

# Electrochemical Atom Transfer Radical Polymerization in Miniemulsion with a Dual Catalytic System

*Marco Fantin, Sangwoo Park, Yi Wang, and Krzysztof Matyjaszewski*

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh,  
Pennsylvania 15213

## Experimental Section

**Materials.** Tetrabutylammonium perchlorate (TBAClO<sub>4</sub>, > 98%), tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>, 98%), copper(II) bromide (CuBr<sub>2</sub>, 99%), methylated cellulose (Tylose, MH = 300), 2-chloromethyl-4-methoxy-3,5-dimethylpyridine hydrochloride (98%), dichloromethane (DCM, > 99.5%), 2,2'-bipyridyl (bpy, 99%), 2-(chloromethyl)pyridine hydrochloride, octadecylamine (99%), sodium dodecyl sulfate (SDS, 99%), hexadecane (HD, 99%) and ethyl  $\alpha$ -bromoisobutyrate (EBiB, 98%) were purchased from Sigma-Aldrich. *N,N*-dimethylformamide (DMF) and sodium bromide (NaBr, 99%) were purchased from Acros. Metal wires (platinum and copper) and platinum gauge were purchased from Alfa Aesar. Tributylhexadecylphosphonium bromide (97%) was purchased from Fluka. Magnesium sulfate anhydrous (MgSO<sub>4</sub>, 98.9%) and sodium hydroxide (NaOH, 99%) were purchased from Fisher. Sodium chloride (NaCl, 99%) was purchased from EMD chemicals. Tris(2-pyridylmethyl)amine (TPMA) was prepared according to a published procedure,<sup>1</sup> *n*-butyl acrylate (BA, 99%, Aldrich) and was passed through a column filled with basic alumina prior to use to remove polymerization inhibitors.

**Synthesis of *N,N*-bis(2-pyridylmethyl)-2-hydroxyethylamine (BPMEA).** BPMEA was synthesized by a modified literature procedure.<sup>2</sup> 2-Picolyl chloride hydrochloride (5.0 g,  $3.1 \times 10^{-2}$  mol) was dissolved in 20 mL of distilled water. Ethanolamine (0.9 mL,  $2.1 \times 10^{-2}$  mol) was slowly injected into the solution. The mixture was stirred and heated to 60 °C. A solution of 2.4 g NaOH

in 10 mL of water was added slowly to the previous mixture. The dark brown solution was stirred for 5 h and cooled to room temperature. The product was extracted with DCM and concentrated. The obtained dark oil was passed through basic alumina with DCM. The solution was concentrated to obtain the desired product.

**Synthesis of bis(2-pyridylmethyl)octadecylamine (BPMODA).** BPMODA was synthesized by a modified literature procedure.<sup>1</sup> 2-(Chloromethyl)pyridine hydrochloride (8.4 g, 51.2 mmol) and octadecylamine (6.57 g, 24.39 mmol) were dissolved in 30 mL of DCM. The NaOH solution was added to the mixture to maintain pH at 8-9 for a week. The organic layer was collected, washed with distilled water three times, and then condensed. The desired product was separated by column chromatography with hexanes/ethyl acetate (4/1, v/v) as eluent. The final product was analyzed by <sup>1</sup>H NMR (see Supporting Information, SI).

**Synthesis of bis[2-(4-methoxy-3,5-dimethyl)pyridylmethyl]octadecylamine (BPMODA\*).** BPMODA\* was synthesized by a modified literature procedure.<sup>3</sup> 2-Chloromethyl-4-methoxy-3,5-dimethyl pyridine hydrochloride (15 g, 67.5 mmol) and octadecylamine (8.67 g, 32.2 mmol) were dissolved in 100 mL of THF. Then, 55 mL of 5 M NaOH<sub>aq</sub> were added to the mixture. The biphasic system was heated at 60 °C for 5 days. The organic layer was collected and washed with brine until pH *ca.* 9. Then, the organic layer was collected, dried over MgSO<sub>4</sub> and concentrated. The desired product was separated by column chromatography with hexanes/ethyl acetate (4/1, v/v) as eluent. The final product was analyzed by <sup>1</sup>H NMR (see SI).

**Typical procedure of a partition experiment.** Aqueous solutions of CuBr<sub>2</sub>/BPMEA (1/2 by mole) were prepared at various concentrations, *i.e.*, 0.1, 1, 2.5, 5, 10, and 20 mM. Catalyst absorbance was recorded by UV-Vis spectroscopy (maximum wavelength,  $\lambda_{\text{max}}$ , was 666 nm). A linear calibration was obtained from the correlation between absorbance and catalyst concentration curves. Solutions of CuBr<sub>2</sub>/BPMEA in water were prepared at two concentrations (2.5 and 5 mM) and then mixed with BA to obtain 15/85 and 30/70 water/BA ratios (by v/v). The mixtures were vigorously stirred using a Vortex Mixer at either RT or 60 °C. The aqueous phase was collected and absorbance at 666 nm was recorded by UV-Vis spectrometer.

