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Manganese Catalyzed Batch and Continuous Flow Cationic RAFT Polymerization Induced by Visible Light

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Supporting Information Placeholder

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ABSTRACT: We present a robust manganese-catalyzed cationic reversible addition-fragmentation chain transfer (RAFT) polymerization induced by visible light. Well-defined poly(vinyl ether)s with controlled molecular weight and molecular weight distributions (MWDs) can be conveniently prepared at room temperature without monomer purification. The commercially available manganese carbonyl bromide is used as the photocatalyst for cationic RAFT polymerization. Moreover, this method has been further applied in both batch and continuous flow system, providing a visible light induced flow cationic polymerization under mild conditions.

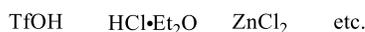
The discovery and fast developments of living cationic polymerization in the 80s to 90s have revolutionized the polymer synthesis,¹⁻³ providing a method of reversibly decreasing the concentration of active species, which has been lately applied to reversible deactivation radical polymerization (RDRP)^{4,5} and promoted great progress in access to polymeric materials with precise and complex architectures. RDRP techniques have received much attention owing to the mild reaction conditions they require and to their excellent compatibility with various monomer and solvent systems. As a result, a large amount of work covers polymerization methodology to mechanism studies and applications.⁶ In parallel, living cationic polymerization has received much interest in recent times, with a focus on the use of external stimuli such as light irradiation, to control the sequences and structures of polymers in mild reaction conditions.⁷⁻¹¹ In 2015, cationic reversible addition-fragmentation chain transfer (RAFT) polymerization was developed by Kamigaito *et al.*, based on typical concepts and mechanism in RDRP techniques.¹² Modelling their system on the chain transfer agent (CTA) used in RAFT polymerization, they synthesized a cationic RAFT agent, which possessed a specific vinyl ether ‘R’ group, able to form an initiating cation after fragmentation. Hence the degenerative chain transfer process, mostly used in RDRP techniques, could be expanded to mediate cationic polymerization. Moreover, the dithioester group present at the polymer chain end could be used for chain extension by either cationic or radical polymerization, providing a novel

approach for the preparation of block copolymers.¹³ In recent years, cationic RAFT polymerization has attracted much interest among polymer chemists. Various external stimulus have been applied to cationic RAFT polymerization, utilizing catalysts such as traditional Bronsted-Lowry acid or Lewis acid,¹⁴ photoredox catalysts^{15,16} and electroredox catalysts (Scheme 1).^{17,18} In addition, the polymerization mechanism can be easily varied between a cationic and radical process, by combining different external stimulus such as light with different wavelengths,¹⁹⁻²¹ to access multiblock copolymers with controlled sequences. More recently, new methodologies for controlled cationic polymerization have been proposed to fabricate precisely defined copolymers.²³⁻²⁵ For instance, Fors and coworkers reported a single-component initiated controlled cationic polymerization under ambient conditions.^{26,27} They synthesized an electron-deficient cyclopentadiene (PCCP) to initiate cationic polymerization, for which termination and chain transfer events could be avoided, due to the tight ion complex formed between the PCCP anion and the oxocarbenium chain end. This system enables a controlled polymerization under ambient conditions, without rigorous monomer purification. Inspired by this method, we recently reported a living cationic polymerization under ambient conditions utilizing a manganese-compound as a weak Lewis acid to construct a similarly tight ion pair.²⁸ However, this method was limited by is the termination reactions required to functionalize the chain end of the polymer for chain extension or post polymerization modifications, typically easily

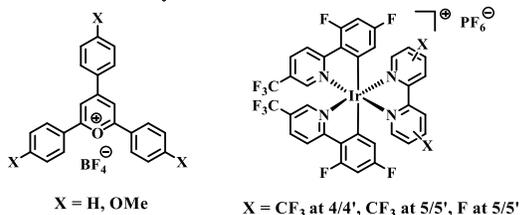
obtained by the RAFT process. These limitations motivated us to study cationic RAFT polymerization under ambient conditions, in which the excellent chain transfer ability of RAFT agent will also significantly inhibit unwanted termination or chain transfer to the nucleophilic impurities.

