Thiourea Dioxide As a Green and Affordable Reducing Agent for the ARGET ATRP of Acrylates, Methacrylates, Styrene, Acrylonitrile, and Vinyl Chloride

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S Supporting Information

ABSTRACT: Thiourea dioxide, a green and inexpensive compound used at industrial scale, was employed as reducing agent for the controlled polymerization of a wide range of monomer families, namely, acrylates (methyl acrylate, 2-hydroxyethyl acrylate, butyl acrylate, methacrylates (2-(dimethylamino)ethyl methacrylate, 2-aminoethyl methacrylate hydrochloride, and methyl methacrylate), styrene, acrylonitrile, and vinyl chloride (nonactivated monomer) by ATRP. Mechanistic studies confirmed that the polymerizations are ruled by the activators regenerated by electron transfer (ARGET) mechanism. It is worth noting that vinyl chloride has never been polymerized by ARGET ATRP. The system proved to be very versatile and robust, working in organic solvents, organic/water mixtures, and aqueous medium at near room temperature with low metal catalyst concentration. Chain extension experiments confirmed the high chain-end functionality of the polymers, allowing the preparation of several well-defined block copolymers.
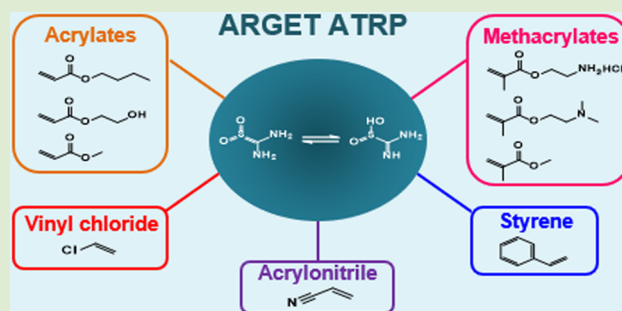
The field of polymeric macromolecular design has been increasingly improved in the last two decades due to the development of reversible deactivation radical polymerization (RDRP) techniques.[1] This set of methods allows the synthesis of polymers with narrow molecular weight distribution and predetermined features, such as molecular weight, architecture, functionality, and topology. Atom transfer radical polymerization (ATRP)[2] is one of the most investigated RDRP techniques, since it can be used for the polymerization of different monomer families at relatively low temperature using commercially available reactants, and the polymerizations can be carried out in bulk, homogeneous media or heterogeneous media, following simple experimental procedures. ATRP reactions are typically initiated from alkyl halide molecules and catalyzed by transition metals (e.g., copper) coordinated with N-containing ligands (Scheme 1).[2] Research trends on ATRP aim to decrease (or eliminate the use) the amount of metal catalyst employed as well as to set reaction conditions for ATRP using inexpensive and eco-friendly compounds (ligands, reducing agents, solvents, etc.). These efforts are pivotal for the development of affordable ATRP processes at an industrial scale. For example, the use of reducing agents that continuously reduce Cu^{II}X/L complexes during polymerization to form Cu^{I}X/L activator species represents a crucial step on the development of ATRP variations that can operate using

Scheme 1. Reaction Scheme of Normal ATRP and Different ATRP Variation Techniques
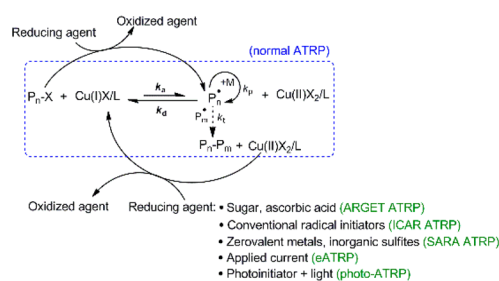
only ppm amounts of metal catalyst. Several types of reducing agents (e.g., radical initiators,[3] ascorbic acid,[4] zerovalent metals,[5] etc.) have been employed for the polymerization of a wide range of monomer families,[6,7] following different polymerization mechanisms (Scheme 1).[2]

