

## Electronic Supporting Information:

### SARA ATRP or SET-LRP. End of controversy?

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## Experimental

### Materials.

All chemicals were purchased from commercial suppliers, *e.g.*, Aldrich, TCI, Alfa Aesar and used as received, unless otherwise stated. Tris(2-(dimethylamino)ethyl)amine (Me<sub>6</sub>TREN) was synthesized as reported in the literature.<sup>1</sup> Oligo(ethylene oxide) monomethyl ether acrylate of molecular weight 480 (OEOA) was passed over a column filled with basic alumina to remove inhibitor prior to use. Metallic copper (Cu<sup>0</sup>, diameter 1 mm) was washed with HCl in methanol and subsequently rinsed with methanol and dried under a stream of nitrogen following literature procedures.<sup>2</sup>

### Instrumentation.

**Ultraviolet-Visible-Near Infrared Spectroscopy (UV-Vis-NIR):** All characterizations were performed using an Agilent 8453 UV-Vis-NIR Spectrometer.

### Procedures.

#### Disproportionation experiment and activation experiment in OEOA/water for Photograph

Cu<sup>I</sup>Br (1.4 mg, 0.0098 mmol) was placed into a Schlenk flask, and the flask was sealed with a glass stopper. The flask containing Cu<sup>I</sup>Br was evacuated and backfilled with nitrogen 4 times. OEOA (1.08g, 2.25 mmol) was added to a second flask, which was sealed with a glass stopper and quickly evacuated in backfilled with nitrogen 4 times. Me<sub>6</sub>TREN (13.8 mg, 0.06 mmol) was added to the second flask, followed by deoxygenated water (5 mL). The mixture was homogenized by vigorous shaking. 5 mL of this 10 mM Me<sub>6</sub>TREN in OEOA/water solution was taken and added with vigorous shaking to the reaction flask containing Cu<sup>I</sup>Br. The reaction flask

was shaken gently for 20 min. Subsequently, 2-hydroxyethyl  $\alpha$ -bromoisobutyrate (HEBiB) (53 mg, 0.25 mmol) was added, the reaction mixture homogenized. The flask was then shaken for an additional 30 min.

### **Cu<sup>I</sup>Br activation experiment in OEOA/water for Photograph**

Cu<sup>I</sup>Br (1.4 mg, 0.0098 mmol) was placed into a Schlenk flask, and the flask was sealed with a glass stopper. The flask containing Cu<sup>I</sup>Br was evacuated and backfilled with nitrogen 4 times. OEOA (1.08g, 2.25 mmol) was added to a second flask, which was sealed with a glass stopper and quickly evacuated in backfilled with nitrogen 4 times. Me<sub>6</sub>TREN (13.8 mg, 0.06 mmol) was added to the second flask, followed by deoxygenated water (5 mL) and HEBiB (63 mg, 0.30 mmol). The mixture was homogenized by vigorous shaking. 5 mL of this 10 mM Me<sub>6</sub>TREN and 50 mM HEBiB in OEOA/water solution was taken and added with gentle shaking to the flask containing Cu<sup>I</sup>Br. The reaction flask was shaken continuously for 30 min.

**Synthesis of oligo(ethylene oxide) 2-bromopropionate:** Oligo(ethylene oxide) monomethyl ether with number-averaged molecular weight 550 (6.64 g, 0.012 mol) was added to a flask. To this flask, 150 mL of dichloromethane (DCM) and triethylamine (6.31 g, 0.062 mol) were added and the reagents were allowed to combine and cooled to 0 °C. Subsequently, 2-bromopropionyl bromide (11.02 g, 0.51 mol) was added and the reaction mixture was stirred at 0 °C for 1 h, followed by stirring at 22 °C for 24 h. The reaction mixture was washed 4 times with 100 mL of dilute hydrochloric acid, followed by 4 washes with a dilute sodium carbonate solution. The majority of the DCM was removed under reduced pressure, and the product was added drop wise to diethyl ether, followed by removal of the volatiles and dissolution of the product in a small amount dichloromethane. The product was precipitated into hexanes, and the viscous liquid collected and dried under reduced pressure to give oligo(ethylene oxide) monomethyl ether 2-bromopropionate (OEObRP) (7.23 g, 0.0105 mol, 88% yield). The purity was established to be greater than 96% by NMR.

