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Inorganic Sulfites: Efficient Reducing Agents and Supplemental Activators for Atom Transfer Radical Polymerization

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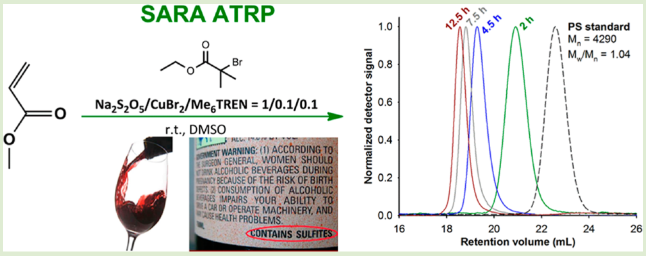
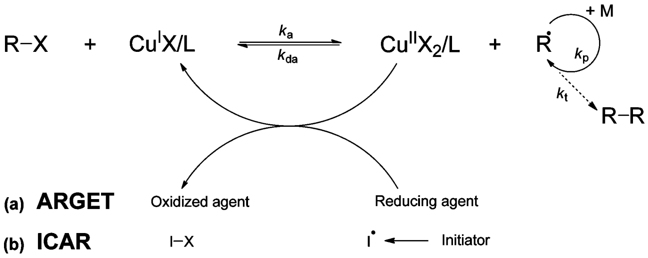
Supporting Information

ABSTRACT: Inorganic sulfites such as sodium dithionite ($Na_2S_2O_4$), sodium metabisulfite ($Na_2S_2O_5$), and sodium bisulfite ($NaHSO_3$) have been studied as reducing agents for atom transfer radical polymerization (ATRP). They act not only as very efficient reducing agents but also as supplemental activators for SARA (supplemental activator and reducing agent) ATRP of methyl acrylate in DMSO at ambient temperature. In combination with Cu(II)Br_2/Me_6TREN, they produced poly(methyl acrylate) with controlled molecular weight, low dispersity (M_w/M_n = 1.05), and well-defined chain-end functionality. Sulfites are eco-friendly, approved by FDA as food and beverage additives, and used commercially in many industrial processes.



Herein we report the use of inexpensive and commonly used sulfites as reducing agents and supplemental activators for atom transfer radical polymerization (ATRP). ATRP is among the most efficient controlled radical polymerization (CRP) processes.[1] It provides access to many polymeric materials with precisely controlled architecture, including stars, brushes, and nanogels, as well as block, gradient, and statistical copolymers with specific functionalities.[2] Recently, new ATRP techniques were developed that permit reduction of transition metal complexes (typically copper with nitrogen-based ligands)[1f] used as redox active ATRP catalysts from ≥1000 ppm to less than 100 ppm in the presence of various reducing agents.[3] The copper catalysts are responsible for forming a dynamic equilibration between tiny amounts of propagating radicals and alkyl halides as dormant species. As shown in Scheme 1, ATRP, as any CRP, is accompanied by a biradical termination process, resulting in the irreversible conversion of Cu(I)/L activators to X-Cu(II)/L deactivators.

Scheme 1. General Mechanism of (a) ARGET ATRP and (b) ICAR ATRP



Consequently, a normal ATRP carried out with ppm amounts of Cu catalyst stops at low monomer conversion when the activator is converted to deactivator. New ATRP procedures employ various mild reducing agents that continuously regenerate the Cu(I) species. In the ARGET[3a,e,4] (activators regenerated by electron transfer) ATRP process various organic (sugars, ascorbic acid, amines, etc.) or inorganic (e.g., tin(II) octoate) reducing agents (RA) have been used. Certain zerovalent transition metals, such as Cu, Fe, Zn, or Mg, act not only as reducing agents, but also as direct supplemental activators in SARA (supplemental activator and reducing agent) ATRP.[3d,e,g,5] ICAR[3b] (initiators for continuous activator regeneration) ATRP employs conventional thermal radical initiators, such as diazo-compounds (AIBN), to react with the Cu(II) and to produce new chains. In recently reported electrochemically mediated ATRP (eATRP),[6] electrical current is used for the reduction process. In a similar way, light can be used in the photochemical activation/reduction process.[7]

Nevertheless, the quest for efficient, inexpensive, safe, and environmentally benign reducing agents continues. Herein we

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would like to report the use of sulfites as a new class of efficient reducing agents (and supplemental activators) for ATRP. Sulfites are commonly used as inexpensive reducing agents in food preservation (especially wine), water treatment, leather, photography, bleach, and many other industrial chemical processes. We tested the three most commonly used sulfites: sodium metabisulfite ($Na_2S_2O_5$), sodium dithionite ($Na_2S_2O_4$), and sodium bisulfite ($NaHSO_3$), as reducing agents in an ATRP of methyl acrylate (MA) carried out at ambient temperature in DMSO solution. As will be further discussed, all sulfites performed as very efficient reducing agents. Subsequently, sodium dithionite (the most effective agent) was used in additional studies, aimed at the exploring range of effective concentrations, targeted molecular weights, and some mechanistic studies that suggest that it acted not only as a reducing agent but also as a supplemental activator, thus, following the SARA ATRP mechanism.

