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Atom Transfer Radical Polymerization Enabled by Sonochemically Labile Cu-carbonate Species

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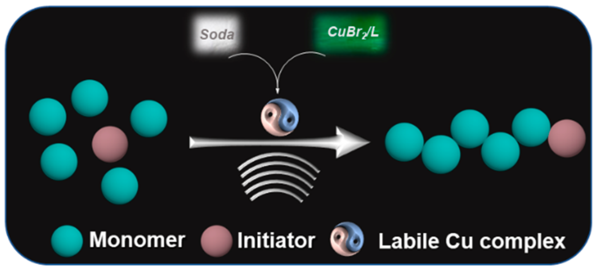
Supporting Information



ABSTRACT: Atom transfer radical polymerization (ATRP) has been previously mediated by ultrasound using a low concentration of copper complex in water (sono-ATRP) or by addition of piezoelectric materials in organic solvents (mechano-ATRP). However, these procedures proceeded slowly and yielded polymers contaminated by new chains initiated by hydroxyl radicals or by residual piezoelectrics. Unexpectedly, in the presence of sodium carbonate, rapid sono-ATRP of methyl acrylate in DMSO was achieved (80% conversion in <2 h) with excellent control of molecular weights and low dispersities ($M_w/M_n < 1.2$). The *in situ* formed Cu^{II}/L-CO$_3$ complex in the the presence of ultrasound generated Cu^I/L species as activators for ATRP and carbonate radical anions. The latter were scavenged by DMSO that was oxidized to dimethyl sulfone. This simple and robust process employs low-intensity ultrasound, air-stable Cu^{II}/L catalysts, and carbonate or bicarbonate salts (washing soda or baking soda) to prepare well-defined polyacrylates.

Many biological reactions proceed without interfering with each other in living cells. These enzyme-catalyzed processes are precisely controlled and entirely switchable.[1] Biomimicking these biological reactions is a long-term goal for chemists. A promising approach is switchable catalysis in which the latent catalysts can be intermittently transformed into catalytically active species by external stimuli and turned back into dormant species.[2] Controlled polymerization regulated by external stimuli has been the subject of intense research[3] since it can provide spatiotemporal control,[4] environmentally benign reaction conditions,[5] and diminished catalyst concentrations.[6]

Ultrasound generates rather unusual reactions conditions—a short duration of extremely high temperatures and pressures in liquids, which cannot be achieved by other energy inputs.[7] Ultrasound offers intriguing opportunities to affect the properties of polymers or nanoparticles.[8] Recent advances in ultrasound-mediated polymerization have further extended the range of ultrasound to the synthesis of well-defined polymers.

Upon exposure to ultrasound, the polymer ligand coordinated to a macromolecular catalyst was stretched and cleaved by strong shear forces resulting from the cavitation, liberating the active transition metal catalysts for ring-opening metathesis polymerization[9] or alkyne−azide cycloaddition click reaction.[10]

Ultrasound was also used as a mechanical trigger to induce electron transfer. Piezoelectric nanoparticles were deformed by the cavitation-induced periodic stress wave, giving rise to the polarization and electric potential. In atom transfer radical polymerization (ATRP),[11] the electric potential reduced Cu^{II} complexes to Cu^I activators to start ATRP.[12] However, such mechanically induced ATRP required either high energy input or proceeded slowly due to limited efficiency. Moreover, hydroxyl radicals were produced sonochemically from water, inducing both reversible addition−fragmentation transfer polymerization (sono-RAFT)[13] and sono-ATRP in aqueous media.[14] However, the resulting polymers were contaminated by new chains generated by hydroxyl radicals or by residual piezoelectrics.

To address the challenges for ATRP mediated by ultrasound, new chemical approaches should be explored. It was previously reported that some Cu^{II}-based complexes comprising labile Cu^{II}−OR bonds could undergo homolytic cleavage to generate Cu^I species and radical anions.[15] Thus, it was hypothesized that a similar concept could be applied to generate Cu^I/L activator ATRP species by ultrasound to start the polymerization. As a proof-of-concept, a rapid sono-ATRP in organic media was successfully carried out with a small amount of Cu^{II}/L deactivator and carbonate salts. This strategy enabled fast polymerization with excellent control and minimal contamination. Sono-ATRP of methyl acrylate (MA) was initially carried out in the presence of Na$_2$CO$_3$ under ultrasonic irradiation using ethyl α-bromoisobutyrate (EBiB) as initiator, CuBr$_2$/TPMA as catalyst, (TPMA = tris(2-pyridylmethyl)-

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amine), and dimethyl sulfoxide (DMSO) as solvent. As shown in Figure 1a, polymerization of MA with Na_2CO_3 gave a linear semilogarithmic kinetic plot and excellent control over molecular weights and dispersity (Figure 1b). The rate of polymerization increased with the concentration of Na_2CO_3. After 2 h sonication with 0.01 wt % Na_2CO_3, polymerization reached 35% conversion, yielding a polymer with M_n = 3300 and M_w/M_n = 1.18 (entry 1, Table S1); with 0.05 wt % Na_2CO_3 and 74% conversion, a polymer with M_n = 6500 and M_w/M_n = 1.13 was obtained (entry 2, Table S1); and with 0.25 wt % Na_2CO_3 and 86% conversion, a polymer with M_n = 7400 and M_w/M_n = 1.16 was achieved (entry 3, Table S1).