### **Disproportionation of Cu<sup>I</sup>Br in water in the presence of Me<sub>6</sub>TREN.**

Cu<sup>I</sup>Br (2.8 mg, 0.020 mmol) was placed into a Schlenk flask equipped with a magnetic stirrer bar and a cuvette. The flask was evacuated and backfilled with nitrogen, and this process was repeated several times. To this flask 0.4 mL of deoxygenated H<sub>2</sub>O was added, followed by

Me<sub>6</sub>TREN (4.6 mg, 0.02 mmol). This reaction mixture was stirred for 20 min to allow full disproportionation of Cu<sup>I</sup> yielding Cu<sup>0</sup> particles and Cu<sup>II</sup>Br<sub>2</sub>/Me<sub>6</sub>TREN.

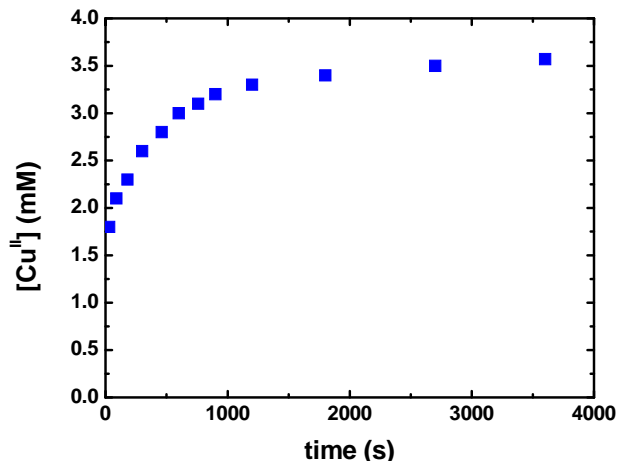
#### **Activation of OEObR<sub>P</sub> by Cu<sup>I</sup>Br in water in the presence of Me<sub>6</sub>TREN.**

To a Schlenk flask, OEObR<sub>P</sub> (74.9 mg, 0.11 mmol), OEObA (0.921 g, 1.9 mmol) were added. The flask was evacuated and backfilled with nitrogen several times. To this flask 4 mL of deoxygenated water and Me<sub>6</sub>TREN (22.5 mg, 0.098 mmol) were added. The resulting solution was bubbled with nitrogen for several minutes. 4.6 mL of the OEObA/OEObR<sub>P</sub>/Me<sub>6</sub>TREN aqueous solution was taken and added to the flask containing the Cu<sup>0</sup> and Cu<sup>II</sup>Br<sub>2</sub>/Me<sub>6</sub>TREN formed by disproportionation. The evolution of Cu<sup>II</sup> was monitored by UV-Vis-NIR spectroscopy.

## **Supporting Data and Information**

### **Measurement of Cu<sup>0</sup> surface area formed by disproportionation**

The surface area of the Cu<sup>0</sup> formed by disproportionation was determined by first disproportionating 50 mM Cu<sup>I</sup>Br with Me<sub>6</sub>TREN in 0.4 mL H<sub>2</sub>O. Subsequently, the suspension containing Cu<sup>II</sup> and Cu<sup>0</sup> was diluted to 5 mL and with 18 wt% OEObA in water and an excess of alkyl halide. By monitoring the increase in Cu<sup>II</sup>, an estimate of the surface area was obtained. However, it is important to note that in this system 20 mM of the alkyl halide OEObR<sub>P</sub> was used and only 2-4 mM of Cu<sup>II</sup> is present. Since the rate coefficients of alkyl halide activation by Cu<sup>0</sup> and comproportionation are comparable ( $k_{a0} = 1.0 \times 10^{-5} \text{ cm s}^{-1}$ , and  $k_{\text{comp}} = 2.4 \times 10^{-5} \text{ cm s}^{-1}$ ),<sup>3</sup> in this system the alkyl halide activation by Cu<sup>0</sup> will dominate by a factor of 4 to 1.5 as the reaction occurs. Therefore, especially in the earliest phase of the reaction, the evolution of Cu<sup>II</sup> can be used to determine the rate of alkyl halide activation. The raw evolution of Cu<sup>II</sup> can be seen in Figure S1.



