Supplementary Information (SI) for Polymer Chemistry.

Supporting Information

Biomass-Derived Photocatalysts for Photocatalytic Atom Transfer Radical Polymerization

Xiaoyu Guo, Xinrang Wang , Chen Wang, Zhuo Dang, Jiquan Liu, Lin Lei**

Key Laboratory of Synthetic and Natural Functional Molecular Chemistry of the Ministry of Education, College of Chemistry and Materials Science, Northwest University, Xi'an 710127, China

Materials

Materials: Methyl methacrylate (MMA, 99%, Aladdin), Glycidyl methacrylate (GMA, 98%, Aladdin), tert-butyl acrylate (tBA, 99%, Aladdin) and butyl methacrylate (BMA, 99%, Aladdin) were passed through an alumina column to remove the inhibitors. Ethyl α-bromophenylacetate (EBPA, 95%, Aladdin) Pentamethyldiethylenetriamine (PMDETA, 99%, Macklin) $CuBr_2$ (99%, Chemical) were used directly. Tetrahydrofuran (THF, 99%) and methanol (≥99.9%) were purchased from Aladdin, Shanghai, China. 5,5-dimethyl-1-pyrroline N-oxide ($C_6H_{11}NO$, DMPO) were purchased from Aladdin reagent.

The white light source used for all experiments was commercial LED light strip (380-780 nm, light intensity:15 m W/cm^2).

Characterization

Fourier transform infrared (FT-IR) spectra were examined on Bruker EQUINOX-55 spectrophotometer in 4000−400 cm^{-1} (KBr pellets). Powder X-ray diffraction (PXRD) patterns were investigated through Bruker D8 ADVANCE X-ray powder diffractometer. Solid UV was measured with a Shimadzu UV-Vis Spectrophotometer UV-3600Plus. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a PHI-5000 (ULVAC-PHI), the C1s peak was calibrated at 284.8 eV. Scanning electron microscopy (SEM) was carried out on a Hitachi SU8010 instrument . ^{1}H NMR spectra were recorded at 298 K on Bruker AVANCE III spectrometers. The nitrogen adsorption/desorption isotherms were measured at a temperature of 77 K using a TriStar II 3020 apparatus manufactured by Micromeritics, with nitrogen serving as the probe gas. For gel permeation chromatography (GPC), the analysis was conducted using an Agilent GPC-1260 liquid chromatography system with a THF phase consisting of a PL 1110-6100 hybrid gel column (10 μm; 300 × 7.5 mm) and a PL 1110-6540 column (5 μm; 300×7.5 mm). The flow rate was set at 1.0 mL min^{-1}, maintaining a temperature of 25 °C. To calibrate the column chromatogram, standard polystyrene (PS) from the THF phase was used, and the conversion to obtain the standard calibration curve for PMMA was performed using the Mark-Houwink Equation. Over a BRUKER A300, EPR spectra were recorded for spin-trapping experiments. Dynamic light scattering (DLS) was employed to determine the particle size and size distribution of the polymer microspheres synthesized via ATRPP. A 0.1 mL portion of the reaction mixture was withdrawn and diluted to 1 mL with Tris buffer (pH 8.5). The DLS analysis was conducted following the water size SOP as the standard operating procedure, and the measurement temperature was maintained at 25 °C.

Synthetic Procedure for γ-CCD-r

First, weigh 1 g of γ-cyclodextrin and evenly disperse it in a 0.1% sulfuric acid solution. Then transfer the suspension to a polytetrafluoroethylene liner and place it in a high-pressure reactor. Conduct hydrothermal carbonization at 453 K for 12 hours. Wash the precipitate six times with deionized water and dry it overnight at 343 K to obtain carbonized γ-cyclodextrin, abbreviated as γ-CCD. Next, weigh 0.1 g of $NaBH_4$ and dissolve it in 20 ml of ACN to prepare a solution. Add 0.1 g of γ-CCD to the solution, and react at 343 K for 12 hours in an oil bath. The resulting sample is washed three times with ACN, then washed three times with deionized water, and finally dried to obtain the reduced product of γ-CCD, referred to as γ-CCD-r.

