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Iodine-Mediated PhotoATRP in Aqueous Media with Oxygen Tolerance

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Water is an environmentally friendly medium for conducting reversible deactivation radical polymerizations. In this paper, we report the investigation of iodine-mediated photocontrolled atom transfer radical polymerization (photoATRP) in aqueous media. The iodine-based initiator was generated by an *in situ* halogen exchange from a commercially available bromine-based initiator, ethyl α -bromophenylacetate, using different iodide salts. Fast and well-controlled polymerization of a water-soluble methacrylate monomer was achieved in water under visible light irradiation, including blue, green and yellow lights. The nature of the reaction medium greatly affected the kinetics and control over the growth of polymers. Polymerizations in water resulted in a well-controlled reaction that provided high monomer conversion and polymers with low dispersities, whereas control over the polymerization was poor in bulk or in an organic solvent, *N,N*-dimethylformamide. Polymerizations were performed over a wide range of visible light in the absence of any photocatalyst. The selection of water as a reaction medium enabled use of iodide salts without the need for solubilizing agents. Moreover, iodine-mediated photoATRP was successfully performed in the presence of residual oxygen, signifying the potential of this polymerization system to tolerate oxygen without performing deoxygenation processes.

Atom transfer radical polymerization (ATRP) is a widely used procedure for synthesizing well-defined polymers.^{1, 2} In ATRP, control over the polymerization is based upon a reversible redox process using catalysts that can efficiently sustain activation and deactivation of polymer chain ends.³⁻⁵ In this regard, copper complexes are one of the most efficient and widely used ATRP catalysts with L/Cu^I and L/Cu^{II}-X (X: Br or Cl) species being the activator and deactivator, respectively.⁶⁻⁸ In

addition, other transition metal-based catalysts such as iron,^{9, 10} ruthenium,¹¹ iridium¹² and also organic photoredox catalysts¹³⁻¹⁵ are capable of catalyzing ATRP with high efficiency.¹⁶

In ATRP reactions, the bond dissociation energy of the carbon-halogen chain ends and affinity of the halogen atom to the catalyst are important criteria for efficient atom transfer processes to succeed. As a result, Br and Cl chain end functionalities are effective in affording well-controlled polymers in the presence of atom transfer catalysts, whereas F chain ends are not suitable due to the high energy required to cleave the C-F bonds.¹⁷ Interestingly, C-I bonds are weaker and therefore can be cleaved easily. However, previous reports have shown low affinity of the I atom to Cu catalysts rendering inefficient ATRP catalysis in the presence of alkyl iodides.¹⁸

Iodine-based polymerizations typically occur via a degenerative transfer process in the presence of iodinated chain transfer agents.¹⁹⁻²⁵ The transfer and dynamic exchange of iodine between propagating radicals and dormant species affords moderate control over polymerization. However, in the presence of compounds such as amines or iodide salts that form complexes with alkyl iodides, the polymerization becomes catalytic undergoing a similar mechanism to ATRP (also referred as reversible complexation mediated polymerization, RCMP²⁶) to catalyze iodine atom transfer, and consequently improves control over polymer chains.

Alkyl iodides are generally light/heat sensitive compounds that require special care for storage and handling. However, for iodine-mediated ATRP reactions, alkyl iodide initiators can be generated *in situ* from more stable alkyl bromides using iodide salts.²⁷ Indeed, the light sensitivity of alkyl iodides can be advantageous for developing photocontrolled iodine-mediated polymerization strategies. Scheme 1 illustrates the general mechanism of iodine-mediated photoATRP via *in situ* generation of the alkyl iodide initiator. In the presence of iodide salts that also act as a catalyst, the C-I bond can be photochemically cleaved to form initiating/propagating radicals and also generating an iodine-based radical.^{26, 28-31} The iodine