**Figure S1.** Evolution of Cu<sup>II</sup> in the activation from Cu<sup>0</sup> powder with 20 mM OEObRP in 18 wt% OEOA in water. Conditions: Pre-disproportionation: [Cu<sup>I</sup>Br]<sub>0</sub> = 50 mM, [Me<sub>6</sub>TREN]<sub>0</sub> = 50 mM in 0.4 mL of H<sub>2</sub>O. Conditions activation, dilution of 0.4 mL with OEOA/OEObRP and H<sub>2</sub>O. Final conditions [Me<sub>6</sub>TREN]<sub>0</sub> = 20 mM, [OEObRP]<sub>0</sub> = 20 mM, [Cu<sup>II</sup>Br<sub>2</sub>/Me<sub>6</sub>TREN]<sub>0</sub> = 2 mM.

To extract the surface area of the Cu<sup>0</sup>, the system can be modeled as:

$$\frac{d[\text{Cu}^{\text{II}}]}{dt} = k_{a0} \frac{S}{V} [\text{OEObRP}] \quad (\text{S1})$$

Although the Cu<sup>II</sup> concentration is measured by UV-Vis-NIR spectrometry, it is easier to solve the problem in terms of the conversion of Cu<sup>0</sup> powder to Cu<sup>II</sup> in solution. In this case, by the stoichiometry of both disproportionation and activation by Cu<sup>0</sup>,

$$[\text{Cu}^{\text{II}}] = [\text{Cu}^{\text{II}}]_0 + [\text{Cu}^{\text{II}}]_0 \text{conv} \quad (\text{S2})$$

This is due to the essentially complete disproportionation in water, leading to half the initially added Cu forming Cu<sup>0</sup> and the other half forming Cu<sup>II</sup>. Therefore, as the Cu<sup>0</sup> activates alkyl halides the concentration of Cu<sup>II</sup> goes from [Cu<sup>II</sup>]<sub>0</sub>, which is the [Cu<sup>II</sup>] upon the addition of the alkyl halides, to 2 [Cu<sup>II</sup>]<sub>0</sub>

Assuming spherical symmetry as the “nascent” Cu<sup>0</sup> is consumed its surface area goes down as  $\text{conv}^{2/3}$  where  $\text{conv}$  again refers to the conversion of the Cu<sup>0</sup> particles to Cu<sup>II</sup>. Therefore this can be rewritten as

$$\frac{[\text{Cu}^{\text{II}}]_0 d\text{conv}}{dt} = k_{a0} \frac{S_0}{V} (\text{conv})^{2/3} [\text{OEObRP}] \quad (\text{S3})$$

Although OEObRP is in a significant molar excess over Cu<sup>0</sup>, there is still a depletion of OEObRP over the reaction. In fact since one activation by Cu<sup>0</sup> removes two alkyl halides, since the

generated  $\text{Cu}^{\text{I}}$  will also activate an alkyl halide. The stoichiometry of the reaction dictates that the OEOPBrP concentration is given by:

$$[\text{OEOPBrP}] = [\text{OEOPBrP}]_0 \left(1 - \frac{4}{5} \text{conv}\right) \quad (\text{S4})$$

This gives the following separable differential equation:

$$\frac{[\text{Cu}^{\text{II}}]_0 d\text{conv}}{dt} = k_{a0} \frac{S_0}{V} [\text{OEOPBrP}]_0 (\text{conv})^{2/3} \left(1 - \frac{4}{5} \text{conv}\right) \quad (\text{S5})$$

Finally, this gives the following solution,

$$g(\text{conv}) = k_{a0} \frac{S_0 [\text{OEOPBrP}]_0}{V [\text{Cu}^{\text{II}}]_0} t \quad (\text{S6})$$

