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## COMMUNICATION

# Improving Photo-controlled Living Radical Polymerization from Trithiocarbonates through the Use of Continuous-flow Techniques

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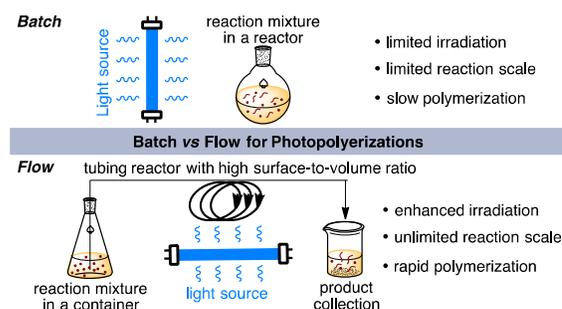
**Herein, we report simple flow reactor designs that enable photo-controlled living radical polymerization (photo-CRP) from trithiocarbonates (TTCs) with significant enhancements in scalability and reaction rates compared to the analogous batch reactions. We also demonstrate the “on/off” photo-switchability of this reaction under flow conditions.**

Photo-polymerizations have been widely applied in academia and industry for several decades.<sup>1</sup> Though historically the most widely used photo-polymerizations are based on non-living free radical chemistry, metal-free photo-controlled/living radical polymerization (photo-CRP) reactions were amongst the very earliest known CRP methods.<sup>2</sup> Over the past decades, photo-CRP variants of the most common living radical polymerizations such as atom transfer radical polymerization (ATRP),<sup>3</sup> nitroxide-mediated radical polymerization (NMP),<sup>4</sup> and reversible addition fragmentation chain transfer polymerization (RAFT)<sup>5</sup>, as well as various related processes,<sup>6</sup> have been developed.

In 2013, we reported<sup>7</sup> the synthesis of telechelic poly(*N*-isopropylacrylamide) (pNiPAAm) through a TTC-mediated photo-CRP process that we believe occurs via a reversible activation/chain transfer “iniferter”<sup>2</sup> mechanism. During these studies, we found that, as expected, greater light intensity increased the reaction rate but had a deleterious effect on molar mass dispersity. The need to use low light intensity and long reaction times to maintain control rendered the process somewhat inconvenient. Furthermore, in contrast to thermal radical polymerizations, photo-CRP reactions typically require new equipment for different reaction scales to ensure uniform irradiation.<sup>8</sup> A simple, scalable photo-CRP technique that would provide control over polymer molecular weight would represent a significant advance in the utility of photo-CRP processes.

In an effort to improve the practicality of photo-CRP, we reasoned that the use of a continuous-flow reactor would be

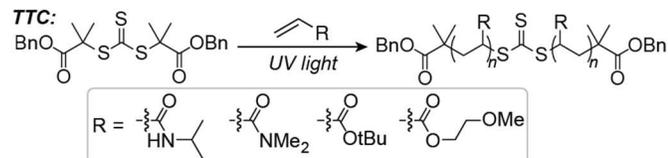
advantageous (Figure 1). Continuous-flow processes are recognized as robust and practical methods due to their easy scale-up, efficient mass- and heat-transfer, potential for automated manufacturing, and increased safety (Figure 1).<sup>9,10,11</sup> Importantly, in contrast to photochemical transformations under batch conditions, flow methods enable more uniform irradiation of the reaction mixtures thanks to the high surface-to-volume ratio in microchannels of flow reactors.<sup>12,13</sup> We hypothesized that these features would accelerate photo-CRP reactions without sacrificing control over molar mass and dispersity. Indeed, Junkers and coworkers recently demonstrated that continuous-flow technology offered benefits in a photo-induced Cu-mediated CRP of methyl methacrylate with molar masses limited to <10 kDa.<sup>12</sup>