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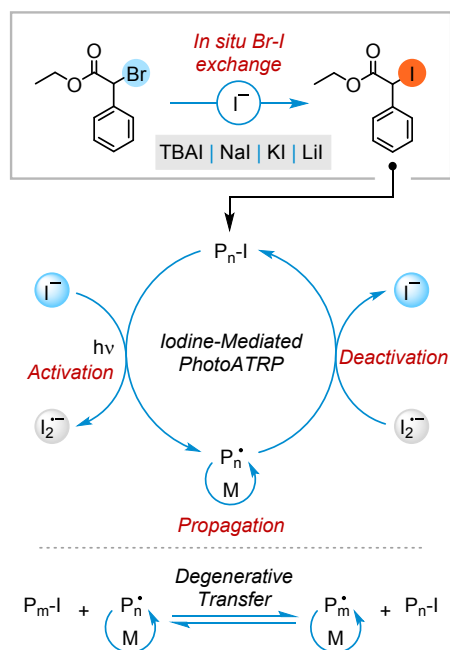
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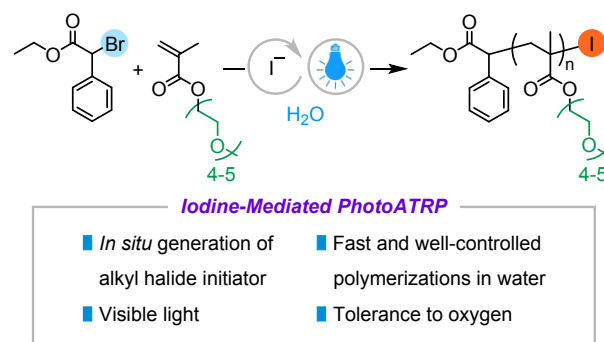
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Scheme 1. Mechanism of iodine-mediated photoATRP by *in situ* generation of the alkyl iodide initiator using iodide salts as the catalyst.

radical complexes with an iodide anion to form an iodine radical anion ($I_2^{\bullet-}$) species, which serve as deactivators for propagating radicals. Furthermore, in an iodine-based polymerization, a degenerative transfer process may also be involved between the growing radicals and iodine-capped dormant species to impart control over the growth of polymer chains.

Water is considered a green solvent for polymerizations and is compatible with different reversible-deactivation radical polymerizations (RDRP) including ATRP, RAFT and other techniques.^{32–35} However, iodine-mediated polymerizations have not been fully investigated in aqueous media. Moreover, RDRP methods have been recently advanced to enable well-controlled polymerizations in the presence of oxygen.³⁶ Indeed, oxygen can be consumed *in situ* by applying various (photo)chemical techniques without the need for performing conventional deoxygenation processes, thereby simplifying the synthesis of polymers with potential utility for new applications.^{36–42}



Scheme 2. Iodine-mediated photoATRP of PEGMA₃₀₀ monomer in water by *in situ* generation of the alkyl iodide initiator under visible light irradiation.

In this paper, iodine-mediated photoATRP was investigated in aqueous media, which enabled fast and well-controlled polymerizations that were also tolerant to residual oxygen without the need for degassing procedures. The alkyl iodide initiator was generated *in situ* by an exchange reaction of Br to I using ethyl α -bromophenylacetate (EBPA) and various iodide salts, which also acted as the catalyst for the polymerization. Polymerizations were conducted under a wide range of visible light as external stimuli enabling temporal control over the polymerization.

Iodine-mediated photoATRP was initially attempted using poly(ethylene glycol) methyl ether methacrylate (average M_n 300, PEGMA₃₀₀) as a water-soluble monomer and ethyl EBPA under blue light irradiation in water (Scheme 2). Tetrabutylammonium iodide (TBAI) was used to generate alkyl iodide initiator by exchanging EBPA's Br to I. Table 1 shows the results of the polymerization of PEGMA₃₀₀ and the effect of concentration of different components involved on the polymerization. High monomer conversion was achieved in less than 2 h under blue light irradiation. Increasing the concentration of TBAI resulted in a well-controlled process providing polymers with low dispersity (\bar{D}) values. For example, in the presence of 1 equiv. of TBAI with respect to EBPA, the polymerization of PEGMA₃₀₀ reached high monomer conversion showing molecular weights close to theoretical values, but with a high \bar{D} of 1.88. However, increasing concentration of TBAI to

Table 1. Results of iodine-mediated photoATRP in water^a

Entry	[PEGMA ₃₀₀]/[EBPA]/[I ⁻]	Iodide salt	[PEGMA ₃₀₀] (vol %)	Time (h)	Conv. (%)	$M_{n,th}$	M_n	\bar{D}
1	100/1/1	TBAI	50	2	91	27400	29900	1.88
2	100/1/2	TBAI	50	2	91	27400	30000	1.43
3	100/1/2	TBAI	33	2	90	27200	27000	1.34
4	100/1/2	TBAI	25	2	83	25100	26600	1.24
5	100/1/4	TBAI	25	2	84	25500	26800	1.18
6	100/1/4	KI	50	2	89	27000	27700	1.35
7	50/1/4	KI	50	2	94	14400	14900	1.26
8	100/1/4	NaI	25	2	83	24800	22900	1.24
9	100/1/4	LiI	25	2	84	25000	24000	1.24
10	100/0/4	TBAI	25	24	0	-	-	-
11	100/1/0	-	25	24	0	-	-	-
12	100/1/4 – in dark	TBAI	25	24	0	-	-	-

^a Reactions were irradiated under blue light LEDs (λ_{max} = 460 nm, 12 mW/cm²).