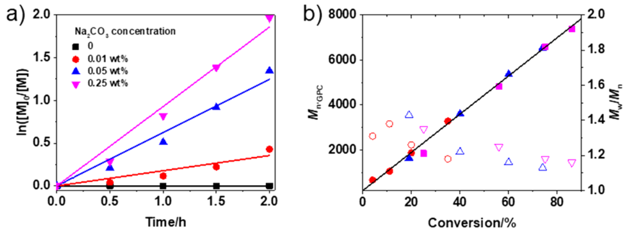


Figure 1. (a) Kinetics of polymerization with various loadings of Na_2CO_3. (b) Evolution of molecular weight (filled symbols) and dispersity (hollow symbols) with conversion. Reaction conditions: $[MA]_0:[EBiB]_0:[CuBr_2]_0:[TPMA]_0$ = 100:1:0.015:0.06 in 50% (v/v) DMSO. Ultrasonic bath (25 °C ± 5 °C, 40 kHz, 110 W). The weight concentration of Na_2CO_3 is relative to the weight of monomer and solvent.

Polymerizations targeting various degrees of polymerizations (DP_t) were carried out in DMSO. The experimental molecular weights matched well the theoretical values. The polymerization with DP_t = 200 reached 82% conversion after 2 h ultrasonication with 0.25 wt % Na_2CO_3, yielding a polymer with M_n = 12 900 and M_w/M_n = 1.08 (entry 6, Table S1). A polymer with M_n = 22 100 and M_w/M_n = 1.06 was formed when the DP_t was set at 400 (entry 7, Table S1). A conversion of 76% after 6 h of ultrasonication was attained in the polymerization with targeted DP_t = 800, giving a polymer with M_n = 48 200 and M_w/M_n = 1.05 (entry 8, Table S1). This procedure could also be employed in the polymerization of ethyl acrylate and poly(ethylene glycol) methyl ether acrylate (M_n = 480), giving well-defined polymers with low dispersity and predetermined molecular weight (entries 9−11, Table S1). Other copper ligands could also be employed for this low ppm system to provide well-defined polymers with predictable molecular weight and low dispersity (entries 4−5, Table S2).

In contrast, no conversion was observed after 2 h ultrasound in the absence of Na_2CO_3 (entry 4, Table S1). Also, with 0.05 wt % Na_2CO_3 (entry 5, Table S1), but without ultrasound, only 5% conversion was reached after 2 h of stirring at room temperature. These experiments highlighted the fundamental role of Na_2CO_3 in the presence of ultrasound and ATRP catalysts. To understand the effect of carbonate anions on Cu complexes, Vis-NIR spectra were recorded under ultrasonication (Figure 2). A strong blue shift was observed in the absorption band of CuBr$_2$/TPMA after addition of Na_2CO_3, indicating a structural change of the complex. Figure 2a showed a fast decrease of the absorbance of Cu^{II} under sonication in the presence of Na_2CO_3. The color changed from green to yellowish during ultrasonication. When the resulting solution was exposed to air, the absorbance of Cu^{II} was restored, suggesting that the formed Cu^I complex was reoxidized to Cu^{II} species in air. Without Na_2CO_3, the absorbance of Cu^{II} under ultrasonication did not change (Figure 2b), demonstrating the importance of Na_2CO_3 in the reduction process.

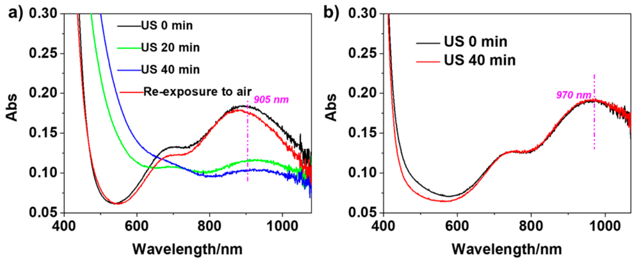


Figure 2. Vis-NIR spectra of CuBr$_2$/TPMA complexes in DMSO under ultrasonication. $[CuBr_2]_0$ = 0.83 mM, $[TPMA]_0$ = 3.3 mM, $[Na_2CO_3]_0$ = 5.5 mM. Ultrasonic bath (25 °C ± 5 °C, 40 kHz, 110 W). (a) With Na_2CO_3 and (b) Without Na_2CO_3.

