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Block Copolymer Sequence Inversion through Photoiniferter Polymerization

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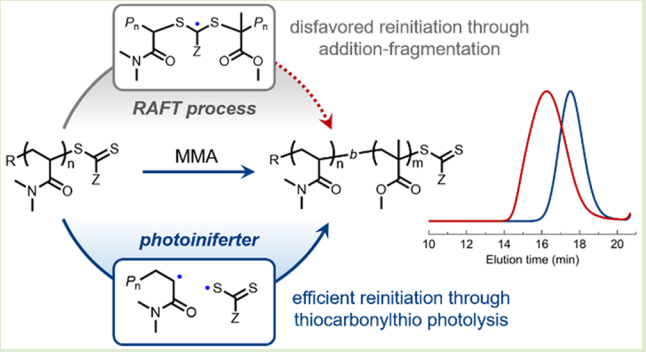
Supporting Information

ABSTRACT: Block copolymers prepared by reversible addition−fragmentation chain transfer (RAFT) polymerization are often restricted to a specific comonomer blocking sequence that is dictated by intermediate radical stability and relative radical leaving group abilities. Techniques that provide alternative pathways for reinitiation of thiocarbonylthio-terminated polymers could allow access to block copolymer sequences currently unobtainable through the RAFT process. We report a method for preparing "inverted" block copolymers, whereby the traditional order of monomer addition has been reversed through the use of photoiniferter-mediated radical polymerization. Specifically, thiocarbonylthio photolysis of xanthate- and dithiocarbamate-functional macromolecular chain transfer agents (macro-CTAs) led to the direct formation of leaving group macroradicals otherwise unaffordable by an addition−fragmentation mechanism. We believe this method could provide a route to synthesize multiblock copolymers of synthetically challenging comonomer sequences.



Reversible-deactivation radical polymerization (RDRP) has enabled significant advances in the field of polymer science by allowing for the synthesis of polymers with intricate composition, structure, and functionality. Reversible addition−fragmentation chain transfer (RAFT) polymerization has emerged as one of the most versatile and widely used RDRP platforms due to its remarkable tolerance toward a variety of polymerization conditions.[1−4] However, like other RDRP methods, the synthesis of block copolymers through RAFT polymerization bears restrictions on the order of monomer addition. Correctly identifying the appropriate macromolecular chain-transfer agent (macro-CTA) suited for efficient fragmentation and reinitiation is critical for the synthesis of well-defined block copolymers.[5,6] The development of new synthetic techniques allowing for indiscriminate sequencing of monomer classes could provide access to materials that are inaccessible through modern RDRP techniques.[7]

Efficient reinitiation of macro-CTAs can be evaluated by considering two series of steps: (1) formation of the macroradical species derived from the parent macro-CTA and (2) macroradical addition to monomer (i.e., cross propagation).[8] During the process of establishing reinitiation (i.e., RAFT pre-equilibrium or initialization), productive fragmentation of the intermediate radical toward macro-R groups, defined here as R groups derived from the macro-CTA, is dependent on the magnitude of k_β in comparison to k_{-add} (Figure 1).[9,10] Fragmentation of the intermediate radical favors the better homolytic leaving group, which decreases in the following order: methacrylates ∼ methacrylamides ≫ styrenics ∼ acrylates ∼ acrylamides ∼ *N*-vinylheteroaromatics > vinyl amides > vinyl esters. As a consequence, block copolymers composed of, for example, methyl methacrylate (MMA) and *N*,*N*-dimethylacrylamide (DMA), require the following blocking order: PMMA-*b*-PDMA, where the more stable radical former (i.e., PMMA) is used as a macro-CTA to ensure efficient chain extension with DMA. Preparation of an identical diblock copolymer, but with an "inverted" sequence (i.e., PDMA-*b*-PMMA) using a PDMA macro-CTA, proves challenging due to differences between k_β and k_{-add} (Figure 1, Pathway A). Preferential fragmentation of the RAFT intermediate toward PMMA (k_{-add}) results in a mixture of PMMA and PDMA homopolymers at low conversion and inefficient or slow chain extension of the PDMA macro-CTA at higher conversion. These long-standing limitations surrounding the inflexible blocking order of RAFT-derived block copolymers have been partly overcome in other RDRP

