

Supporting Information

Redox-Switchable Atom Transfer Radical Polymerization

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EXPERIMENTAL

Materials

Methyl acrylate (MA; Sigma-Aldrich, 99%) was purified by passing through a basic alumina column to remove polymerization inhibitor prior to use. Ethyl α -bromoisobutyrate (EBiB; Sigma-Aldrich, 98%), copper(II) bromide (CuBr₂; Sigma-Aldrich, 99%), L-ascorbic acid (AscAcid, Sigma-Aldrich), ferrocenium hexafluorophosphate (FcPF₆; Sigma-Aldrich, 97%) and *N,N*-dimethylformamide (DMF; Fisher Chemical) were used as received. Tris[2-(dimethylamino)ethyl]amine (Me₆TREN) was received from Koei Chemical Co., Ltd. (Japan).

Instrumentation

Proton nuclear magnetic resonance (¹H NMR) measurements were performed on a Bruker Advance 500 MHz spectrometer. Number-average molecular weight (M_n) and dispersity (D) of the polymers were determined by size-exclusion chromatography (SEC). The SEC instrument was equipped with a Waters 515 pump and a Waters 2414 differential refractometer using PSS columns (SDV 10⁵, 10³, and 500 Å) with THF as eluent at 35 °C and a flow rate of 1 mL/min. Linear poly(methyl methacrylate) standards were used for calibration. UV-vis spectra were recorded using Agilent 8453 spectrophotometer.

General ATRP Procedures

ARGET ATRP of MA

A 20 mL vial equipped with a stir bar was sealed with a rubber septum and subjected to vacuum and backfilled with nitrogen for 5 times. MA and DMF were degassed separately for 40 min. DMF (2 mL), MA (2 mL, 22.2 mmol, 200 equiv.), CuBr₂ (1.0 mg, 4.4×10⁻⁶ mol, 0.04 equiv.), Me₆TREN (1.2 μL, 4.4×10⁻⁶ mol, 0.04 equiv.), and EBiB (16.3 μL, 0.111 mmol, 1 equiv.) were added into the vial under nitrogen. The vial was placed in a water bath at 25 °C. A degassed solution of AscAcid (50 μL, 88.8 mM in DMF; 0.78 mg, 0.04 equiv.) was added to start the reaction. Samples were taken periodically for ¹H NMR and SEC analyses.

Redox Switchable ATRP using AscAcid/FcPF₆ as Redox Switches

A 20 mL vial equipped with a stir bar was sealed with a rubber septum and subjected to vacuum and backfilled with nitrogen for 5 times. MA and DMF were degassed separately for 40 min. DMF (2 mL), MA (2 mL, 22.2 mmol, 200 equiv.), CuBr₂ (1.0 mg, 4.4×10⁻⁶ mol, 0.04 equiv.), Me₆TREN (1.2 μL, 4.4×10⁻⁶ mol, 0.04 equiv.), and EBiB (16.3 μL, 0.111 mmol, 1 equiv.) were added into the vial under nitrogen. The vial was placed in a water bath at 25 °C. A degassed solution of AscAcid (50 μL, 88.8 mM in DMF; 0.78 mg, 0.04 equiv.) was added to start the reaction. A degassed solution of FcPF₆ (50 μL, 44.4 mM in DMF; 0.735 mg, 2.22×10⁻⁶ mol) was added to polymerization solution after 1 h. Samples were taken periodically for ¹H NMR and SEC analyses.

Redox Switchable ATRP using AscAcid/O₂ as Redox Switches

A 2-dram vial equipped with a stir bar was sealed with a rubber septum and subjected to vacuum and backfilled with nitrogen for 5 times. MA and DMF were degassed separately for 40 min. DMF (2 mL), MA (2 mL, 22.2 mmol, 200 equiv.), CuBr₂ (1.0 mg, 4.4×10⁻⁶ mol, 0.04 equiv.), Me₆TREN (1.2 μL, 4.4×10⁻⁶ mol, 0.04 equiv.), and EBiB (16.3 μL, 0.111 mmol, 1 equiv.) were added into the vial under nitrogen. The vial was placed in a water bath at 25 °C. A degassed solution of AscAcid (50 μL, 88.8 mM in DMF; 0.78 mg, 0.04 equiv.) was added to start the reaction. After 1 h, the polymerization solution was bubbled with air for 1 min. The reaction was bubbled with nitrogen for 2 min before adding a second batch of AscAcid (50 μL, 88.8 mM in DMF; 0.78 mg, 0.04 equiv.). Samples were taken periodically for ¹H NMR and SEC analyses.

