Supporting information for:
Lights on! Significant photo enhancement effect on ATRP by ambient laboratory light

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Experimental Section

Materials

Methyl methacrylate (MMA, 99%) was purchased from Sigma-Aldrich and purified before use by passing through a basic alumina column to remove the inhibitor. Ethyl 2-bromoisobutyrate (EBiB, 98%), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, 99%), copper(II) bromide ($CuBr_2$, 99%), copper(I) bromide (CuBr, 99.99%), *N,N*-dimethylformamide (DMF), tin(II) 2-ethylhexanoate ($Sn(EH)_2$), ascorbic acid and methanol (all from Sigma-Aldrich) were used as received.

Procedures for ATRP Polymerizations

Classical ATRP (Cu^I/Cu^{II})

In a Schlenk flask with a mixture of DMF (2.0 mL), methanol (1 mL), EBiB (46.6 μL, 0.374 mmol), PMDETA (24.9 μL, 0.1138 mmol), and MMA (4 mL, 37.40 mmol) was and a stirring bar were put into a reaction tube. Four freeze-pump-thaw cycles were applied in order to remove oxygen. Under nitrogen flow, the Cu(I)Br (5.4 mg, 0.0374 mmol) and Cu(II)Br_2 (0.836 mg, 0.00374 mmol) catalyst was then quickly introduced. The mixture was vigorously stirred until the catalyst was completely dissolved. The polymerization solution was then separated into relatively two reaction tubes (#2L and #2D). One reaction tube (#2L) was placed in the middle of two standard fluorescent lamps (type L 58 W/880 "SKYWHITE" from Osram, Germany with 58 W, 8000 K color temperature and a luminous flux of 4900 lm at 25 °C for the entire lamp) emitting light in the spectral range of 400-750 nm at an approximate distance of 1 m to each lamp and the reaction mixture was stirred throughout the experiments (in order to simulate the lighting environments of ATRP in normal chemistry laboratory, the room light was retained during the whole polymerization). Dark reaction (#2D) was conducted by covering the other reaction tube with aluminum foil and stirred at room temperature. After a certain time, the polymerization was stopped. The product was dissolved in acetone. Finally, the resultant polymer was isolated by precipitation in methanol and dried under vacuum at 30 °C for 24 h. Reprecipitation was performed until a colorless powder was obtained. The polymer products were dried in a vacuum to a constant weight and analyzed. Monomer conversion was determined by ^1H NMR spectroscopy by the ratio of the OCH_3 signal intensity in polymer (3.60 ppm) and monomer (3.75 ppm). The molar mass and dispersity of the polymer were measured by GPC.

Optimized classical ATRP at 55 °C: In a Schlenk flask with a mixture of DMF (3.0 mL), PMDETA (20 μL, 0.047 mmol), and MMA (2 mL, 18.5 mmol) was and a stirring bar were put into a reaction tube. Four freeze-pump-thaw cycles were applied in order to remove oxygen. Under nitrogen flow, the CuBr (4.7 mg, 0.033) and $CuBr_2$ (3.1 mg, 0.011 mmol) were quickly introduced. The mixture was vigorously stirred until the catalyst was completely dissolved. Finally, the initiator EBiB (13.9 μL, 0.093 mmol) was added. The polymerization solution was then separated into relatively two reaction tubes (#4H and #4D) and reacted in a heating bath at 55 °C. The following processes were similar to that of in classical ATRP at room temperature. The same procedure was performed on entries #3H and #3D, however the

DP = 200 where the concentration of catalyst, ligand and initiator were doubled.

Classical ATRP (initial Cu^I only)

In a Schlenk flask with a mixture of DMF (2.0 mL), methanol (1 mL), EBiB (46.6 μL, 0.374 mmol), PMDETA (24.9μL, 0.1138 mmol), and MMA (4 mL, 37.40 mmol) was and a stirring bar were put into a reaction tube. Four freeze-pump-thaw cycles were applied in order to remove oxygen. Under nitrogen flow, the CuBr (5.4 mg, 0.0374) for #5L and #5D, or CuBr (5.4 mg, 0.0374 mmol) and ascorbic acid (0.49 mg, 0.0028 mmol) for #6L and #6D were then quickly introduced. The mixture was vigorously stirred until the catalyst was completely dissolved. The polymerization solution was then separated into relatively two reaction tubes (#5L and #5D, or #6L and #6D). The following processes were similar to that of in classical ATRP.

