

Photoinduced Atom Transfer Radical Polymerization with ppm-Level Cu Catalyst by Visible Light in Aqueous Media

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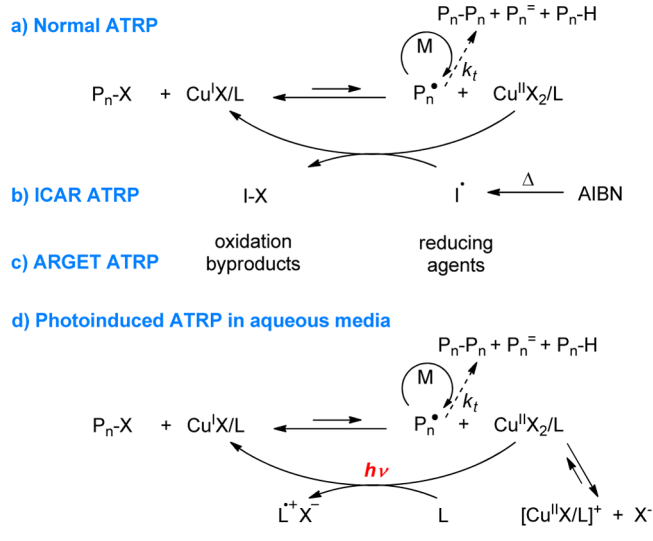
S Supporting Information

ABSTRACT: Photoinduced ATRP was successfully performed in aqueous media. Polymerization of oligo-(ethylene oxide) methyl ether methacrylate (OEOMA) in the presence of CuBr₂ catalyst and tris(2-pyridylmethyl)-amine ligand when irradiated with visible light of 392 nm wavelength at 0.9 mW/cm² intensity was well controlled. Linear semi-logarithmic kinetic plots and molecular weights increasing with conversion were observed. Polymers of OEOMA were synthesized with low dispersity ($M_w/M_n = 1.12$) using only 22 ppm of copper catalyst in the presence of excess bromide anions in highly diluted (90% v/v) aqueous media. The effects of copper concentration, salt, and targeted degrees of polymerization were investigated. The polymerization could be directly regulated by external stimulation, i.e., switching the irradiation on/off, with a good retention of chain-end functionality, as proved by clean chain extension of the OEOMA polymers. This new system could enable applications for controlled aqueous radical polymerization due to its low catalyst loading in the absence of any other chemicals.

Reversible deactivation radical polymerization (RDRP) procedures are versatile polymerization methods, allowing the synthesis of polymers with precisely controlled architecture, narrow molecular weight distribution, and highly retained chain-end functionalities.^{1,2} Atom transfer radical polymerization (ATRP),³ nitroxide-mediated polymerization (NMP),⁴ and reversible addition–fragmentation chain-transfer polymerization (RAFT)⁵ are the most widely used RDRP techniques. ATRP is governed by a transition-metal-catalyzed activation and deactivation equilibrium. The transition metal in the lower oxidation state activates alkyl halides by halogen transfer to form radicals. These radicals initiate and propagate the polymerization before being deactivated by the higher oxidation state catalyst complex.

Traditional ATRP systems required high catalyst concentration to maintain the activity throughout the polymerization (Scheme 1a).⁶ Recently, ATRP using ppm-level Cu catalysts was developed by continuously regenerating the activators through reduction of the higher oxidation state deactivator complexes (Scheme 1b,c). These techniques include initiators for continuous activator regeneration (ICAR) ATRP,⁷ activators regenerated by electron-transfer (ARGET) ATRP,⁸ supplemental activators and reducing agent (SARA) ATRP,⁹

Scheme 1. Illustration of ATRP Equilibria



also called SET-LRP,¹⁰ electrochemically mediated ATRP (eATRP),¹¹ and photoinduced ATRP.¹² Other photoinduced RDRP methods, including photoinduced electron transfer (PET)-RAFT,¹³ cobalt-mediated radical polymerization (CMRP),¹⁴ and organoiodine-mediated radical polymerization (IRP),¹⁵ have been recently developed.¹⁶

