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Visible-Light-Controlled Living Radical Polymerization from a Trithiocarbonate Iniferter Mediated by an Organic Photoredox Catalyst

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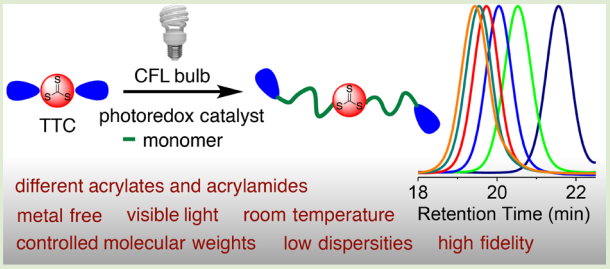
Supporting Information

ABSTRACT: Living radical polymerization of acrylates and acrylamides from trithiocarbonate iniferters using a compact fluorescent lamp (CFL) bulb and 10-phenylphenothiazine as an organic photoredox catalyst is reported. With this system, chain growth can be efficiently switched between "on" and "off" in response to visible light. Polymer molar masses increase linearly with conversion, and narrow molar mass distributions are obtained. The excellent fidelity of the trithiocarbonate-iniferter enables the preparation of triblock copolymers from macro-iniferters under the same visible-light mediated protocol, using UV light without a photoredox catalyst or under traditional thermally induced RAFT conditions. We expect that the simplicity and efficiency of this metal-free, visible-light-mediated polymerization will enable the synthesis and modification of a range of materials under mild conditions.

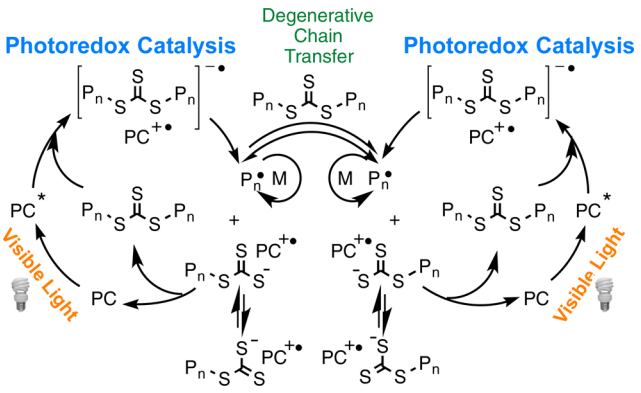


Controlled radical polymerizations (CRP) have been widely employed for the synthesis of polymers with well-defined composition, topology, and architecture.[1] In recent years, methods that enable switchable, external control over the chain growth process have been developed.[2] These techniques have led to innovative new strategies for macromolecular engineering. For example, electrochemically mediated atom transfer radical polymerization (ATRP) has been applied to star polymer synthesis,[3] aqueous polymerization,[4] and polymer-brush formation on various surfaces.[5] Alternatively, photo-CRP reactions that use light as an external stimulus offer opportunities for spatiotemporal control over chain growth.[6] Recently, extensive efforts have been dedicated to the development of novel photo-CRP reactions (e.g., ATRP,[7] reversible addition−fragmentation chain transfer, RAFT, polymerization,[8] Co-mediated,[9] Te-mediated,[10] and others[11]). With the exception of a few examples,[7g,h,8a,11f,j] most of these processes rely on metal photoredox catalysts (PCs) or UV light.[1c,12] For example, Boyer and co-workers recently showed that an Ir-based PC could mediate CRP from trithiocarbonate (TTC) iniferters under visible light.[11b] More recently, the same group reported the use of chlorophyll, which possesses a redox-active Mg-porphyrin, for this reaction.[11c]

In 2013, we reported the synthesis of telechelic poly(*N*-isopropylacrylamide) (PNiPAAm) using a metal-free UV-controlled photo-CRP based on direct excitation of a TTC iniferter.[11d,13] We recently improved upon the efficiency and scope of this method by employing continuous flow technology.[14] Despite these developments, the need to use UV light has drawbacks; UV light requires special equipment and it can induce irreversible TTC decomposition reactions, especially at high light intensities and low TTC concentrations.[15−17] Building on our studies[11d] and inspired by Boyer's examples (vide supra),[11b,c,j] we set out to develop a metal-free, visible-light promoted CRP from TTC iniferters.