Kinetics and polymerization data:

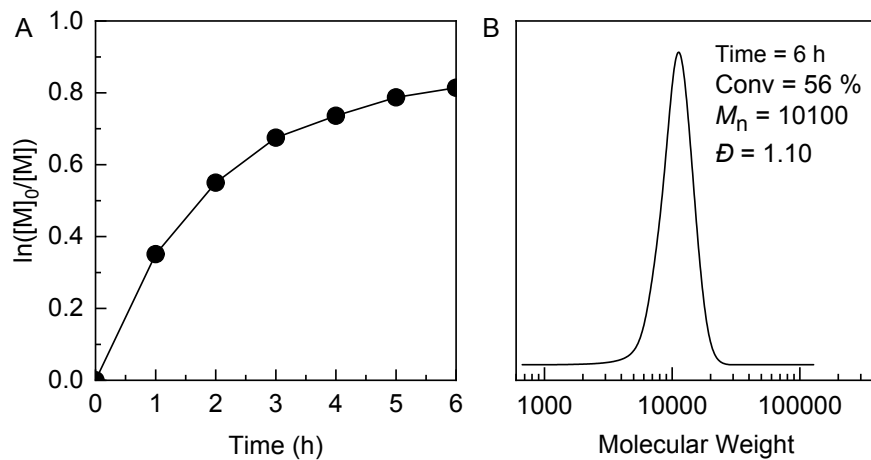


Figure S1. ARGET ATRP of MA using Me_6TREN in DMF. Reaction conditions: $[\text{MA}]/[\text{EBiB}]/[\text{CuBr}_2]/[\text{Me}_6\text{TREN}]/[\text{AscAcid}] = 200/1/0.04/0.04/0.04$ in 50 vol% DMF at 25 °C. AscAcid added initially.

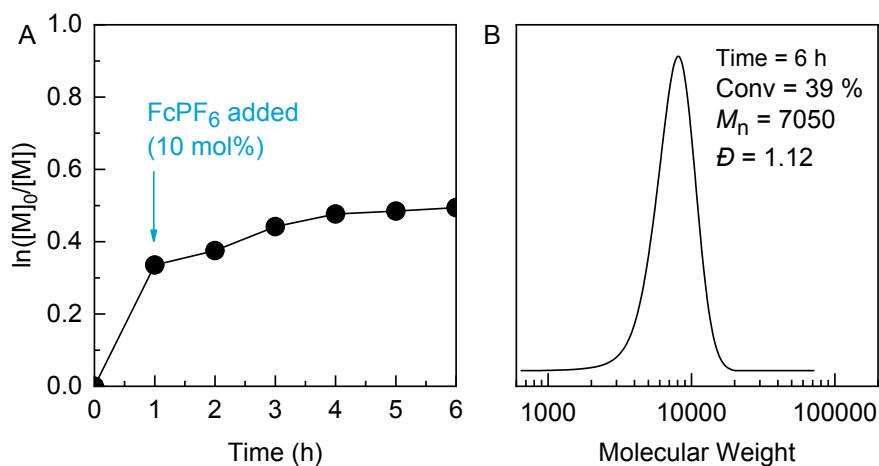


Figure S2. Redox control in ATRP. Reaction conditions: $[\text{MA}]/[\text{EBiB}]/[\text{CuBr}_2]/[\text{Me}_6\text{TREN}]/[\text{AscAcid}] = 200/1/0.04/0.0/0.04$ in 50 vol% DMF at 25 °C. AscAcid added initially. FcPF_6 (10 mol% with respect to Cu) added at 1 h.

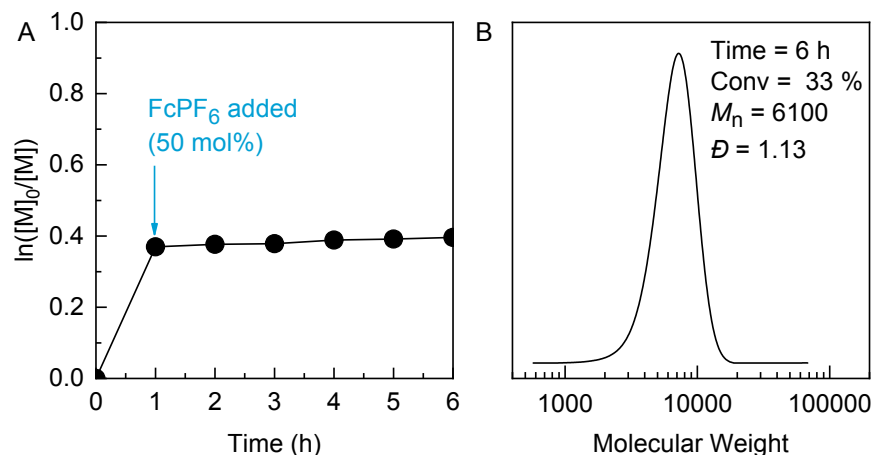


Figure S3. Redox control in ATRP. Reaction conditions: $[MA]/[EBiB]/[CuBr_2]/[Me_6TREN]/[AscAcid] = 200/1/0.04/0.0/0.04$ in 50 vol% DMF at 25 °C. AscAcid added initially. FcPF₆ (50 mol% with respect to Cu) added at 1 h.