Environmentally friendly solvents including supercritical carbon dioxide,¹⁷ ionic liquids,¹⁸ and water¹⁹ are desirable to replace volatile and potentially hazardous organic solvents in ATRP systems. Aqueous systems provide better thermal control and higher rate of polymerization; however, a few challenges are still associated with homogeneous aqueous ATRP. The large ATRP equilibrium constant can result in a high radical concentration,^{19e,20} and partial dissociation of halide ion from deactivator complex can lead to inefficient deactivation and Cu^I disproportionation (Scheme 1d). Hydrolysis of the carbon–halogen bond results in loss of chain-end functionalities.²¹ All of these side reactions lead to formation of dead chains and broad molecular weight distribution. In order to overcome these barriers, high concentrations of Cu were used.^{19a,b,21,22}

Recently, our group reported low ppm-level Cu-based ATRP for ICAR,^{19c} ARGET,^{19d} and SARA ATRP²³ in aqueous media

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Table 1. Results of Photoinduced Aqueous ATRP of OEOMA₅₀₀ with Different Cu Concentrations^a

entry	conditions ([M] ₀ /[I] ₀ /[Cu] ₀ /[L] ₀)	Cu concn (ppm)	time (h)	convrsn (%) ^b	M _{n,th} ^c	M _{n,GPC} ^d	M _w /M _n ^d
1	450/1/9/36	20000	4	60	137000	97000	1.07
2	450/1/3/12	6600	6	54	123500	101000	1.20
3	450/1/1/4	2200	6	69	157250	125000	1.26
4	450/1/0.1/0.4	220	4	94	213000	142000	1.26
5	450/1/0.1/0.4 with 5 mM NaBr	220	4	78	177000	114000	1.11
6	450/1/0.1/0.4 with 5 mM NaCl	220	6	44	101000	16000	4.05
7	450/1/0.05/0.2	110	3	70	160000	230000	1.56
8	450/1/0.01/0.04	22	3	80	182000	322000	1.96
9	450/1/0.01/0.04 with 5 mM NaBr	22	4	85	193000	213000	1.25
10	450/1/0.01/0.04 with 30 mM NaBr	22	4	55	126000	103000	1.17

^aReaction conditions: [OEOMA₅₀₀]₀/[PEO₂₀₀₀BPA]₀/[CuBr₂]₀/[TPMA]₀ = 450/1/x/4x in 90% (v/v) water with irradiation by 392 nm at 0.9 mW/cm² at room temperature. ^bConversion determined by ¹H NMR. ^cCalculated on the basis of conversion (i.e., M_{n,th} = M_{PEOBPA} + [OEOMA₅₀₀]₀/[PEO₂₀₀₀BPA]₀ × conversion × M_{monomer}). ^dDetermined by GPC in THF, based on linear PMMA as calibration standard.