Previous work:

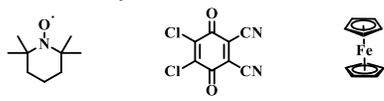
a) Bronsted-Lowry acid or Lewis acid:



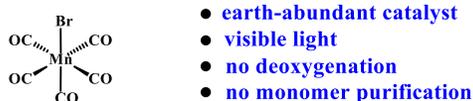
b) Photoredox catalysts



c) Electrodox catalysts



This work: Manganese catalyst



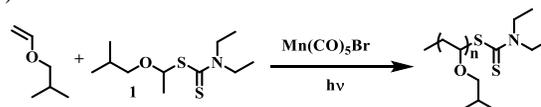
Scheme 1. Different catalysts for cationic RAFT polymerization.

Since strict purification of reagents and inert atmosphere are typically required in cationic RAFT polymerization, we first screened cationic RAFT polymerization catalyzed by several typical Lewis acids without degassing and strict purification of monomers. Control reactions were also performed in glove box, using purified monomers (Table S1). Surprisingly, the molecular weights and molecular weight distributions (MWDs) of products obtained from control did not show marked differences, indicating the cationic RAFT polymerization is tolerant to impurities. However, we observed that the traditional Lewis acid and protonic acid are unstable in air, as they react with air moisture. Moreover, the solubility of common Lewis acids is poor in vinyl ethers, making the polymerization heterogeneous, and thus hindering the control of the polymerization. In contrast to the versatility of our system, typical other photocatalyst such as onium (Scheme 1) or PCCP need complex synthesis, and other system such as iridium-based photocatalysts are typically very expensive.

Manganese, as an earth-abundant transition metal, is a potential candidate for new catalyst development in sustainable chemistry.²⁹ Our recent work on controlled cationic polymerization utilizing halide abstraction reaction between manganese carbonyl and organic halides showed acceptable control under mild conditions.^{30,31} The good solubility in vinyl ethers, and the halide abstraction ability of manganese carbonyl compounds indicate their potential to oxidize cationic RAFT agents into initiating cation, under appropriate conditions. To avoid the oxygen-sensitive radical reactions between manganese carbonyl and organic halides, a bench-stable catalyst, manganese carbonyl bromide (Mn(CO)₅Br), was chosen as the single catalyst, as it has been reported to generate high vacant state manganese,³² which may abstract the dithiocarbonyl group in cationic RAFT agents. This hypothesis was first examined by UV-vis absorption spectrum. The intensity of absorption peak before

300 nm of Mn(CO)₅Br with isobutyl vinyl ether (IBVE) in hexane decreased along with increasing of irradiation time under blue LED, and the intensity of the peak after 300 nm first decreased, then increased. Moreover, the shape of the absorption peak changed, indicating the irreversible decomposition of Mn(CO)₅Br (Figure S2a) and the formation of the dimer, [Mn(CO)₄Br]₂ (the UV-vis spectrum was shown in Figure S2b). The absorption peak of the cationic RAFT agent (**1**, Table 1) with IBVE in hexane showed no change (Figure S3), which can be attributed to the stability of **1** under the same conditions. However, we observed the absorption peak of Mn(CO)₅Br with **1** and IBVE in hexane at around 390 nm, increasing with irradiation time, implying the abstraction reaction between manganese and dithioester group due to the increased molar index of refraction of the manganese compound (Figure S4).

Table 1. Polymerization of IBVE in bulk with various conditions at 25 °C under irradiation of blue LED (Light intensity = 10 mW cm⁻²).



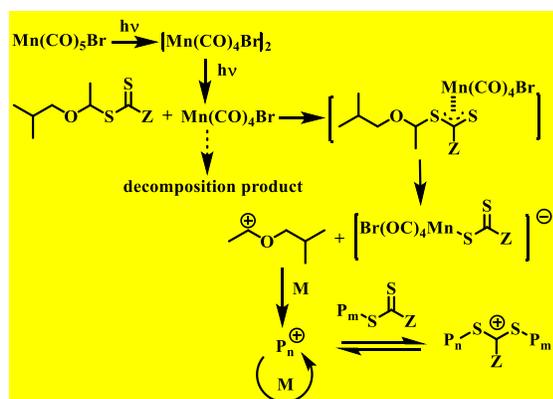
Entry	[IBVE] ₀ /[1] ₀ / [Mn ₂ (CO) ₅ Br] ₀	Time (h)	Conv.%	^a M _{n,th}	^b M _{n,SEC}	<i>D</i>
1	100 : 1 : 0.05	8	72.3	7500	9400	1.12
2	100 : 1 : 0.1	3	88.5	9100	11700	1.11
3	100 : 1 : 0.2	0.7	95.5	9800	12000	1.11
4	100 : 1 : 0.4	0.4	94.5	9700	12000	1.12
5	50 : 1 : 0.1	2	93.7	4900	6500	1.09
6	200 : 1 : 0.4	0.5	87.4	17800	22200	1.19
7	400 : 1 : 0.8	0.5	84.8	34000	34000	1.24

