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# ATRP of Methyl Acrylate with Metallic Zinc, Magnesium, and Iron as Reducing Agents and Supplemental Activators

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Atom transfer radical polymerization (ATRP) provides access to well-defined polymers with complex architecture, such as block and graft copolymers, stars or brushes.[1−5] Typically, ATRP is initiated by alkyl halides in the presence of $Cu^I$ complexes with N-based ligands as catalysts.[6−12] Alternative ATRP initiating systems were developed, based on reverse ATRP, simultaneous normal and reverse initiating systems and activators generated by electron transfer (AGET).[13−17] In these systems, oxidatively stable $Cu^{II}$ complexes were reduced to the $Cu^I$ complexes at the beginning of the reaction with radicals formed by decomposition of radical initiators or various reducing agents, such as $tin^{II}$ 2-ethylhexanoate, ascorbic acid or sugars. These initiating systems laid foundation for the development of the next generation of ATRP systems, carried out in the presence of small amounts (ppm) of the Cu-complex in which the activator catalyst complexes, the $Cu^I$ species, are continuously regenerated during the polymerization. In initiators for continuous activator regeneration (ICAR) ATRP,[18] the deactivating $Cu^{II}$ species, formed by unavoidable termination reactions, are continuously reduced to reform the activating $Cu^I$ species by reaction with conventional radical initiators. In activators regenerated by electron transfer (ARGET) ATRP[18−26] an excess of various mild reducing agents, that do not form molecules capable of initiating an ATRP, is used. Reducing agents include such organic reducing agents as glucose, ascorbic acid, hydrazine, phenols, amines, or even excess of ligands[27] but also inorganic reducing agents such as $tin^{II}$ 2-ethylhexanoate,[20] or zerovalent copper.[28−31] In search of new reducing agents we explored other inorganic species, such as zerovalent metals, $Zn^0$, $Mg^0$, and $Fe^0$.

ATRP of MA initiated by methyl 2-bromopropionate (MBP) and catalyzed by $CuBr_2/Me_6TREN$ was studied in the presence of $Zn^0$, $Mg^0$, and $Fe^0$ (Table 1). With the initial molar ratio of reagents; $[MA]_0/[MBP]_0/[Me_6TREN]_0/[CuBr_2]_0 = 200/1/0.1/0.02$, in 33.3% (v/v) DMSO ($[MA]_0 = 7.4$ M), at 25 °C, the polymerizations reached 82%, 84% and 88% conversion in 4, 11, and 72 h, in the presence of $Zn^0$, $Mg^0$ and $Fe^0$, respectively (surface areas for all metals were the same, ca. 33 $mm^2$). Thus, the apparent order of activity of the reducing agents was $Zn^0 > Mg^0 > Fe^0$. The molecular weights of the PMA formed in these reactions agreed with theoretical values and $M_w/M_n$ values were lower than 1.1.

When PMDETA was used as the ligand instead of $Me_6TREN$, the same order of activity was found but overall level of control was lower. With $Zn^0$ as the reducing agent, after 8 h reaction, a polymer with $M_n = 14\,800$, $M_w/M_n = 1.47$ was formed in 80% yield. With $Mg^0$, 19 h was required to obtain 90% conversion yielding a polymer with $M_n = 15\,900$, $M_w/M_n = 1.25$. When $Fe^0$ was used, 72% conversion was reached after 56 h, producing a polymer with $M_n = 13\,300$ with the lowest value of $M_w/M_n = 1.12$.

The ATRP equilibrium is defined as:

$$K_{ATRP} = \frac{[R^\bullet][Cu^{II}X_2/L]}{[RX][Cu^IX/L]}$$

Thus, higher $[R^\bullet]$ (faster polymerization) is for catalyst with larger value of $K_{ATRP}$ and lower ratio of $Cu^{II}/L$ and $Cu^I/L$. This ratio depends also on the redox process with reducing agents. Apparently, much higher $K_{ATRP}$ for $Me_6TREN$-based system results in faster polymerization. However, the reduction process also maintains higher $[Cu^{II}/Me_6TREN]$ than $[Cu^{II}/PMDETA]$, as evidenced by formation of polymers with lower $M_w/M_n$ values for the former system. $Fe^0$ is a weaker reducing agent than $Zn^0$ or $Mg^0$ and results in higher $[Cu^{II}/PMDETA]$, leading to slower polymerization and polymers with lower $M_w/M_n$.

