time and (b) evolution of M_n and PDI with conversion for the polymerization of BnMA using *p*-cyanobenzaldehyde as the organic catalyst at ambient temperature irradiated with 23 W CFL bulbs. Reaction was conducted with the molar ratio of [BnMA]:[$CF_3(CF_2)_5$-I]:[*p*-cyanobenzaldehyde]:[DMA]=

60:1:50:3.

Photopolymerization of PEGMA with 2,4-dimethoxy benzaldehyde as an organocatalyst

The concentration of PEGMA in DMF (6.0 g) was about 24 wt%. Specifically, the molar ratio of reagents [PEGMA]/[$CF_3(CF_2)_5$-I]/[2,4-dimethoxy benzaldehyde]/[DMA] was 24/1/-/5, 24/1/20/-, and 24/1/20/5, respectively.

Chain extensions using aldehydic molecule as organic catalyst

One-pot synthesis of PPEGMA with PPEGMA-I as a macroinitiator and p-anisaldehyde as an organocatalyst

The polymer PPEGMA was synthesized by one-pot process with sequential monomer addition. The molar ratio of [PEGMA]/[$CF_3(CF_2)_5$-I]/[*p*-anisaldehyde]/[DMA] was 47/2/10/5 and the concentration of PEGMA in DMF (6 g) was about 26%. After 24 h of irradiation under 23 W CFL bulbs, a small portion of the reactant was sampled to determine the conversion of PEGMA (90.1%) and the Mn and PDI of the macroinitiator PPEGMA-I (Mn,GPC=10200; PDI=1.33). Then, 4.3156 g of deoxygenated PEGMA was introduced into the reactant. The reactant samples were taken using a syringe under a positive pressure of argon at different time intervals, and then purified by diethyl ether. The precipitates were dried at 40°C in vacuum.

One-pot synthesis of PPEGMA with PPEGMA-I as a macroinitiator and 2,4-dimethoxy benzaldehyde as an organocatalyst

The polymer PPEGMA was synthesized by one-pot process with sequential monomer addition. The molar ratio of [PEGMA]/[$CF_3(CF_2)_5$-I]/[2,4-dimethoxy benzaldehyde]/[DMA] was 48/2/5/10 and the concentration of PEGMA in DMF (6 g) was about 26%. After 16 h of irradiation under 23 W CFL, a small portion of the reactant was sampled to determine the conversion of PEGMA (82.3%) and the M_n and PDI of the macroinitiator PPEGMA-I ($M_{n,GPC}$=15400; PDI=1.23). Then, 2.2095 g of deoxygenated PEGMA was introduced into the reactant. The reactant samples were taken using a syringe under a positive pressure of argon at different time intervals, and then purified by diethyl ether. The precipitates were dried at 40°C in vacuum.

The synthesis of block copolymer with PPEGMA-I as a macroinitiator and p-anisaldehyde as an organocatalyst

The PPEGMA-I macroinitiator ($M_{n,GPC}$=14200 g mol^{-1}; PDI=1.39) was synthesized under the molar ratio of [PEGMA]/[$CF_3(CF_2)_5$-I]/[*p*-anisaldehyde]/[DMA]=42/2/5/5 for 20.5 h. Then the PPEGMA-Br macroinitiator (0.770 g, 0.054 mmol), MMA (2.61 g, 26 mmol), *p*-anisaldehyde (0.142 g, 1.0 mmol), DMA (0.131 g, 1.1 mmol) and 6.0 g of DMF were added to a dry one-necked round-bottom Pyrex flask. The polymerization process was performed under the similar conditions as previously mentioned. The reaction mixture was irradiated with 23 W CFL bulbs for 100 h before the polymer was purified as mentioned above. Monomer conversion of the reaction was 74.8%.

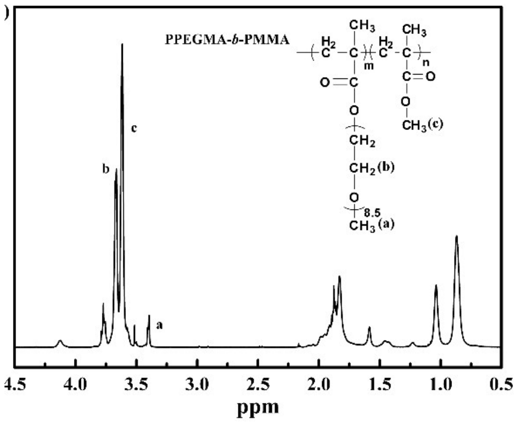

Fig. S7 ^1H NMR spectrum of PPEGMA-*b*-PMMA block copolymer obtained from the PPEGMA-I macroinitiator and *p*-anisaldehyde-based photopolymerization.