After addition of the carbonate anions, the intensity of the voltammetric curve representing the redox couple Br−$Cu^{II}TPMA^+$/Br−Cu^ITPMA (black line in Figure 3a) gradually decreased. Both the cathodic and anodic peak decreased, while a new peak couple appeared at more negative potentials, whose intensity steadily increased over time. After 30 min of ultrasonication, only the new peak couple was observed, and the signal intensity remained constant, indicating that the new complex was stable in solution. Concurrently, we recorded the increase of intensity of a broad peak at more positive potential, due to the oxidation of Br^- to Br_2 (Figure S1); this suggested that some Br anions were no longer coordinated to the Cu center. When the experiment was repeated without ultrasound, the new peak couple formed slowly, in more than 120 min (Figure 3b). Thus, the electrochemical investigation suggests that the following equilibrium takes place:

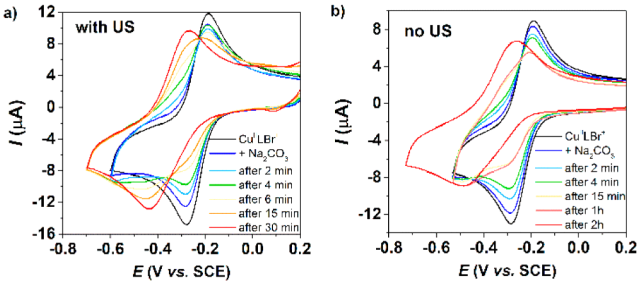


Figure 3. CVs of (a) 1 mM and (b) 0.83 mM CuBr$_2$/TPMA in DMSO + 0.1 M Et_4NBF_4 in the absence (black line) and presence of 6.7 mM Na_2CO_3, recorded with (a) and without (b) applying ultrasound to the electrochemical cell in between each scan. CVs were recorded on a GC electrode, at scan rate 0.2 V s^{-1}.

$$BrCu^{II}TPMA^{+} + CO_3^{2-} \rightleftharpoons (CO_3)Cu^{II}TPMA + Br^{-} \qquad (1)$$

The formation of the carbonate complex is 4−5 times faster in the presence of ultrasounds. A similar behavior was observed by CV in anhydrous DMSO (Figure S2), although the formation of the new peak couple was slower. This indicated that DMSO is essential for the reaction equilibrium rather than the minimal amount of water. Moreover, a peak couple at the same potential values appeared after addition of Na_2CO_3 to $Cu^{II}TPMA^{2+}$ with noncoordinating triflate anions, i.e., in the absence of Br anions (Figure S3).

Moreover, a significant anodic current was measured by linear sweep voltammetry under ultrasonication (Figure S4a), showing that approximately 35% of total Cu was present as Cu^I species. The experiment clearly indicates that Cu^I can be generated from Cu^{II} species by ultrasound in the presence of carbonate salts. The homolytic cleavage of $(CO_3)Cu^{II}TPMA$ should generate the Cu^I species and a carbonate radical anion (eq 2). This process is faster under ultrasonication, as indicated by both Vis-NIR and ultrasound experiments (Figure S4b).

$$(CO_3)Cu^{II}TPMA \rightleftharpoons Cu^{I}TPMA^{+} + CO_3^{\bullet -} \qquad (2)$$

The $CO_3^{\bullet -}$ is a strong oxidant, and therefore it can oxidize the excess ligand, if present, or solvent, DMSO. The oxidation of sulfoxides to sulfones by the carbonate radical anion was previously reported, ultimately generating CO_3^{2-} and CO_2.[16] Since DMSO is present in much larger amounts than the ligand, its oxidation is more likely. To support this hypothesis, ^1H NMR spectra were recorded *in situ* (Figure S5) and showed that dimethyl sulfone—the oxidized product of DMSO—was produced during ultrasonication. Furthermore, the sono-ATRP of MA was well controlled, regardless of the [Cu]/[TPMA] ratio (entries 1−3, Table S2). This indicated that excess ligand does not play any role in this carbonate-mediated polymerization. Conversely, DMSO is scavenging $CO_3^{\bullet -}$.