From the kinetic study (Figure 1), it can be concluded that $Zn^0$ showed highest reducing activity among three metals studied in an ATRP, although Mg has the most negative reducing potential (−2.7 V vs SHE in comparison with −0.76 V for Zn and −0.45 V for Fe).[32] An induction period was observed in the presence of $Mg^0$, plausibly because the surface of $Mg^0$ was oxidized by air that could reduce its reactivity. $Fe^0$ led to the slowest polymerization after a long induction period. The best control was observed, probably due to the slow reducing process with $Fe^0$. UV−vis studies showed that $Zn^0$ and $Mg^0$ could reduce $CuBr_2/L$ to $CuBr/L$ nearly completely; however, the reduction process proceeded to much lower extent and was much slower with $Fe^0$ as reducing agent (Figure S1, Supporting Information).

The products of the redox process for metal $Zn^0$ and $Mg^0$ are $Zn^{II}$ and $Mg^{II}$ halides. However, for $Fe^0$ there are two possible products $Fe^{III}$ and $Fe^{II}$ halides. However, since the value of $E_{1/2}(Fe^{3+}/L/Fe^{2+}/L)$ is 500 mV more positive than $E_{1/2}(Cu^{2+}/L/Cu^+/L)$ with ligand of $Me_6TREN$ (300 mV more positive with PMDETA), this indicates the preference of formation of $Cu^{II}/L$ and $Fe^{II}/L$ rather than $Cu^I/L$ and $Fe^{III}/L$ (Table S1, Supporting Information). Thus, $Fe^{II}/L$ is not an efficient reducing agent, and a slow reduction should involve $Fe^0$ .

The molecular weights of the resulting PMA prepared in the presence of all three metals were close to the theoretical values. The molecular weight distribution was relatively broad at low conversion but very low values of $M_w/M_n$ (< 1.1) were obtained after the conversion exceeded 50%.

To evaluate the role of zerovalent metals, additional experiments were performed in the absence of $CuBr_2$ but in the presence or the absence of $Me_6TREN$ ligand (Table 2).

**Table 1. ATRP of MA with Metallic $Zn^0$, $Mg^0$, and $Fe^0$ as Reducing Agents**[a]

| ligand | metal | time/h | conv/% | $M_{n,GPC}$ | $M_{n,th}$ | $M_w/M_n$ |
|---|---|---|---|---|---|---|
| $Me_6TREN$ | $Zn^0$ | 4 | 82 | 15 100 | 14 100 | 1.08 |
| $Me_6TREN$ | $Mg^0$ | 11 | 84 | 13 800 | 14 500 | 1.07 |
| $Me_6TREN$ | $Fe^0$ | 72 | 88 | 17 800 | 15 100 | 1.06 |
| PMDETA | $Zn^0$ | 8 | 80 | 14 800 | 13 700 | 1.47 |
| PMDETA | $Mg^0$ | 19 | 90 | 15 900 | 15 400 | 1.25 |
| PMDETA | $Fe^0$ | 56 | 72 | 13 300 | 12 400 | 1.12 |

[a] $[MA]_0/[MBP]_0/[ligand]_0/[CuBr_2]_0 = 200/1/0.1/0.02$, in 33.3% (v/v) DMSO ($[MA]_0 = 7.4$ M), at 25 °C. $Zn^0$ wire ($d$ = 1 mm, $L$ = 10 mm), $Mg^0$ ribbon (width = 3 mm, thickness = 0.15 mm, $L$ = 5 mm), and $Fe^0$ wire ($d$ = 0.5 mm, $L$ = 20 mm) were used. All surface areas are 33 $mm^2$.

No polymerization of MA was observed in the absence of $Me_6TREN$. Polymerizations proceeded in the presence of a ligand,

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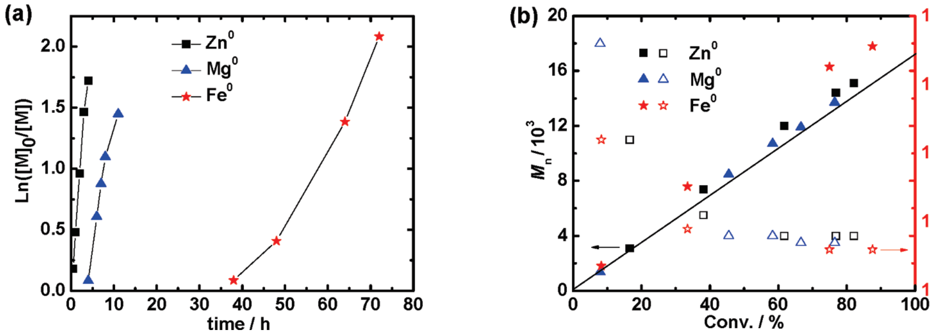