Thiourea dioxide (TDO) is an inexpensive reducing agent,[8] also known as "green industrial reductant", which is commercially available, easy to handle, and easy to store. It

has been successfully used in many industries, such as textile, paper, and dye, among others.[9] Due to its versatility, TDO can also find application in other distinct areas like organic synthesis, synthesis of metal sulfides, and bitumen modifications.[10] However, to the best of our knowledge, the use of this reducing agent in ATRP has never been studied. There is only one work reporting the use of TDO as a cocatalyst, in combination with octyl viologen in the presence of buffer NaHCO$_3$, for the synthesis of well-defined poly(vinyl chloride) (PVC) by single electron transfer/degenerative chain transfer living radical polymerization (SET-DTLRP).[11] However, results showed that no polymer was obtained when TDO was used alone as a catalyst.

In this work, TDO was successfully used for the regeneration of CuBr/ligand activator complexes during the ATRP of several monomer families. TDO is poorly soluble in common organic solvents and its solubility in water is also limited (3 mg/100 mL). Therefore, different solvents/mixtures were tested for the polymerization of methyl acrylate (MA), as the model monomer, mediated by TDO/CuBr$_2$/Me$_6$TREN in order to study the influence of the solvent mixture composition on the kinetics and control over the polymerization. The reaction in pure ethanol, despite being controlled, was very slow and stopped at low monomer conversion (Figure 1, red
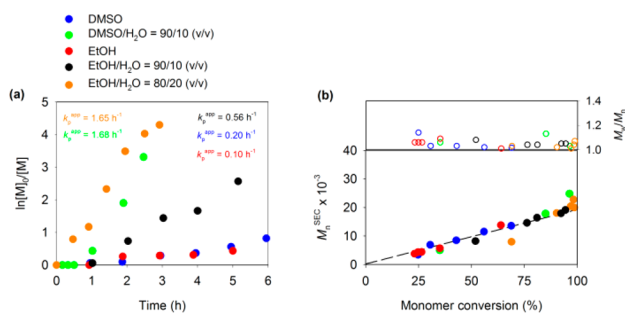

Figure 1. Kinetic plots of (a) $\ln[M]_0/[M]$ vs time and (b) M_n^{SEC} and M_w/M_n vs monomer conversion for the TDO/CuBr$_2$/Me$_6$TREN-catalyzed ATRP of MA in different solvents. Conditions: $[MA]_0/[EBiB]_0/[TDO]_0/[CuBr_2]_0/[Me_6TREN]_0$ = 222/1/1/0.1/0.25, $[MA]_0/[solvent]_0$ = 2/1 (v/v); T = 30 °C.

symbols), most probably due to the lack of reducing agent availability. However, increasing the solubility of TDO in the solvent mixture by adding 10% of water to EtOH allowed the reaction to proceed at higher rate and the monomer reached conversion near 100% in 5 h (Figure 1, black symbols). Nevertheless, an induction period of about 25 min was observed, potentially due to the slow dissolution of TDO in the mixture. Increasing the water content of the solvent mixture up to 20% led to even faster polymerization with no induction period. The same behavior was observed when DMSO was used as the polymerization solvent. In the pure solvent, the reaction was very slow, whereas in DMSO/H$_2$O = 90/10 (v/v) the rate of polymerization was higher (Figure 1, blue vs green symbols). For the range of solvent mixtures investigated, the control over the PMA-Br molecular weight was always excellent throughout the polymerizations ($Đ$ < 1.15, Figure 1b). A well-defined high molecular weight PMA-Br (M_n^{SEC} = 58.5 × 10^3, $Đ$ = 1.13) was also prepared in EtOH/H$_2$O = 90/10 (v/v) using only 100 ppm of CuBr$_2$ to confirm the ability of the system to work with a very low catalyst loading.