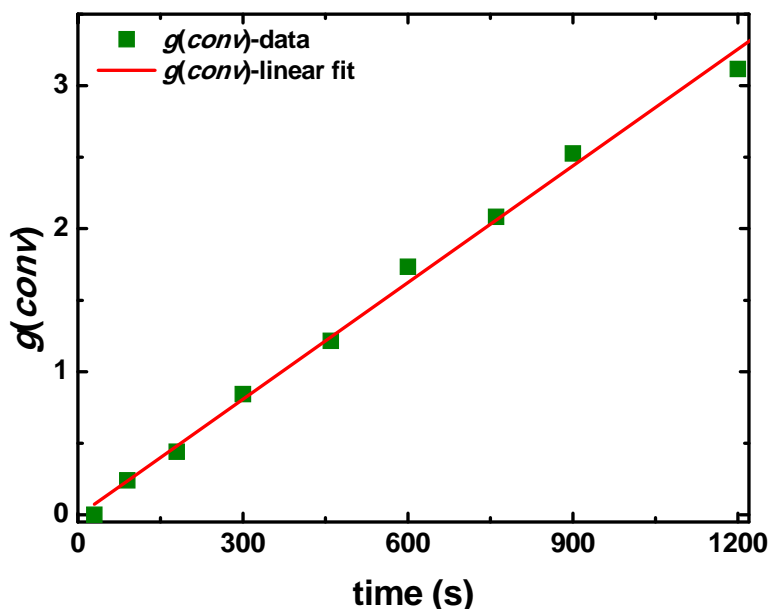
where,

$$g(\text{conv}) = \int_0^{\text{conv}} \frac{dc}{(c)^{2/3} \left(1 - \frac{4}{5} c\right)} \quad (\text{S7})$$

Therefore, plotting  $g(\text{conv})$  against time should be linear with slope:

$$\text{slope} = k_{a0} \frac{S_0 [\text{OEOPBrP}]_0}{V [\text{Cu}^{\text{II}}]_0} \quad (\text{S8})$$

As can be seen in Figure S2, the plot of  $g(\text{conv})$  against time is indeed linear, up to rather high conversion of  $\text{Cu}^0$  to  $\text{Cu}^{\text{II}}$ . The slope of the plot of  $g(\text{conv})$  against time is  $\text{slope} = 2.7 \times 10^{-3} \text{ s}^{-1}$ . Substituting the known  $k_{a0} = 1.0 \times 10^{-5} \text{ cm s}^{-1}$ ,  $V = 5 \text{ cm}^3$ , and  $[\text{OEOPBrP}]_0/[\text{Cu}^{\text{II}}]_0 = 10$ , gives  $S_0 = 130 \text{ cm}^2$ . This surface area was for 2.8 mg of  $\text{Cu}^{\text{I}}\text{Br}$  that underwent disproportionation. By mass balance, complete disproportionation of 2.8 mg of  $\text{Cu}^{\text{I}}\text{Br}$  gives 0.64 mg of  $\text{Cu}^0$ , since only half of the Cu forms  $\text{Cu}^0$ . Therefore, a surface area of  $130 \text{ cm}^2$  for 0.64 mg  $\text{Cu}^0$  gives a specific surface area of approximately  $20 \text{ m}^2/\text{g}$  of  $\text{Cu}^0$ . This calculation also implies that the surface area generated by disproportionation is  $46 \text{ cm}^2$  for every 1 mg of  $\text{Cu}^{\text{I}}\text{Br}$  disproportionated.



**Figure S2.** Plot of  $g(conv)$  vs. time, as well as a linear fit to the  $g(conv)$  data. The function fitted to the data is  $g(conv) = 2.7 \times 10^{-3} t - 8.3 \times 10^{-3}$ .

## Simulations

All simulations were performed using the PREDICI® program (version 6.3.2) using the methods previously described in the literature.<sup>3,4</sup> In both models R-X and R• represent small molecule initiators and radicals, while P<sub>n</sub>-X and P<sub>n</sub>• represent polymeric dormant chains and radicals, respectively. For heterogeneous reactions, for convenience, overall rate coefficients, defined as  $k^{\text{over}} = k^{\text{app}} \times S/V$  were used, as outlined in earlier work.<sup>4</sup> In aqueous system model, dissociation of halide from Cu<sup>II</sup>X/L and Cu<sup>I</sup>X/L complexes is taken into account. The importance of this reaction in aqueous media has been shown in previous work.<sup>3</sup>

Simulations of lifting experiments were performed with assumption that the surface area of Cu<sup>0</sup> remaining in the reaction mixture after removal of wire is approximately 1% of the original surface area of the wire, based on the 10 fold polymerization rate reduction. Therefore, the rates of comproportionation, disproportionation, activation by Cu<sup>0</sup>, and deactivation by Cu<sup>I</sup> were 100 times slower when the wire was lifted out of the solution.

Typical polymerization model in DMSO solvent, including Cu<sup>I</sup> and Cu<sup>0</sup> induced radical loss, employed for lifting experiments is presented in the scheme S1. Rate coefficients used in the model experiments are presented in table S1.