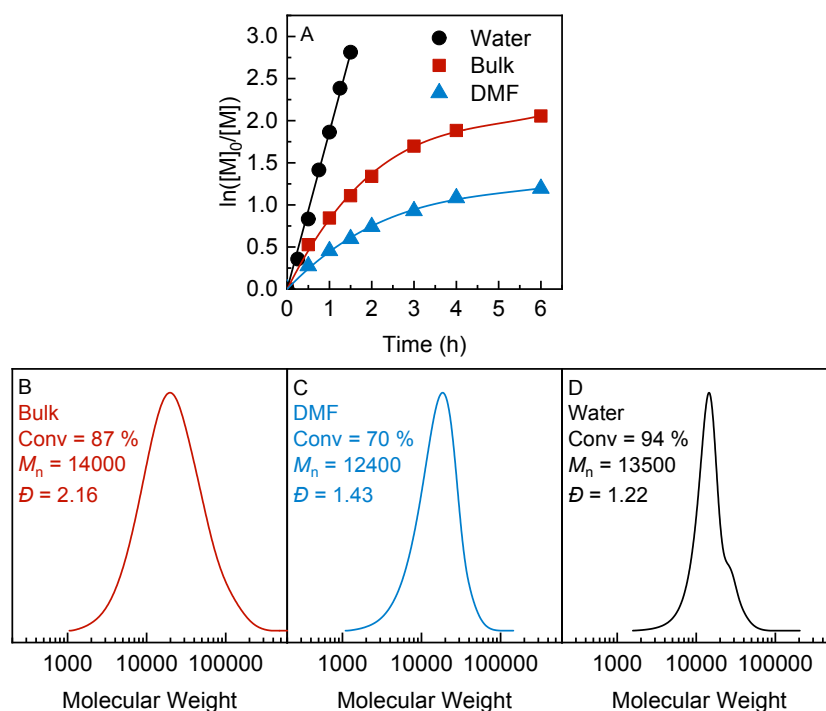


Figure 1. Iodine-mediated photoATRP of PEGMA₃₀₀ in different reaction media demonstrating a fast and well-controlled polymerization obtained in water compared to bulk or in DMF. (A) Kinetics and (B) SEC results of the polymerizations. Reaction conditions: [PEGMA₃₀₀]/[EBPA]/[TBAI] = 50/1/4 in 50 vol % solvent (water or DMF) or bulk. Irradiated under blue LEDs ($\lambda_{\text{max}} = 460 \text{ nm}$, 12 mW/cm^2).

2 equiv., with respect to initiator, improved control over the polymerization and provided polymers with \bar{D} of 1.43 (Entries 1 and 2, Table 1). These observations suggest that in the presence of high concentration of the iodide salt control over the polymerization was achieved mainly through an ATRP mechanism with iodide salts acting as the catalysts under photochemical conditions. In the absence of excess iodide salts, control may be attributed predominately to a degenerative mechanism.

Furthermore, under more dilute conditions, the rate of polymerization slightly decreased but resulted in well-controlled polymers, showing lower \bar{D} values. For instance, in the presence of 2 equiv. of TBAI with respect to initiator, decreasing concentration of the monomer from 50 to 33 and 25 vol % in water resulted in decreasing \bar{D} from 1.43 to 1.34 and 1.24, respectively (Entries 2-4, Table 1). In the presence of 4 equiv. of TBAI and 25 vol % monomer, the polymerization was well-controlled giving low dispersity $\bar{D} = 1.18$ (Entry 5, Table 1). Importantly, in all these polymerizations experimental molecular weights agreed well with theoretical values, indicating high initiation efficiency. In addition, alkali metal iodide salts including potassium, sodium and lithium iodides were also used to perform and efficiently control the polymerization of PEGMA₃₀₀ in water (Entries 6-9, Table 1 and Figures S4-S6). Notably, these organic and alkali metal iodide salts were readily soluble in the reaction medium and therefore were used without additional solubilizing agents, as was previously required for the *in situ* exchange of Br-I when conducting polymerization in organic media.³⁰

Control experiments performed in the absence of either EBPA, iodide salts, or light did not lead to initiation of a polymerization, indicating the importance of the contributing components for a successful iodine-mediated photoATRP under visible light (Entries 10-12, Table 1).