General procedure for the catalytic polymerization of oxygen-tolerant ATRP using γ-CCD-r: Methyl methacrylate (MMA, 1 g, 9.99 mmol, 200 equiv), ethyl α-bromophenylacetate (EBPA, 12 mg, 0.049 mmol, 1 equiv),γ-CCD-r, 0.5 mg, tetrahydrofuran (THF, 1 g, 13.9 mmol), $CuBr_2$ (0.00065 g), and PMDETA (0.0021 g) were accurately weighed and placed into 5 mL centrifuge tubes. The mixtures were sonicated for 5 minutes to ensure homogeneity, then transferred into 10 mL pressure-resistant glass vials. The vials were tightly sealed and irradiated under white LED light. At designated time intervals, small aliquots were withdrawn from the reaction mixture for gel permeation chromatography (GPC) analysis to determine the number-average molecular weight (M_n) and polydispersity index ($Đ$).

Upon completion of the reaction, the polymer solution was diluted with tetrahydrofuran (THF) and purified by repeated precipitation in cold methanol (twice). The precipitated polymer was then collected, thoroughly dried, and weighed to determine the monomer conversion rate.

General procedure for the synthesis of macromolecular initiator (PMMA-Br): Methyl methacrylate (MMA, 1 g, 9.99 mmol, 200 equiv), ethyl α-bromophenylacetate (EBPA, 12 mg, 0.049 mmol, 1 equiv), catalyst (γ-CCD-r, 0.5 mg), tetrahydrofuran (THF, 1 g, 13.9 mmol), $CuBr_2$ (0.00065 g), and PMDETA (0.0021 g) were accurately weighed and placed into 5 mL centrifuge tubes. The mixture was sonicated for 5 minutes to ensure complete dissolution and homogeneity. The resulting solution was then transferred to a 10 mL reaction tube. Subsequently, the reaction mixture was irradiated under a white LED light source for 3 hours to facilitate polymerization.

After the reaction, the crude product was dissolved in a small amount of THF and precipitated dropwise into 30 mL of methanol to remove unreacted monomer and initiator. The molecular weight (M_n) and polydispersity index (PDI) of the product were determined by gel permeation chromatography (GPC).

General Procedure of chain extension experiment: In the chain extension polymerization of methyl methacrylate (MMA), a mixture comprising MMA (0.25 g, 50 equiv), PMMA-Br (0.177 g, 1 equiv), and γ-CCD-r (0.000125 g) was fully dissolved in THF (0.375 g, 60% w/w). The solution was irradiated under white light in the oxygen-tolerant conditions for 4 hours. The block copolymer PMMA-*b*-PMMA was isolated by precipitation in methanol.

For the chain extension polymerization of butyl methacrylate (BMA), a mixture of BMA (0.25 g, 50 equiv), PMMA-Br (0.23 g, 1 equiv), and γ-CCD-r (0.000125 g) was dissolved in THF (0.375 g, 60%

w/w). The reaction was conducted under white light and oxygen-tolerant conditions for 5 hours. The block copolymer PMMA-*b*-PBMA was isolated by precipitation in methanol.

Similarly, for the chain extension polymerization of glycidyl methacrylate (GMA), a solution was prepared from GMA (0.25 g, 50 equiv), PMMA-Br (0.46 g, 1 equiv), γ-CCD-r (0.000125 g), and THF (0.375 g, 60% w/w). After irradiation under white light for 5 hours under oxygen-tolerant conditions, the polymerization was completed. The product, PMMA-*b*-PGMA, was obtained by precipitation in methanol.

In the chain extension polymerization of benzyl methacrylate (BzMA), a mixture of BzMA (0.25 g, 50 equiv), PMMA-Br (0.25 g, 1 equiv), and γ-CCD-r (0.000125 g) was dissolved in THF (0.375 g, 60% w/w) and irradiated under white light for 4 hours under oxygen-tolerant conditions. The block copolymer PMMA-*b*-PtBA was isolated by precipitation in petroleum ether.

Superoxide radical anion assay using NBT: In a 5 mL centrifuge tube, 0.2 mg of γ-CCD-r, 0.012 g of EBPA, 2 mL of a 5×10^{-5} mol/L aqueous NBT solution, and 1 mL of deionized water were combined. The mixture was sonicated for 10 minutes and subsequently exposed to illumination under a white lamp.

The ATRPP reaction was conducted with γ-CCD-r as the catalyst：After sonicating a mixture of 0.9 mL of DVB and 29.1 mL of acetonitrile containing 3.3 mg of γ-CCD-r and 0.09 g of EBIB for 5 minutes, the resulting solution was transferred to a 50 mL round-bottom flask. The reaction mixture was then stirred at a gentle speed under irradiation with white light.

