Lamp vs. Laser: A Visible Light Photoinitiator that Promotes Radical Polymerization at Low Intensities and Cationic Polymerization at High Intensities

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Abstract

A visible light absorbing, anthraquinone derivative 1-tosyloxy-2-methoxy-9,10-anthraquinone (**QT**) mediates both cationic and radical polymerizations depending on the intensity of visible light used. A previous study showed that this initiator generates *para*-toluenesulfonic acid through a stepwise, two-photon excitation mechanism. Thus, under high intensity irradiation, **QT** generates acid in sufficient quantities to catalyze the cationic ring opening polymerization of lactones. However, under low intensity (lamp) conditions, the two-photon process is negligible, and **QT** photooxidizes DMSO, generating methyl radicals which initiate the RAFT polymerization of acrylates. This dual capability was utilized to switch between radical and cationic polymerizations to synthesize a copolymer using a one-pot procedure.

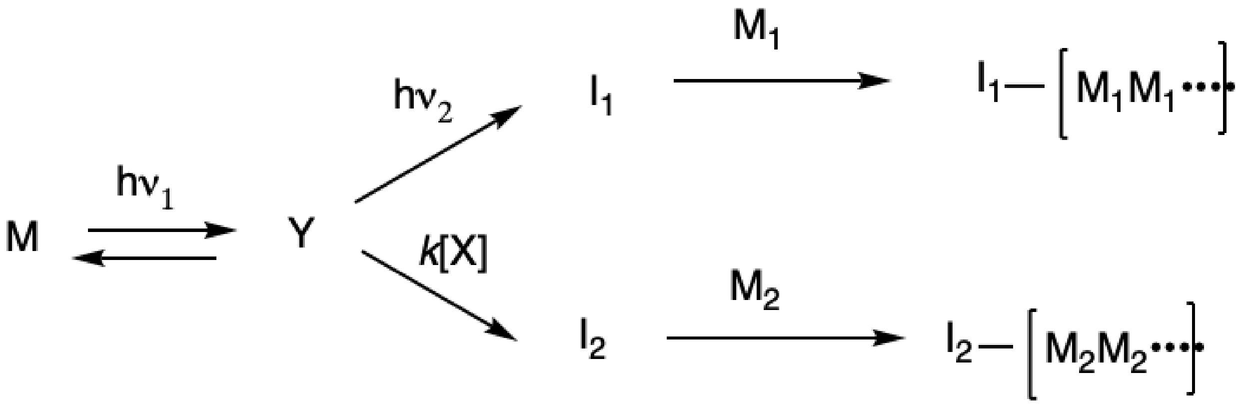
Introduction

The preparation of polymers and related materials through photoinitiation procedures has been important for many decades.[1–4] The use of light to create or modify polymers, gels, liposomes, and related materials is attractive because light can be used to achieve high spatial resolution, provide temporal specificity, and can break and form energetic chemical bonds in situations where high temperatures and/or harsh reagents would not be tolerated. Early photoinitiation systems used UV light to break strong covalent bonds, creating reactive radicals, which in turn added to various vinyl monomers, promoting polymerization through chain addition reactions. Subsequent developments adapted the photoinitiation strategy to more sophisticated processes including: visible light promoted initiation,[5,6] cationic polymerizations,[7] controlled radical polymerizations (e.g. ATRP, RAFT),[8–10] ring-opening polymerizations (ROP),[11,12] and high resolution multiphoton fabrication methods.[13–16]

As the demand for the synthesis of increasingly sophisticated polymeric materials rises, the need for new methods of controlled polymerization processes also increases. For example, there is much current interest in macromolecules that have novel architectures such as block, brush, and star type copolymers. Traditionally the synthesis of such molecules required complex procedures, such as separation and purification of intermediate products and/or carefully managed sequential additions of monomers and initiators. To simplify such preparations, several research groups have begun to explore so-called "one-pot" methods for achieving controlled copolymerization.[17–20] These methods use mixtures of monomers that polymerize through distinct mechanisms (e.g. radical vs. cationic). Control of the product's structure and composition is realized by using an external stimulus to switch between mechanisms. For example, combining two chromatically orthogonal photoinitiators makes it possible to switch between radical initiation and cationic initiation by varying the photolysis wavelength.[17,21–24] This approach enables synthesis of copolymers having carefully controlled acrylate and vinyl ether blocks. Other successful approaches control monomer incorporation through modulating pH, redox state, and temperature.[25–31]