**Figure 1** Photo-CRP under batch or flow conditions.

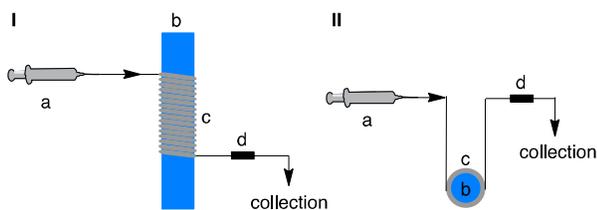
Herein, we report the development of a simple flow reactor design that enables the scalable photo-CRP of acrylates and acrylamides from TTCs (Scheme 1) with dramatic enhancements in reaction rate and versatility. This new method provides polymer products with narrow molecular weight distributions ( $M_w/M_n = 1.06-1.22$ ) even for molar mass values above 100 kDa. Furthermore, we expand this technique to several acrylate and acrylamide monomers

(Scheme 1), and we demonstrate for the first time that the “on/off” switchability of this reaction is preserved under flow conditions. A novel multi-valve flow reactor design enables the collection of different molar mass polymer samples from the same reaction run simply by opening and closing collection valves located at different points along the flow path. The low cost and commercial availability of all components of this system, and its plug and play capability with different monomers and trithiocarbonates, will make it a useful platform for scalable photo-CRP.

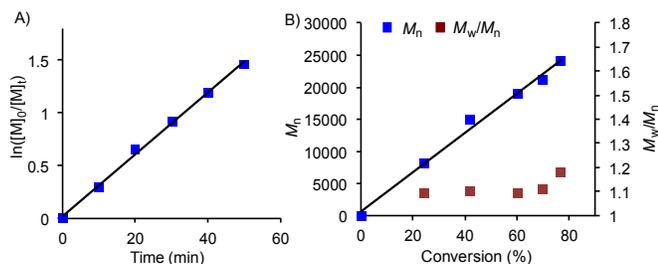


**Scheme 1** Photo-CRP reaction and monomer scope investigated in this work. Bn = benzyl; TTC = trithiocarbonate

To increase the practicality of this method, we sought to use only commercially available components for the setup. Since the photo-CRP reaction is sensitive to oxygen, all parts used to build the setup such as syringes, tubing reactors, and connectors were carefully chosen to minimize air permeability during the flow process (see the Supporting Information, SI, for details). We first investigated the photo-CRP of *N*-isopropylacrylamide (NiPAAm) from a bis-benzyl TTC (Scheme 1) with setup A shown in Figure 2. In this setup, the reaction solution was first loaded in a stainless steel syringe and injected with a syringe pump into a reactor made of Halar® tubing, which was wrapped around a UV lamp (peak emission at 352 nm, for detailed information about the reactor, flow rate etc., see SI). In this setup, the UV exposure time, which is related to the flow residence time, can be easily adjusted by changing the flow rates. After irradiation the reaction mixture was passed through a back pressure regulator to prevent backflow before collection. The collected sample solutions were analyzed via <sup>1</sup>H NMR and gel permeation chromatography (GPC) to determine monomer conversion.

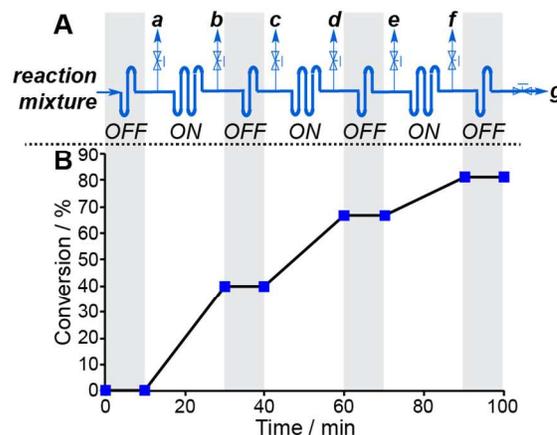


**Figure 2** Continuous-flow Setup A for photo-CRP, I: view from the side; II: view from the top. See the supporting information for details.