The synthesis of block copolymer with PBnMA-I as a macroinitiator and p-cyanobenzaldehyde as an organocatalyst

The PBnMA-I macroinitiator ($M_{n,GPC}$=12500 g mol^{-1}; PDI=1.85) was synthesized using the initiator as described in the procedure for the homopolymerization of PBnMA with *p*-cyanobenzaldehyde as an organic catalyst. Then the PBnMA-Br macroinitiator (0.532 g, 0.042 mmol), MMA (2.03 g, 20 mmol), *p*-cyanobenzaldehyde (1.31 g, 10 mmol), DMA (0.121 g, 1.0 mmol), and 6.0 g of DMF were added to a dry one-necked round-bottom Pyrex flask. The polymerization process was performed under the similar conditions as previously mentioned. The reaction mixture was irradiated with 23 W CFL for 65 h before the polymer was purified as mentioned above. Monomer conversion of the reaction was 67.8%.

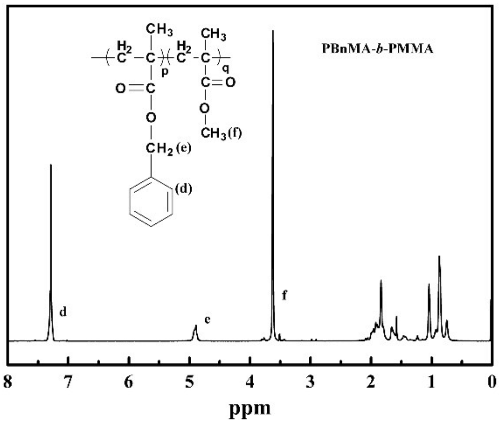

Fig. S8 ^{1}H NMR spectrum of PBnMA-*b*-PMMA block copolymer obtained from the PBnMA-I macroinitiator and *p*-cyanobenzaldehyde-based photopolymerization.

The synthesis of block copolymer with PPEGMA-I as a macroinitiator and 2,4-dimethoxy benzaldehyde as an organocatalyst

The PPEGMA-I macroinitiator ($M_{n,GPC}$=13000 g mol^{-1}; PDI=1.18) was synthesized under the molar ratio of [PEGMA]/[$CF_3(CF_2)_5$-I]/[2,4-dimethoxy benzaldehyde]/[DMA]=42/2/5/5 for 23 h. Then the PPEGMA-I macroinitiator (1.98 g), 0.516 g of BnMA, 0.660 g of 2,4-dimethoxy benzaldehyde, 0.087 g of DMA, and 6.0 g of DMF were added to a dry one-necked round-bottom Pyrex flask. The polymerization process was performed under the similar conditions as previously mentioned. The reaction mixture was irradiated with 23 W CFL bulbs for 23 h before the polymer was purified as mentioned above. Monomer conversion of the reaction was 33.9%.

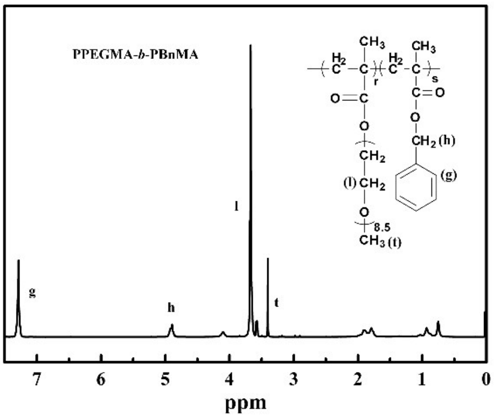

Fig. S9 ^{1}H NMR spectrum of PPEGMA-*b*-PBnMA block copolymer obtained from the PPEGMA-I macroinitiator and 2,4-dimethoxy benzaldehyde-based photopolymerization.

The micellization of amphiphilic block copolymers

About 10 mg of PPEGMA-*b*-PMMA (or PPEGMA-*b*-PBnMA) was dissolved in 1 mL of THF. Then, the solution was dropwise added into 20 mL of deionized water with stirring in a beaker at 50°C for 1.5 h to allow venting of THF.

The self-assembled micellar aggregates based on the as-prepared amphiphilic block copolymers were characterized by SEM. As illustrated in Fig. S11, micellar aggregates were observed from the self-assembly of amphiphilic block copolymers of PPEGMA-*b*-PMMA and PPEGMA-*b*-PBnMA in aqueous medium. Typical DLS histogram of amphiphilic block copolymer micelle in deionized water is shown in Fig. S12, the effective diameter of PPEGMA-*b*-PMMA micelle was about 139 nm, while its polydispersity was 0.175. In addition, the effective diameter of PPEGMA-*b*-PBnMA micelle was about 192 nm, while its polydispersity was 0.233.