Scheme S1. Kinetic model for RDRP in DMSO in the presence of Cu<sup>0</sup> used in simulations

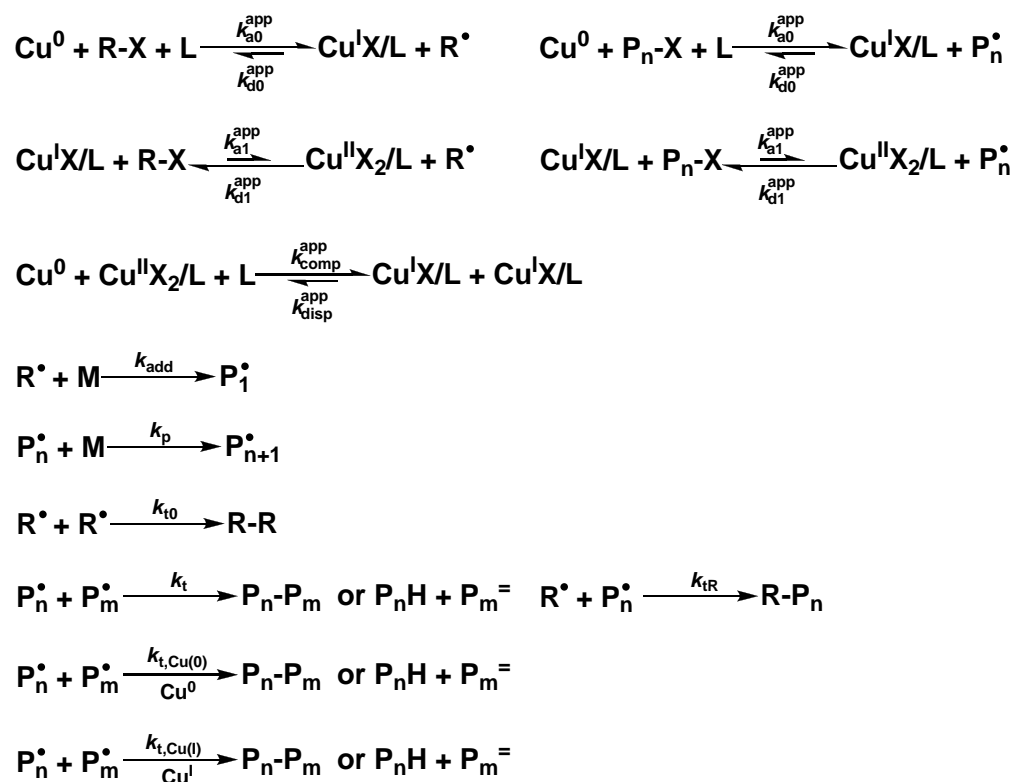


Table S1. Rate coefficients for RDRP in DMSO in the presence of Cu<sup>0</sup>

Rate coefficient <sup>a</sup>	$k$ or $k^{\text{app}}$	Reference
$k_{\text{a}0}$	$1.0 \times 10^{-4} \text{ cm s}^{-1}$	5
$k_{\text{d}0}$	$1.2 \times 10^{-1} \text{ cm s}^{-1}$	4
$k_{\text{comp}}$	$3.5 \times 10^{-3} \text{ cm s}^{-1}$	2
$k_{\text{disp}}$	$3.1 \times 10^{-6} \text{ cm s}^{-1}$	2
$k_{\text{a}1}$	$2.0 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$	4
$k_{\text{d}1}$	$2.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	4, 6
$k_{\text{p}}$	$15600 \text{ M}^{-1} \text{ s}^{-1}$	7
$k_{\text{add}}$	$5.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	8

$k_t^{b,c}$	$1.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	9
$k_{t,\text{Cu}(0)}^{b,c}$	$1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	4
$k_{t,\text{Cu}(I)}^{b,c}$	$4.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	10
$k_{tR}^d$	$1.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	7, 9
$k_{t0}$	$2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	11

<sup>a</sup> L = Me<sub>6</sub>TREN, X = Br, R-X = MBrP, reaction medium is MA/DMSO = 2/1 (v/v);

<sup>b</sup> During the presence of Cu<sup>0</sup> wire in the reaction mixture  $k_{t,\text{Cu}(0)}$  was used. While Cu<sup>0</sup> was lifted, the effect of remaining Cu<sup>0</sup> on termination was  $k_t$  and  $k_{t,\text{Cu}(I)}$  were used.

<sup>c</sup>  $k_t = k_{tc} + k_{td}$ , where  $k_{tc}$  and  $k_{td}$  are combination and disproportionation termination rate coefficients respectively. It was assumed, that conventional termination occurs exclusively by combination of macroradicals, while Cu<sup>0</sup> induced termination occurs by disproportionation

<sup>d</sup> It was also assumed that  $k_{tR} \approx k_t$ .

