**Electronic Supporting Information** 

## Photoredox Catalyst-Mediated Atom Transfer Radical Addition for Polymer Functionalization under Visible Light<sup>+</sup>

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## **Experimental Section**

**Materials:** Methyl methacrylate (99%), allyl methacrylate (98%), tris[2-phenylpyridinato-C<sup>2</sup>,*N*]iridium(III) (99%), polybutadiene (90% 1,2-vinyl), diethyl bromomalonate (92%), methyl  $\alpha$ bromophenylacetate (97%), ethyl  $\alpha$ -bromoisobutyrate (98%),  $\alpha$ -bromoisobutyric acid (98%), hexylamine (99%), methyl acrylate (99%), methacryloyl chloride (97%), allyl alcohol ( $\geq$ 99%), Nmethyl-1-pyrrolidone (NMP,  $\geq$ 99%), and 1-iodoperfluorohexane (99%) were all purchased from Aldrich and used as received. *N*,*N*-dimethylformamide (DMF, 99.8%, Ajax Chemical), dimethyl sulfoxide (DMSO, Ajax Chemical), *n*-hexane (Ajax Chemical), ethyl acetate (Ajax Chemical), diethyl ether (Ajax Chemical), petroleum spirit (Ajax Chemical) were also used as received. 2,2'-Azobis(2methylpropionitrile) (AIBN, Aldrich, 99%) was freshly recrystallized from methanol before use. Chain transfer agent, 4-cyanopentanoic acid dithiobenzoate (CPADB), was synthesized according to literature procedures.<sup>1</sup> **Instrumentation.** Gel permeation chromatography (GPC) was performed using tetrahydrofuran (THF) or dimethylacetamide (DMAc) as the eluent. The GPC system was a Shimadzu modular system comprising an auto injector, a Phenomenex 5.0  $\mu$ m beadsize guard column (50 × 7.5 mm) followed by three Phenomenex 5.0  $\mu$ m bead-size columns (10<sup>5</sup>, 10<sup>4</sup>, and 10<sup>3</sup> Å), and a differential refractive-index detector. The system was calibrated with narrow molecular weight distribution polystyrene standards with molecular weights of 200 to 10<sup>6</sup> g mol<sup>-1</sup>.

Nuclear magnetic resonance (NMR) spectroscopy was carried out on a Bruker DPX 300 spectrometer operating at 300.17 MHz for <sup>1</sup>H and 75.48 MHz for <sup>13</sup>C using CDCl<sub>3</sub> and DMSO- $d_6$  as solvents and tetramethylsilane (TMS) as a reference. Data was reported as follows: chemical shift ( $\delta$ ) measured in ppm downfield from TMS; multiplicity; proton count. Multiplicities were reported as singlet (s), broad single (bs), doublet (d), triplet (t), and multiplet (m).

**Visible light reactor setup.** Photoredox reactions were carried out in a Rayonet reactor (Model RPR-200) equipped with six Nec 8 Watt Natural Tri-Phosphorus fluorescent tubes (48 Watts).



**Synthesis of random copolymer poly(allyl methacrylate-r-methyl methacrylate)** P(AM-*r*-MMA). The monomers allyl methacrylate and methyl methacrylate were copolymerized at 65 ° C using

CPADB as RAFT chain transfer agent (CTA), AIBN as radical initiator and DMSO as solvent. The polymerization mixture was purged with nitrogen for 30 min before reaction. After 24 h reaction, the reaction mixture was precipitated in methanol and dried under high vacuum overnight to yield pink powder with  $M_n = 21\ 000\ \text{g/mol}$ , PDI = 1.16.

**RAFT End removal of P(AM-***r***-MMA) via aminolysis.** Random copolymer P(AM-*r*-MMA) (0.5 g) was dissolved in THF (20 mL) containing methyl acrylate (0.24 g). The mixture was degassed for 20 min. Degassed hexylamine (0.08 g) was added into above solution slowly by injection. The reaction mixture was kept overnight. After complete reaction, the reaction mixture was precipitated in petroleum ether (300 mL). The white precipitate was collect and dried under high vacuum overnight to yield a white powder, with  $M_n = 22\ 800\ \text{g/mol}$ , PDI = 1.25.