Effect of polymerization medium. Using water as a solvent resulted in a well-controlled iodine-mediated photoATRP of PEGMA₃₀₀ monomer under blue light irradiation. The efficiency of polymerization in aqueous media was further demonstrated by conducting the polymerization in bulk or in an organic solvent, *N,N*-dimethylformamide (DMF). Tetrabutylammonium iodide (TBAI) was used to exchange the initiator's Br to I. Kinetics of the polymerization in bulk showed a decrease in the rate of the polymerization over time yielding 87 % monomer conversion in 6 h (Figure 1-A). Size exclusion chromatography (SEC) analysis of the polymer obtained in bulk showed a broad molecular weight distribution with a high \bar{D} of 2.16 (Figure 1-B). The uncontrolled polymerization in bulk can be related to the poor solubility of TBAI in the monomer, and consequently inefficient Br-I exchange and hence poor catalysis. Under these conditions, using DMF as an organic solvent, a decrease in the rate of polymerization was observed as the polymerization progressed with 70 % monomer conversion in 6 h. A relatively high \bar{D} of 1.43 was obtained in DMF (Figure 1-C). Fast generation of radicals under a strong blue light irradiation and relatively slow rate of propagation in DMF led to the termination of polymer chains and hence a decrease in the rate of polymerization. However, conducting the polymerization of PEGMA₃₀₀ monomer in water resulted in a fast and

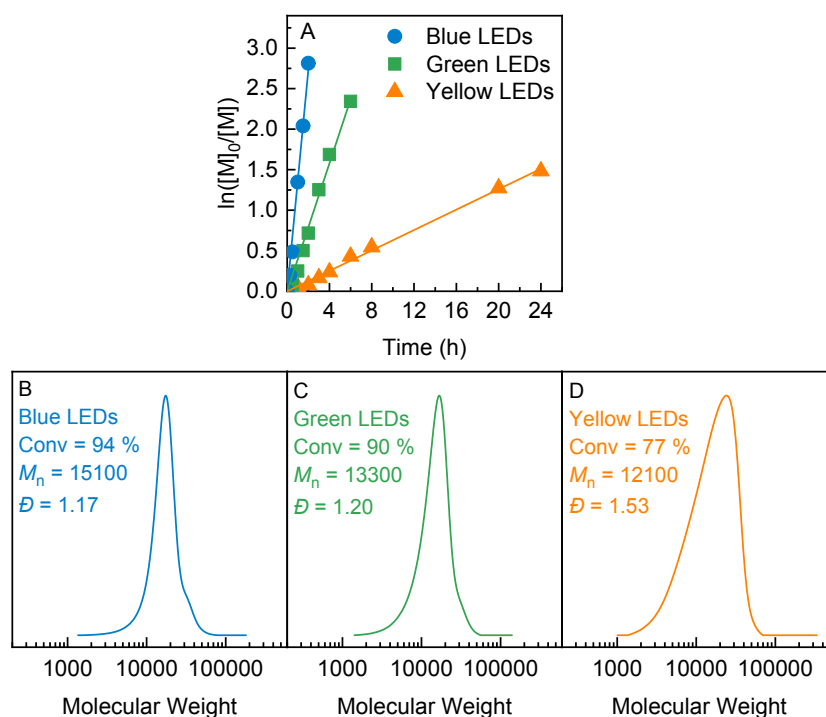


Figure 2. Iodine-mediated photoATRP of PEGMA₃₀₀ in aqueous media demonstrating well-controlled polymerizations achieved under a wide range of visible light irradiation. (A) kinetics and (B) SEC results of the polymerizations. Reaction conditions: [PEGMA₃₀₀]/[EBPA]/[TBAI] = 50/1/4, monomer 75 vol % in water, irradiated under blue (λ_{max} = 460 nm, 12 mW/cm²), green (λ_{max} = 520 nm, 4.5 mW/cm²), and yellow (λ_{max} = 595 nm, 0.6 mW/cm²) LEDs.

well-controlled process ensured by a rapid formation of the radicals under a strong blue light and a high rate of propagation in water. Linear semi-logarithmic kinetics were observed with the polymerization reaching 94 % monomer conversion in 90 min providing polymers with low \bar{D} of 1.22 (Figure 1-D and Figure S1). Notably, SEC traces of the polymers obtained in water showed a shoulder appearing at higher molecular weights as the reaction reached high monomer conversions. The appearance of this shoulder can be attributed to the presence of di-functional impurities in the monomer, resulting in branching at higher conversions, which can be suppressed by conducting the polymerizations under dilute conditions (Figures S1-S3).