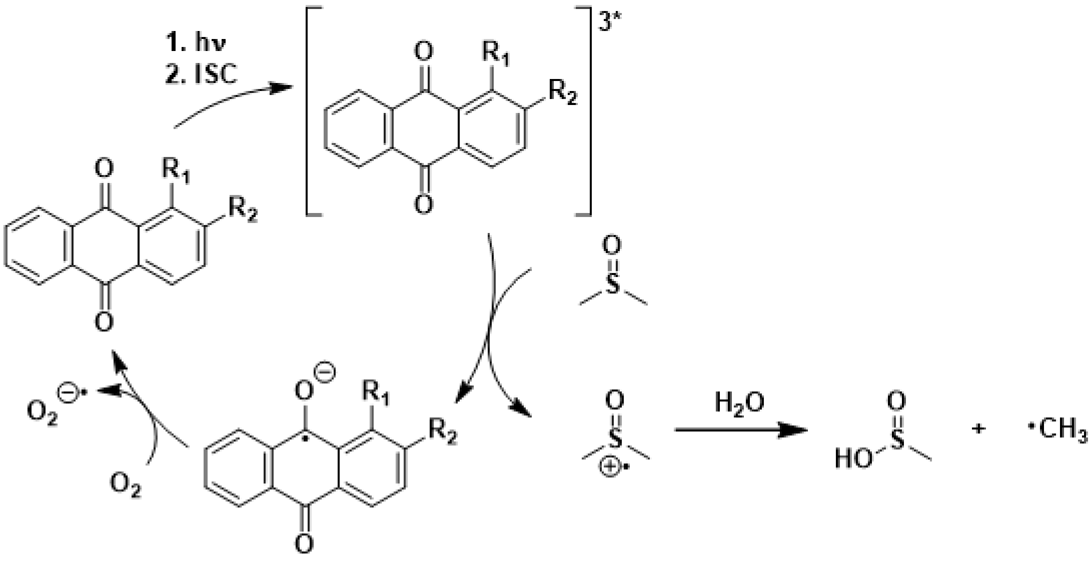
The current study aims to develop a photoinitiator whose mechanism is controlled by the intensity of light applied to the system. In principle, intensity-dependent mechanisms can be achieved in cases where biphotonic excitation of a substrate (M, Scheme 1) produces initiating species (I_1) that are distinct from those produced through monophotonic excitation (I_2). There are numerous examples of photoinitiators that are activated through bi- and multi-photon excitation.[16,32–35] However, the majority of these species are activated through non-resonant two-photon absorption (nr-TPA) wherein two photons, which individually are insufficiently energetic to populate an excited state, are absorbed simultaneously. Such systems would not be suitable for the current purposes as they would be transparent, and thus unreactive, under low intensity conditions. Alternatively, there are several photoinitiators and other molecular switches that can be activated via sequential two-photon excitation (s-TPA).[36–39] In these cases the initial photon ($h\nu_1$) creates an intermediate state (Y, e.g. excited triplet state or a high energy photoisomer). The latter can either absorb a second photon ($h\nu_2$), causing a desired photochemical reaction, or revert back to the original state. In the present context, the aim is to exploit the short-lived intermediate state (Y) to carry out an alternative one-photon initiation process. An important consideration was that the one-photon initiation process needs to have a quantum efficiency that is both high enough to provide for significant reactivity under low intensities, but also low enough to allow the two-photon pathway to predominate at high intensities. To that end we anticipated that use of a co-initiator (X) would provide a means of tuning the efficiency of the one-photon process via the concentration of the co-initiator.