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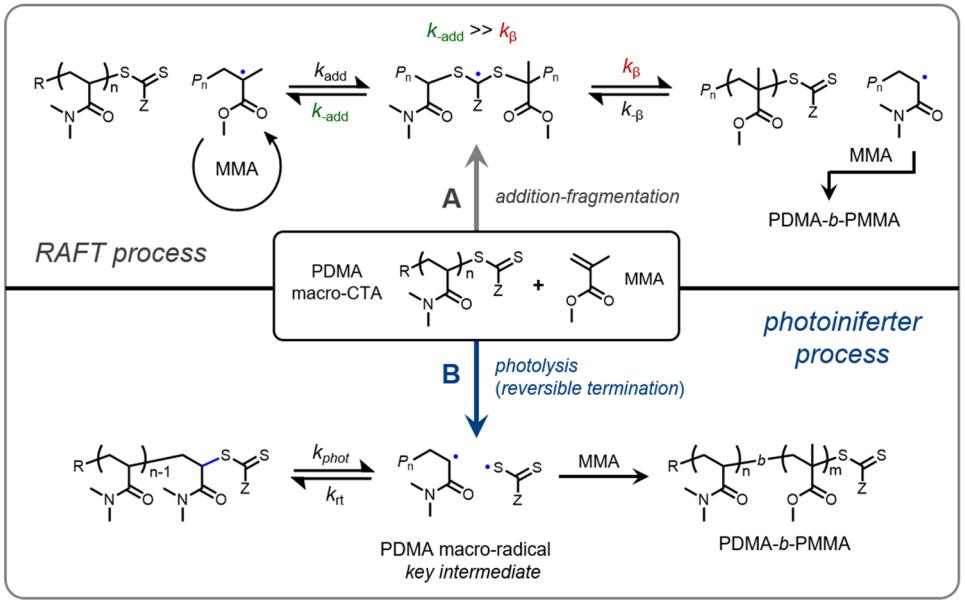

Figure 1. Pathways outlining mechanistic considerations for poly(*N*,*N*-dimethylacrylamide) (PDMA) macromolecular chain transfer agent (macro-CTA) undergoing chain extension with methyl methacrylate (MMA) to produce PDMA-*b*-PMMA through either RAFT polymerization (A) or photoiniferter polymerization (B).

methods such as ATRP through the use of either halogen exchange or photoredox catalysis.[11,12]

One alternative route toward reinitiation of thiocarbonylthio-derived RAFT polymers is through direct photolysis of the carbon−sulfur bond (Figure 1, Pathway B).[13−16] Due to the role of photolysis-driven initiation, thiocarbonylthio CTAs are known as photoinitiator-transfer-terminator (photoiniferter) agents.[17] Early work from the 1980s by Otsu and co-workers involved the use of dithiocarbamate photoiniferters as reversible terminating agents for living free-radical polymerization.[18] Seeing that such techniques predate RAFT polymerization, it is worth noting that much of the work was performed without detailed knowledge of degenerative chain transfer and blocking order restrictions. Interestingly, however, Otsu and co-workers reported the synthesis of PS-*b*-PMMA, whereby a PS dithiocarbamate macrophotoiniferter underwent photomediated chain extension with MMA.[19] Due to the lack of productive fragmentation (i.e., $k_{-add} > k_\beta$) needed for reinitiation through an addition−fragmentation mechanism, it is assumed that block copolymers formed in this fashion are synthesized primarily through photolysis-driven reinitiation.

Inspired by the early work of Otsu and co-workers, we hypothesized thiocarbonylthio C−S bond photolysis could provide a convenient route to generate R group macroradical intermediates otherwise disfavored by the RAFT process. Herein, we report the use of thiocarbonylthio-derived macro-CTAs to provide sequence-inverted diblock copolymers under mild polymerization conditions.