**Cyclic voltammetry (CV) analysis of catalysts.** CV was performed on 1 mM CuBr<sub>2</sub>/L catalyst solutions (L = bpy or BPMEA for aqueous phase catalyst; BPMODA or BPMODA\* for

organic phase catalysts;  $\text{CuBr}_2/\text{L}$  mole ratio = 1/2). In aqueous phase, 0.1 M of NaBr (0.63 g, 3 mmol) was used as a supporting electrolyte in a total volume of 30 mL.  $\text{Br}^-$  anions ensure that most of  $\text{Cu}^{\text{II}}$  is present in the form of  $\text{Br-Cu}^{\text{II}}/\text{L}^+$  in the aqueous phase.<sup>4</sup> Organic phase catalysts were prepared in BA/anisole solution (1/1, by v/v) with 0.1 M TBAPF<sub>6</sub> or TBAClO<sub>4</sub> as a supporting electrolyte ( $\text{PF}_6^-$  and  $\text{ClO}_4^-$  are non-coordinating anion that should not interact with the copper complex). CV spectra were recorded at a Pt disk working electrode (WE) with a Pt mesh counter electrode (CE) and a saturated calomel (SCE) reference electrode (RE). Scan rate ( $\nu$ ) was 100 mV/s.

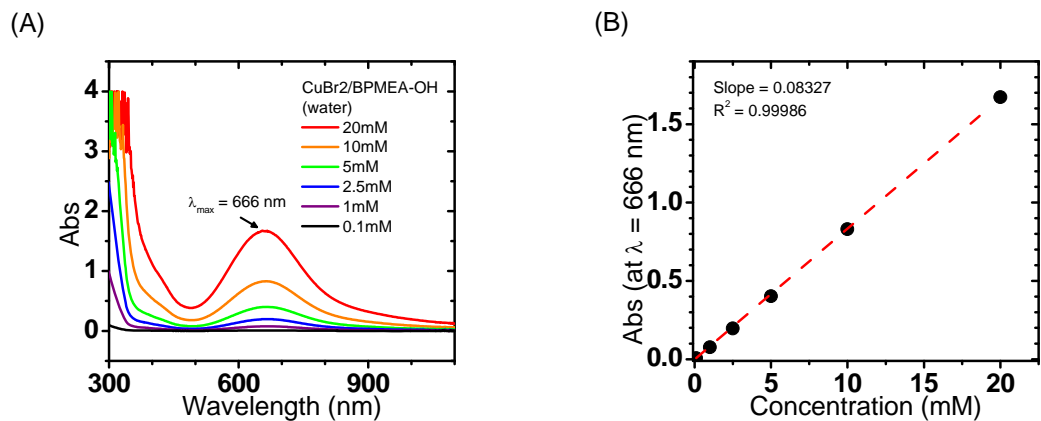
**Conventional *e*ATRP with  $\text{CuBr}_2/\text{BPMODA}^*$  catalysts.** TBAClO<sub>4</sub> (2.05 g, 6 mmol),  $\text{CuBr}_2$  (28 mg,  $1.26 \times 10^{-1}$  mmol), and BPMODA\* (71 mg,  $1.26 \times 10^{-1}$  mmol) were placed in a seven-neck electrolysis cell maintained at 60 °C under a slow N<sub>2</sub> purge. Then, 18 mL of N<sub>2</sub> purged BA (126 mmol) and DMF (12 mL) were added to the reaction. To evaluate the impact of hexadecane (HD) on the polymerization, the same amount of HD used in the miniemulsion polymerization was added to this conventional homogenous reaction (1.04 mL, 3.55 mmol). A CV was recorded at 100 mV/s with this electrode setup: Pt disk WE; a Pt mesh CE separated from polymerization mixture by a glass frit filled with Tylose gel (saturated in TBAClO<sub>4</sub>); a Ag/AgI/0.1 M TBAI (Ag/AgI/I<sup>-</sup>) in DMF reference electrode. Appropriate applied potential was selected from the CV results ( $E_{\text{app}} = E_{\text{pc}} - 80$  mV, where  $E_{\text{pc}}$  = cathodic peak potential). EBiB (65  $\mu\text{L}$ ,  $4.44 \times 10^{-1}$  mmol) was injected into the reaction solution and a second CV was recorded to confirm the electrochemical catalytic ( $EC''$ ) process. The Pt mesh electrode was then used as the WE for the polymerization using the chronoamperometry (CA) method. Samples were withdrawn periodically to follow monomer conversion by <sup>1</sup>H NMR. Number-average molecular weight ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) were determined by gel permeation chromatography (GPC).