Post-functionalization of P(AM-*r*-MMA) with radical initiators, R-Xs, mediated by visible light. In a typical experiment, a 5 mL glass vial was equipped with a rubber septum and charged with DMSO (2.0 mL), P(AM-*r*-MMA) (20 mg, 0.038 mmol olefin, 1 equiv.), radical initiator diethyl bromomalonate (45.5 mg, 0.19 mmol, 5 equiv.),  $Ir(ppy)_3$  (0.25 mg, 0.00037 mmol, 0.010 equiv.). The mixture was then degassed by N<sub>2</sub> for 30 min in the dark. The mixture was then irradiated by fluorescence tubes (48 Watts). After the reaction was complete (24 h), the reaction mixture was precipitated in MeOH. The white precipitate was collected and dried under vacuum, then submitted for <sup>1</sup>H NMR (CDCl<sub>3</sub>) and GPC (DMAc) measurements to determine the degree of functionalization (*f*), molecular weight and polydispersity.

Degree of functionalization (*f*) was calculated as:

$$f = \left(1 - \frac{\frac{I_{5.3ppm}}{2}}{\frac{I_{3.65ppm}}{12}}\right) \times 100\%$$

where  $I_{5.3ppm}$ : integration of the signal at  $\delta$  5.3 ppm attributed to the unreacted CH<sub>2</sub> group of terminal olefins;  $I_{3.65ppm}$ : integration of the signal at  $\delta$  3.65 ppm attributed to the methyl group of MMA repeating units.

Model reactions for atom transfer radical addition (ATRA) of haloalkanes to olefins mediated by visible light. In a typical experiment, a 5 mL glass vial was equipped with a rubber septum and charged with DMSO- $d_6$  (1.0 mL), allyl alcohol (14.5 mg, 0.25 mmol, 1 equiv.), radical initiator diethyl bromomalonate (89.6 mg, 0.375 mmol, 1.5 equiv.), Ir(ppy)<sub>3</sub> (1.64 mg, 0.0025 mmol, 0.010 equiv.). The mixture was then degassed by N<sub>2</sub> for 30 min in the dark. The mixture was then irradiated by fluorescence tubes (48 Watts). The reaction can be monitored by <sup>1</sup>H NMR. After the reaction was judged complete by TLC analysis, the reaction mixture was diluted by 20 mL dichloromethane and washed by deionized water three times. The oil layer was collected and dried with anhydrous sodium sulphate. After filtration and concentration, light yellow oil was obtained and purified by column chromatography using hexane/ethyl acetate (4/1, v/v) as elute.  $R_f = 0.15$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) 4.19 (m, 5H, (CH<sub>3</sub>CH<sub>2</sub>OOC)<sub>2</sub>CH, CH<sub>2</sub>CHBrCH<sub>2</sub>OH), 3.82 (m, 2H, CH<sub>2</sub>CHBrCH<sub>2</sub>OH), 3.72 (m, 1H, (CH<sub>3</sub>CH<sub>2</sub>OOC)<sub>2</sub>CH), 2.55~2.3 (m, 2H, CH<sub>2</sub>CHBrCH<sub>2</sub>OH), 1.28 (m, 6H, (CH<sub>3</sub>CH<sub>2</sub>OOC)<sub>2</sub>CH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 171.2, 66.9, 61.90, 61.81, 55.55, 50.03, 33.6, 14.05, 14.01.

**Post-modification of 1,2-polybutadiene.** A 5 mL glass vial was equipped with a rubber septum and charged with NMP (2.0 mL), PB (10 mg, 0.157 mmol olefin, 1 equiv.), radical initiator diethyl bromomalonate (75 mg, 0.315 mmol, 5 equiv.),  $Ir(ppy)_3$  (1.1 mg, 0.0017 mmol, 0.010 equiv.). The mixture was then degassed by N<sub>2</sub> for 30 min in the dark. The mixture was then irradiated by fluorescence tubes (48 Watts). After the reaction was complete (24 h), the reaction mixture was precipitated in MeOH. The oily precipitate was collected and dried under vacuum, then submitted for <sup>1</sup>HNMR (CDCl<sub>3</sub>) and GPC (THF) measurements.

Degree of functionalization (*f*) was calculated as:

$$f = \frac{\frac{I_{4.2ppm}}{5}}{\frac{I_{4.9ppm}}{2} + \frac{I_{4.2ppm}}{5}} \times 100\%$$

where  $I_{4.2ppm}$ : integration of the signal at  $\delta$  4.2 ppm attributed to five protons (3' and 6 in Figure S12);  $I_{4.9ppm}$ : integration of the signal at  $\delta$  4.9 ppm attributed to unreacted CH<sub>2</sub> group of terminal olefins.