The kinetic plots of ATRP of MA conducted at ambient temperature (30 °C) in dimethylsulfoxide (DMSO) using $Na_2S_2O_4$, $Na_2S_2O_5$, and $NaHSO_3$ as reducing agents are shown in Figure 1. The targeted number average molecular weight at full conversion was $M_n = 20000$. The catalyst was added at 10 mol % versus initiator (ethyl 2-bromoisobutyrate), and a reducing agent was added at an equimolar concentration to the initiator.

The rate of polymerization was first order with respect to monomer concentration with all three reducing agents (Figure 1), and the molecular weights determined by GPC were in good agreement with the theoretical values, indicating an efficient initiation and excellent control during polymerization. This is confirmed by low dispersity values of the obtained polymers (M_w/M_n always <1.1) from the beginning of the polymerization to high conversion. A comparison of the kinetic data indicates that $Na_2S_2O_4$ provided the fastest polymerization of MA, indicating it is a more efficient reducing agent, allowing faster (re)generation of active Cu(I)Br/L catalyst. Reactions with sodium metabisulfite were 3.5 times slower and, with sodium bisulfite, about 2.3 times slower.

Because dithionite ($Na_2S_2O_4$) was the most efficient reducing agent, it was used in subsequent studies that are presented in Table 1. The ratio of $[Na_2S_2O_4]_0/[CuBr_2]_0$ was varied between 0.5/0.1 and 2/0.1, Table 1, entries 1−3, and Supporting Information (SI), Figure 1). Independent of the ratio used, the control over the PMA molecular weight during polymerization was excellent. Molecular weights determined by GPC matched very well the theoretical values and low PDI values were obtained for the PMA. A higher $[Na_2S_2O_4]_0/[CuBr_2]_0$ ratio leads to a faster polymerization. However, the increase in the polymerization rate was relatively small, due to the limited solubility of $Na_2S_2O_4$ in the DMSO/MA mixture.

The ATRP of MA was also studied with different monomer/initiator ratios, that is, different targeted degrees of polymerization, DP (Table 1, entries 1, 4, 5, and SI, Figure 2). The polymerization rate decreased with increased targeted DP, due to the lower number of growing macroradicals. It is remarkable to note that even for the DP = 1100, the PMA dispersity values were very low ($M_w/M_n = 1.05$) even at very high monomer conversion (96.5%), indicating minimal contribution of side reactions with $Na_2S_2O_4$.

The next series of experiments were carried out to elucidate the mechanism of ATRP in the presence of sulfites.

No polymer was formed during the initial experiment with only MA, initiator, and $Cu(II)Br_2/Me_6TREN$ deactivator (i.e., in absence of $Na_2S_2O_4$), Table 1, entry 6. However, polymerization of MA did occur without $Cu(II)Br_2/Me_6TREN$ in the presence of $Na_2S_2O_4$, both in the absence and in the presence of the ATRP initiator (Table 1, entry 8, SI, Figure 3, and Table 1, entry 7, SI, Figure 4).