**Miniemulsion polymerization by *e*ATRP.** A stock solution of BA (50 mL, 348.76 mmol),  $\text{CuBr}_2$  (78 mg, 0.35 mmol), and BPMODA\* (198 mg, 0.35 mmol) was prepared. HD (0.50 mL, 1.71 mmol), EBiB (29  $\mu\text{L}$ ,  $1.97 \times 10^{-1}$  mmol, to target degree of polymerization (DP) = 283) were added to 8 mL of the BA containing stock solution (the amount of EBiB was adjusted for different targeted DPs). SDS (329 mg, 1.14 mmol), NaBr (411 mg, 4 mmol),  $\text{CuBr}_2$  (9 mg, 0.04 mmol), and BPMEA (10 mg, 0.04 mmol) were dissolved in 32 mL of distilled water. The organic and aqueous

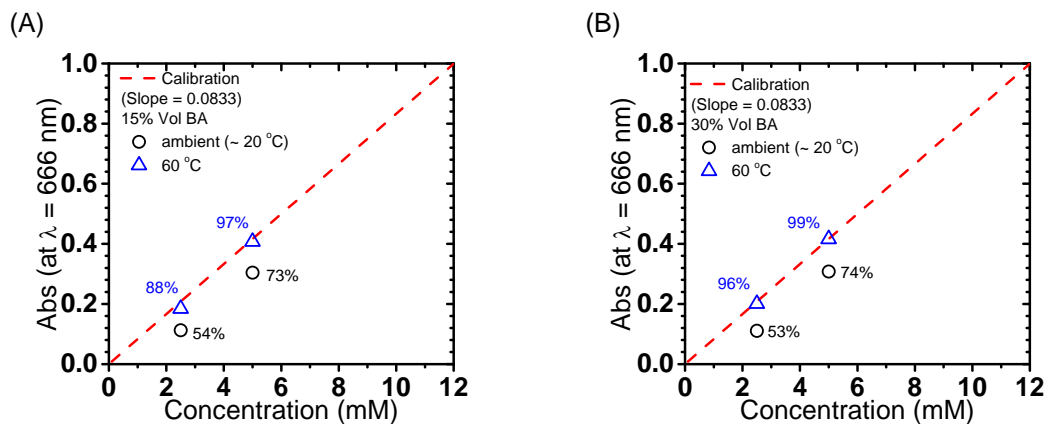
solutions were mixed (total volume  $\approx$  40 mL), placed in an ice bath, and dispersed by a probe sonicator, amplitude = 70% for 15 min; (application and rest time of 1 s each). Nitrogen was bubbled through the miniemulsion solution for 30 min, prior to recording a CV at 100 mV/s with a Pt disk WE, and the same CE and RE described above. The CV allowed for accurate selection of the applied potential ( $E_{\text{app}} = E_{1/2}$ ,  $E_{\text{pc}}$ , or  $E_{\text{pc}} - 80$  mV, where  $E_{1/2}$  is the half-sum of the cathodic and anodic peak potential). A Pt mesh (geometrical area ca. 6 cm<sup>2</sup>) WE was used for electrolysis under proper  $E_{\text{app}}$ . Mass transport of reactants to the electrode appears to be very important in microemulsion.<sup>5</sup> To ensure maximum reproducibility, the electrode was placed about 1 cm from the top of the stirring bar (length = 2.0 cm), which was stirred at 750 rpm. Samples were withdrawn periodically to follow the monomer conversion by gravimetric analysis, while  $M_n$  and  $M_w/M_n$  were determined by GPC.

**Apparatus and characterization.** Ultrasound treatment was carried out using Ultrasonics W-385 sonicator. UV-Vis spectra were recorded by Agilent 8453 with a glass cuvette (length = 1 cm). <sup>1</sup>H NMR (300 MHz) spectra were measured on a Bruker Advance 300 spectrometer using CDCl<sub>3</sub> as a solvent.  $M_n$  and  $M_n/M_w$  were determined by GPC equipped with Polymer Standards Services (PSS) columns (guard, 10<sup>5</sup>, 10<sup>3</sup>, and 10<sup>2</sup> Å) and a differential refractive index detector (Waters, 2410), with THF as eluent at a flow rate 1.00 mL/min ( $T = 35$  °C). GPC traces were processed by WinGPC 8.0 software (PSS) using a calibration based on linear polystyrene (PSty) standards. CVs and CAs were recorded by a Gamry Ref 600 potentiostat. During the *e*ATRP, a condenser was connected to the reaction cell and maintained at -10 °C using a circulating chiller (NESLAB Inc., RTE-111). Particle size and size distribution were determined by using a Zetasizer Nano from Malvern Instruments, Ltd.