Investigation of the influence of TDO on the polymerization features revealed that reaction rate increased with increasing TDO concentration (Table S1), similarly to what was observed for other ATRP systems using reducing agents.[4,12,13] However, unexpectedly, the induction period of the polymerization increased with increasing TDO concentration (Table S1). We hypothesized that TDO could have some role as radical scavenger when present in large amounts in the polymerization. To confirm that hypothesis, two model experiments were conducted in which MA was allowed to react by free radical polymerization (FRP) in the presence or absence of TDO. Results showed that monomer conversion was much higher (69% vs 11%, Table S2) when TDO was not used in the polymerization, which confirms that somehow TDO is interacting with propagating radicals. This behavior is under investigation and will be reported elsewhere. Nevertheless, for the range of TDO concentration studied for the TDO-mediated ATRP of MA, the control over the molecular weight of the polymer was not affected by this event, as judged by the low dispersity and the excellent agreement between theoretical and experimental molecular weights (Table S1). When using a new reducing agent for ATRP, it is important to evaluate its exact role during reaction which will determine the polymerization mechanism. In this case, the reaction could be ruled either by the SARA ATRP mechanism, if TDO shows both reducing and supplemental activation ability or by ARGET ATRP, if TDO is only able to act as a reducing agent of CuBr$_2$. UV spectra (Figure S1) of TDO/CuBr$_2$/Me$_6$TREN in degassed mixtures mimicking polymerization conditions (solvent and monomer/solvent mixture) were recorded over time and showed that TDO is able to efficiently reduce the deactivator complex to form the CuBr/Me$_6$TREN activator species. To investigate the potential supplemental activation behavior, several model experiments were conducted in which TDO was allowed to react either with alkyl halide initiator (EBiB) or copper-free PMA-Br macroradical (CEF = 98%; [copper] < 0.002 ppm) in MA/EtOH/H$_2$O = 67/30/3 (v/v/v) mixtures (Table S3). Results showed that TDO alone is not able to activate either EBiB or PMA-Br (Table S3, entries 3 and 5) during 5 h, which corresponds to the time required for MA to reach high conversion on a controlled polymerization (with deactivator complex) under similar conditions. However, after 22 h, high molecular weight PMA was formed in the presence of EBiB and TDO (Table S3, entry 4). This result was unexpected and shows that TDO might be able to interact with initiator, as a potential side reaction of the polymerization. To further investigated this, it was hypothesized that the type of initiator or influence of light could be responsible for the observed behavior. However, control experiments conducted in the dark (with EBiB) and with light using MBP as a secondary initiator produced similar results (Table S3, entries 6−8). The deep investigation of this interaction is out of the scope of this work, since it does not contribute to the polymerization under the studied conditions (no activation of alkyl halides by TDO was observed during the time required for complete MA polymerization), and thus, it will be reported elsewhere. The possible interaction between TDO and monomer was also evaluated and the results showed that TDO is not able to form radicals and to initiate the polymerization of MA (Table S3, entry 1). It is also worth mentioning that no polymerization occurred in the absence of TDO (Table S3, entry 2). In summary, the results suggest that the TDO-mediated ATRP is ruled by the ARGET ATRP

mechanism, in which TDO is exclusively responsible for the regeneration of the activator by reduction of $CuBr_2/Me_6TREN$ complex, since TDO is not able to activate PMA-Br dormant chains. For comparison purposes, the polymerization of MA using other reducing agents reported for ARGET ATRP, namely, ascorbic acid[4] and glucose[14] was conducted under the same conditions. Results (Table S5) showed that TDO is superior than glucose and presents similar behavior to the one of ascorbic acid regarding the efficient mediation of the polymerization.

A low molecular weight PMA-Br sample obtained at high monomer conversion (98%) by $TDO/CuBr_2/Me_6TREN$-catalyzed ARGET ATRP was fully characterized by SEC, MALDI, and ^1H NMR analyses. The agreement between the different molecular weights and the low dispersity ($M_n^{NMR} = 4.8 \times 10^3$; $M_n^{th} = 4.9 \times 10^3$; $M_n^{SEC} = 4.8 \times 10^3$; Đ = 1.06) of the polymer are indicative of a well-defined structure. The MALDI spectrum presented in Figure 2 confirms the chemical
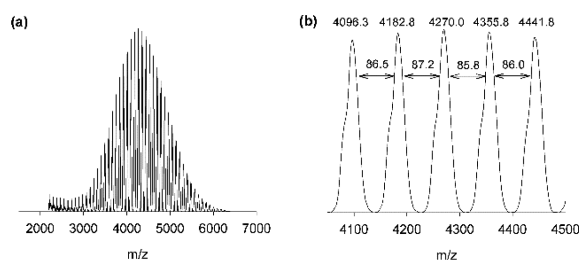
Figure 2. MALDI-TOF-MS in the linear mode (using HABA as matrix) of PMA-Br ($M_n^{NMR} = 4.8 \times 10^3$; $M_n^{th} = 4.9 \times 10^3$; $M_n^{SEC} = 4.8 \times 10^3$; Đ = 1.06): (a) m/z from 2000 to 6500 and (b) m/z from 4050 to 4500.