The proposed mechanism for this process is provided in Scheme 1. Electron transfer from a photoexcited PC (PC*) activates a TTC molecule and provides a radical ($P_n^{\bullet}$) that can undergo either propagation or degenerative chain transfer (RAFT process). As in the UV-induced iniferter process, the

Scheme 1. Proposed Mechanism for Photo-CRP in the Presence of a Photoredox Catalyst and a Trithiocarbonate (TTC) Iniferter



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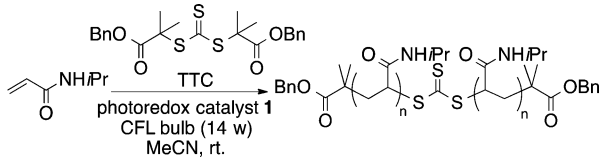
key to the excellent photocontrol of this system is that the TTC fragment (a radical in the UV case; a putative TTC anion + $PC^{+\bullet}$ ionic complex in the visible-light case) can deactivate the propagating polymer chain to generate a polymeric TTC and ground state PC. These species can re-enter the catalytic cycle under light (e.g., reversible activation). This PC-based method is advantageous because exogenous radicals from initiators such as AIBN (e.g., traditional RAFT polymerization) are avoided, which minimizes the formation of dead chains. Furthermore, the TTC does not absorb light in the visible range; undesired irreversible UV photoreactions are avoided.[16] Thus, the key for our studies was to find an organic PC that could replace metal-based PCs.

We first evaluated several known organic PCs in the presence of NiPAAm and TTC using a 14 W CFL bulb as the light source. As shown in Table 1, 10-phenylphenothiazine (PTH)

Table 1. Optimization of Reaction Conditions for Photo-CRP with Organic PCs[a]



entry	photoredox catalyst (mol %)	conv. (%)	$M_{n,theory}$	$M_{n,GPC}$	M_w/M_n
1		<3			
2	PTH **1a** (0.5)	93	26700	28300	1.14
3[b]	PTH **1a** (0.5)	55	16000	398000	1.75
4	PTH **1a** (0.02)	85	24500	23200	1.02
5	PTH **1a** (0.001)	7			
6[c]	PTH **1a** (0.02)	0			
7	eosin Y **1b** (0.05)	0			
8	methylene blue **1c** (0.05)	0			

[a]Reaction conditions: NiPAAm (2.0 M), TTC (8 mM, 0.4 mol %), and PC **1** (as shown in the table) in MeCN at room temperature with irradiation from 14 W CFL bulbs for 3 h (M_n = number-average molar mass; M_w = weight-average molar mass). [b]The reaction was run in the absence of TTC. [c]The reaction was run in the absence of light. See the Supporting Information for details.

gave the best results in this system. Indeed, PTH was also recently employed by the Hawker[7g] and Matyjaszewski[7c] groups to conduct metal-free photo-ATRP reactions. In our studies, when 0.5 mol % PTH and 0.4 mol % TTC were used, although 93% conversion of NiPAAm was achieved in 3 h based on ^{1}H NMR analysis (entry 2), gel permeation chromatography (GPC) revealed the presence of a low molecular weight impurity (Figure S1). Using 0.5 mol % PTH in the absence of TTC afforded polymers with a broad molar mass distribution (entry 3). We reasoned that at low TTC/PC ratios or in the absence of TTC, degenerative chain transfer, which requires free TTC, cannot occur efficiently. To gain better control over this system, different TTC/PC ratios were examined (see Supporting Information for details). To our delight, when 0.02 mol % PTH was used in the presence of 0.4 mol % TTC, the polymerization showed satisfactory results in both reactivity and dispersity. Further decreasing the concentration of PTH to 0.001 mol % gave poor conversion (7% after 3 h).

Given the proposed mechanism shown in Scheme 1, which suggests that growing polymer chains are deactivated in the absence of light to form a macro-TTC and ground state PTH, it should be possible to reversibly trigger the growth of polymer chains in this system via switching the light source "ON" and "OFF". To confirm this switchability, we conducted a series of ON/OFF cycles. As shown in Figure 1, both the % conversion

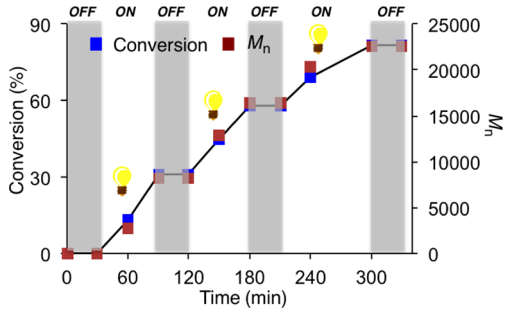


Figure 1. "ON"/"OFF" experiments of photo-CRP from TTC with PTH photoredox catalyst.

and number-average molar mass (M_n) increased during the first 60 min ON cycle. There was no further conversion or mass increase when the reaction was left in the dark for 30 min. Exposure to light for another 60 min lead to increased conversion and M_n. The second and third cycles further confirmed the fidelity of this process. The fact that both the conversion and M_n increased together during each ON cycle strongly suggests that each chain is reversibly activated in response to light, as opposed to the alternative possibility that irradiation induces the growth of new chains through irreversible radical formation.