a) Calculated based on conversion ($M_{n,th} = [IBVE]_0/[1]_0 \times M_{IBVE} \times \text{conversion} + M_1$); b) Determined by SEC using polystyrene (PS) as standard in tetrahydrofuran (THF)

These observations inspired us to further developed a cationic RAFT polymerization catalyzed by Mn(CO)₅Br, under visible light. The polymerization was carried out with **1**, Mn(CO)₅Br and IBVE without extra purification and deoxygenation. Table 1 summarises the results, and it shows that the concentration in Mn(CO)₅Br has remarkable effects on the polymerization rate (Entry 1-4, Table 1). The polymerization rate increased by increasing the amount of Mn(CO)₅Br, while the molecular weight is only depend on the molar ratio between monomer to **1** (Entry 5-7, Table 1). The MWDs are all narrow, demonstrating the excellent controllability of this method. Furthermore, controlled experiments were also performed to examine the effect of each component in the polymerization. No polymerization occurred without **1** or Mn(CO)₅Br or light (Entry 1-3, Table S2), indicating both these compounds are required for a successful polymerization. Furthermore, a photo switch 'on/off' experiment was performed to explore the polymerization mechanism. No polymerization occurred during the first 5 min of photo-irradiation, then polymerization oc-

curred after 1 h, after turning off the light, with monomer conversion reaching 89.8%, thus confirming the photo-induced nature of the polymerization (Table S3).

Based on the results mentioned above, the mechanism depicted in Scheme 2 was proposed. The dimer of $\text{Mn}(\text{CO})_5\text{Br}$ was first formed under irradiation with visible light.³³ It was followed by decomposition of the manganese dimer under the continuous light irradiation, which generates a high vacant state manganese complex.³² This manganese complex can oxidize **1** to form a cation and manganese-dithiocarbamate complex and may further decompose to other side products as proposed by the literature.³³ The chain propagating reaction proceeds via the RAFT mechanism, producing well-controlled poly(vinyl ether)s with high chain end fidelity. It is worth noting that the decomposition of $\text{Mn}(\text{CO})_5\text{Br}$ can not only occur under light irradiation, but also upon heating. Interestingly, the polymerization is still controlled at temperatures as low as 60 °C (Table S4), which is unusual compared to traditional living cationic polymerizations. These results demonstrate further the versatility of this cationic RAFT polymerization.



Scheme 2. Proposed mechanism of the polymerization.

Kinetic studies showed a linear relationship of $\ln([M]_0/[M])$ with time (Figure S6A), indicating a constant concentration in active species during polymerization. An induction period of several minutes was observed, which may be attributed to the initial generation of cations. In addition, the molecular weights increase linearly with monomer conversion, although experimental values are slightly higher than theory, possible due to the consumption of small amounts of **1** to generate the initial cation (Figure S6B) or the minor impurities in the synthesized **1** (Figure S7). The MWDs remains narrow, even at high monomer conversions. Moreover, the symmetric and unimodal SEC traces shifted to high molecular weights with an increase in monomer conversion (Figure S6C). These results demonstrate the living characteristics of this polymerization.