structure of the polymer with one series of peaks, which are separated by an interval corresponding to the MA repeating unit (86.1 mass unit). The series was attributed to a PMA-Br polymer chain showing ion forms of single alkali metal adduct $[R\text{-}(MA)n\text{-}Br + Na^+]$, where R-Br is the initiator EBiB, as previously observed.[12] Besides the confirmation of the polymer chemical structure, the ^1H NMR spectrum (Figure S6) also allowed the determination of the high chain-end functionality (98%) of PMA-Br, by the ratio between the $-C(CH_3)_3$ signal (c) from the EBiB fragment and the $-$ CHBr active chain-end signal (g) of the polymer.

Pure PMA-Br macroinitiator was reinitiated with Sty in DMF, giving a well-defined PMA-b-PS-Br block copolymer (Figure 3a), that confirms the "livingness" of the polymer
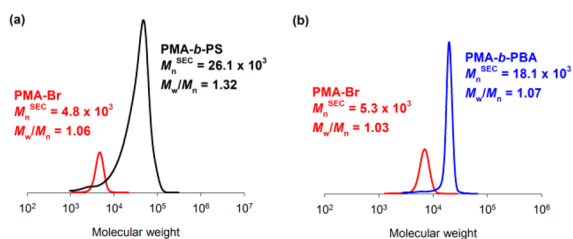
Figure 3. SEC traces of (a) PMA-Br macroinitiator (red line) and PMA-b-PS block copolymer (black line) obtained after chain extension by TDO-mediated ARGET ATRP at 70 °C and (b) PMA-Br macroinitiator (red line) and PMA-b-PBA block copolymer (blue line) obtained after a "one-pot" chain extension by TDO-mediated ARGET ATRP at 30 °C.

obtained by this new ARGET system. The slight increase of the dispersity of the copolymer was attributed to the higher reactivity of styrene in comparison to MA.[15] In fact, when PMA-Br was reinitiated with a monomer with similar reactivity (n-BA)[15] by "one-pot" ARGET ATRP, there was a clear shift of the SEC trace of the macroinitiator (Figure 3b), giving a PMA-b-PBA-Br block copolymer with very narrow molecular weight distribution (Đ = 1.07) and no tailing.

The polymerization of different monomer families, including functional monomers (Figure 4) was investigated using TDO
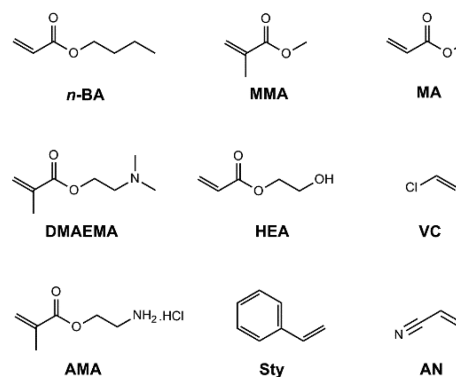
Figure 4. Chemical structure of the monomers polymerized by TDO-mediated ARGET ATRP.

as the reducing agent to evaluate the range of application and robustness of this new ARGET ATRP system. The results summarized in Table 1 show that the system is very versatile and robust, as it was successfully employed for the controlled polymerization of a wide portfolio of monomers (Sty, AN, acrylates, and methacrylates) near room temperature in organic solvents (DMSO or DMF; Table 1, entries 9 and 12), water/organic solvent mixtures (EtOH/H_2O and DMSO/H_2O; Table 1, entries 1−8 and entry 11) and even in aqueous medium (Table 1, entry 10). Representative kinetics of AN, VC, and Sty are presented in SI (Figures S2−S4). Chemical structures of the polymers were confirmed by ^1H NMR spectroscopy and results are also available in SI.