## Selected results of Partition Experiments

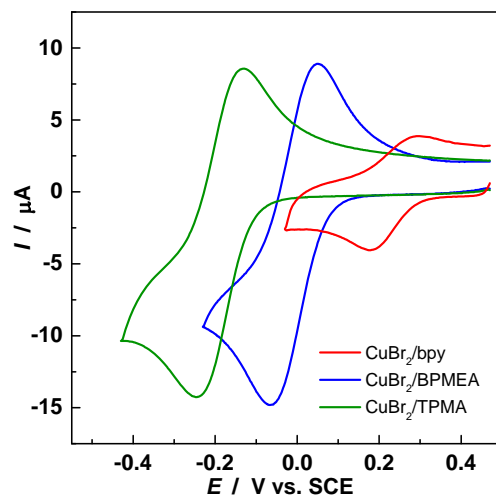


**Figure S1.** (A) UV-Vis spectra of CuBr<sub>2</sub>/BPMEA at different concentrations (0.1 to 20 mM). (B) Calibration curve (absorbance vs. concentration) obtained from the UV-Vis spectra ( $R^2 = 0.99986$ ).

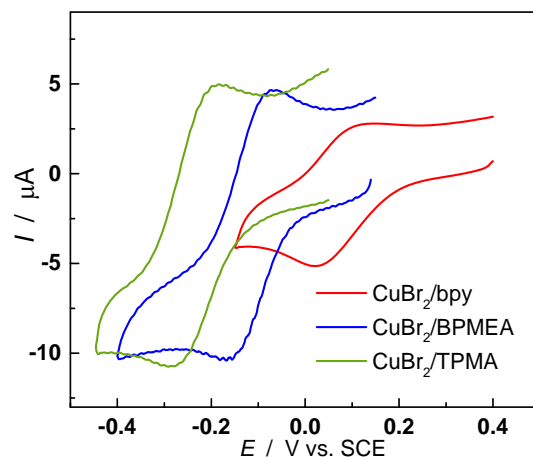


**Figure S2.** Partition experiments of CuBr<sub>2</sub>/BPMEA in (A) 85/15 and (B) 70/30 water/BA mixtures (by v/v).  $T$  = ambient ( $\sim 20$  °C) or 60 °C. Calibration curve was obtained from Figure S1.

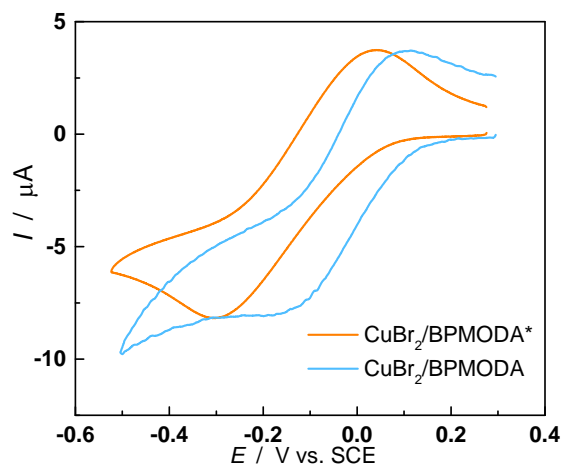
### Cyclic Voltammetry Investigation of the Catalysts



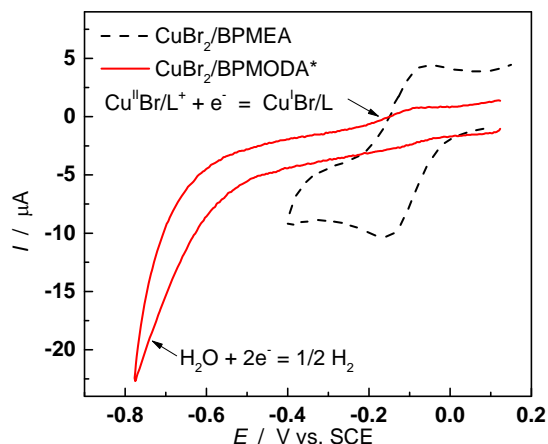
**Figure S3.** Cyclic voltammetry of 1 mM  $\text{CuBr}_2/\text{L}$  in BA/anisole 50/50 + 0.1 M  $n\text{-Bu}_4\text{NPF}_6$  at Pt disk electrode.  $v = 0.1 \text{ V s}^{-1}$ .  $T = 60 \text{ }^\circ\text{C}$ . Anisole was added to have sufficient solubility of all complexes and sufficient conductivity. Lower current for  $\text{CuBr}_2/\text{bpy}$  (1/2 molar ratio) is due to lower solubility of this complex.