In addition, a series of control experiments, either without copper or without EBiB, showed no conversion after ultrasonication, indicating that $CO_3^{\bullet -}$ did not initiate polymerization and that its interaction with Cu(II) was required to start ATRP (entries 1−3, Table S3). Thus, the reduction of $CO_3^{\bullet -}$ by DMSO is necessary to shift both equilibria in eqs 1 and 2 toward the products, i.e., toward the generation of the ATRP activator, $Cu^I/TPMA^+$. When the sono-ATRP of MA was performed in sulfolane, a fully oxidized solvent, under the same conditions as used in DMSO, essentially no conversion was observed (entry 4, Table S3). Thus, DMSO was oxidized by $CO_3^{\bullet -}$ produced by ultrasonic decomposition of Cu^{II}-carbonate species (eq 2). The effect of other carbonates or bicarbonates was explored, including potassium carbonate, sodium bicarbonate, and ammonium bicarbonate (Table S4). All of them showed controlled polymerization in the presence of ultrasound, suggesting the ease and robustness of this procedure.

Temporal control of the sono-ATRP was also examined. As shown in Figure 4a, the polymer chain propagation can be reversibly and intermittently switched on/off by ultrasound. A continuation of the polymer chain growth was attained after re-exposure to ultrasonic irradiation, while only a slightly increasing conversion was observed without ultrasound, due to continuing radical termination that resulted in the conversion of Cu(I) activators to Cu(II) deactivators. Excellent control over the polymerization was achieved, yielding polymers with low *Đ* and molecular weights agreeing well with the theoretical values (Figure 4b).

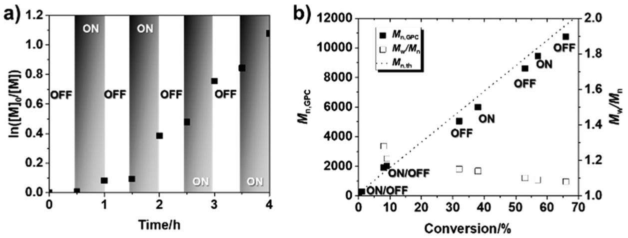
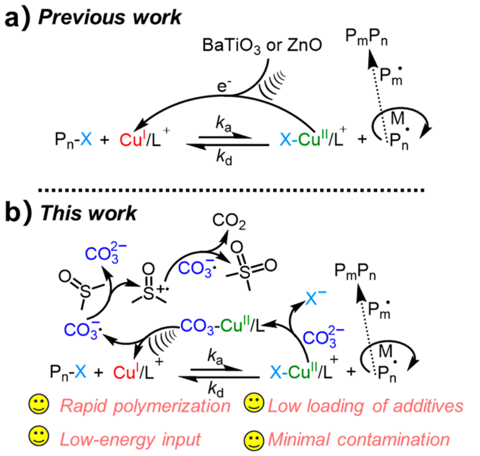


Figure 4. Temporal control in sono-ATRP with 0.025 wt % Na_2CO_3 under ultrasound agitation through intermittent switching on/off ultrasound bath (25 °C ± 5 °C, 40 kHz, 110 W). (a) Kinetics and (b) molecular weight and dispersity of polymers. Reaction conditions: $[MA]_0$:$[EBiB]_0$:$[CuBr_2]_0$:$[TPMA]_0$ = 200:1:0.03:0.12 in 50% (v/v) DMSO.

To examine the chain-end fidelity of the polymers synthesized by this procedure, chain extension was carried out. The first block was synthesized under standard conditions $[MA]_0$:$[EBiB]_0$:$[CuBr_2]_0$:$[TPMA]_0$ = 200:1:0.03:0.12 in 50% (v/v) DMSO and 0.05 wt % Na_2CO_3. After 6 h ultrasonication, the polymerization reached 91% conversion, giving PMA-Br with M_n = 7600 and M_w/M_n = 1.09. Then, another 2 mL of degassed MA was added for chain extension. As shown in Figure S7, after 8 h ultrasonication, the GPC trace cleanly shifted, showing a polymer with M_n = 10 500 and M_w/M_n = 1.08.

In summary, Scheme 1 provides a comparison between previous work on sono-ATRP and the novel rapid sono-ATRP in the presence of carbonate anions, enabling fast polymerization (conversion >80% in <2 h) with low-intensity ultrasonic irradiation as well as excellent control.

Scheme 1. (a) Mechano-ATRP Enabled by Piezoelectric Materials and (b) Sono-ATRP Enabled by *in Situ* Formed Cu-carbonate Species[a]



[a] Counter ion X^- is omitted for Cu complex in the equilibrium.

The presented results demonstrated that the carbonate anions reacted with $CuBr_2$ to form $(CO_3)Cu^{II}/TPMA$ which under ultrasonication underwent homolytic cleavage into carbonate radical anions and Cu^I species, thus catalytically activating ATRP. This facile and robust approach will extend the application of ultrasound-mediated ATRP to the synthesis of the well-defined and pure polymers or polymer-based hybrids.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.9b00029.

Chemicals, details of experimental procedures, CV curves, results for control experiments, and ^1H NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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