AGET ATRP

In a Schlenk flask with a mixture of DMF (2.0 mL), methanol (1 mL), EBiB (46.6μL, 0.374 mmol), PMDETA (24.9μL, 0.1138 mmol), and MMA (4 mL, 37.40 mmol) was and a stirring bar were put into a reaction tube. Four freeze-pump-thaw cycles were applied in order to remove oxygen. Under nitrogen flow, the $Cu(II)Br_2$ (8.4 mg, 0.0374 mmol) catalyst and $Sn(EH)_2$ (6.24 μL, 0.0187 mmol) or ascorbic acid (0.32 mg, 0.0187 mmol) was then quickly introduced. The mixture was vigorously stirred until the catalyst was completely dissolved. The polymerization solution was then separated into relatively two reaction tubes (#7L and #7D, or #8L and #8D). The following processes were similar to that of in classical ATRP.

ARGET ATRP

In a Schlenk flask with a mixture of DMF (3.0 mL), methanol (1.5 mL), EBiB (35 μL, 0.281 mmol), PMDETA (37.35 μL, 0.084 mmol), and MMA (6 mL, 56.1 mmol) was and a stirring bar were put into a reaction tube. Four freeze-pump-thaw cycles were applied in order to remove oxygen. Under nitrogen flow, the $Cu(II)Br_2$ (0.63 mg, 0.00281 mmol) catalyst and $Sn(EH)_2$ (27.88 μL, 0.084 mmol) was then quickly introduced. The mixture was vigorously stirred until the catalyst was completely dissolved. The polymerization solution was then separated into relatively three reaction tubes (#1L, #1H and #1D). The reaction of 6H was performed under normal ambient irradiation with hood light with two fluorescence lamps (type Master TL-D 58W/840 from Philips®) shows a light emission intensity at 6.19±0.29 mW/cm^2 including room light. The other two reaction tubes and following processes were similar to that of in classical ATRP.

Kinetics: In a Schlenk flask with a mixture of DMF (4 mL), methanol (2 mL), EBiB (93 μL, 0.748 mmol), PMDETA (50 μL, 0.225 mmol), $Cu(II)Br_2$ (16.8 mg, 0.0748 mmol), and MMA (8 mL, 74.8 mmol) was and a stirring bar were put into a reaction tube. Four freeze-pump-thaw cycles were applied in order to remove oxygen. Under nitrogen flow, the reduce agent ascorbic acid (6.6 mg, 0.0374 mmol) was then quickly introduced. The mixture was vigorously stirred until the solids were completely dissolved. The polymerization solution was then separated into relatively three reaction tubes for reactions at different light irradiation. After indicated polymerization times, aliquots of the reaction mixture were collected and the polymer product was isolated by precipitation in methanol. The polymer products were dried in a vacuum to a constant weight and analyzed. Monomer conversion was determined by ^1H NMR spectroscopy by the ratio of the OCH_3 signal intensity in polymer (3.60 ppm) and monomer (3.75 ppm). The molar mass and dispersity of the polymer were measured by GPC.

Characterization

Gel permeation chromatography (GPC) was performed on a PL-GPC-120 (Polymer Laboratories) running under WinGPC software (PSS, Mainz, Germany) with two consecutive

Gram columns (2×100 Å) with *N,N*-dimethylacetamide (DMAc) (5 gL^{-1} LiBr, 70 ℃, 1 mL min1) as eluent and calibrated against PMMA standards from PSS, Mainz, Germany. Conversions were determined by end group analysis using ^1H NMR spectroscopy data recorded on a Bruker DRX 500 spectrometer at 500 MHz at room temperature in $CDCl_3$.

A digital lux light meter, with AR823$^+$ detector (Luzchem Research, Inc., Ottawa, Canada) was used to measure the intensity of ambient light with two fluorescent lamps (L, 5.35±0.15 mW/cm^2) and fumy hood light (H, 6.19±0.29 mW/cm^2). The laboratory ceiling lights consisting of 6 fluorescent lamps (type Master TL-D 58W/840 from Philips®) were on in both of the two measurements.