We hypothesized that photolysis-driven reinitiation could provide access to block copolymers of an inverted blocking order. Trithiocarbonates, xanthates, and dithiocarbamates represent three of the most commonly used thiocarbonylthio photoiniferter agents, and acrylamides are among the most well-studied monomer classes used in photoiniferter polymerization processes.[20] Therefore, we chose to synthesize PDMA macro-CTAs bearing either trithiocarbonate (PDMA-TTC), xanthate (PDMA-Xan), or dithiocarbamate switchable RAFT agent (PDMA-SRA) functionality (Figure 2). Using previously

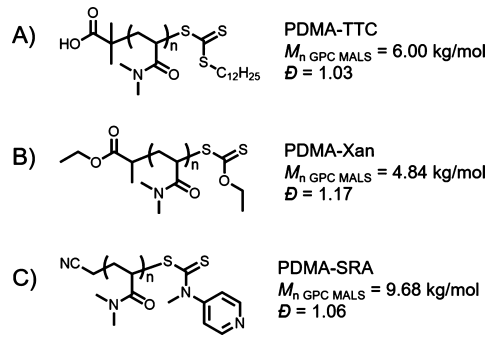

Figure 2. PDMA photoiniferters containing (a) trithiocarbonate (PDMA-TTC), (b) xanthate (PDMA-Xan), and (c) switchable RAFT agent (PDMA-SRA) thiocarbonylthio end groups.

established methods,[20,21] DMA was polymerized in the presence of either a trithiocarbonate or switchable raft agent using RAFT polymerization with an appropriate azo thermal initiator, whereas xanthate-mediated photoiniferter polymerization was used to obtain PDMA-Xan. Low number-average molecular weights (less than 10 kg/mol) were targeted to easily monitor shifts in molecular weight and molecular weight distribution of the attempted diblock formations by gel-permeation chromatography (GPC).

We first sought to examine the ability of PDMA-TTC photoiniferters to reinitiate methyl methacrylate by exciting the $\pi \rightarrow \pi^*$ transition (λ_{max} = 312 nm, Figure 3A) of the trithiocarbonate using UV light irradiation (Scheme 1). After 2 h of continuous light exposure, a mixture of uninitiated PDMA-TTC and PDMA-*b*-PMMA was observed by GPC analysis (Figure 4A). As expected, linear pseudo-first-order kinetics were observed (Figure S2), which is consistent with previous reports detailing MMA photoiniferter polymerization.[22] The presence of residual PDMA-TTC is likely a result of slow photolysis due to low TTC absorption in the UV range (Figure 3A), which is consistent with previous kinetic studies of PDMA-TTC photoiniferters.[20] Dormant PDMA-

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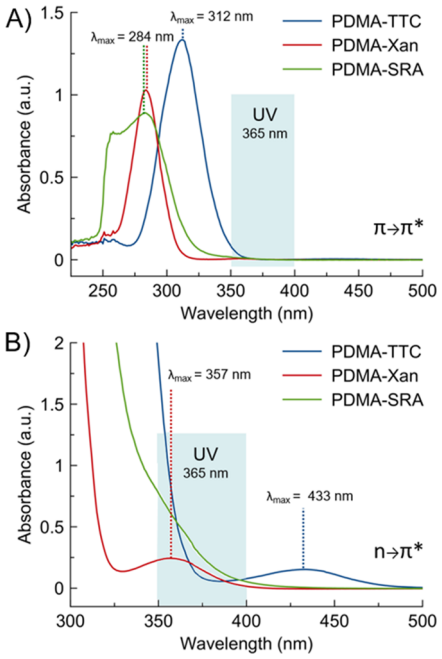
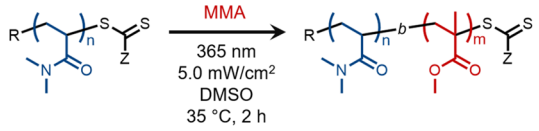


Figure 3. UV−vis spectra of PDMA macro-CTAs.