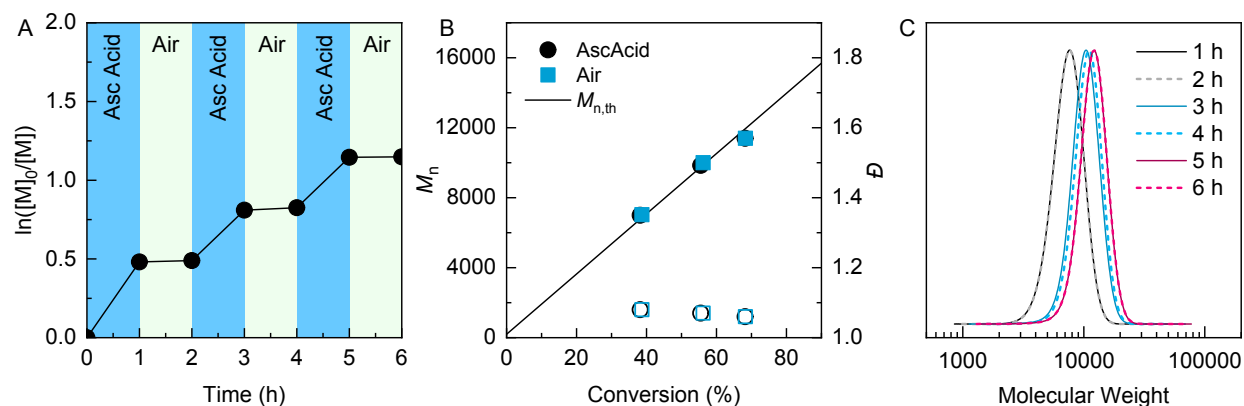


Figure S4. (A) Kinetics of temporal control using AscAcid and oxygen as redox agents. (B) Number-average molecular weight (M_n , solid points) and dispersity (\bar{D} , open points) as a function of monomer conversion. (C) SEC traces: solid lines after addition of AscAcid and dashed lines after air bubbling. Reaction conditions: $[MA]/[EBiB]/[CuBr_2]/[Me_6TREN]/[AscAcid] = 200/1/0.04/0.04/0.04$ in 50 vol% DMF at 25 °C. AscAcid added at 0, 2 and 4 h. Air bubbled for 1 min at 1, 3, and 5 h. Nitrogen bubbled for 2 min at 2 and 4 h.

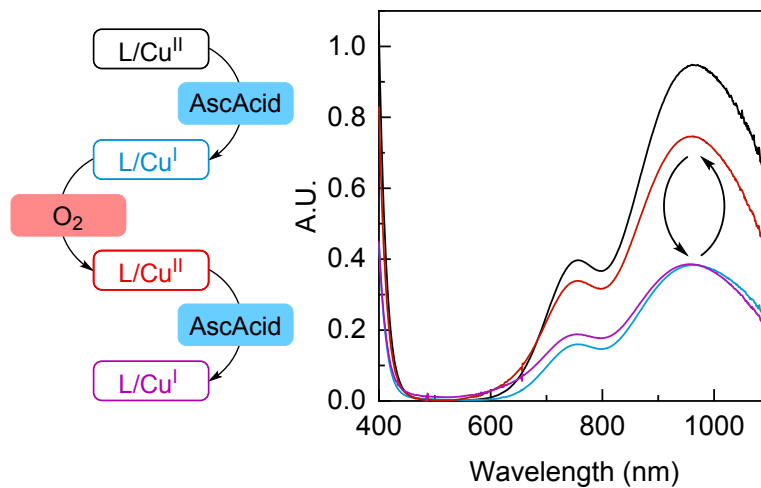


Figure S5. Evolution of the Vis-NIR spectra of Cu catalyst after sequential addition of AscAcid and oxygen. $[\text{CuBr}_2/\text{Me}_6\text{TREN}] = [\text{AscAcid}] = 2.22 \text{ mM}$ in DMF. Oxygen was introduced by bubbling with air for 1 min.