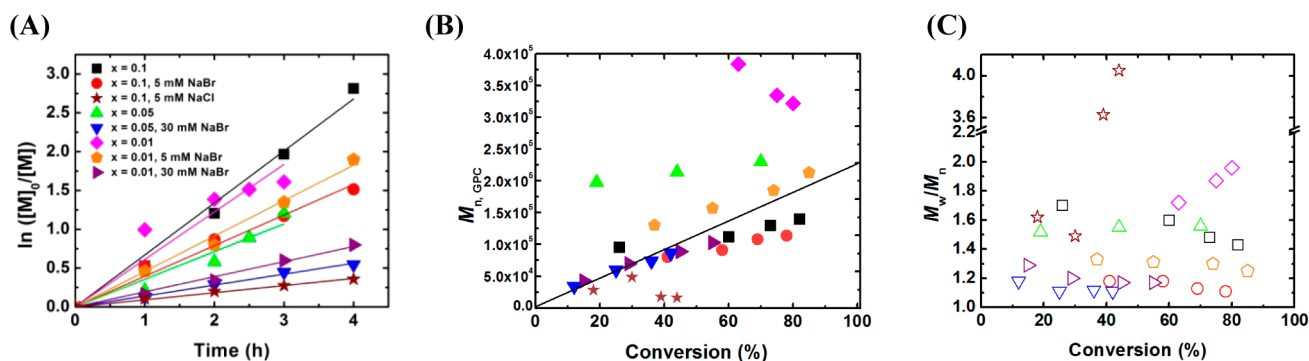


Figure 1. Effect of salt concentration in photoinduced ATRP of OEOMA₅₀₀ in water with ppm of Cu catalyst. (A) Semi-logarithmic kinetic plots. Evolution of (B) number-average molecular weight (M_n , filled symbols) and (C) molecular weight distribution (M_w/M_n , open symbols) with conversion under the following conditions: [OEOMA₅₀₀]₀/[PEO₂₀₀₀BPA]₀/[CuBr₂]₀/[TPMA]₀ = 450/1/x/4x in 90% water with 392 nm at 0.9 mW/cm² irradiation at room temperature.

with efficient control over the polymerization rate and narrow molecular weight distributions. However, ICAR, ARGET, and SARA ATRP introduce new reactants, i.e., conventional radical initiators, reducing agents, and transition-metal salts, to the system which could limit the range of applications for the products. Also, Haddleton previously reported that photoATRP of acrylate in aqueous solution presented poor control.¹²ⁱ Herein, photoATRP was extended to aqueous media using low ppm levels of Cu/tris(2-pyridylmethyl)amine (TPMA) catalyst to provide well-controlled polymerizations. This system features low catalyst concentrations, as low as 22 ppm molar with respect to monomer, under benign conditions, i.e., irradiation with visible light at room temperature in aqueous media, so they can be widely adapted to biological applications.

Photoinduced ATRP in water was first attempted for the polymerization of oligo(ethylene oxide) methyl ether methacrylate (OEOMA, $M_n = 500$) using poly(ethylene oxide)-bromophenylacetate (PEO₂₀₀₀-BPA) as a macroinitiator under visible light irradiation (392 nm at 0.9 mW/cm²). TPMA was used as a ligand since it forms a stable Cu^I complex without any significant disproportionation in water, and it could efficiently reduce air-stable Cu(II) deactivator to Cu(I) activator under photochemical conditions.^{12b} The effect of Cu concentration

was investigated, and results are summarized in Figure S1 and Table 1. Polymerizations at high concentration Cu (20 000 ppm vs monomer) gave a linear semi-logarithmic kinetic plot versus conversion. Excellent control over the reaction was obtained. The experimental molecular weights were in good agreement with the theoretical values with dispersities as low as 1.07 (entry 1, Table 1). The UV-vis spectra showed that the system absorbed in the near-UV and visible light range (Figure S2), which confirmed a photoinduced ATRP mechanism. The possibility of photochemical cleavage of C-Br bond could not be excluded;^{12o} however, compared to photoreduction of Cu(II) by ligands, it had limited contribution to radical generation (only major photoactivation pathway are shown in Scheme 1d).^{12a}

Photoinduced ATRP with 6600, 2200, and 220 ppm of Cu ($x = 3, 1,$ and $0.1,$ respectively) still provided well-defined polymers ($M_w/M_n = 1.20$ – 1.26 , entries 2–4, Table 1). The reaction with lower loadings of Cu catalyst, 110 and 22 ppm, gave polymers with much higher M_n compared to theoretical M_n as well as broad distribution ($M_w/M_n = 1.56$ and 1.96 , entries 7 and 8, Table 1, respectively). It is worth noting that the molecular weight decreased with increasing conversion when only 22 ppm of Cu catalyst was used, indicating a poorly

controlled polymerization. This could be attributed to the low deactivator concentration resulting from dissociation of the halogen atom from the $\text{CuBr}_2/\text{TPMA}$ complex, which is one of the major challenges associated with aqueous ATRP, especially with low Cu concentration.^{19c,d} However, the addition of excess of halide salt shifts the equilibrium toward deactivator complex $\text{Br}-\text{Cu}^{\text{II}}\text{Br}/\text{TPMA}$, promoting efficient deactivation (Scheme 1d).^{19c,d}