Scheme 1. Light intensity dependent mechanisms



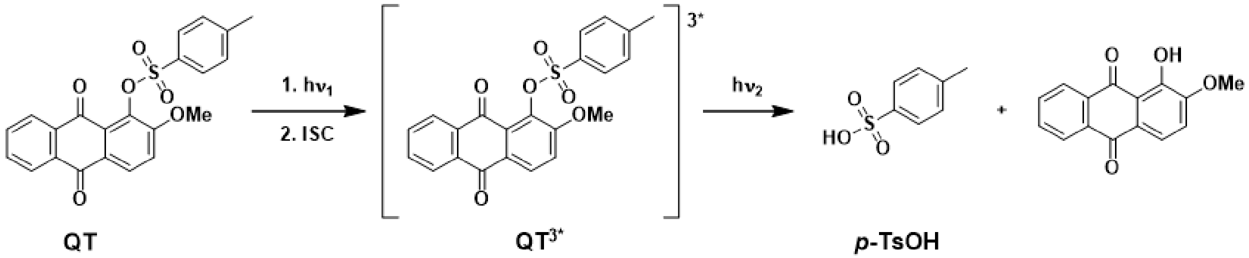
Prior work demonstrated that substituted anthraquinone derivatives could be used in conjunction with thiolate chain-transfer agents to initiate RAFT (reversible addition fragmentation chain-transfer) polymerization of acrylate monomers using visible light.[40] This process relied on a reaction of the anthraquinone triplet state with DMSO, generating radical pairs. The oxidized DMSO was presumed to react with water to generate highly reactive methyl radicals.[41] The latter initiated RAFT polymerization, providing acrylate polymers with controlled molecular weights and narrow polydispersities.

Scheme 2. Generation of initiating methyl radicals via photooxidation of DMSO



In a separate study a sulfonatoxy-substituted anthraquinone derivative was found to generate high yields of strong acids under high intensity visible irradiation (e.g. 100 W/cm^2 at 447 nm).[42] As outlined in Scheme 3, excitation of 1-tosyloxy-2-methoxy-9,10-anthraquinone **QT** with UV or short wavelength visible light is followed by intersystem crossing to generate its triplet state. This triplet state then absorbs a second photon which allows for bond scission and subsequent reactions leading to the generation of *p*-toluenesulfonic acid (*p*-TsOH). It was shown that this procedure could be used to effect sequential two-photon initiation of the cationic polymerization of ethyl vinyl ether.

Scheme 3. Mechanism of two-photon photoacid generation from **QT**



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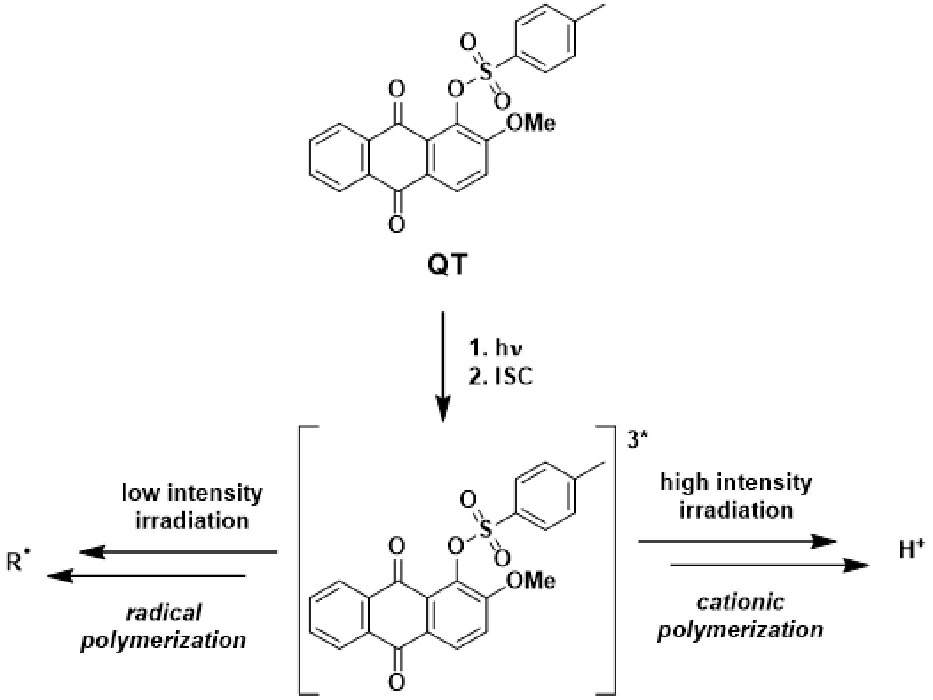
The work described herein demonstrates that **QT** can photoinitiate both cationic ring-opening polymerization of cyclic lactones as well as mediate radical polymerization of acrylates depending on the intensity of visible light irradiation used, demonstrating a dual capability of one photosensitizer. As described in Scheme 4, irradiation of **QT** generates its first excited triplet state. Under high intensity irradiation, the triplet state will be re-excited causing bond dissociation to generate acid capable of catalyzing cationic polymerization. In contrast, when low intensity irradiation is used, the triplet state of **QT** oxidizes DMSO, leading to the formation of radicals which can initiate radical polymerization. In addition, copolymers can be synthesized utilizing both radical and cationic polymerization in a one-pot process. Having a photosensitizer that is capable of mediating more than one type of polymerization allows for the preparation of more complex materials while maintaining simplicity of the reaction mixture.

