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# Osmium-Mediated Radical Polymerization

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Continuous development of controlled/“living” radical polymerization (CRP) processes have resulted in unprecedented control over polymer molecular weight and molecular weight distribution and have further allowed the synthesis of macromolecules with well-defined compositions, architectures, and functionalities.[1,2] Among the available CRP techniques, atom transfer radical polymerization (ATRP) has become particularly important and continues to prove invaluable as a synthetic tool.[3−7] The working mechanism of ATRP involves a halogen-capped polymer chain and a transition metal complex in reversible equilibrium with a polymeric radical and the corresponding higher oxidation state metal halide complex (Scheme 1).[8,9] Current trends in ATRP research include correlating catalyst, alkyl halide, and monomer structure[10−12] with reaction parameters and evolution of molecular weight distribution,[13−16] synthesizing new ligands to realize higher control over polymerization[17,18] and aid in catalyst separation/recovery,[19] and expanding the use of transition metals that can serve as catalysts from efficient Cu-based systems[6,8] to include Ru,[20,21] Fe,[22−24] Ni,[25,26] Re,[27] Rh,[28] Mo,[29−31] and Co.[32]

Because the group eight metal complexes $Fe^{II}Br_2(PPh_3)_3$[22] and $Ru^{II}Cl_2(PPh_3)_3$[20] have been successfully used in ATRP, $Os^{II}$ was believed a reasonable candidate to expand the range of available transition metals capable of serving as ATRP catalysts. Additionally, $Os^{II}Cl_2(PPh_3)_3$[33] (**1**) and the trichloride analogue $Os^{III}Cl_3(PPh_3)_3$[34] (**2**) that would be generated during ATRP have previously been isolated and characterized. This study now aims to investigate the ability of these two compounds to respectively mediate direct ATRP, where the equilibrium in Scheme 1 is established from the left with an alkyl halide initiator and the activating metal species, and reverse ATRP, where the equilibrium is established from the right with polymerization initiated by a conventional free radical initiator in the presence of the deactivating metal species.

Additionally, this coordinatively unsaturated $Os^{II}$ catalyst was investigated for its potential to control polymerization by an alternative mechanism. In stable free radical polymerization (SFRP), a SFR (or persistent radical) reversibly couples with a propagating alkyl radical to generate an equilibrium between a propagating and a dormant species that can result in a controlled polymerization (Scheme 1). The persistent radicals capable of mediating SFRP, first developed as nitroxide-mediated polymerization,[35] have recently been expanded from organic species to include transition metal complexes. While Co is the most widely used metal in SFRP,[36,37] examples of Fe[38] and now Mo[30] SFRP systems are known. Interestingly, some of these same Mo complexes are also capable of serving as ATRP catalysts under appropriate conditions.[30] The following studies will investigate the ability of Os to mediate ATRP and SFRP and will also begin to probe the potential interplay of these two radical polymerization mechanisms on a single metal catalyst.

**Scheme 1. Mechanism for ATRP and SFRP**

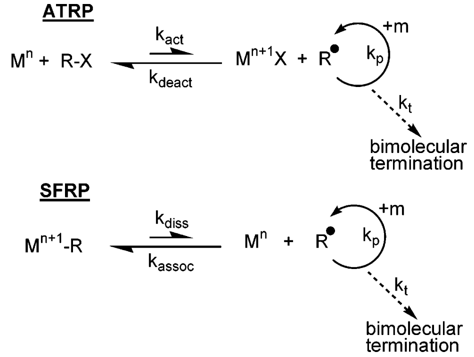

**Table 1. Alkyl Halide-Initiated, $Os^{II}Cl_2(PPh_3)_3$-Mediated Polymerization**

| monomer | initiator | time (h) | conv (%) | $M_n$ (g/mol) | theor $M_n$ | $M_w/M_n$ |
|---|---|---|---|---|---|---|
| Sty[a] | PEB | 20 | 90 | 15 453 | 18 923 | 1.11 |
| Sty[b] | PEB | 6 | 83 | 16 182 | 17 466 | 1.22 |
| BA[a] | MBP | 24 | 73 | 19 180 | 18 880 | 1.63 |
| BA[b] | MBP | 2 | 71 | 36 413 | 18 367 | 1.66 |
| MMA[a] | EBiB | 2.5 | 80 | 18 678 | 16 214 | 1.62 |

[a] [Monomer]:[**1**]:[initiator] = 200:1:1. [b] [Monomer]:[**1**]:[initiator]:[$Al(OiPr)_3$] = 200:1:1:4; 100 °C, bulk, 10% DPE internal standard.