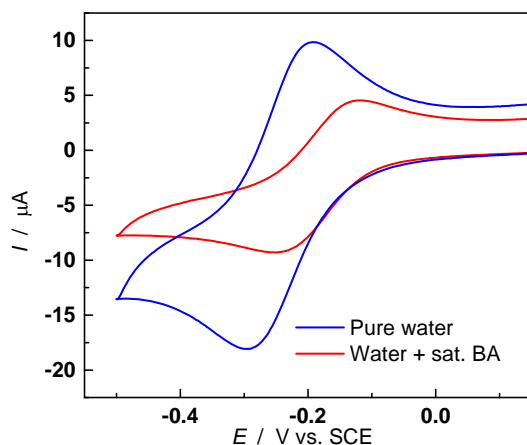
**Figure S4.** Cyclic voltammetry of 1 mM  $\text{CuBr}_2/\text{L}$  in miniemulsion (recipe in Table 3) on a Pt disk electrode.  $v = 0.1 \text{ V s}^{-1}$ .  $T = 60 \text{ }^\circ\text{C}$ . The shape of the CV is only slightly affected by the surfactant molecules absorbed onto the electrode surface.



**Figure S5.** Cyclic voltammetry of 1 mM  $\text{CuBr}_2/\text{L}$  in BA/anisole 50/50 + 0.1 M  $n\text{-Bu}_4\text{NClO}_4$  at Pt disk electrode.  $v = 0.1 \text{ V s}^{-1}$ .  $T = 60 \text{ }^\circ\text{C}$ .



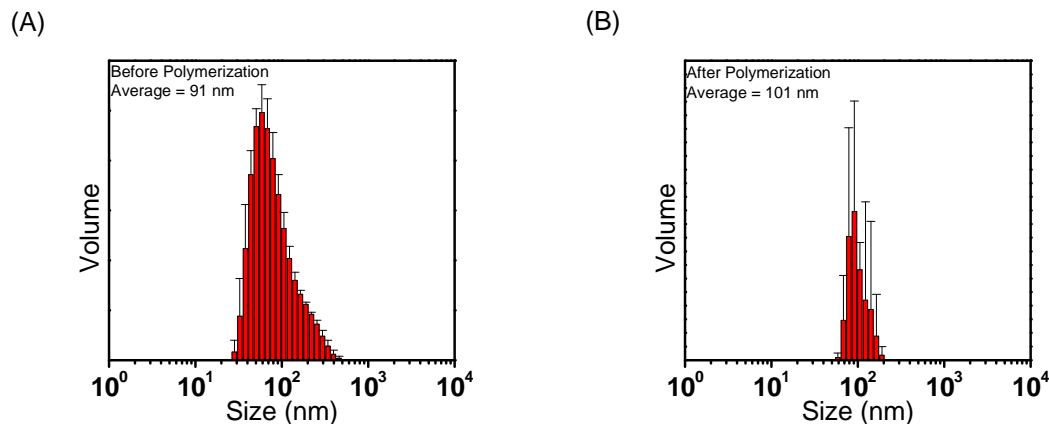
**Figure S6.** Cyclic voltammetry of 1 mM  $\text{CuBr}_2/\text{L}$  in miniemulsion (recipe in Table 3) on a Pt disk electrode.  $v = 0.1 \text{ V s}^{-1}$ .  $T = 60 \text{ }^\circ\text{C}$ . The reduction peak of  $\text{CuBr}_2/\text{BPMODA}^*_{\text{org}}$  can be barely distinguished from the capacitive current, indicating a poor connection between the electrode and the organic phase droplets that contain the catalyst. The small current could also indicate the absorption of some  $\text{CuBr}_2/\text{BPMODA}^*_{\text{org}}$  on the electrode surface.



**Figure S7.** Cyclic voltammetry of 1 mM  $\text{CuBr}_2/\text{BPMEA}$  in water + 0.1 M NaBr with or without BA on Pt disk electrode.  $v = 0.1 \text{ V s}^{-1}$ .  $T = 25 \text{ }^\circ\text{C}$ . The presence of BA accounts for most of the  $E_{1/2}$  observed when changing solvent from water to miniemulsion. The lower current in the presence of BA could be due by adhesion of BA on the electrode surface, which lowers the active electrochemical area for the reduction of  $\text{Cu}^{\text{II}}\text{Br}/\text{L}$ .

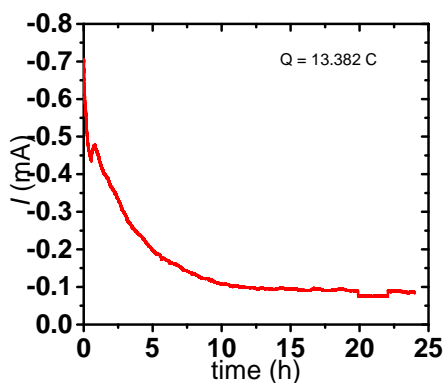


## Dynamic Light Scattering Before and After Miniemulsion *e*ATRP



**Figure S8.** Particle sizes of miniemulsion polymerization (A) before polymerization and (B) after polymerization (Table 4, entry 10, in main text). A monomodal trace was observed in each case.