Remarkably, the nonactivated VC was also polymerized in a controlled manner (Table 1, entry 11 and Figure S2), affording PVC with dispersity (Đ = 1.50) similar to the one obtained by RAFT,[16,17] NMP,[16,18] or Cu(0)-mediated SARA ATRP.[5,19,20] In a previous work, TDO has already been used as cocatalyst in SET-DTLRP of VC in THF/H_2O, but PVC was obtained only in the presence of sodium bicarbonate ($NaHCO_3$) as buffer and the electron-transfer cocatalyst octyl viologen.[11] Since there are no reports of ARGET ATRP of VC,[21,22] the mechanism of TDO-mediated polymerization of VC was also investigated. Table S4 shows the results of the model experiments carried out to elucidate the mechanism of TDO-mediated ATRP of VC. No polymer was formed during the initial experiment with only VC, initiator ($CHBr_3$), and $CuBr_2/TREN$ deactivator[5,19,20,22,23] (i.e., in the absence of TDO; Table S4, entry 1). Results also showed that the reducing agent does not react with monomer (Table S4, entry 2). In a similar way to what was observed for the MA polymerization, TDO was not able to activate a copper-free Br-PVC-Br macroiniator (Table S4, entry 3). Also, the possible activation of initiator ($CHBr_3$) by TDO, leading to the formation of uncontrolled polymer, only occurred for a reaction time higher than the one required to obtain full VC

Table 1. Experimental Conditions and Molecular Weight Results for the Polymerization of Different Monomers by TDO-Mediated ARGET ATRP

entry	conditions	t (h)	conv. (%)	$M_n^{th} \times 10^{-3}$	$M_n^{SEC} \times 10^{-3}$	Đ
1[a]	$[MA]_0/[EBiB]_0/[CuBr_2]_0/[Me_6TREN]_0/[TDO]_0$ = 210/1/0.1/0.25/1	5.2	81	16.9	17.9	1.05
2[a]	$[MA]_0/[EBiB]_0/[CuBr_2]_0/[Me_6TREN]_0/[TDO]_0$ = 56/1/0.1/0.25/1	3.3	98	4.9	4.8	1.06
3[a]	$[DMAEMA]_0/[EBiB]_0/[CuBr_2]_0/[Me_6TREN]_0/[TDO]_0$ = 242/1/0.1/0.25/1	4.8	84	32.2	26.5	1.26
4[a]	$[n\text{-}BA]_0/[EBiB]_0/[CuBr_2]_0/[Me_6TREN]_0/[TDO]_0$ = 224/1/0.1/0.25/1	2.0	72	20.7	13.2	1.05
5[a]	$[MMA]_0/[EBiB]_0/[CuBr_2]_0/[Me_6TREN]_0/[TDO]_0$ = 233/1/0.1/0.25/1	3.9	76	17.8	22.1	1.25
6[a]	$[MMA]_0/[EBPA]_0/[CuBr_2]_0/[Me_6TREN]_0/[TDO]_0$ = 236/1/0.1/0.25/1	10.5	33	8.1	7.2	1.43
7[a]	$[HEA]_0/[EBiB]_0/[CuBr_2]_0/[Me_6TREN]_0/[TDO]_0$ = 224/1/0.1/0.25/1	6.0	80	25.3	26.4	1.13
8[b]	$[AMA]_0/[EBPA]_0/[CuBr_2]_0/[TPMA]_0/[TDO]_0$ = 91/1/0.5/2/1	20.7	94	14.4	18.0	1.14
9[c]	$[Sty]_0/[EBiB]_0/[CuBr_2]_0/[Me_6TREN]_0/[TDO]_0$ = 230/1/0.1/0.25/1	45.0	12	3.1	2.4	1.08
10[d]	$[AMA]_0/[HEBiB]_0/[CuBr_2]_0/[TPMA]_0/[TDO]_0$ = 91/1/0.5/2/1	3.0	96	17.4	18.5	1.12
11[e]	$[VC]_0/[CHBr_3]_0/[CuBr_2]_0/[TREN]_0/[TDO]_0$ = 222/1/0.5/1/1	6.0	21	3.1	4.0	1.50
12[f]	$[AN]_0/[BPN]_0/[CuBr_2]_0/[TPMA]_0/[TDO]_0$ = 195/1/0.1/0.25/1	24.0	38	4.1	4.0	1.20