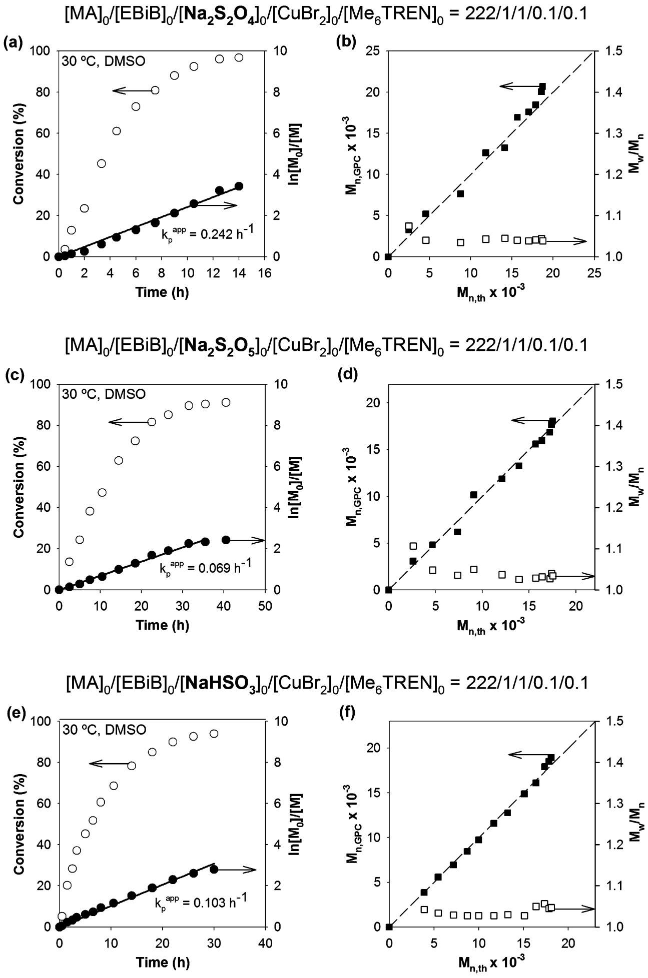

Figure 1. Kinetic plots of MA conversion and $\ln[M]_0/[M]$ vs time (a, c, and e) and plot of number average molecular weights ($M_{n,GPC}$) and dispersity (M_w/M_n) vs theoretical number-average molecular weights ($M_{n,th}$; b, d, and f) for ATRP of MA in the presence of $CuBr_2/Me_6TREN$ with different reducing agents (RA = $Na_2S_2O_4$ (a, b), $Na_2S_2O_5$ (c, d), and $NaHSO_3$ (e, d, f). Conditions: $[MA]_0/[EBiB]_0/[RA]_0/[CuBr_2]_0/[Me_6TREN]_0$ = 222/1/1/0.1/0.1 at 30 °C in DMSO; $[MA]_0/[DMSO]$ = 2/1 (v/v).

In both cases, the polymerization of MA occurred, but in an uncontrolled manner, as evidenced by very high dispersity values. Surprisingly, the reaction was much faster in the presence of the ATRP initiator, suggesting that sulfites can act as supplemental activators for alkyl halides.

The reduction process of $Cu(II)Br_2/Me_6TREN$ by $Na_2S_2O_4$ in pure DMSO was studied by UV−vis spectroscopy (Figure 2), which showed that the dithionite acted as a powerful reducing agent, converting half of Cu(II) species into Cu(I) activators within about 20 min. This indicates that the sulfites act both as supplemental activators and reducing agents, following the SARA ATRP mechanism. The very slow polymerization initiated solely by $Na_2S_2O_4$ could be due to a very small contribution from dissociation of dithionite anions to $SO_2^{\bullet-}$ radical anions that can directly initiate polymerization.

Table 1. SARA ATRP of MA in the Presence of $CuBr_2/Me_6TREN$ and $Na_2S_2O_4$ at 30 °C in DMSO (33 vol % DMSO)

entry	$[MA]_0/[EBiB]_0/[Na_2S_2O_4]_0/[CuBr_2]_0/[Me_6TREN]_0$	k_p^{app} (h^{-1})	time[a] (h)	conv.[a] (%)	$M_{n,th}$[a]	$M_{n,GPC}$[a]	M_w/M_n[a]
1	222/1/1/0.1/0.1	0.242	14.0	96.7	18700	20700	1.04
2	222/1/0.5/0.1/0.1	0.190	19.8	97.5	18800	20800	1.03
3	222/1/2/0.1/0.1	0.257	10.0	91.4	19500	21200	1.06
4	70/1/1/0.1/0.1	0.366	8.8	95.6	5900	6400	1.07
5	1100/1/1/0.1/0.1	0.115	30.5	96.5	88600	91800	1.05
6	222/1/0/0.1/0.1		50.0	0			
7	222/1/1/0/0	0.275	7.4	89.0	17200	2100	11.09
8	222/0/1/0/0	0.018	6.8[b]	8.3[b]	1600[b]	3100[b]	4.55[b]
	$[MMA]_0/[EBiB]_0/[Na_2S_2O_4]_0/[CuBr_2]_0/[Me_6TREN]_0$						
9	222/1/1/0.1/0.1		20.0	97.6	22800	26400	1.12
	$[Sty]_0/[EBiB]_0/[Na_2S_2O_4]_0/[CuBr_2]_0/[Me_6TREN]_0$						
10	222/1/1/0.1/0.1[c]		150.0	16.4	3800	4700	1.06
11	222/1/1/0.1/0.1[c,d]		100.0	87.3	20400	28700	1.15

[a] Values obtained from the last sample from the kinetic studies. [b] After 7 h an insoluble polymer was formed. [c] DMF was used as solvent. [d] Reaction temperature T = 60 °C.