Plots of $\ln([M]_0/[M]_t)$ versus light exposure time (Figure 2a), M_n versus % conversion (Figure 2b), as well as the gel permeation chromatography (GPC) traces for polymers obtained after different exposure times (Figure 2c), further demonstrate the high degree of control in this polymerization over several ON/OFF cycles. After a short inhibition period, which is commonly observed in related photo-CRP reactions,[7j,8a,11b,c] linear relationships were observed for both $\ln([M]_0/[M]_t)$ versus exposure time (Figure 2a) and M_n versus % conversion (Figure 2b), while the values of M_w/M_n remained quite low (1.02−1.03) throughout the entire process (conversion > 80%). These features strongly suggest that this photo-CRP reaction is both highly controlled and reversibly activated in response to visible light.

Next, we applied this method to the polymerization of other monomers such as *N*,*N*-dimethylacrylamide (DMA), ethylene glycol methyl ether acrylate (EGMEA), and *tert*-butyl acrylate (*t*BA). As shown in Table 2, polymers with narrow molar mass distributions were obtained for all acrylates and acrylamides tested. Satisfactory conversions were achieved for all monomers after 3 h of irradiation. The molar masses measured by GPC analysis are consistent with the corresponding results calculated based on conversions, which suggest that the polymerizations are well controlled for each monomer. Following those experiments, the monomer/TTC ratio was increased to 2000/1 to prepare polymers with higher degrees of polymerization. In this case, 159 kDa PNiPAAm with M_w/M_n = 1.19 was produced after 3 h of irradiation. We have not been able to synthesize PNiPAAm with such a large molar mass in our analogous studies using UV excitation of TTCs,[11d,14] which further attests to the robustness of the current visible-light controlled system.

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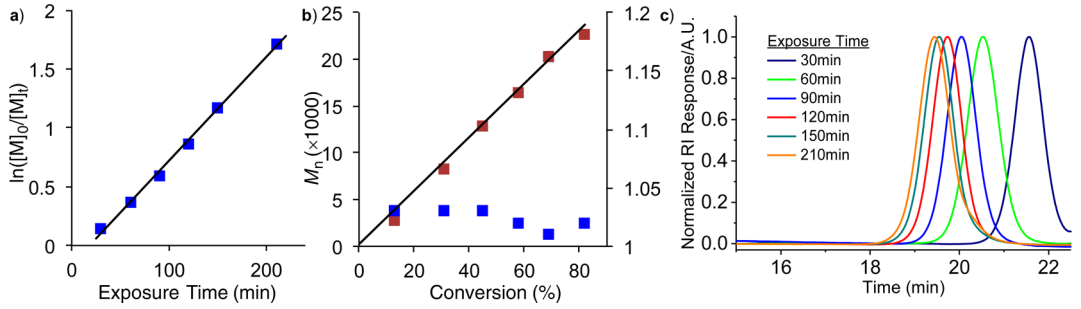

Figure 2. Photo-CRP from TTC with PTH catalyst while cycling the light source "ON" and "OFF". (a) Irradiation time vs $\ln([M]_0/[M]_t)$, with $[M]_0$ and $[M]_t$ being the concentration of monomers at time points 0 and t, respectively; (b) % conversion vs M_n and % conversion vs M_w/M_n; (c) GPC traces after different irradiation times.

Table 2. Photo-CRP of Acrylates and Acrylamides with PTH Catalyst[a]

monomer	DMA	EGMEA	*t*BA	NiPAAm
M/TTC	500/1	500/1	500/1	2000/1
conv. (%)	90	78	76	70
$M_{n,theory}$	45000	51300	49700	159000
$M_{n,GPC}$	50900	52300	51300	168600
M_w/M_n	1.05	1.08	1.02	1.19

[a]Reaction conditions: monomer (2.0 M), TTC (4 mM for DMA, EMGEA, and *t*BA, 1 mM for NiPAAm), and PC **1** (0.02 mol % for DMA, EMGEA, and *t*BA, 0.01 mol % for NiPAAm) in MeCN at room temperature with irradiation from 14 W CFL bulbs.

To validate the structure of the polymers generated via this photo-CRP method, MALDI-TOF (matrix-assisted laser desorption/ionization time-of-flight) mass spectroscopy, NMR, GPC, IR, and UV–vis spectroscopy were performed on purified PDMA samples. The MALDI-TOF spectrum of PDMA (Figure 3A) exhibited a single set of peaks; each peak was separated by the mass of one monomer unit. The observed m/z values are consistent with the expected values for the macro-TTC structures with different degrees of polymerization. Meanwhile, the MALDI-TOF results agreed with the GPC analysis and the calculated M_n from ^{1}H NMR spectroscopy. In a representative ^{1}H NMR spectrum (Figure S2), resonances that correspond to the protons from the benzyl chain ends were observed at 5.08 and 7.39 ppm. The peaks at 310 nm in the UV–vis (Figure S3) and 1727 cm^{-1} in the FTIR (Figure S4) spectra, respectively, are characteristic of the TCC unit. Collectively, these data provide strong support for the proposed macro-TTC structure.