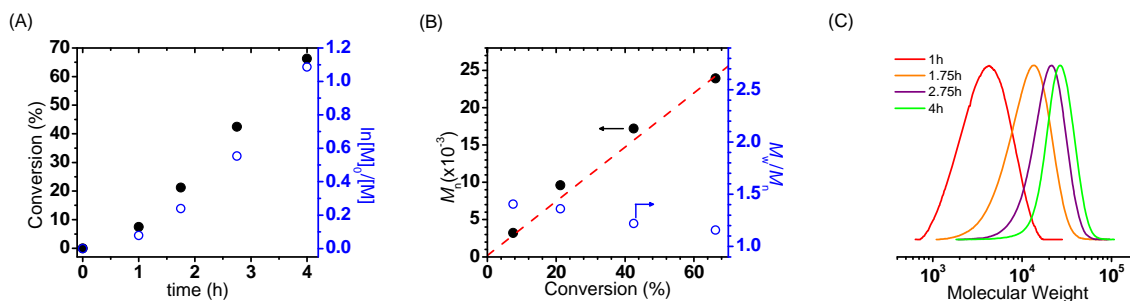
## Example of Chronoamperometry During Miniemulsion *e*ATRP



**Figure S9.** Chronoamperometry recorded during miniemulsion *e*ATRP with  $\text{CuBPMDEA}_{\text{aq}}/\text{CuBPMODA}_{\text{org}}$  as catalyst couple. The current profile showed that  $\text{Cu}^{\text{I}}/\text{L}_{\text{aq}}$  was produced at a high rate at the beginning of the polymerization, and then slowly regenerated with an approximate constant cathodic current.

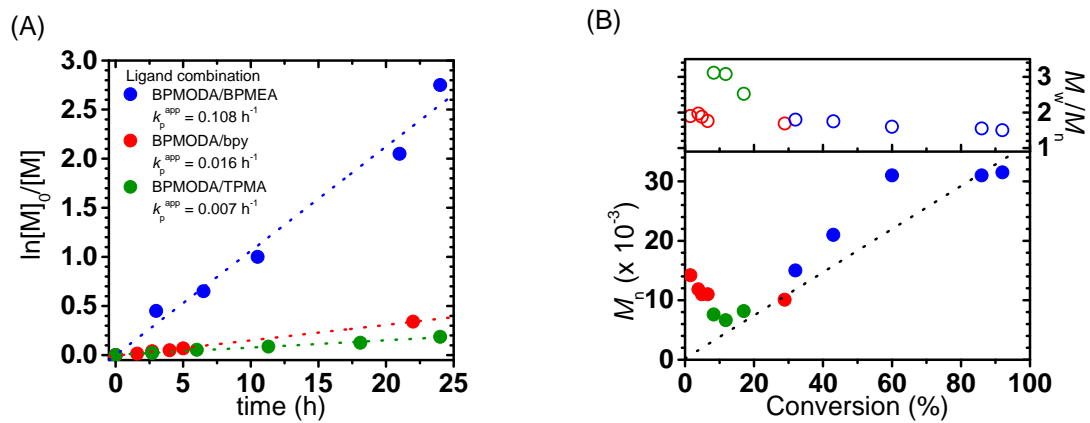
### Conventional *e*ATRP in Homogenous Solvent with CuBr<sub>2</sub>/BPMODA\* as Catalysts

Conventional *e*ATRP was carried out using CuBr<sub>2</sub>/BPMODA\* with HD to confirm catalytic activity of BPMODA\* and effect of HD on the polymerization. Target DP of polymers was 283, identical reaction conditions of the organic phase in the miniemulsion polymerization (Figure S10). The ratio for the polymerization was [BA]/[EBiB]/[CuBr<sub>2</sub>]/[BPMODA\*] = 283/1/0.3/0.3 and 5 wt% of HD was used at 60 °C under  $E_{app} = E_{pc} - 80$  mV. After 0.5h of induction time periods, linear first-order kinetic was observed. MW was linearly increased with increasing monomer conversion and low  $\bar{D}$  was observed ( $M_w/M_{n,final} = 1.16$ ). GPC trace of growing PBA showed clean peak shift from low MW to high MW without any shoulders. Although the polymerization mixture contained HD, no adverse effects were observed in conventional *e*ATRP.