Effect of light sources on polymerization. Iodine-mediated photoATRP in water was successfully initiated and controlled with a wide range of visible light sources. Figure 2-A shows the kinetics of the polymerization of PEGMA₃₀₀ monomer in the presence of TBAI under blue, green and yellow light LEDs. Irradiation under blue light LEDs (460 nm) resulted in 94 % monomer conversion in 2 h (M_n = 15 100, \bar{D} = 1.17), Figure 2-B and Figure S3.

Under a green light (520 nm) irradiation, polymerization was slower and reached ~ 90 % monomer conversion in 6 h and provided polymers with well-controlled properties (M_n = 13300, \bar{D} = 1.20), Figure 2-C. Polymerizations under blue and green lights showed linear semi-logarithmic kinetics with a lower rate of polymerization observed under green LEDs. Importantly, well-controlled polymerizations were achieved in both cases with molecular weights in agreement with theoretical values

and $\bar{D} < 1.2$. Under yellow light LEDs (595 nm), a slow polymerization of PEGMA₃₀₀ monomer was observed giving ~ 77 % conversion in 24 h, and polymers showed a \bar{D} of 1.43, Figure 2-D. These results demonstrate the efficiency of iodine-mediated photoATRP in aqueous media achieved over a wide range of visible light in the presence of simple iodide salts.

Notably, iodine-mediated photoATRP was successfully performed in the absence of any added conventional photoinitiator/photocatalyst. Therefore, in the presence of iodide salts, direct photolysis of the labile C-I bond by visible light may be responsible for the formation of radicals and therefore successful polymerizations.

Temporal control. Kinetics of the polymerization was mediated

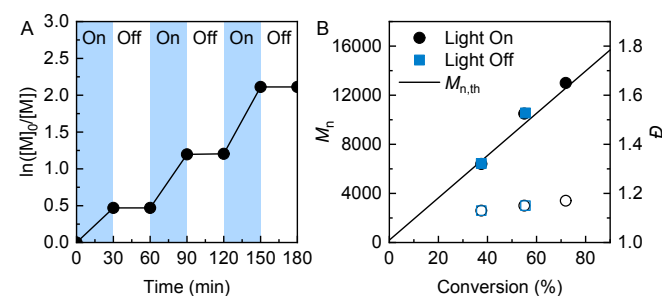


Figure 3. Temporal control in iodine-mediated photoATRP in water, demonstrating control of polymer chain growth under light irradiation. Reaction conditions: [PEGMA₃₀₀]/[EBPA]/[TBAI] = 50/1/4 in 75 vol % water. Irradiated under blue LEDs (λ_{max} = 460 nm, 12 mW/cm²). (A) Kinetics of the polymerization upon multiple light on/off switches. (B) Number-average molecular weight (M_n , solid points) and dispersity (\bar{D} , open points) as a function of monomer conversion.