Scheme 1. Photomediated Chain Extension of PDMA Macro-CTAs with MMA



Z = S-$C_{12}H_{25}$ (PDMA-TTC)
O-CH_2CH_3 (PDMA-Xan)
N-methyl-*N*-(pyridin-4-yl) (PDMA-SRA)

TTC chains are unlikely to undergo productive fragmentation via an addition−fragmentation pathway with growing methyl methacrylate-terminated polymer chains. Furthermore, slow photolysis of the PDMA-TTC macro-CTA would result in an artificially high molar ratio of [MMA]:[PDMA macroradical], in turn producing a high PMMA number-average degree of polymerization during the polymerization.

We sought to explore other methods of increasing the photolysis rate of PDMA-TTC, thus providing faster reinitiation for effective blocking. Unlike UV light, blue-light irradiation facilitates photolysis through excitation of the trithiocarbonate n → π^* transition (λ_{max} = 433 nm, Figure 3B).[15,23] Therefore, we hypothesized this alternative excitation pathway could lead to enhanced TTC photolysis due to more appreciable overlap between TTC absorption and blue-light emission. Similar to previous attempts with UV light, a combination of high molecular weight PDMA-*b*-PMMA and PDMA-TTC was obtained after irradiating for 12 h (Figure S3). In a final attempt to enhance the rate of PDMA-TTC reinitiation, Eosin Y, serving as a photoredox catalyst (0.5 mol % relative to PDMA-TTC), was added to the polymerization mixture with the anticipation of facilitating rapid reactivation of PDMA-TTC chain ends through photoinduced electron/energy transfer RAFT (PET-RAFT) polymerization.[24−26] However, reactivation through the eosin Y-mediated photoredox process was not effective enough to lead to the formation of well-defined PDMA-*b*-PMMA block copolymers (Figure S4). We anticipate that the use of a photoredox catalyst having a higher redox potential could lead to enhanced reactivation as compared to Eosin Y; however, given the air sensitivity and expensive nature of such catalysts, these studies were not pursued further.

Unlike trithiocarbonates, xanthates undergo rapid photolysis under UV light irradiation.[20,27] Overlapping absorption of the xanthate n → π^* transition (λ_{max} = 357 nm, Figure 3B) and emission of UV light (λ_{max} = 365 nm) from common UV photoreactors facilitate efficient excitation and lead to rapid photolysis.[28] Furthermore, Ajayaghosh and co-workers have previously demonstrated moderate control over photoiniferter polymerization of MMA with xanthates.[29,30] Due to the low transfer constant between MMA and xanthates, chain growth is expected to be predominately regulated through reversible termination. Therefore, we hypothesized that PDMA-XAN macro-CTAs could provide rapid reinitiation of MMA in the presence of UV light. Gratifyingly, UV-induced photoiniferter chain extensions of PDMA-XAN led to efficient PDMA-*b*-PMMA block copolymer formation (Figure 4B). A high blocking efficiency was observed (ca. 98%) through deconvolution of the purified PDMA-*b*-PMMA GPC chromatogram (Figure S5), indicative of highly efficient conversion of