Grafting reaction onto polymer microspheres：A mixture was prepared consisting of 50 mg of synthesized polymer microspheres, 0.3 mg of γ-CCD-r, and 4 mL of MMA. After sonication for 5 minutes, the mixture was transferred into a 5 mL round-bottom flask and irradiated with white light to initiate the reaction.

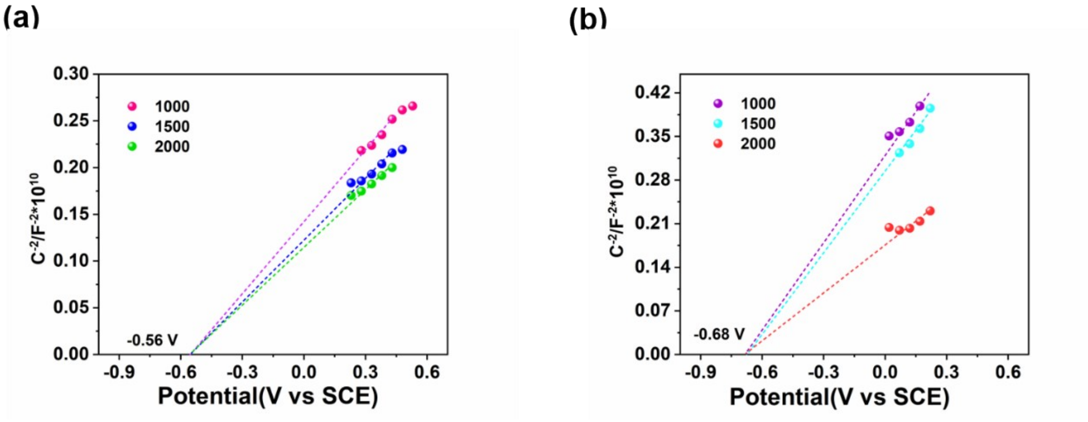


Figure S1. (a) The Mott-Schottky curve for the γ-CCD. (b) The Mott-Schottky curve for the γ-CCD-r.

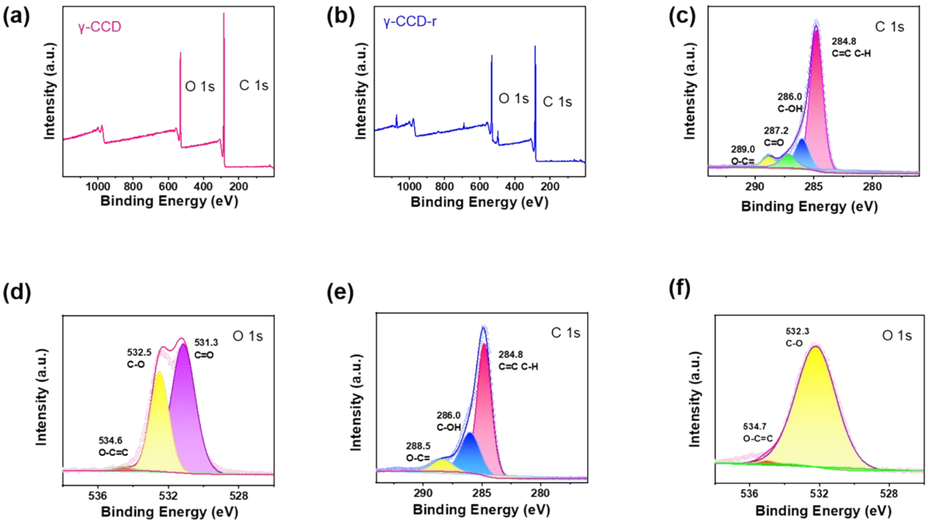


Figure S2. (a) Full Survey XPS Spectrum of γ-CCD (b) Full Survey XPS Spectrum of γ-CCD-r (c) C 1s XPS spectrum of γ-CCD (d) O 1s XPS spectrum of γ-CCD (e) C 1s XPS spectrum of γ-CCD-r (f) O 1s XPS spectrum of γ-CCD-r.