**Figure 3** Photo-CRP under flow conditions with Setup A. **A)** Irradiation time (residence time in flow) vs.  $\ln([M]_0/[M]_t)$ , with  $[M]_0$  and  $[M]_t$  being the concentrations of monomers at time points 0 and  $t$ , respectively; **B)** conversion vs.  $M_n$  and conversion vs.  $M_w/M_n$ .

As shown in Figure 3, the photo-CRP with NiPAAm/TTC in a 250/1 ratio proceeded with excellent control under flow conditions. Plots of both  $\ln([M]_0/[M]_t)$  versus exposure time (Figure 3A), and the number-average molecular weight ( $M_n$ ) versus conversion (Figure 3B) gave linear relationships, while the value of  $M_w/M_n$  remained low (1.09-1.18) throughout the entire process. The observed increase in dispersity at high conversions may be due to irreversible trithiocarbonate decomposition or chain coupling at low monomer concentrations. When the tubing reactor was immersed in an 80 °C oil bath without light irradiation, there was no conversion as determined by <sup>1</sup>H NMR analysis. The photo-CRP exhibited a ~four-fold increased reaction rate under flow conditions (~60 min to reach 80% conversion) compared to its batch counterpart (~240 min to reach 74% conversion) under otherwise identical reaction conditions.



**Figure 4** “On”/“off” experiments for photo-CRP under flow conditions.

Next, to demonstrate that the polymers generated via photo-CRP can be reactivated by irradiation under flow conditions, we conducted “on”/“off” cycles with the setup shown in Figure 4A. In this setup, the tubing reactors were completely covered with aluminum foil for places where light was “off” (10 min residence time); the tubing reactors were wrapped around UV lamps for places where light was on (20 min residence time). A series of collection valves were placed at various positions along the tubing (see Figure 4A). When the flow started, only one outlet from  $a$  to  $g$  was switched on for collecting samples, which were immediately analyzed by <sup>1</sup>H NMR and GPC (see SI). As demonstrated in Figure 4B, after the first irradiation for 20 min (sample collected via outlet  $b$ ), there was no further conversion in the dark for 10 min (sample collected via outlet  $c$ ). Continued irradiation led to reactivated polymer growth. The second and third cycles (Figure 4B) further confirmed the ability to control the photo-CRP process using light.

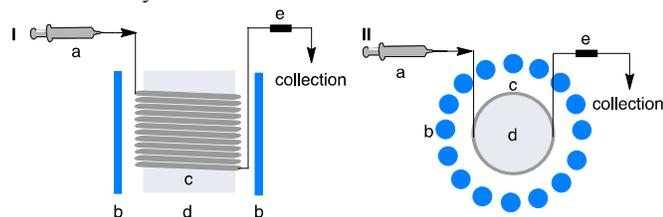
**Table 1** Comparison of photo-CRP under flow conditions<sup>a</sup> with setup A (Figure 2) or B (Figure 5).

Entry	Flow Setup	Time	Conversion <sup>b</sup>	$M_n$ <sup>c</sup>	$M_w/M_n$ <sup>c</sup>
1	A	30min	65%	39000	1.23
2	A	60min	80%	41000	1.43
3	B	30min	50%	26900	1.10

<sup>a</sup>Reaction conditions: NiPAAm (2.0 M), 1 (4.0 mM) in MeCN with irradiation from a 8 W UV lamp (peak emission at 352 nm) under flow conditions.  $M_n$  = number average molar mass;  $M_w$  = weight average

molar mass. <sup>b</sup>The conversion of monomer was determined by <sup>1</sup>H NMR spectroscopy. <sup>c</sup> $M_n$  and  $M_w/M_n$  were determined by GPC analysis.