Scheme 4. Using 1-tosyloxy-2-methoxyanthraquinone **QT** to mediate cationic or radical photopolymerizations depending on the intensity of visible light irradiation



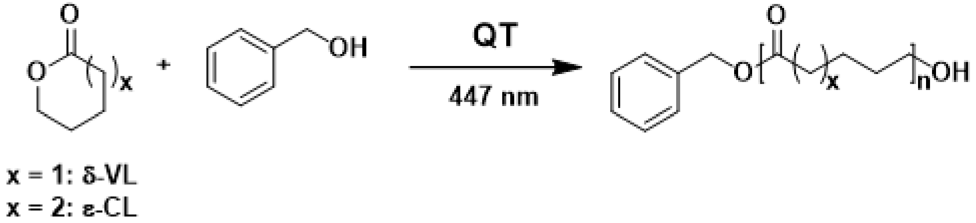
Results and Discussion

Cationic Ring-Opening Polymerization

The ring-opening polymerization (ROP) of lactones is a prominent technique for preparing polyesters however, only in recent years has it been mediated by light.[12,43,44] In 2013, Dove and coworkers demonstrated that, upon UV irradiation, triarylsulfonium photoacid generators (PAGs) can act as effective photoinitiators for the cationic ROP of lactones and carbonates.[9] Then, in 2016, Boyer and coworkers provided the first example of cationic ROP of lactones with visible light. They demonstrated that a reversible merocyanine-based photoacid can be activated using visible light and the resulting acid is capable of initiating polymerization to form well-defined polymers.

Our earlier study demonstrated that high intensity visible light photolysis of **QT** produces *p*-toluenesulfonic acid (*p*-TsOH), which is sufficiently acidic to initiate the cationic polymerization of ethyl vinyl ether,[42] thus demonstrating that **QT** could be used as a photoinitiator for the polymerization of vinyl ethers. The biphotonic nature of this process was established, in part, by observation of a quadratic dependence of the polymerization rate on light intensity. To determine if this process could be applied to the formation of polyesters via ring-opening of lactones, a series of experiments described in Scheme 5 and Table 1 were carried out. Specifically, a series of polymers from the ROP of ε-caprolactone (ε-CL) and δ-valerolactone (δ-VL) catalyzed by visible light irradiation (447 nm CW laser, 10-100 W/cm^2 W) of **QT** were synthesized. Unlike the case for the vinyl ethers, it was found that satisfactory conversions of monomer required the addition of an alcohol co-initiator. Benzyl alcohol was used for this purpose as its distinct ^{1}H NMR signals in the free alcohol and in the polymeric product facilitate analysis. Varying degrees of polymerization were targeted and the results are summarized in Table 1.

Scheme 5. Ring-opening polymerization of δ-VL and ε-CL catalyzed by visible light irradiation of **QT**