Therefore, photoinduced aqueous ATRP was investigated at low Cu concentration in the presence of added halide salts. The results are summarized in Table 1 and Figure 1. The rate of polymerization decreased with addition of 5 mM NaBr and control over the molecular weight and dispersity improved (entries 4 and 8 vs 5 and 9, Table 1). The photoinduced ATRP reaction using 22 ppm of Cu catalyst with 30 mM salt gave the best result, reaching 55% conversion after 4 h forming a polymer with $M_n = 103\,000$ and $M_w/M_n = 1.17$ (entry 10, Table 1). It is interesting to note that such a high molecular weight could be obtained and still with a narrow molecular weight distribution. A similar reaction using 220 ppm of Cu catalyst with 5 mM NaCl gave polymer with a bimodal distribution ($M_n = 16\,000$, $M_w/M_n = 4.05$, entry 6, Table 1), indicating a poor control in the presence of chloride anions and alkyl bromide initiators.

Table 2 and Figure S3 summarize the results of photoinduced ATRP in water targeting different DP_T of OEOMA₅₀₀

Table 2. Results for Photoinduced ATRP of OEOMA with Various DP_T in Aqueous Media^a

entry	DP_T	time (h)	convrsn (%) ^b	$M_{n,\text{th}}$ ^c	$M_{n,\text{GPC}}$ ^d	M_w/M_n ^d
1	450	4	78	177000	114000	1.11
2	250	4	70	90000	79200	1.21 ^f
3	200	4	59	61000	56300	1.16 ^f
4	100	4	39	21500	17500	1.16 ^f
5	450 ^e	4	61	84000	84800 ^f	1.18
6	200 ^e	4	47	30000	31900 ^f	1.10
7	100 ^e	4	40	14000	17100 ^f	1.10

^aReaction conditions: $[\text{OEOMA}_{500}]_0/[\text{PEO}_{2000}\text{BPA}]_0/[\text{CuBr}_2]_0/[\text{TPMA}]_0 = \text{DP}_T/1/0.1/0.4$ in 90% water with 5 mM NaBr at room temperature with irradiation by 392 nm at 0.9 mW/cm². ^bConversion determined by ¹H NMR. ^cCalculated on the basis of conversion (i.e., $M_{n,\text{th}} = M_{\text{PEOBPA}} + \text{DP} \times \text{conversion} \times M_{\text{monomer}}$). ^dDetermined by GPC in THF, based on linear PMMA as calibration standard. ^eOEOMA₃₀₀ as monomer. ^fDetermined by GPC in water, based on linear PEG as calibration standard.

and OEOMA₃₀₀. The monomer concentration was kept constant in all the experiments, while the concentrations of initiator, Cu, and ligand were varied with respect to the target DP. Polymerization of OEOMA₅₀₀ with targeted $\text{DP}_T = 250$ reached 70% conversion after 4 h of irradiation and provided a polymer with $M_n = 79\,200$ and $M_w/M_n = 1.21$ (entry 2, Table 2). The polymerization was slightly slower than under the previous conditions targeting a $\text{DP}_T = 450$, due to a higher concentration of CuBr_2 . With lower DP_T targeted, the conversion reached 59% and 39% for $\text{DP}_T = 200$ and 100 after 4 h, respectively (entries 3 and 4, Table 2). Similarly, ATRP of OEOMA₃₀₀ with different targeted $\text{DP}_T = 450$, 200, and 100 provided all well-defined polymers with predictable M_n and narrow M_w/M_n values ranging from 1.10 to 1.18 (entries 5–7, Table 2).