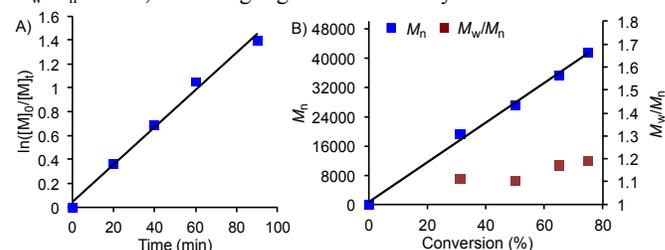
To produce polymers with higher molecular weights, we next tried to increase the NiPAAm/TTC ratio to 500/1 using setup A. However, in this case, the dispersity increased dramatically when the irradiation time was greater than ~30 min (Table 1, entries 1 and 2). To avoid irreversible TTC decomposition at low concentration, we hypothesized that decreasing the intensity of light might prove favorable; a new setup B (Figure 5) was assembled. In this setup, the tubing reactor was wrapped around a glass bottle, which was placed in the middle of a chamber where it was surrounded by UV lamps at a distance of 3 cm (see SI for details). The greater distance from the lamps translates into a decreased light intensity. We were pleased to find that the photo-CRP showed excellent control when conducted in setup B. In 30 min residence time, 50% conversion of NiPAAm and a low  $M_w/M_n$  value (1.10) was observed as determined by <sup>1</sup>H NMR and GPC analysis.



**Figure 5** Continuous-flow Setup B for photo-CRP. I: view from the side; II: view from the top. See the supporting information for details.

With setup B in hand, we next evaluated the photo-CRP of NiPAAm (NiPAAm/initiator = 500/1) with different exposure times (residence times) under flow conditions. As shown in Figure 6, good linear relationships were observed for plots of both  $\ln([M]_0/[M]_t)$  versus exposure time (Figure 6A), and  $M_n$  versus conversion (Figure 6B). PNiPAAm was produced with different  $M_n$  values ranging from

19,400 to 41,600 g/mol with narrow molecular weight distributions,  $M_w/M_n < 1.20$ , which highlights the versatility of this method.



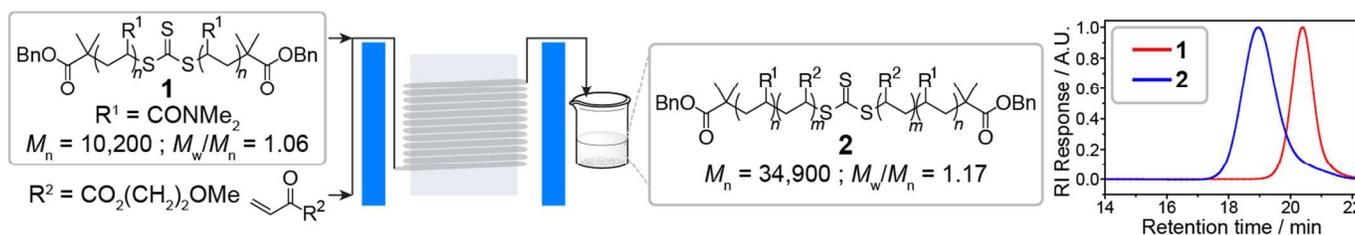
**Figure 6** Photo-CRP under flow conditions with Setup B. A) Irradiation time (residence time in flow) vs.  $\ln([M]_0/[M]_t)$ , with  $[M]_0$  and  $[M]_t$  being the concentrations of monomers at time points 0 and  $t$ , respectively; B) conversion vs.  $M_n$  and conversion vs.  $M_w/M_n$ .

Following our studies of photo-CRP of NiPAAm with setups A and B under flow conditions, we decided to apply this technique to polymerization of other monomers, such as *tert*-butyl acrylate (*t*BA), ethylene glycol methyl ether acrylate (EGMEA) and *N,N*-dimethylacrylamide (DMA) (structures shown in Scheme 1). As shown in Table 2, after short exposure times (40-90 min), polymers with narrow molar mass distributions ( $M_w/M_n = 1.11$ -1.21) were obtained for all cases with either setup A or B in satisfactory conversions. Furthermore, polymers with different molar masses were obtained by easily changing parameters in flow. The theoretical molecular weights calculated based on conversions were consistent with corresponding results obtained by GPC measurement, which suggests that the polymerizations were well controlled under flow conditions. Following these successful experiments, the monomer/TTC ratio was increased to 2000/1, and photo-CRP was examined using DMA with setup B. In this case, the poly(DMA) with over 100 kDa molar mass with a good  $M_w/M_n$  value ( $M_w/M_n = 1.22$ ) was obtained, which is difficult using flow methods.<sup>10c</sup>