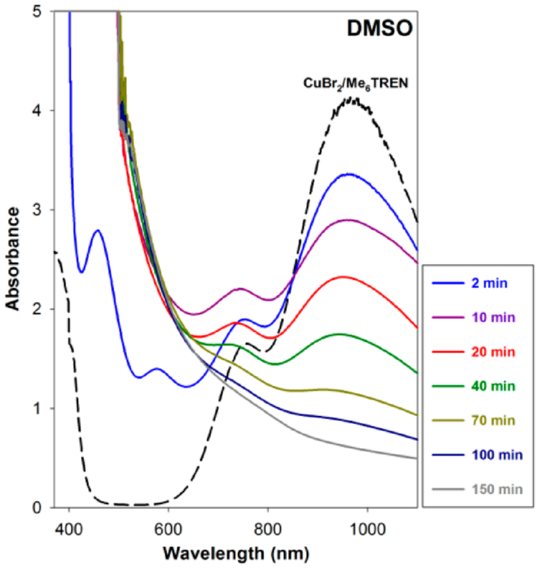

Figure 2. UV–vis spectra of reduction of $Cu(II)Br_2/Me_6TREN$ by $Na_2S_2O_4$ in DMSO recorded at different reaction times (30 °C); $[Na_2S_2O_4]_0/[CuBr_2]_0/[Me_6TREN]_0$ = 0.1/0.01/0.01 mmol/mL.

The "living" nature of the PMA-Br chain-ends was confirmed by carrying out a chain extension experiment (Figure 3). The ^1H NMR (SI, Figure 5) and MALDI-TOF-MS (SI, Figure 6a,b) also confirm a high degree of chain end functionality of PMA synthesized in the presence of sulfites.

Figure 3 shows the complete shift of the entire molecular weight distribution from relatively low molecular weight PMA ($M_{n,GPC}$ = 4100, M_w/M_n = 1.05) to a higher molecular weight ($M_{n,GPC}$ = 28400, M_w/M_n = 1.05). The new catalytic system reported in this manuscript was successfully extended to polymerization of styrene and methyl methacrylate (Table 1, entries 9–11).

The conditions used in SARA ATRP with sulfites are similar to the so-called SET-LRP[8] process in the presence of zerovalent copper. However, mechanistically, SET-LRP follows SARA ATRP, with copper acting as a supplemental activator and reducing agent.[9]

To conclude, inorganic sulfites are a new class of very efficient reducing agents and supplemental activators for SARA ATRP. These new reducing agents in combination with Cu(II) species produce polymers with controlled molecular weight, low dispersity, and well-defined chain-end functionality. Sulfites are eco-friendly reducing agents that are applied commercially in many industrial processes and approved by FDA as food and beverage additives. These new inorganic reducing agents should assist in more efficient ATRP and also atom transfer radical addition and cyclization processes,[10] as well as the implementation of SARA ATRP for larger scale production of well-defined polymers.

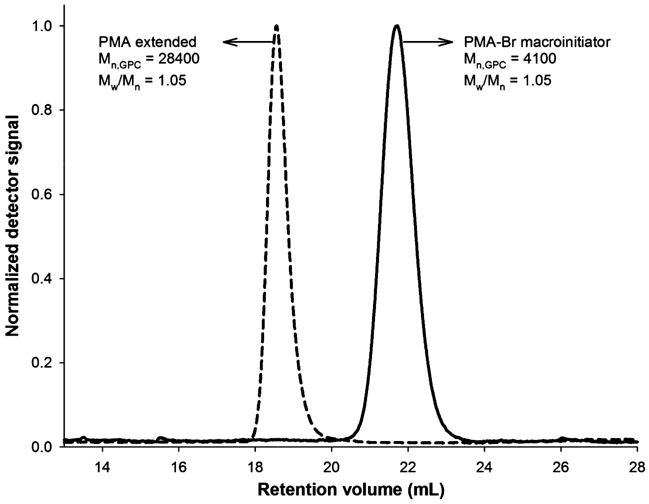

Figure 3. GPC traces of the PMA before (right curve) and after the chain extension (left curve) experiment.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials, instrumentation, experimental conditions, and experimental results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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