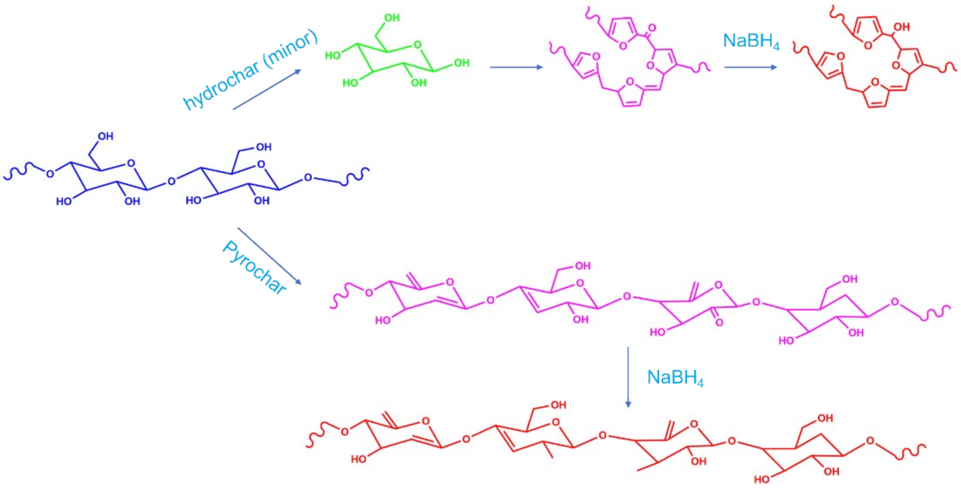
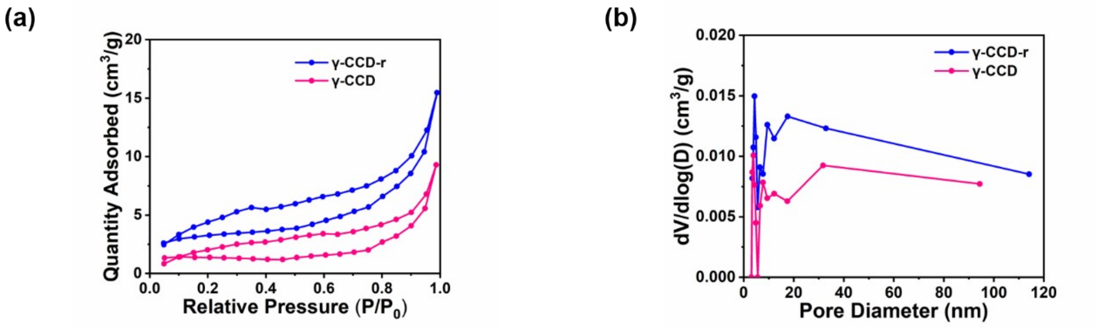


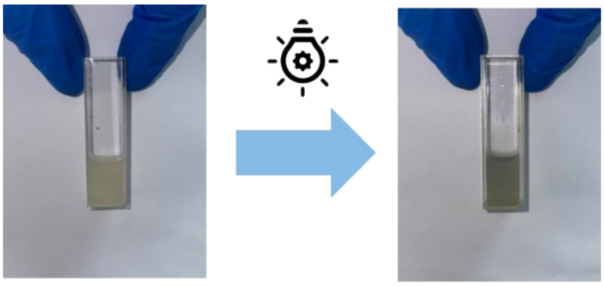
Figure S3. The synthesis process for γ-CCD-r.



(c)

Sample	S_{BET}（m^2/g）	Pore Width(nm)	V_{BJH}（cm^3/g）
γ-CCD	3.853	3.844	0.012
γ-CCD-r	10.540	4.309	0.018

Figure S4. (a) The nitrogen adsorption-desorption isotherms of γ-CCD and γ-CCD-r. (b) The pore size distribution curves of γ-CCD and γ-CCD-r and (c) BET analysis results.



0 min **10 min**

Figure S5. Color change under white light irradiation.

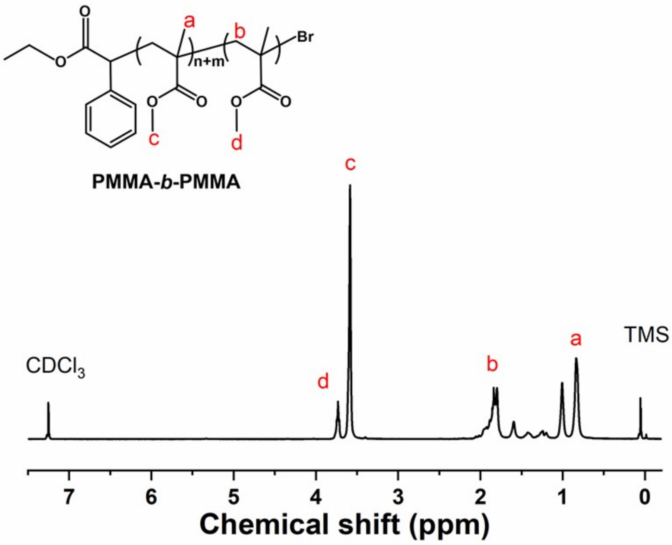


Figure S6. The ^{1}H NMR spectrum of PMMA-*b*-PMMA.