The structure of PIBVE was further characterized by proton nuclear magnetic resonance (¹H NMR) and matrix assisted laser desorption time-of-flight mass spectrometry (MALDI-TOF MS). The signal of the proton on the carbon atom connecting to dithiocarbamate group at the polymer chain end (peak f in Figure S8), demonstrates the polymerisation occurs via the RAFT process. A signal at ca.10 ppm was assigned to an aldehyde group, which might be caused by the elimination of an isobutyl group from the polymer terminal. In the MALDI-TOF spectrum (Figure S9), the difference between the main series of peaks is calculated to 100.12 m/z, which matches well the molecular weight of IBVE. The peak of A₄₅ can be assigned to PIBVE with olefin terminal, which was generated from the

elimination of the dithiocarbamate group at the chain end, occurring in the MALDI-TOF MS process. The peak of PIBVE with an aldehyde chain end is confirmed by ¹H NMR results (peak f in Figure S8). The B₄₅ signal is assigned to PIBVE with hydroxyl terminal, originated from the termination of the cationic propagating species by moisture. The C₄₅ signal can be assigned to PIBVE with methoxy group at the chain end generated by the termination of methanol. The D₄₅ signal arises from the β elimination at the α end of PIBVE. Overall, these data confirm the relatively good chain end fidelity of the PIBVE prepared by this method. Chain extension experiments were further performed to confirm the end group fidelity. SEC analysis shows a shift of the MWD to high molecular weights, with a small tail at low molecular weights (Figure S10), which was attributed to the ‘dead chain’ bearing the aldehyde chain end discussed above.

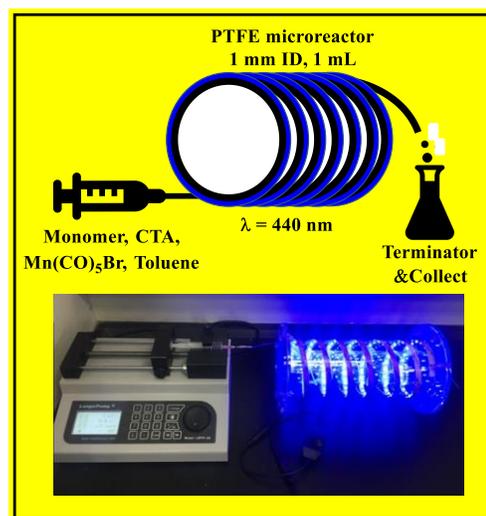


Figure 1. Flow setup for cationic RAFT polymerization.

The versatility of this method motivated us to investigate the use of cationic polymerization in continuous flow reactors under mild conditions. Flow chemistry has been widely used for various polymerization systems, benefiting from fast mixing, stemming from a short diffusion time and fast heat transfer.³⁴ The development of light regulated flow polymerization to yield well controlled MWDs had become an efficient approach to synthesized precisely defined polymers.³⁵⁻³⁷ However, continuous flow cationic polymerization is still very limited owing to its inherent limitations, including inhibition due to moisture-sensitive Lewis acid, and low temperatures. The first flow cationic polymerization was reported in 2004 by Yoshida *et al.* who used a ‘cation pool’ approach, which is still the commonly accepted method to undertake flow cationic polymerization.³⁸⁻⁴⁰ Lu *et al.* developed fast flow cationic polymerization by decreasing the concentrations of added base in traditional living cationic polymerization.^{41,42} The obvious drawbacks of these methods include the need for low temperatures, as the monomers and initiators have to be cooled before mixing, and the polymerization must be performed in a cool bath, which adds complexity to the process. On the other hand, in our visible light induced cationic RAFT polymerization, the monomers and initiators can be mixed together directly, the polymerization can be triggered by switching the light on, and all of these operations

can be performed at room temperature. We built a fully opened photo flow reactor to test our system, based on a sample inject pump and 129 low-energy blue LED lights attached to a 10 cm i.d. poly(methyl methacrylate) (PMMA) pipe, with polytetrafluoroethylene (PTFE) tubing coiled around the outside of a 5.5 cm o.d. PMMA pipe, allowing throughput of reaction mixtures (Figure 1). The results of flow polymerization with different flow rates are depicted in Table 2. PIBVE with controlled molecular weights and narrow MWDs (< 1.2) was obtained in all cases, showing the excellent control of this system. It is worth noting that a flow reactor-based photoinduced cationic RAFT polymerization was also reported during the preparation of this manuscript,⁴³ although the work was limited to the continuous-flow synthesis of pyrylium tetrafluoroborates in order to simplify the synthesis of the photocatalyst.

Table 2. Flow polymerization with $[\text{IBVE}]_0 : [\mathbf{1}]_0 [\text{Mn}(\text{CO})_5\text{Br}]_0 = 100 : 1 : 0.2$ in toluene with different flow rates at 25 °C under visible light (Light intensity = 38.7 mW cm⁻²). $V_{\text{IBVE}} : V_{\text{toluene}} = 1 : 1$.