Irradiation was required for the initiation and regeneration of soluble Cu^{I} in photoinduced ATRP reactions. The major advantage of these systems is the feasibility of stopping or restarting the reaction at any time by simple turning the light off or on. The experiment with on/off light switching cycles showed almost no conversion after removal of the light source and a clear continuation of the reaction after re-exposure to the light (Figure 2A). The slight increase in conversion between 3 and 4 h can be attributed to some residual amount of Cu^{I} present in the system. Additionally, efficient control was achieved with low dispersities and molecular weight agreeing well with the theoretical values (Figure 2B).

To confirm the utility of this photoinduced ATRP in aqueous media, chain extension of the homopolymer of OEOMA₅₀₀ was conducted with OEOMA₃₀₀. The polymerization was carried out under typical conditions and provided the block copolymer with $M_n = 115\,000$ and $M_w/M_n = 1.13$ (cf. Supporting Information). After 1 h of irradiation, the extension of polymer with OEOMA₃₀₀ reached 12% conversion, giving P(OEOMA₅₀₀)-*b*-P(OEOMA₃₀₀) $M_n = 139\,000$ and $M_w/M_n = 1.22$.

In summary, aqueous photoinduced ATRP was successfully performed under irradiation at 0.9 mW/cm² with 392 nm visible light. The effect of catalyst concentration was investigated by reducing the Cu loading from 20 000 to 22 ppm. The reaction was not well controlled with 220 ppm or less Cu catalyst without excess halides due to the instability of the deactivator in aqueous media. The addition of 5 or 30 mM NaBr overcame this problem, and excellent control over molecular weight and dispersity was attained using only 22 ppm

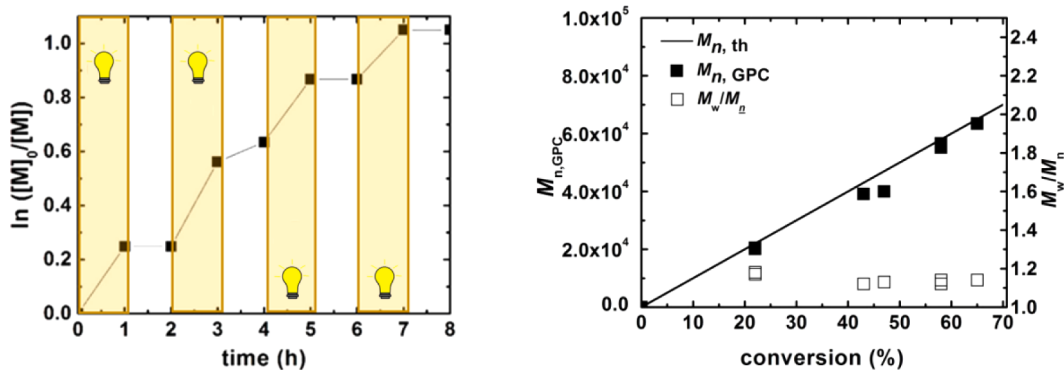


Figure 2. (A, left) Semi-logarithmic kinetic plots for on/off polymerization under conditions $[\text{OEOMA}]_0/[\text{PEOBPA}]_0/[\text{CuBr}_2]_0/[\text{TPMA}]_0 = 200/1/0.1/0.4$ with 5 mM NaBr in 90% water under 392 nm irradiation (0.9 mW/cm²). (B, right) Evolution of number-average molecular weight (M_n , filled symbols) and molecular weight distribution (M_w/M_n , open symbols) with conversion.

of Cu catalyst in the reaction medium. The development of a process using low concentrations of catalyst in aqueous media with irradiation by visible light at room temperature makes this a procedure valuable for wide range of applications.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b11599.

Experimental procedures for preparation and characterization of all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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