Initially, the concentration of **QT** relative to the initiator was set to 0.1 (Table 1, Entries 2 & 8) and the targeted degree of polymerization was 50. The irradiation time is the time required for **QT** to generate its maximum amount of acid. Because acid serves as a catalyst in the polymerization, once **QT** produces its maximum concentration of acid, the polymerization can propagate in the absence of continued irradiation. For both lactones, high monomer conversion was observed. Both polymers showed good agreement between the theoretical molecular weight and the measured molecular weight and both polymers displayed a narrow polydispersity, determined using gel permeation chromatography (GPC), indicating a controlled polymerization. Increasing the ratio of **QT** from 0.1 to 0.25 (Table 1, Entries 3 & 9) did not have any significant effect on the outcome of the polymerization, but did require longer irradiation times in order to fully convert **QT**. For both monomers, high conversions were still achieved with similar polydispersities. Omitting **QT** from the reaction mixture resulted in a lack of monomer conversion (Table 1, Entries 1 & 7). Additionally, including **QT** but not irradiating the sample also resulted in a lack of monomer conversion (Table 1, Entries 6 & 12). These control experiments demonstrate that irradiation of **QT** is necessary to catalyze the polymerization reaction. Various degrees of polymerization were targeted (Table 1, Entries 4-5, 10-11) and in all cases the theoretical and experimental molecular weights were in good agreement with narrow polydispersities.

Table 1. Ring opening polymerization of ε-CL and δ-VL with varying concentrations of **QT** and varying targeted degrees of polymerization

Entry	Monomer	[QT][a]	$[M]_0/[I]_0$	Irradiation Time (min)	Polymerization Time (hr)	% Monomer Conversion[b]	$M_{n, theo}$[c]	$M_{n, GPC}$[d]	PDI[d]
1	ε-CL	0	50	60	24	0	--	--	--
2	ε-CL	0.10	50	30	48	88	5130	5606	1.25
3	ε-CL	0.25	50	90	48	71	4160	5110	1.19
4	ε-CL	0.10	25	30	24	86	2562	3336	1.24
5	ε-CL	0.10	100	30	96	73	8440	6846	1.19
6	ε-CL	0.10	50	0	24	0	--	--	--
7	δ-VL	0	50	60	24	0	--	--	--
8	δ-VL	0.10	50	30	5	73	3612	4899	1.17
9	δ-VL	0.25	50	90	2	83	4263	5224	1.22
10	δ-VL	0.10	25	30	0.75	86	2261	3729	1.19
11	δ-VL	0.10	100	30	18	97	9820	10836	1.28
12	δ-VL	0.10	50	0	24	0	--	--	--

[a]Molar equivalents relative to the amount of initiator, [b]Determined by ^{1}H NMR, [c]Calculated by the equation: $M_{n, theo} = MW_{initiator} + (\% \text{ conv.} \times [M]_0/[I]_0 \times MW_{monomer})$, [d]Determined by GPC using THF as a solvent and calibrated using polystyrene standards

In order to understand how laser power affects the rate of polymerization, the polymerization of ε-CL catalyzed by the photolysis of **QT** was monitored over time with varying powers of 447 nm irradiation. Figure 1 (left) shows that the most pronounced effect is during the first 15 minutes of irradiation and after that, the rate of polymerization is relatively linear with time. When plotted, the monomer conversion after 15 minutes of photolysis as a function of laser power displays a quadratic trend which is consistent with a biphotonic generation of acid (Figure 1, right). The negligible polymerization rate at low powers opens the possibility of combining ROP with other photomediated polymerizations.