Simulations of pre-disproportionation experiments were performed starting after pre-disproportionation stage, when monomer and initiator mixture is injected into pre-disproportionated mixture. Surface area of Cu<sup>0</sup> generated via disproportionation was calculated based on conducted pre-disproportionation experiment, where Cu<sup>I</sup>/Me<sub>6</sub>TREN is allowed to fully disproportionate, followed by activation of generated Cu<sup>0</sup> by alkyl halide, for which activation rate constant is known, and measuring Cu<sup>II</sup> concentration spectrophotometrically as highlighted in Figure S1-S2.

Typical polymerization model in H<sub>2</sub>O, employed for pre-disproportionation experiments is presented in the scheme S2. Rate coefficients used in the model experiments are presented in table S2. For convenience, overall rate coefficients, defined as  $k^{\text{over}} = k^{\text{app}} \times S/V$  were used, as outlined in earlier work.<sup>4</sup> Values of disproportionation and comproportionation rate constants are based on the overall rate coefficients determined experimentally rather than on specific speciation.



Scheme S2. Kinetic model for RDRP in H<sub>2</sub>O in the presence of Cu<sup>0</sup> used in simulations

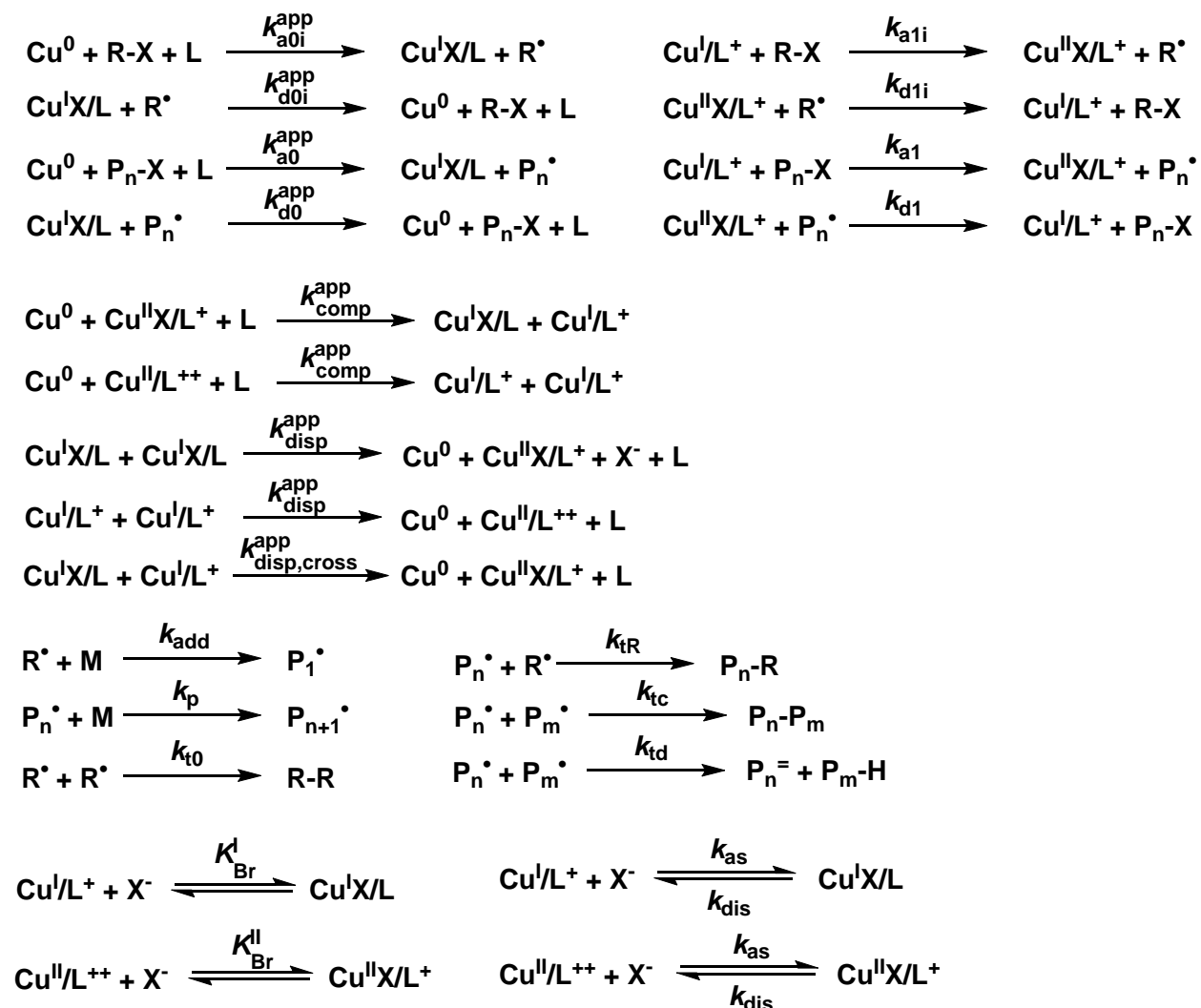


Table S2. Rate coefficients for RDRP in H<sub>2</sub>O in the presence of Cu<sup>0</sup>

Rate coefficient <sup>a</sup>	$k$ or $k^{\text{app}}$	Reference