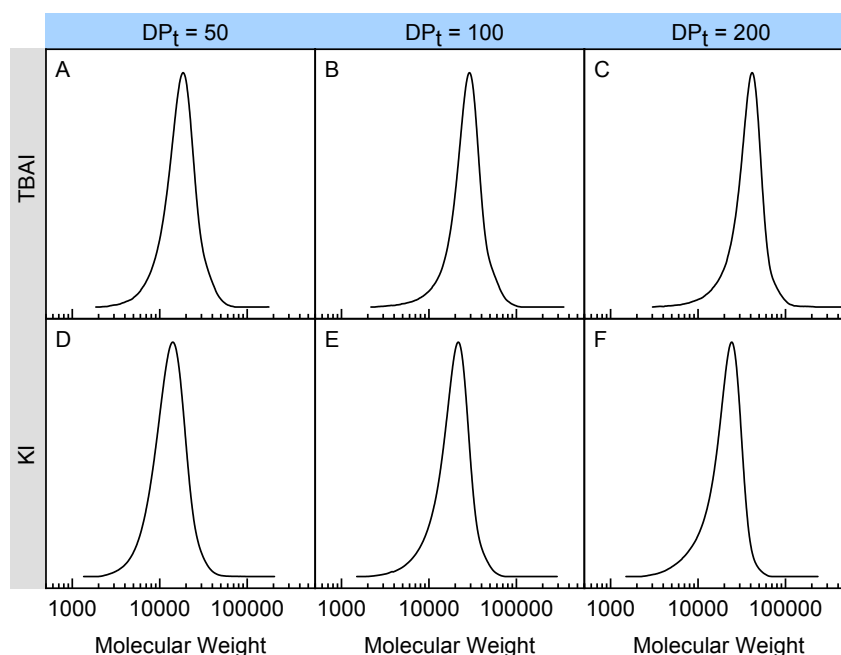


Figure 4. SEC traces of the polymers synthesized in the presence of residual oxygen. Reaction conditions: $[\text{PEGMA}_{300}]/[\text{EBPA}]/[\text{I}^-] = \text{DP}_t/1/4$ ($\text{DP}_t = 50, 100$, and 200) in $75 \text{ vol } \% \text{ water}$ (total volume 8 mL). Irradiated under blue LEDs ($\lambda_{\text{max}} = 460 \text{ nm}$, 12 mW/cm^2) for 2 h . Polymerizations were performed without deoxygenation of the solutions in full, capped vials.

by switching the light on and off. As shown in Figure 3, iodine-mediated photoATRP of PEGMA_{300} in water was activated only under blue light irradiation and was switched off by removing the light. Importantly, control over the polymerization was maintained during multiple light on/off switches with molecular weights in line with theoretical values and low $\bar{D} < 1.2$.

Polymerizations in the presence of residual oxygen. Iodine-mediated photoATRP was controlled in the presence of residual oxygen without performing typical deoxygenation processes. Oxygen tolerant polymerizations of PEGMA_{300} were conducted under blue light irradiation using TBAI or KI as the catalyst and targeting degrees of polymerization (DP_t) of 50–200. Results of the polymerizations showed well-controlled polymers obtained in the presence of residual oxygen reaching high monomer conversions and providing polymers with low $\bar{D} < 1.2$ (Table 2). As shown in Figure 4, the polymers synthesized in the presence of residual oxygen showed monomodal, narrow molecular weight distributions, indicating a high level of control over polymers achieved under these conditions.

Table 2. Results of iodine-mediated photoATRP in the presence of residual oxygen (without deoxygenation)

Entry	Iodide salt	DP_t	Conv. (%)	$M_{n,\text{th}}$	M_n	\bar{D}
1	TBAI	50	93	14200	15300	1.19
2	TBAI	100	85	25800	25000	1.18
3	TBAI	200	64	38600	34000	1.17
4	KI	50	74	11300	11500	1.20
5	KI	100	62	18800	17000	1.21
6	KI	200	44	26600	18500	1.20

^a Reaction conditions: $[\text{PEGMA}_{300}]/[\text{EBPA}]/[\text{I}^-] = \text{DP}_t/1/4$ ($\text{DP}_t = 50, 100$, and 200) in $75 \text{ vol } \% \text{ water}$ (total volume 8 mL). Irradiated under blue LEDs ($\lambda_{\text{max}} = 460 \text{ nm}$, 12 mW/cm^2) for 2 h . Polymerizations were performed without deoxygenation of the solutions in full, capped vials.

In summary, iodine-mediated photoATRP was investigated in aqueous media. Polymerizations were catalyzed by iodide salts that were also used to initially generate alkyl iodide initiator *in situ*. Use of water as a solvent resulted in fast polymerizations, providing high monomer conversions with polymers showing well-controlled properties. Importantly, iodine-mediated photoATRP was initiated and controlled under a wide range of visible light irradiation including blue, green, and yellow lights in the absence of conventional photocatalysts. Furthermore, polymerizations were successfully controlled in the presence of residual oxygen signifying the potential of iodine-mediated photoATRP for use in applications without the need for performing deoxygenation processes.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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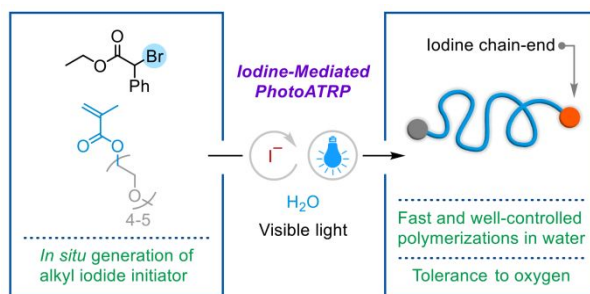
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Iodine-mediated photoATRP was conducted in aqueous media enabling fast and well-controlled polymerizations under visible light without deoxygenation.