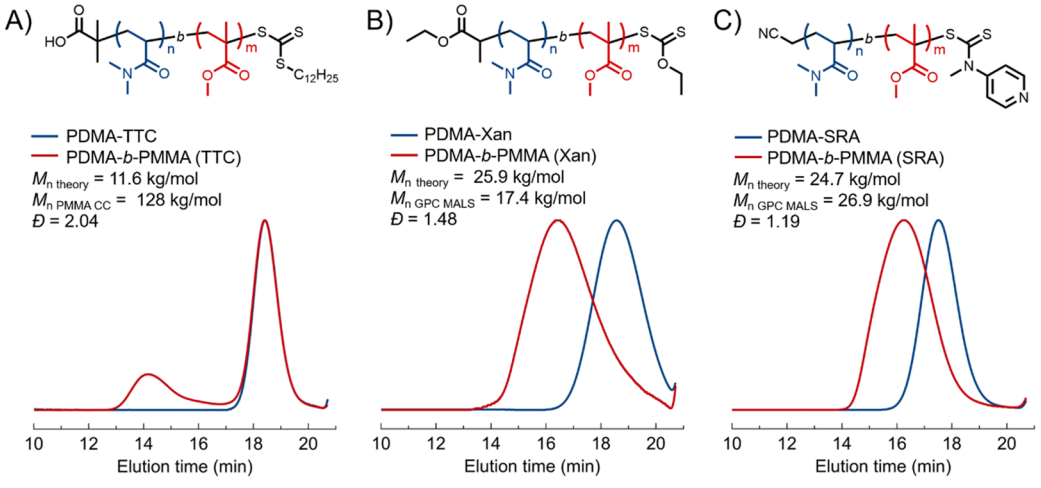


Figure 4. GPC chromatograms of PDMA-*b*-PMMA prepared from PDMA macro-CTAs.

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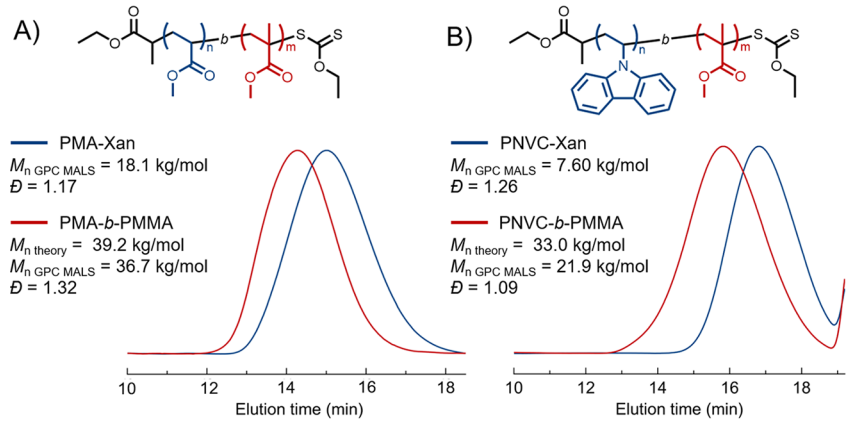

Figure 5. Preparation of (A) PMA-*b*-PMMA and (B) PNVC-*b*-PMMA using the xanthate photoiniferter approach.

the PDMA-Xan macro-CTA into the respective PDMA-*b*-PMMA block copolymer. Kinetic studies of photomediated chain extension of PDMA-Xan with MMA revealed linear pseudo-first-order kinetics, indicating a constant radical concentration was maintained throughout the polymerization. Additionally, the rapid conversion of PDMA-Xan macro-CTA into the corresponding PDMA-*b*-PMMA diblock copolymer was observed by monitoring the shift in molecular weight with time by GPC (Figure S6). Furthermore, PDMA-Xan photomediated chain extensions exhibited faster polymerization kinetics when compared to PDMA-TTC (Figure S7). In comparison to photomediated chain extension, exogenously initiated thermal chain extension of PDMA-Xan with MMA through RAFT polymerization led to a mixture of PMMA homopolymer and PDMA-Xan, as expected, demonstrating the promise of our proposed light-mediated method for inverting blocking sequences (Figure S8).