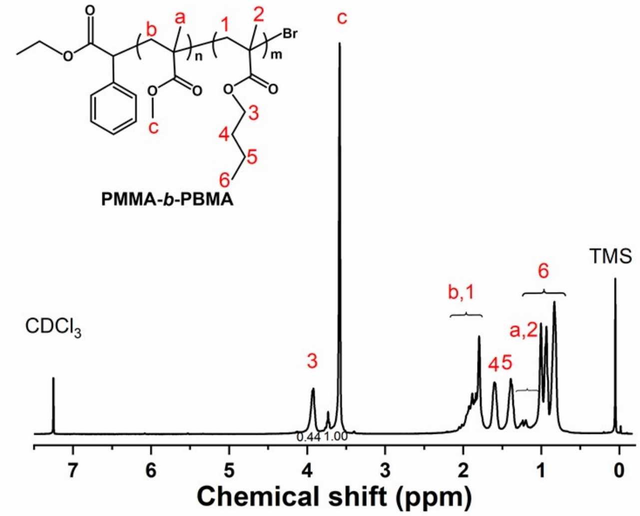


Figure S7. The ^{1}H NMR spectrum of PMMA-b-PBMA. $M_{n,NMR}$= (0.44/2)/(1/3)×35($DP_{PMMA-Br}$)×142.2 g/mol+ 7000 g/mol（$M_{n,PMMA-Br}$）= 11000 g/mol

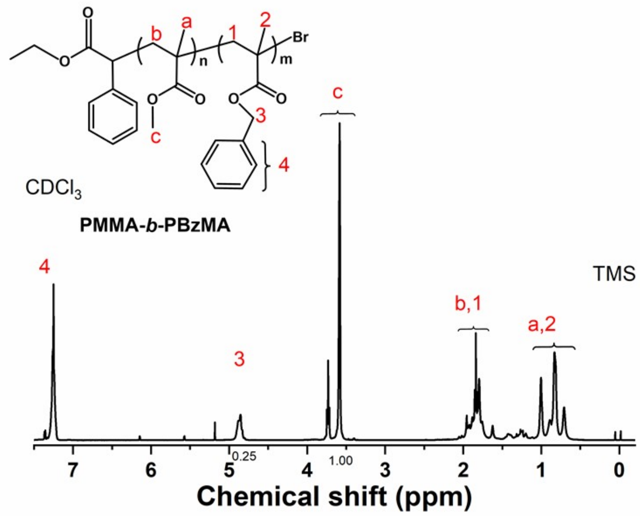


Figure S8. The ^{1}H NMR spectrum of PMMA-*b*-PBzMA. $M_{\mathrm{n,NMR}}$ = (0.25/2)/(1/3)×35(DP$_{\mathrm{PMMA\text{-}Br}}$)×176.21 g/mol+ 7000 g/mol（$M_{\mathrm{n,PMMA\text{-}Br}}$）= 10000 g/mol

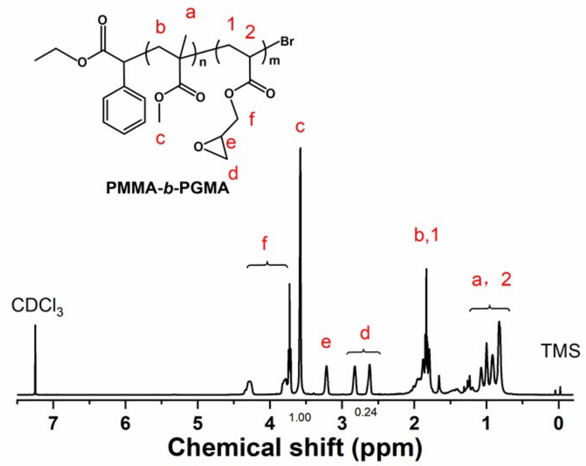


Figure S9. The ^{1}H NMR spectrum of PMMA-*b*-PGMA. $M_{\mathrm{n,NMR}}$= 0.24/(1/3)×35(DP$_{\mathrm{PMMA\text{-}Br}}$)×142.15 g/mol+ 7000 g/mol（$M_{\mathrm{n,PMMA\text{-}Br}}$）= 10000 g/mol