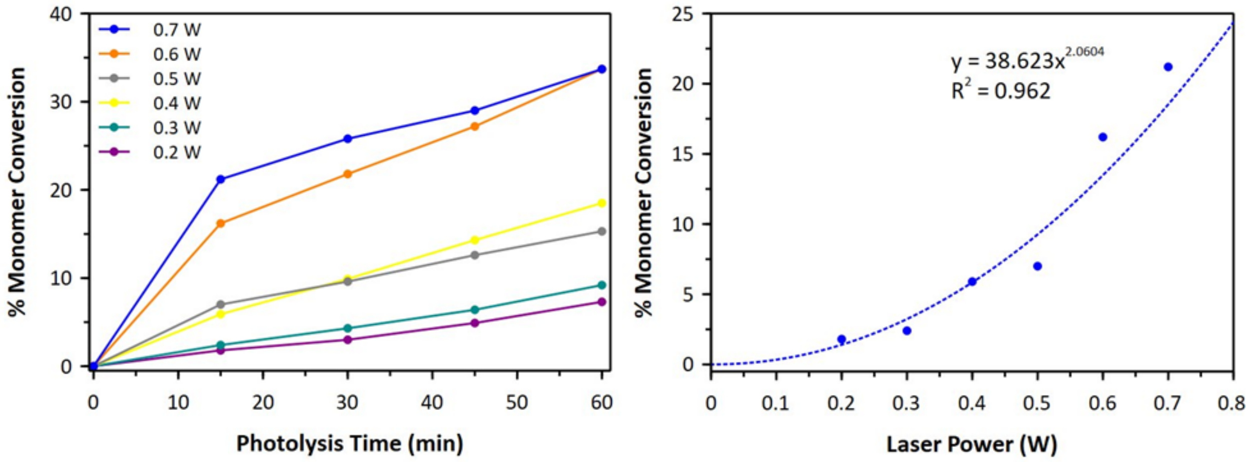


Figure 1. Left: Monitoring conversion of ε-CL over time from photolysis of **QT** at varying powers of 447 nm irradiation. Monomer conversion monitored using ^{1}H NMR. Right: Conversion of ε-CL after 15 minutes of irradiation as a function of 447 nm laser power

RAFT Polymerization

A previous study showed that a combination of a substituted anthraquinone derivative, 2-acetamidoanthraquinone and DMSO, could be used as a visible light RAFT photoinitiation system. To demonstrate that **QT** can similarly photooxidize DMSO, initiating RAFT polymerization, polymerizations of acrylate monomers were carried out using 419 nm broadband irradiation, as described in Scheme 6. Using 4-cyanopentanoic acid dithiobenzoate (CPADB) as the chain transfer agent, the polymerizations of methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) using were carried out in both the presence and absence of **QT** and the results are summarized in Table 2. In all cases, monomer conversion was observed however the polymerization in the presence of **QT** led to significantly higher monomer conversion, consistent with the results of previous work,[16] indicating that **QT** is behaving similarly. The polymerization that occurs in the absence of **QT** is attributed to a photoiniferter mechanism caused by the UV emission of the 419 nm bulbs overlapping with the absorption tail of CPADB allowing direct absorption of the chain transfer agent, also observed in our previous work.

Scheme 6. RAFT polymerization of acrylate monomers via photooxidation of DMSO by **QT**

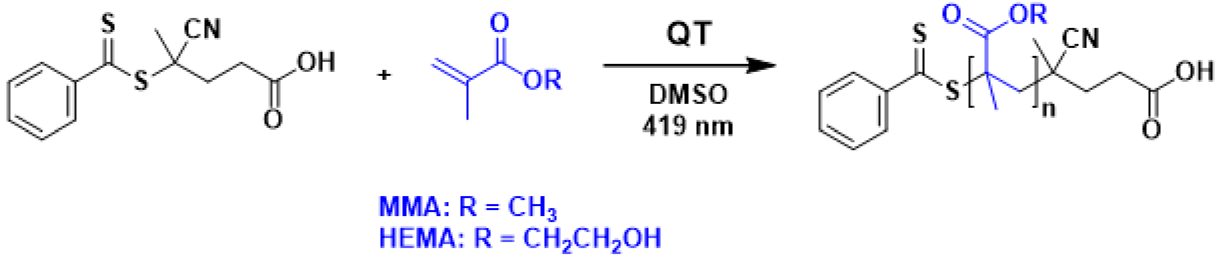


Table 2. RAFT polymerization of acrylate monomers in the presence and absence of **QT**