Next, we evaluated the use of this method to prepare block copolymers containing varied MMA number-average degrees of polymerization. However, monomer to macro-CTA ratios greater than 300:1 led to asymmetric molecular weight distributions favoring a high molecular weight shoulder (Figure S9). Photolysis studies were performed to provide further insight into molecular weight growth. Small-molecule xanthates were synthesized from potassium *O*-ethyl xanthate and an appropriate alkyl halide to structurally mimic acrylic and methacrylic xanthates. Photolysis studies were then carried out in DMSO-d_6 using 15 equiv of 1-ethylpiperidine hypophosphite (EPHP) as a hydrogen atom donor (Figure S10). From these studies, we found that methacrylic R groups undergo photolysis faster than acrylic R groups. Assuming the rate of hydrogen atom abstraction from EPHP is greater than the rate of reversible termination, this suggests that terminal xanthate groups of methacrylic chain ends undergo photolysis faster than PDMA- or PMA-derived macro-CTAs. A faster rate of photolysis later in the polymerization could explain the shape of the molecular weight distributions when targeting higher degrees of polymerization. The asymmetry of molecular weight distributions was ultimately suppressed by lowering the initial monomer concentration from 1.5 to 0.2 M (Figure S11). It is hypothesized that lower propagation rates help establish a proper balance between the relative rates of PDMA photolysis (i.e., reinitiation) and propagation.

We then investigated poly(methyl acrylate) (PMA) and poly(*N*-vinylcarbazole) (PNVC) xanthate macro-CTAs to serve as efficient photoiniferters for the block copolymerization of MMA. Rapid photolysis rates of PNVC-xanthate derivatives have been previously reported and, therefore, prompted us to investigate the construction of PNVC-*b*-PMMA diblock copolymers.[28] Indeed, chain extension of PNVC-xanthate with MMA led to the formation of PNVC-*b*-PMMA ($M_{n\ GPC\ MALS}$ = 21.9 kg/mol, Đ = 1.09, Figure 5B). Similarly, PMA-*b*-PMMA could be efficiently prepared ($M_{n\ GPC\ MALS}$ = 36.7 kg/mol, Đ = 1.32, Figure 5A) with good agreement between theoretical and experimental molecular weights.

Lastly, we sought to evaluate the potential for dithiocarbamate PDMA macro-CTA derived from a switchable RAFT agent (PDMA-SRA) to achieve similar diblock copolymerization. We anticipated that the use of dithiocarbamate-switchable RAFT agents could provide access to block copolymer sequences which complement previous work on unifying more activated and less activated monomer classes.[31,32] UV−vis spectroscopy of PDMA-SRA revealed similar electronic transitions compared to PDMA-Xan (Figure 3A). Specifically, the absorption of PDMA-SRA dithiocarbamate $\pi \rightarrow \pi^*$ transition (λ_{max} = 284 nm, Figure 3A) matched that of PDMA-Xan. We reasoned that these observed similarities in absorption could translate into rapid C−S bond photolysis of PDMA-SRA. To test this, we performed chain extension reactions under identical reaction conditions as PDMA-Xan-mediated PDMA-*b*-PMMA synthesis. Indeed, clean blocking efficiency was observed with good agreement between theoretical and experimental molecular weights (Figure 4C). We again attribute this enhanced blocking efficiency (ca. 78%, Figure S12) to rapid C−S bond photolysis, as is the case with PDMA-Xan.

In conclusion, we have developed a method to invert the blocking order of RAFT-derived polymers through the use of thiocarbonylthio photolysis. We found a strong dependence on the identity of both the R- and Z-group of the macro-CTA in facilitating efficient blocking. Importantly, this method provides a new route to circumvent fundamental issues inherent to the mechanism of RAFT polymerization in the context of block copolymer formation. We are currently investigating the use of this method to construct multiblock copolymers containing methacrylic interior blocks which otherwise are unobtainable through sequential blocking. We envision this method will allow for rapid advancements in block copolymer self-assembly due to the ability to access previously unstudied comonomer sequences.

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■ ASSOCIATED CONTENT

Supporting Information

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Materials, methods, experimental details, and supporting figures (PDF)

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The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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NOTE ADDED AFTER ASAP PUBLICATION

Due to a production error, this paper was published ASAP on October 15, 2019, with errors in the Figure 2 caption. The corrected version was reposted on October 17, 2019.

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