[a][monomer]$_0$/[solvent] = 2/1 (v/v), solvent: EtOH/H$_2$O = 90/10 (v/v), T = 30 °C. [b][monomer]$_0$ = 2 M, solvent: IPA/H$_2$O = 50/50 (v/v), T = 35 °C. [c][monomer]$_0$/[solvent] = 2/1 (v/v), solvent: DMF, T = 30 °C. [d][monomer]$_0$ = 2 M, solvent: H$_2$O, T = 35 °C. [e][monomer]$_0$/[solvent] = 1/1 (v/v), solvent: DMSO/H$_2$O = 95/5 (v/v), T = 42 °C. [f][monomer]$_0$/[solvent] = 1/1.5 (v/v), solvent: DMSO, T = 30 °C.

conversion in a controlled polymerization under the same conditions (Table S3, entries 4 and 5, and Figure S2). Therefore, the results suggest that the polymerization of VC is also ruled by the ARGET ATRP mechanism. The "living" character of the previously obtained Br-PVC-Br macroinitiator (M_n^{th} = 1.8 × 10^3; M_n^{SEC} = 3.1 × 10^3; Đ = 1.60) was further confirmed by a successful preparation of a PMA-b-PVC-b-PMA (M_n^{th} = 39.2 × 10^3; M_n^{SEC} = 39.7 × 10^3; Đ = 1.30) triblock copolymer by TDO-mediated ARGET ATRP in DMSO/H$_2$O = 95/5 (v/v). The chromatograms shown in Figure S5 demonstrate a clear shift of the macroinitiator molecular weight distribution toward very high molecular weight values, with decrease of the dispersity of the block copolymer. The structure of the PMA-b-PVC-b-PMA block copolymer was confirmed by ^{1}H NMR (Figure S17).

The use of TDO as a reducing agent for ARGET ATRP presents a combination of different advantages over conventional reducing agents used in related techniques (e.g., ascorbic acid, Cu(0), light, etc.). First, it is effective for the controlled polymerization of a wide range of monomers, in different solvents, which is important for the preparation of complex polymeric structures by "one-pot" polymerization (one-step reaction) for advanced applications. In addition, compared to Cu(0), which is one of the most used reducing agents in ATRP, there is no buildup of copper concentration during polymerizations with TDO. This fact facilitates or even avoids the need of further polymer purifications, depending on the final application. Finally, the use of eco-friendly solvents, an industrial affordable and safe reducing agent, and reactions performed at near room temperature, make this system a feasible process to be potentially used at industrial scale from both economic and environmental standpoints.

In conclusion, a new wide-range ATRP system using TDO as the reducing agent was reported for the polymerization of acrylates, methacrylates, Sty, AN and nonactivated VC near room temperature. Mechanistic studies conducted for the polymerization of MA and VC revealed that the polymerization mediated by TDO is based on the ARGET ATRP mechanism. The polymerizations could be conducted in organic solvents, organic/water mixtures and aqueous medium affording polymers with very low dispersity. The high chain-end functionality of both PMA-Br and Br-PVC-Br was confirmed by the successful synthesis of well-defined diblock

and triblock copolymers (PMA-b-PS, PMA-b-PVC-b-PMA, and PMA-b-PBA-Br).

ASSOCIATED CONTENT

S **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacro-lett.9b00139.

> Materials, techniques, methods, polymerization details, UV−vis spectra, chromatograms and ^{1}H NMR spectra (PDF)

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Author Contributions
All authors have given approval to the final version of the manuscript.

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Notes
The authors declare no competing financial interest.

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