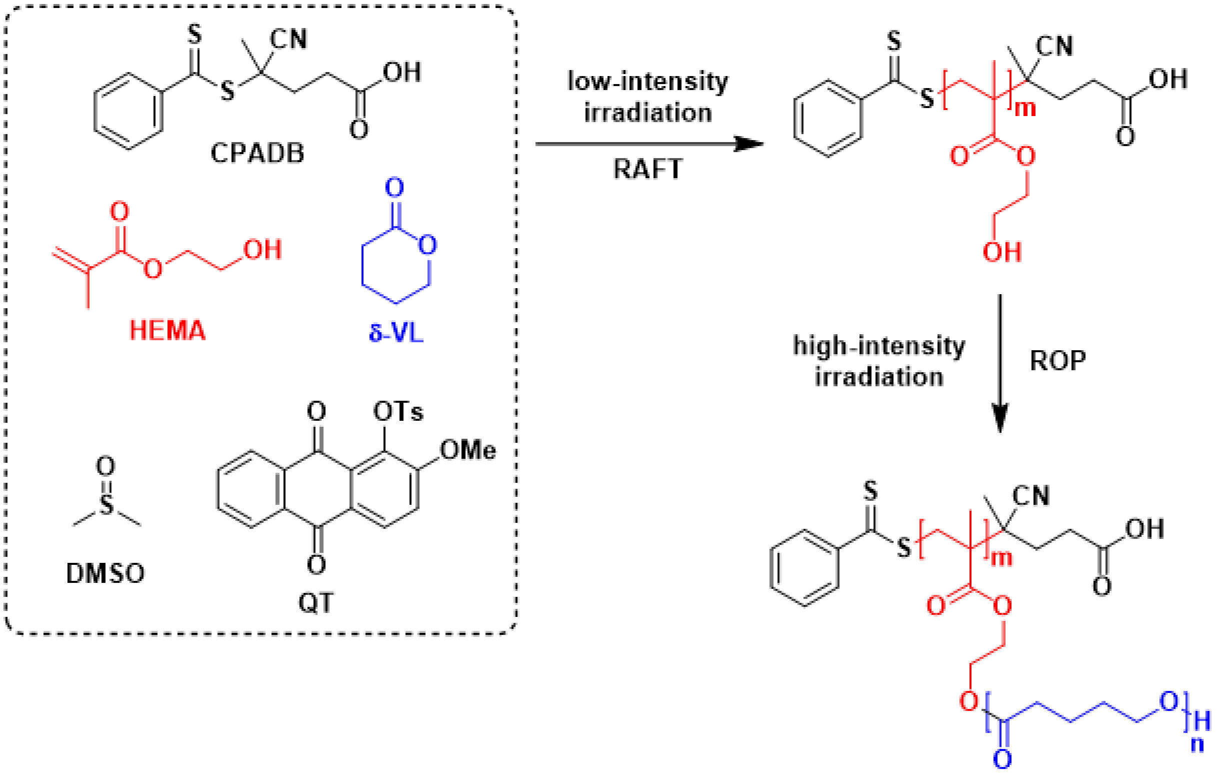
Entry	Monomer	[M]/[CPADB]	[QT]/[CPADB]	Photolysis Time (hr)	% Monomer Conversion[a]
1	MMA	100	0	18	46
2	MMA	100	0.1	18	76
3	MMA	100	0.5	18	63
4	HEMA	100	0	18	71
5	HEMA	100	0.1	18	97
6	HEMA	100	0.5	18	93

[a] Determined by ^{1}H NMR

One-Pot Brush Copolymerization

Knowing that **QT** is capable of polymerizing acrylates under low intensity irradiation and can initiate cationic polymerization under high intensity irradiation, a one-pot brush copolymerization, as shown in Scheme 7, was carried out. The hypothesis is that under low intensity irradiation (419 nm broadband lamps), polymerization of HEMA via RAFT polymerization should be the dominant reaction. Then, by switching to high intensity irradiation (447 nm CW laser), **QT** will generate acid and the ROP of δ-VL should begin to take place.

Scheme 7. One-pot brush copolymerization



As Figure 2 shows, when the sample is irradiated with broadband 419 nm irradiation, there is a significant conversion of HEMA (80%) while the conversion of δ-VL is minimal (9%). When the light source is switched to the high intensity 447 nm CW laser, conversion of HEMA continues however there is a sharp increase in the conversion of δ-VL due to acid generation from **QT**. GPC analysis of the isolated material provided support for copolymer formation as evidenced by the observation single peak (Figure S6) with a narrow molecular weight distribution (PDI = 1.26).