Entry	Flow rate (mL min ⁻¹)	Time (min)	Conv. %	^a $M_{n,\text{th}}$	^b $M_{n,\text{SEC}}$	\bar{D}
1	0.04	22	45.1	4800	6000	1.20
2	0.03	30	70.7	7300	8400	1.14
3	0.02	48	74.3	7700	8800	1.15
4	0.015	57	82.0	8500	10300	1.12

a) Calculated based on conversion ($M_{n,\text{th}} = [\text{IBVE}]_0/[\mathbf{1}]_0 \times M_{\text{IBVE}} \times \text{conversion} + M_1$); b) Determined by SEC using polystyrene (PS) as standard in tetrahydrofuran (THF).

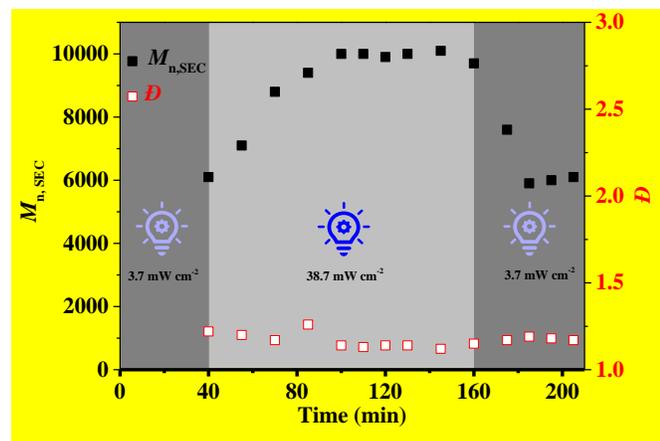


Figure 2. Tuning the molecular weights by adjusting intensities of photo irradiation in flow polymerization with $[\text{IBVE}]_0 : [\mathbf{1}]_0 [\text{Mn}(\text{CO})_5\text{Br}]_0 = 100 : 1 : 0.2$ in toluene at constant flow rate of 0.03 mL min⁻¹. $V_{\text{IBVE}} : V_{\text{toluene}} = 1 : 1$.

The introduction of light in our system also provides the advantage of temporal control of the polymerization. As shown in Scheme 2, the polymerization rate is highly depending on the decomposition of $\text{Mn}(\text{CO})_5\text{Br}$, which can be controlled by tuning the light intensity. Therefore, the molecular weight can be easily tuned by changing the light intensity in the flow reactor, at constant flow rate. Figure 2 shows a variety of products collected at different time after tuning the light intensity. We observed that the molecular weight increased gradually from 6100 g mol⁻¹ to 10100 g mol⁻¹ after tuning the light intensity from 3.7

mW cm⁻² to 38.7 mW cm⁻², and then decreased to 6000 g mol⁻¹ again after tuning the light back to 3.7 mW cm⁻². This process is a convenient method over control of molecular weights. Moreover, the light intensity could also be tuned by a computer algorithm, thus opening up applications in artificial intelligence polymer synthesis.

In conclusion, we have demonstrated the use of visible light to mediate cationic RAFT polymerization, catalyzed by manganese carbonyl bromide as a robust and facile method to design well-defined poly(vinyl ether)s with good chain end fidelity. Our process uses a commercially available catalyst, room temperature, unpurified monomers and does not require deoxygenation. The versatility of our method enabled us to expand it to flow reactions. In this process, the control of light provides temporal control over molecular weight, thus opening up great potential for further applications.

■ ASSOCIATED CONTENT

Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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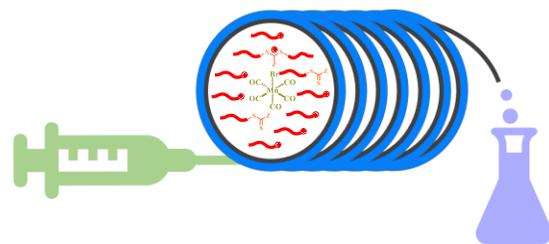
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Visible Light Induced Cationic RAFT Polymerization in Continuous Flow Reactor

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Visible light induced cationic RAFT polymerization catalyzed by manganese compound under mild conditions was presented, which was further applied in both batch and continuous flow polymerization.