$k_{a0}$	$5 \times 10^{-6} \text{ cm s}^{-1}$	3
$k_{a0i}$	$5.6 \times 10^{-5} \text{ cm s}^{-1}$	3
$k_{d0}$	$8 \times 10^{-2} \text{ cm s}^{-1}$	3
$k_{d0i}$	$8 \times 10^{-3} \text{ cm s}^{-1}$	3
$k_{\text{comp}}$	$2.4 \times 10^{-5} \text{ cm s}^{-1}$	3
$k_{\text{disp}}$	$5 \times 10^{-4} \text{ cm s}^{-1}$	3

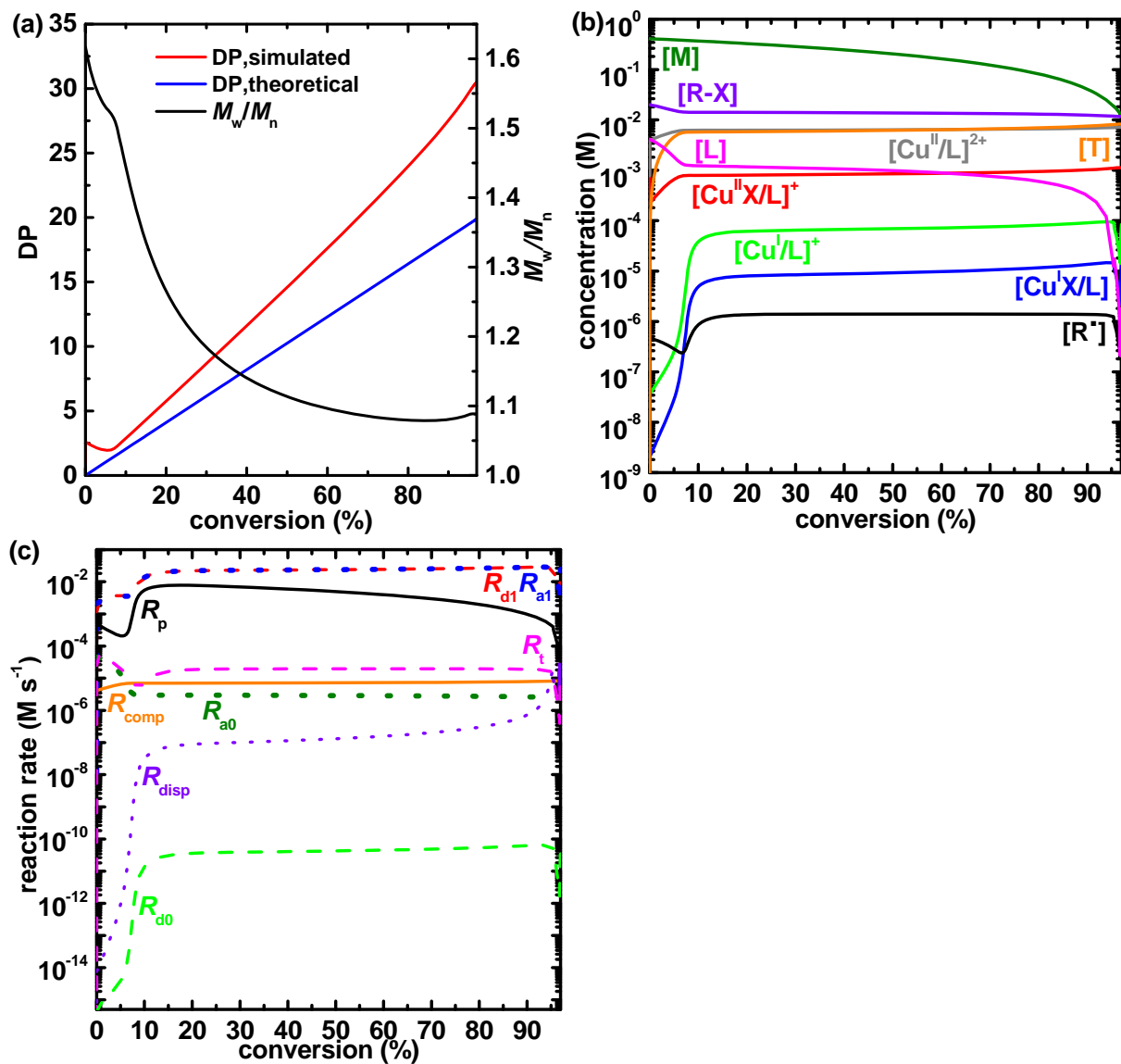
$k_{\text{disp,cross}}$	$10^{-3} \text{ cm s}^{-1}$	3
$k_{\text{al}}$	$2.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	3
$k_{\text{ali}}$	$2.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	3
$k_{\text{dl}}$	$2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	3
$k_{\text{dli}}$	$2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	3
$k_{\text{p}}^b$	$1.73 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	12
$k_{\text{add}}$	$1.1 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$	8
$k_{\text{tc}}^b$	$1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	9
$k_{\text{td}}$	$0 \text{ M}^{-1} \text{ s}^{-1}$	13
$k_{\text{tR}}$	$5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	3
$k_{\text{t0}}$	$2.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	3
$k_{\text{as}}$	$1.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	this work
$k_{\text{dis}}$	$1.0 \times 10^4 \text{ s}^{-1}$	this work
Equilibrium const.	$K$	Reference
$K_{\text{Br}}^{\text{I}}$	$14 \text{ M}^{-1}$	3
$K_{\text{Br}}^{\text{II}}$	$14 \text{ M}^{-1}$	3