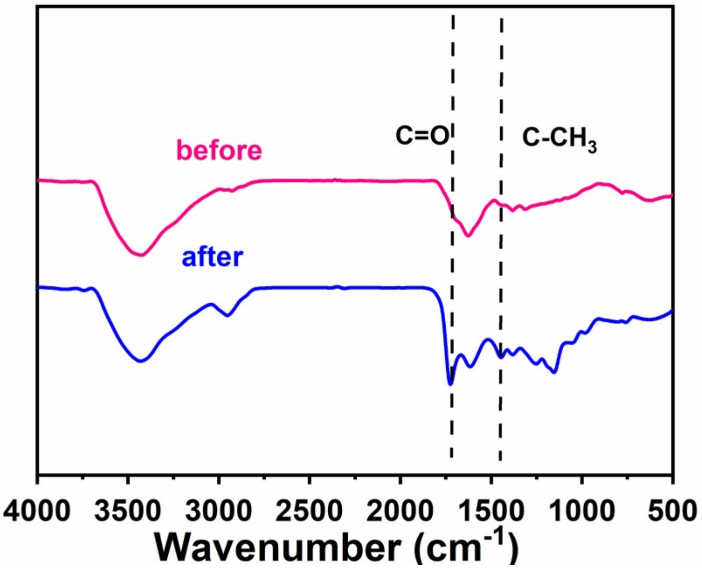


Figure S10. FT-IR spectra of the catalyst before and after cycling.

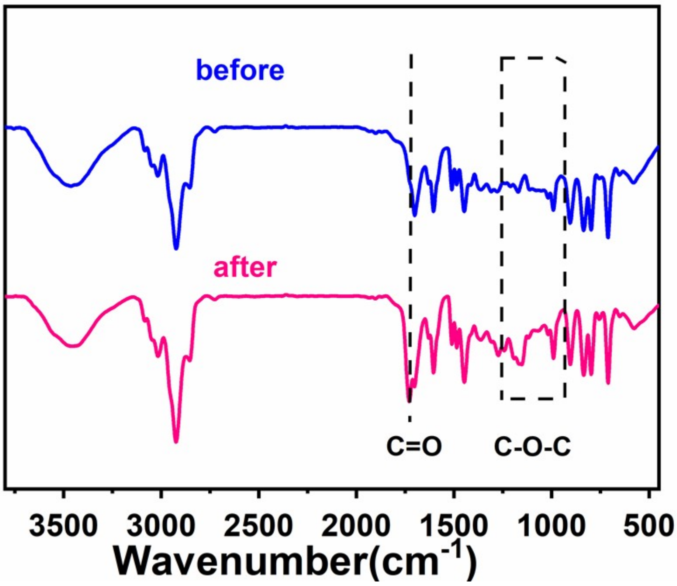
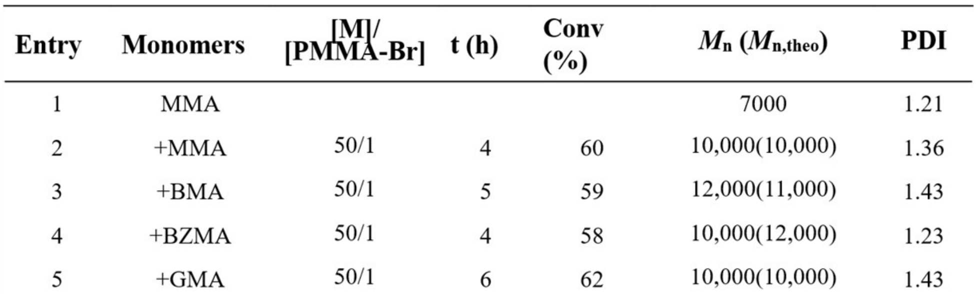


Figure S11. FT-IR Spectra of polymer microspheres before and after grafting.

Table S1. ATRP block copolymer with γ-CCD-r as photocatalyst



Entry	Monomers	[M]/[PMMA-Br]	t (h)	Conv (%)	M_n ($M_{n,theo}$)	PDI
1	MMA				7000	1.21
2	+MMA	50/1	4	60	10,000(10,000)	1.36
3	+BMA	50/1	5	59	12,000(11,000)	1.43
4	+BZMA	50/1	4	58	10,000(12,000)	1.23
5	+GMA	50/1	6	62	10,000(10,000)	1.43