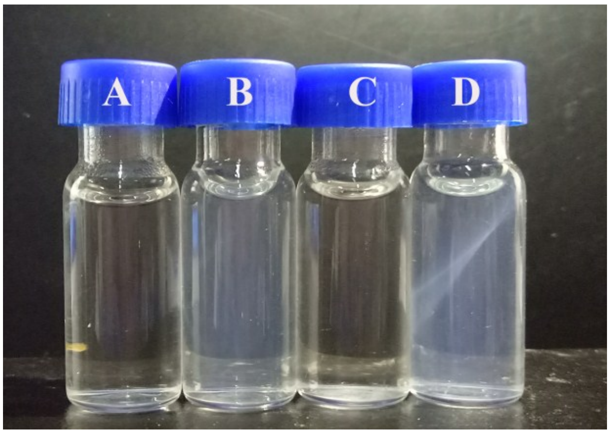

Fig. S10 Pictures of (A) PPEGMA-*b*-PMMA in THF, (B) PPEGMA-b-PMMA micelle, (C) PPEGMA-*b*-PBnMA in THF, and (D) PPEGMA-*b*-PBnMA micelle.

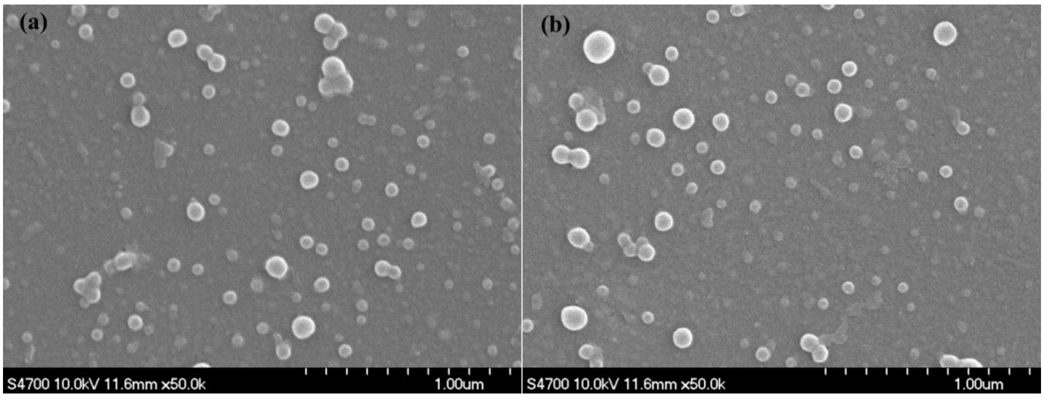

Fig. S11 SEM images of (a) PPEGMA-*b*-PMMA, and (b) PPEGMA-*b*-PBnMA block copolymers prepared from 0.5 mg mL^{-1} aqueous solution.

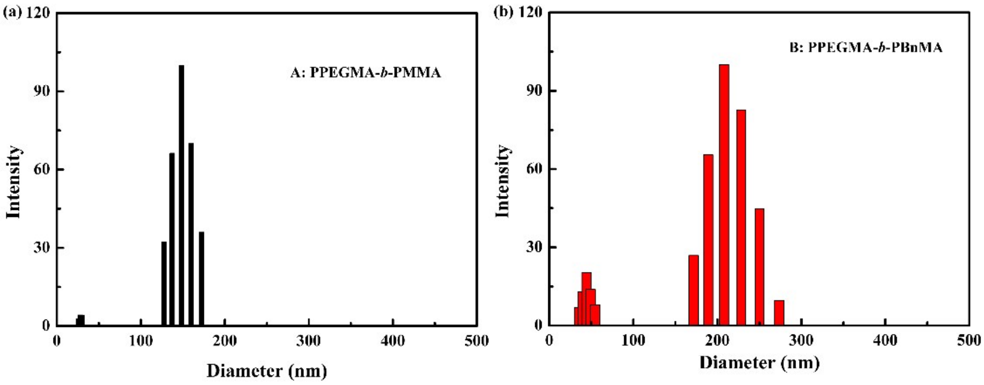

Fig. S12 Typical DLS histogram of amphiphilic block copolymer micelle of (a) PPEGMA-*b*-PMMA, and (b) PPEGMA-*b*-PBnMA in deionized water, respectively.