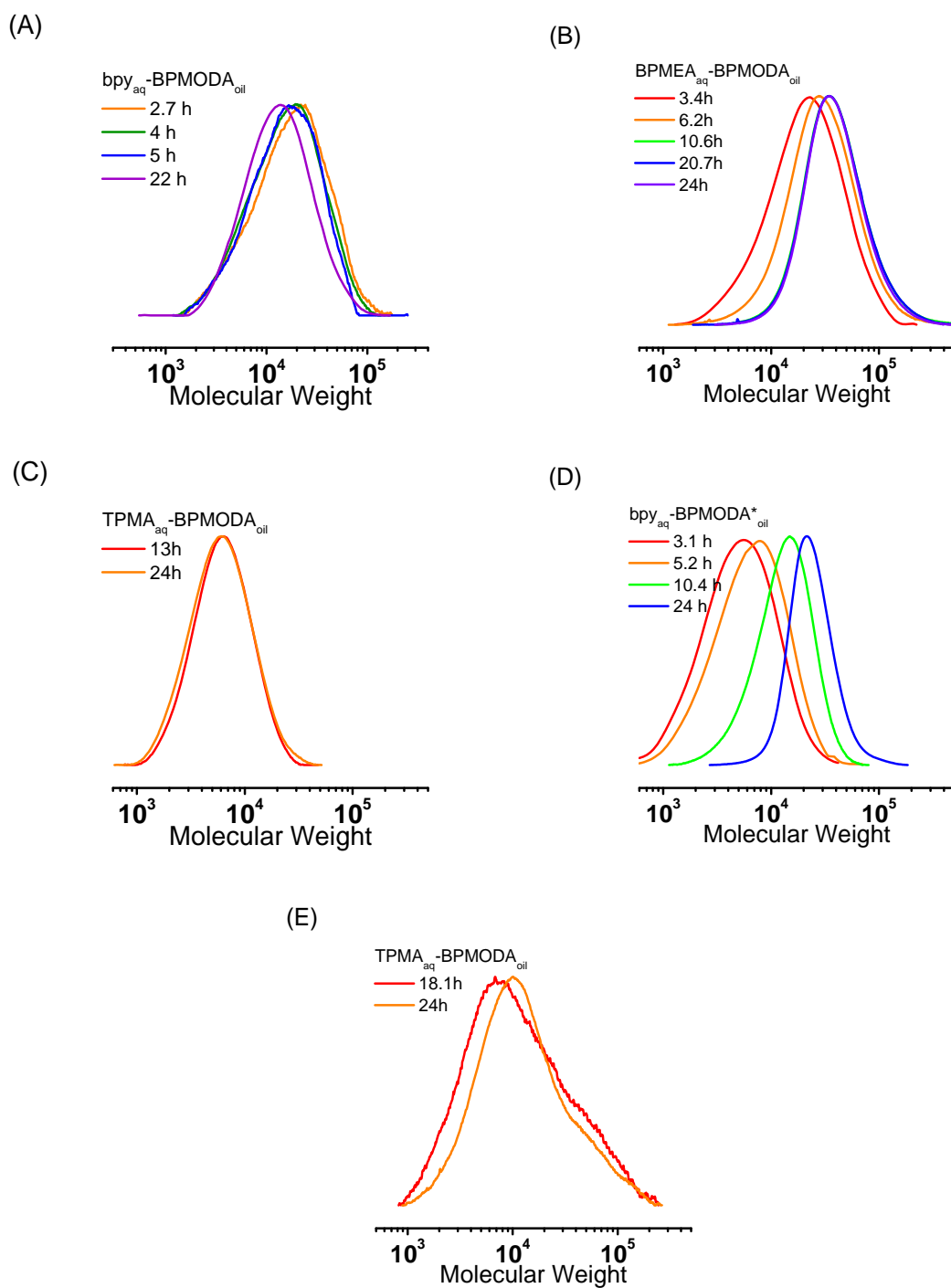
**Figure S10.** Conventional *e*ATRP of BA with CuBr<sub>2</sub>/BPMODA\*. (A) Monomer conversion vs. time, (B) MW and  $\bar{D}$  vs. monomer conversion, and (C) GPC trace. Reaction condition: [BA]/[EBiB]/[CuBr<sub>2</sub>]/[BPMODA\*] = 283/1/0.3/0.3; [BA]<sub>0</sub> = 4.19 M (in DMF); 5 wt% of HD (vs. wt of BA); [TBAClO<sub>4</sub>] = 0.2 M;  $E_{app} = E_{pc} - 80$  mV.

### Miniemulsion *e*ATRP with CuBr<sub>2</sub>/BPMODA<sub>org</sub>



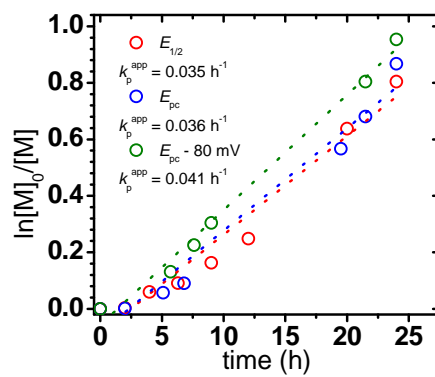
**Figure S11.** (A) Logarithmic kinetic plot and (B) MW and  $D$  evolution vs. monomer conversion for the miniemulsion *e*ATRP with  $\text{Cu}^{\text{II}}$ /BPMODA\*<sub>org</sub> and different aqueous phase catalysts.