Synthesis of model polymer poly(allyl methacrylate-r-methyl methacrylate) (P(AM-r-

MMA)) and its aminolysis



**Scheme S1** Synthetic route for model polymer poly(allyl methacrylate-*r*-methyl methacrylate) (P(AM*r*-MMA)) by reversible addition-fragmentation chain transfer (RAFT) polymerization and subsequent aminolysis.



**Fig. S1** A) <sup>1</sup>H NMR spectrum of model polymer poly(allyl methacrylate-*r*-methyl methacrylate) (P(AM-*r*-MMA)) after aminolysis; B) UV-vis spectra of model polymer before and after aminolysis.



**Fig. S2 GPC** curves for functionalized P(AM-*r*-MMA) with diethyl bromomalonate (1) at the comparable degrees of functionalization at different catalyst ratios: blue for 1 mol%, and red for 2 mol%.



**Fig. S3** <sup>1</sup>H NMR monitoring of post-functionalization of aminolyzed P(AM-*r*-MMA) with diethyl bromomalonate (**1**) in the presence of 1 mol% catalyst (Ir(ppy)<sub>3</sub>) and visible light in DMSO, recorded in CDCl<sub>3</sub>.



**Fig. S4** <sup>1</sup>H NMR spectrum stack for products of before (top) and after (bottom) post-functionalization of aminolyzed P(AM-*r*-MMA) with 1-iodoperfluorohexane (**5**) in the presence of 1 mol% catalyst (Ir(ppy)<sub>3</sub>) and visible light, recorded in CDCl<sub>3</sub>.

**Table S1** Degree of functionalization (*f*) obtained by visible light-mediated ATRA of diethyl bromomalonate (**1**) onto aminolyzed P(AM-*r*-MMA) at 1 mol% catalyst in different solvents after 26 h irradiation

Solvents	DMSO	DMF	NMP
f	72.1%	53.0%	58.2%



**Fig. S5** <sup>1</sup>H NMR monitoring of model reaction of diethyl bromomalonate (1) to allyl alcohol in the presence of 1 mol% catalyst ( $Ir(ppy)_3$ ) and visible light in DMSO-*d*<sub>6</sub>. Diethyl bromomalonate (1): allyl alcohol = 1.5 : 1.



Fig. S6 <sup>1</sup>H NMR spectra for the starting material (black curve) of methyl  $\alpha$ -bromophenylacetate (2) and product (red curve) of model reaction of methyl  $\alpha$ -bromophenylacetate (2) to allyl alcohol in the presence of 1 mol% catalyst (Ir(ppy)<sub>3</sub>) and visible light in DMSO-*d*<sub>6</sub>. Methyl  $\alpha$ -bromophenylacetate (2): allyl alcohol = 2 : 1.



**Fig. S7** <sup>1</sup>H NMR spectrum for the product of model reaction of ethyl  $\alpha$ -bromoisobutyrate (**3**) to allyl alcohol in the presence of 1 mol% catalyst (Ir(ppy)<sub>3</sub>) and visible light in DMSO-*d*<sub>6</sub>. ethyl  $\alpha$ -bromoisobutyrate (**3**) : allyl alcohol = 3 : 1.



**Fig. S8** <sup>1</sup>H NMR spectrum for the product of model reaction of 1-iodoperfluorohexane (5) to allyl alcohol in the presence of 1 mol% catalyst ( $Ir(ppy)_3$ ) and visible light in DMSO-*d*<sub>6</sub>. 1-iodoperfluorohexane (5): allyl alcohol = 1.5 : 1.



**Fig. S9** <sup>19</sup>F NMR spectrum for the product of model reaction of 1-iodoperfluorohexane (5) to allyl alcohol in the presence of 1 mol% catalyst  $(Ir(ppy)_3)$  and visible light in DMSO- $d_6$ . 1-iodoperfluorohexane (5): allyl alcohol = 1.5 : 1.



**Fig. S10** <sup>1</sup>H NMR spectrum of product of diethyl bromomalonate (1) to allyl alcohol.



Fig. S11 H-H COSY spectrum of product of diethyl bromomalonate (1) to allyl alcohol.



**Fig. S12** <sup>1</sup>H NMR spectrum stack for products of before (black curve) and after (blue curve) postfunctionalization of polybutadiene with diethyl bromomalonate (1) in the presence of 1 mol% catalyst ( $Ir(ppy)_3$ ) and visible light. The red curve is the product of control experiment without photocatalyst, which present the same spectrum as starting material (black cruve) recorded in CDCl<sub>3</sub>

## References

1. Xu, J.; Tao, L.; Boyer, C; Lowe, A. B; Davis, T. P. Macromoleules 2010, 43, 20-24.