**Table 2** Photo-CRP under flow conditions with setup A or B.

Entry	Monomer	[M]:[Initiator 1]	Flow Setup	Time (min)	Conversion (%) <sup>b</sup>	$M_{n,theo}$ <sup>c</sup>	$M_{n,GPC}$ <sup>d</sup>	$M_w/M_n$ <sup>d</sup>
1	<i>t</i> BA	250:1	A	60min	81%	26400	29800	1.21
2	<i>t</i> BA	500:1	B	90min	82%	52900	54200	1.19
3	EGMEA	250:1	A	60min	88%	29100	30300	1.21
4	EGMEA	500:1	B	80min	81%	53100	55800	1.17
5	DMA	250:1	A	40min	87%	22000	25500	1.11
6	DMA	250:1	A	40min	87% (84%, 2.95 g) <sup>e</sup>	22000	24900	1.11
7	DMA	500:1	B	80min	84%	42000	43300	1.18
8	DMA	2000:1	B	40min	55%	109400	105800	1.22

<sup>a</sup>Reaction conditions: monomer (2.0 M), **1** (4 or 8 mM) in MeCN with irradiation from a 8 W UV lamp (emission at 352 nm) under flow conditions. See the Supporting Information for details. <sup>b</sup>The conversions of monomer were determined by <sup>1</sup>H NMR spectroscopy. <sup>c</sup> $M_n$  calculated according to conversions. <sup>d</sup>The values of  $M_{n,GPC}$  and  $M_w/M_n$  were determined by GPC analysis. <sup>e</sup>Isolated yield on a 36 mmol scale.



**Figure 7** Synthesis of PDMA-*b*-PEGME-*b*-PDMA triblock copolymer **2** under photo-flow conditions. 60 min residence time; see SI for details.

One of the major advantages of flow chemistry involves the ease-to-scale-up reactions. To further demonstrate the robustness of our flow technique, we successfully conducted the photo-CRP of DMA under the same flow conditions of a small-scale synthesis by just prolonging the collecting time (Table 2, entries 5 and 6). In a period of 400 minutes of collection time, we were able to generate 2.95 grams (84% isolated yield, from 36 mmol of monomer) of PDMA with a satisfactory molecular weight distribution ( $M_w/M_n = 1.11$ ). Greater scales could be achieved by running the flow system for a longer period of time, or through construction of multiple flow paths around the same light source.

Finally, we sought to evaluate the potential of setup B for the formation of a block copolymer. A PDMA homopolymer synthesized in setup A (1, Figure 7) was used as a macro-TTC for the synthesis of triblock PDMA-*b*-PEGMEA-*b*-PDMA 2 in setup B. GPC analysis (Figure 6) confirmed that the chain extension was successful. In addition, the molecular weight distribution remained narrow after chain extension.

In conclusion, we have developed a simple, scalable, and efficient technique for photo-CRP from TTCs. This method represents, to our knowledge, the first example of metal-free and switchable photo-CRP conducted under flow conditions. Importantly, the design enables the accelerated synthesis of high molecular weight polymers that have not been achieved in batch or flow syntheses. Notably, two flow setups were designed for reactions with different monomer/TTC ratios enabling control over the molecular weights and molecular weight distributions. Moreover, we have also successfully performed a multistep flow sequence to access block-polymers. To increase the practicality of this protocol, all components used to assemble our flow setups are available from commercial sources; the benefits of these simple setups should translate to many of the other known photo-CRP reactions. We expect that the operational simplicity of this flow technique and its ability to produce high quality polymers in high quantities will make it a useful method for both academia and industry.

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## Notes and references

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## COMMUNICATION

## TOC

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