## GPC Traces of Miniemulsion *e*ATRP with Dual Catalyst



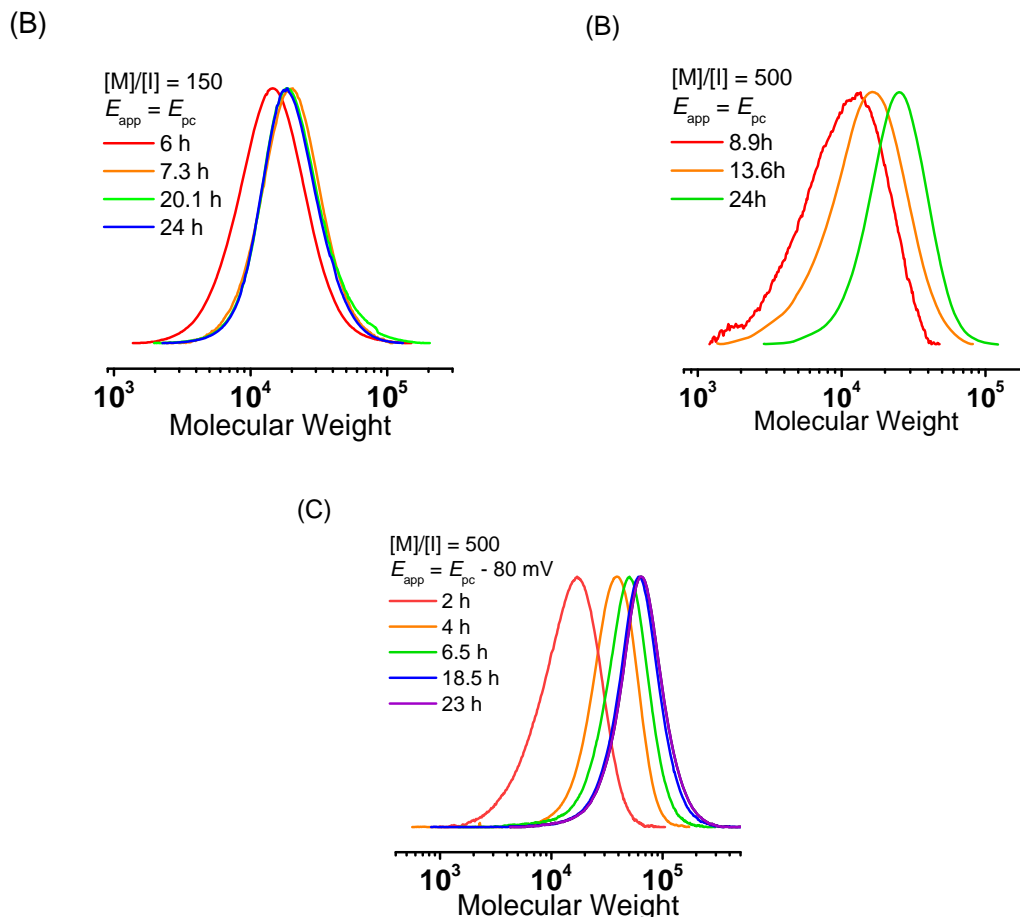
**Figure S12.** GPC traces for the dual catalyst experiments in [Table 4](#) entries 6-9 and 11 (main text).

### Kinetic Plot of Miniemulsion *e*ATRP with Different $E_{\text{app}}$ s



**Figure S13.** First-order kinetic plot of miniemulsion *e*ATRP with the dual catalyst CuBPMEA<sub>aq</sub>/CuBPMODA\*<sub>org</sub> at various  $E_{\text{app}}$ s.

## GPC Traces of Miniemulsion *e*ATRP with Different Target DP and $E_{app}$



**Figure S14.** GPC traces for the dual catalyst experiments in Table 5, entries 4-6 (main text).

## References

- (1) Xia, J.; Matyjaszewski, K. Controlled/"Living" Radical Polymerization. Atom Transfer Radical Polymerization Catalyzed by Copper(I) and Picolylamine Complexes. *Macromolecules* **1999**, *32*, 2434-2437.
- (2) Kickelbick, G.; Paik, H.-j.; Matyjaszewski, K. Immobilization of the Copper Catalyst in Atom Transfer Radical Polymerization. *Macromolecules* **1999**, *32*, 2941-2947.
- (3) Elsen, A. M.; Burdynska, J.; Park, S.; Matyjaszewski, K. Active Ligand for Low PPM Miniemulsion Atom Transfer Radical Polymerization. *Macromolecules* **2012**, *45*, 7356-7363.
- (4) Fantin, M.; Isse, A. A.; Gennaro, A.; Matyjaszewski, K. Understanding the Fundamentals of Aqueous ATRP and Defining Conditions for Better Control. *Macromolecules* **2015**, *48*, 6862-6875.
- (5) Rusling, J. F. Green synthesis via electrolysis in microemulsions. *Pure and applied chemistry* **2001**, *73*, 1895-1905.