<sup>a</sup> L = Me<sub>6</sub>TREN, X = Br, R-X = HEBiB, reaction medium is 18 wt% OEOA in H<sub>2</sub>O.

<sup>b</sup> Value for Dodecyl Acrylate

### Halide association/dissociation dynamics

In order to evaluate the effect of dynamics of halide association/dissociation on the polymerization a series of simulations were performed under following conditions: OEOA/H<sub>2</sub>O = 18/82 (wt/wt), [OEOA]<sub>0</sub>:[HEBiB]<sub>0</sub>:[Cu<sup>II</sup>Br<sub>2</sub>]<sub>0</sub>:[Me<sub>6</sub>TREN]<sub>0</sub> = 100:1:0.01:0.2, [OEOA]<sub>0</sub> = 0.41 M, 10 cm of Cu<sup>0</sup> wire ( $d = 1 \text{ mm}$ ) in  $V = 6 \text{ mL}$  with 0 mM or 30 mM of NaBr added at 22 °C. The simulations were based on the model outlined in Scheme S2 and Table S2, with variable halide association and dissociation rate constants, while maintaining  $K_{\text{Br}}^{\text{II}} = 14 \text{ M}^{-1}$ . The outcome of polymerizations (Fig. S3 a, b, c) does not change if dynamics of halide association/dissociation is sufficiently fast and thus appropriate values of  $k_{\text{as}} = 1.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{\text{dis}} = 1.0 \times 10^4 \text{ s}^{-1}$  were used in simulations. Identical plots were obtained using larger values of  $k_{\text{as}}$  and  $k_{\text{dis}}$ .



**Figure S3.** Simulation of OEOA polymerization under the conditions:  $[OEOA]_0:[HEBiB]_0:[Cu^{II}Br_2]_0:[Me_6TREN]_0 = 20:1:0.2:0.4$ , 18 wt% OEOA in H<sub>2</sub>O.  $V = 6$  mL,  $S = 250$  cm<sup>2</sup>, ca. 10000 ppm Cu<sup>II</sup> at the beginning. (a) gives the DP and  $M_w/M_n$ , (b) gives the concentrations of all species in solution and (c) gives the rates of reaction.

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