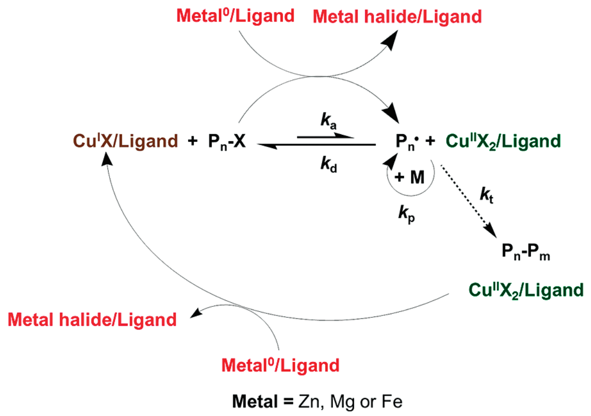
**Figure 1.** (a) Kinetic plots of ln($[M]_0$/[M]) vs time and (b) Evolution of number-average molecular weights $M_n$ and $M_w/M_n$ values vs conversion for ATRP of MA with $Zn^0$, $Mg^0$ and $Fe^0$ as reducing agent. $[MA]_0/[MBP]_0/[Me_6TREN]_0/[CuBr_2]_0 = 200/1/0.1/0.02$, in 33.3% (v/v) DMSO ($[MA]_0 = 7.4$ M), at 25 °C. $Zn^0$ wire ($d = 1$ mm, $L = 10$ mm), $Mg^0$ ribbon (width $= 3$ mm, thickness $= 0.15$ mm, $L = 5$ mm), $Fe^0$ wire ($d = 0.5$ mm, $L = 20$ mm). A constant surface area ~33 mm$^2$ for all metals was used.

**Table 2. $Zn^0$, $Mg^0$, and $Fe^0$ Initiated Free Radical Polymerization of MA without $CuBr_2$[a]**

| ligand | metal | time/h | conv/% | $M_{n,GPC}$ | $M_{n,th}$ | $M_w/M_n$ |
|---|---|---|---|---|---|---|
| $Me_6TREN$ | $Zn^0$ | 19 | 44 | 220 000 | 7600 | 2.07 |
| $Me_6TREN$ | $Mg^0$ | 48 | 31 | 130 000 | 5400 | 1.83 |
| $Me_6TREN$ | $Fe^0$ | 17 | 16 | 43 600 | 2900 | 1.82 |
| none | $Zn^0$ | 36 | ~0 | | | |
| none | $Mg^0$ | 36 | ~0 | | | |
| none | $Fe^0$ | 36 | ~0 | | | |

[a] $[MA]_0/[MBP]_0/[ligand]_0 = 200/1/0.1$, in 33.3% (v/v) DMSO ($[MA]_0 = 7.4$ M), at 25 °C. Zn wire ($d = 1$ mm, $L = 10$ mm), Mg ribbon (width $= 3$ mm, thickness $= 0.15$ mm, $L = 5$ mm), and Fe wire ($d = 0.5$ mm, $L = 20$ mm) were used . All surface areas were 33 mm$^2$.

**Scheme 1. ATRP of MA with Zero-Valent Metal as Supplemental Activator and Reducing Agent**



but without $CuBr_2$, however, they were much slower than reactions conducted in the presence of $CuBr_2$ for all three systems. Molecular weights were much larger than predicted for quantitative initiation ($M_{n,th}$) and molecular weights distributions were very broad. This may indicate a more conventional redox initiated polymerization with the higher oxidation state metal complexes acting as very poorly deactivating species.

However, it appears that all three metals (or metal oxides on the surface) can react with alkyl halides and can initiate a polymerization. Therefore, they can act not only as reducing agents but also as supplemental activators. Thus, the mechanism of ATRP with a zerovalent metal as reducing agent may be slightly different compared to that with organic reducing agents such as ascorbic acid, glucose, or amines, since the zerovalent metal can directly, albeit slowly, react with the alkyl halide in the presence of a ligand. The reactions involved in zerovalent metal mediated ARGET ATRP are shown in Scheme 1. Such a dual role of supplemental activator (SA) and reducing agent (RA) can be termed as SARA ATRP.

In summary, well-controlled ATRP of MA was performed with three zerovalent metals, $Zn^0$, $Mg^0$, and $Fe^0$, as reducing agents to continuously regenerate the activator CuBr/ligand from $CuBr_2$/ligand complex, formed due to radical termination. The metals alone, in the presence of ligands, can also act as supplemental activators but they form inefficient deactivators. The observed activity of $Zn^0$ was higher than that of $Mg^0$ which exceeded that of $Fe^0$.

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**Supporting Information Available:** Experimental section, UV-vis spectra for the reduction with different metals, and cyclic voltametry data. This material is available free of charge via the Internet at http://pubs.acs.org.

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