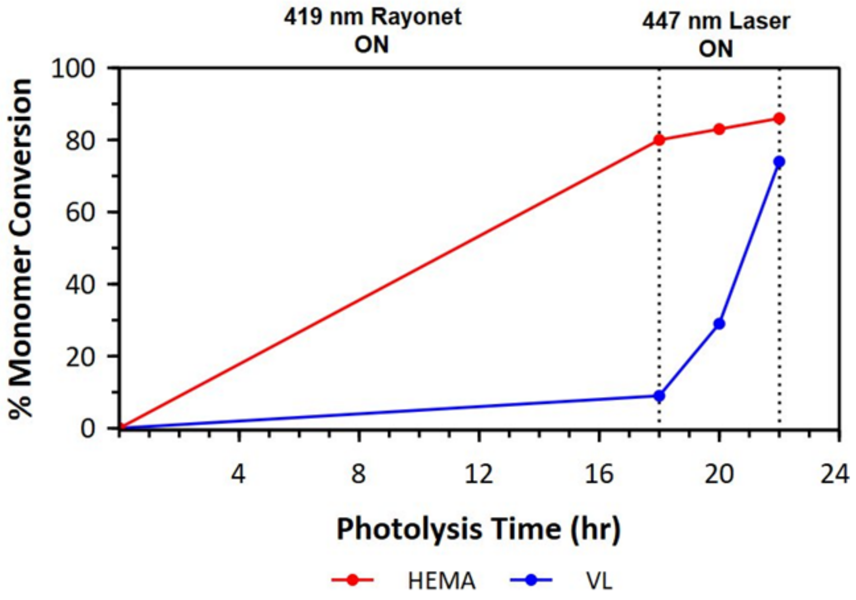


Figure 2. Monitoring conversion of HEMA and δ-VL under different intensities of visible light irradiation of **QT**. Monomer conversion is monitored using ^{1}H NMR.

To ensure that the acrylate does not intrinsically polymerize more rapidly than the lactone, a similar sample was irradiated with only the high intensity 447 nm CW laser. In this case, both monomers show immediate conversion however, δ-VL reached 60% conversion within 4 hours whereas HEMA only reached 20% conversion. (Figure 3).

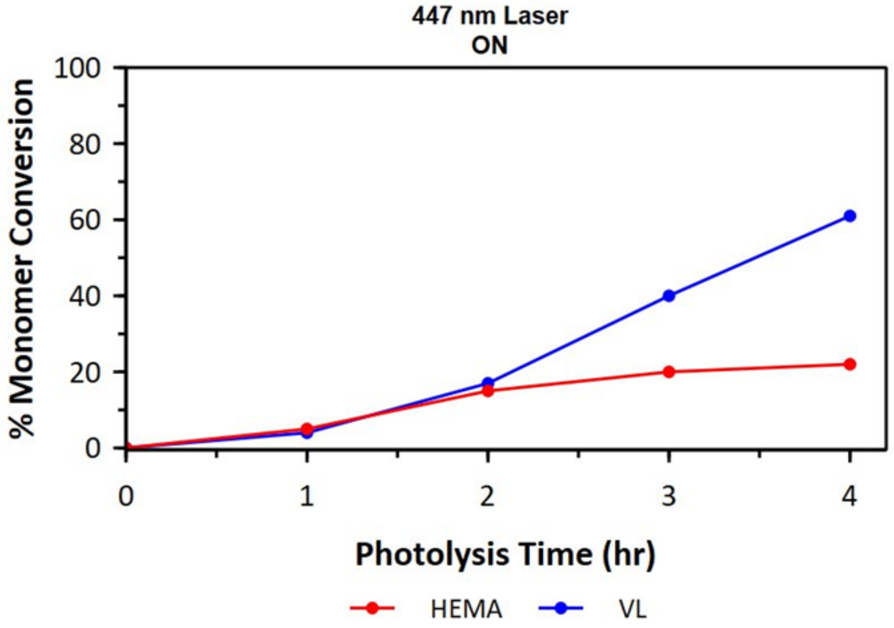


Figure 3. Monitoring conversion of HEMA and δ-VL during photolysis of **QT** with a 447 nm CW laser. Monomer conversion monitored using ^{1}H NMR.

Conclusions

The experiments described in this paper demonstrate that a single catalyst, 1-tosyloxy-2-methoxyanthraquinone **QT**, is capable of mediating both cationic and radical polymerizations depending on the intensity of visible light irradiation. Under high intensity irradiation, photoacid generation occurs producing strong acid capable of catalyzing cationic ring opening polymerization of lactones. Under low intensity irradiation, **QT** is able to photooxidize DMSO which leads to formation of methyl radicals capable of initiating RAFT polymerization. The dependence on light intensity allowed for the one-pot synthesis of a brush copolymer where a single photocatalyst can mediate two types of polymerizations. This demonstrates a strategy that allows simple reaction mixtures to be used to synthesize more complex materials.

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