Macro-TTCs prepared from this method should be able to serve as iniferters for subsequent chain extension via PTH catalyzed photoredox CRP, UV-induced CRP, or traditional RAFT polymerization with a thermal radical initiator. We conducted a series of chain extension experiments with a PDMA macro-TTC (M_n = 4500, M_w/M_n = 1.02) to assess the ability to synthesize triblock copolymers via these methods. GPC analysis shows that for all three cases tested: photopolymerization in the presence of PTH with a CFL bulb at room temperature (Figure 3B), photopolymerization under direct UV excitation (365 nm) of the macro-TTC at room temperature (Figure 3C), and RAFT polymerization in the presence of AIBN (PDMA/AIBN = 20/1) at 70 °C (Figure 3D), triblock copolymer products with low molar mass distributions and virtually no low molecular weight tailing were obtained. These results further attest to the excellent fidelity of the TTC unit within the macro-TTC agent obtained from PTH catalyzed photo-CRP. They also highlight the versatility of these macro-TTCs for application in alternative polymerization methodologies.

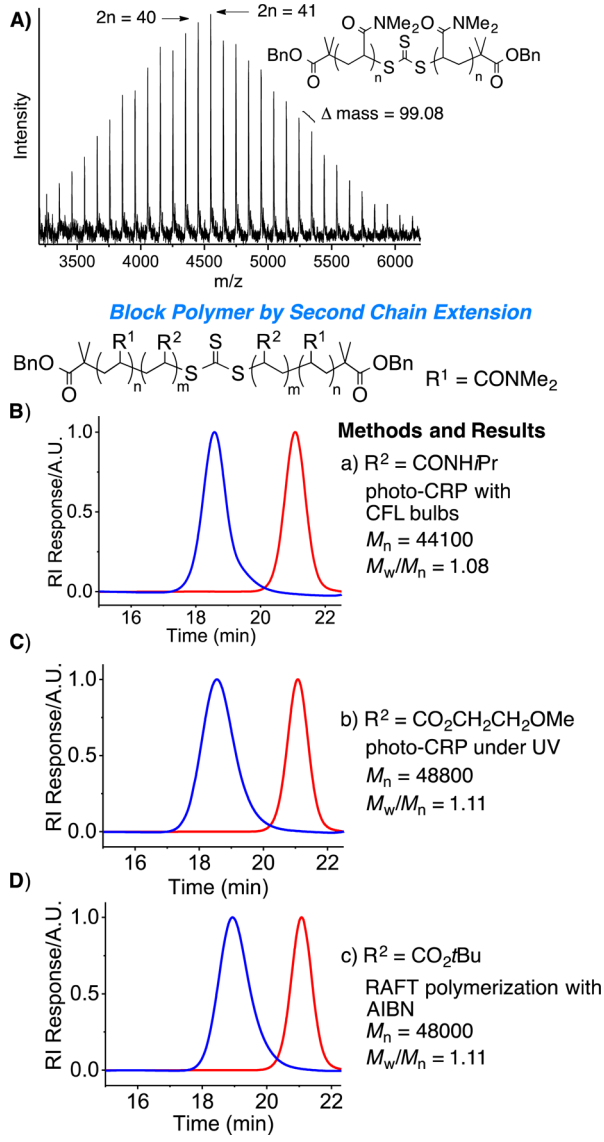

Figure 3. (A) MALDI-TOF mass spectrometry results of photo-CRP from TTC with PTH catalyst. (B–D) Synthesis of triblock copolymers starting from a PDMA macroinitiator prepared via photo-CRP with irradiation from CFL bulbs (red trace = starting macroinitiator PDMA, blue trace = block polymer).

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In conclusion, we have developed a metal-free photo-CRP from a TTC iniferter that proceeds via organic photoredox catalysis. This approach provides polymers from a variety of acrylate and acrylamide monomers with good molecular weight control, narrow molar mass distributions, and excellent structural fidelity. The latter feature enables the preparation of triblock copolymers from divergent polymerization processes. Perhaps most importantly, this method is simple; only a typical household CFL bulb is needed as the light source. We expect that this method will be useful for the synthesis of a variety of TTC-functionalized polymeric architectures.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and additional supplementary data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00241.

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Notes

The authors declare no competing financial interest.

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