The ability of **1** to act as an ATRP catalyst was first investigated with the alkyl bromide initiators 1-phenylethyl bromide (PEB), ethyl 2-bromoisobutyrate (EBiB), and methyl 2-bromopropionate (MBP) to homopolymerize styrene (Sty), methyl methacrylate (MMA), and butyl acrylate (BA), respectively. Polymerization was successful in all cases. The polymers generated in reactions of bulk monomer at 100 °C typically possessed molecular weights close to theoretical values based on conversion (measured against a diphenyl ether (DPE) internal standard) and were observed to follow first-order linear kinetics, indicating the Os complex had mediated a controlled polymerization (Table 1).

The polymerization of Sty initiated by PEB was well controlled and achieved 90% conversion in 20 h with $M_w/M_n = 1.11$. The observed $M_n = 15\,500$ g/mol at this conversion was slightly lower than the calculated theoretical value of 18 900 g/mol, possibly resulting from new chains formed by thermal self-initiation (Figure 1). The polymerization of BA initiated by MBP needed 24 h to reach 73% conversion with $M_w/M_n = 1.63$. At this time, the observed $M_n = 19\,180$ g/mol agreed very well with the theoretical value of 18 880 g/mol (Figure 2S). The polymerization of MMA initiated by EBiB was comparatively faster than polymerizations of Sty or BA, reaching 80% conversion in only 2.5 h with $M_w/M_n = 1.62$ (Figure 3S).

Certain aluminum additives have been known to increase the rate of ATRP and in some cases even decrease $M_w/M_n$, particularly aluminum isopropoxide ($Al(OiPr)_3$).[39] Recent studies suggest the nature of the catalytic effect of $Al(OiPr)_3$ in ATRP is the result of a

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**Table 2. Osmium-Mediated Styrene Polymerization**

| conditions[a] | initiator | solvent | time (h) | conv (%) | $M_n$ (g/mol) | $M_w/M_n$ |
|---|---|---|---|---|---|---|
| ATRP[b] | PEB | DMF | 20 | 68 | 15 220 | 1.48 |
| ATRP[b] | PEC | DMF | 20 | 74 | 19 800 | 1.43 |
| reverse ATRP[c] | AIBN | DMF | 20 | 27 | 4 690 | 1.64 |
| SFRP[d] | AIBN | toluene | 48 | 71 | 43 980 | 2.81 |
| SFRP[d] | AIBN | DMF | 48 | 76 | 31 860 | 3.19 |

[a] 100 °C, 10% DPE internal standard, 50% (v/v) solvent. [b] [Sty]:[**1**]:[PEX] = 200:1:1. [c] [Sty]:[**2**]:[AIBN] = 200:1:2/3. [d] [Sty]:[**1**]:[AIBN] = 200:1:2/3.

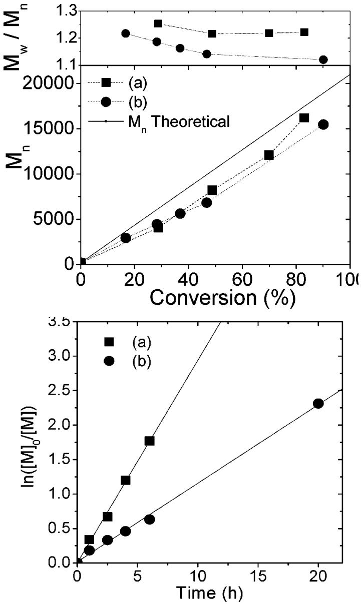

**Figure 1.** (a) [Sty]:[**1**]:[PEB]:[Al(OiPr)$_3$] = 200:1:1:4. (b) [Sty]:[**1**]:[PEB] = 200:1:1; 100 °C, bulk ("ATRP" conditions).

more favorable Lewis acid–base interaction with the oxidized metal complex vs the halide-capped polymer chain that shifts the ATRP equilibrium more toward the active state.[40] While Ru$^{II}$Cl$_2$(PPh$_3$)$_3$ often requires the use of such additives to mediate ATRP,[41] the Os analogue of this complex was sufficiently active to mediate controlled polymerizations of all three monomers without any additives.

However, the effect of this additive on the two slower polymerizations (Sty and BA) was investigated. The rate of styrene polymerization increased with the addition of 4 equiv of Al(OiPr)$_3$ relative to **1** (80% conversion was reached in ~6 h with Al(OiPr)$_3$ vs 16 h without the additive), but $M_w/M_n$ was slightly higher (1.2 vs 1.1). A linear increase in $M_n$ with conversion and linear first-order kinetics were still observed in the presence of Al(OiPr)$_3$ (Figure 1). These observations are consistent with the proposition that Al(OiPr)$_3$ coordination to the Os$^{III}$ species could reduce the deactivation rate constant and shift the ATRP equilibrium more toward the active state, as the addition of Al(OiPr)$_3$ resulted in a faster but less controlled Sty polymerization. The effect of this additive in the BA polymerization was even more pronounced, as 70% conversion was reached in only 2 h compared with 24 h without Al(OiPr)$_3$. While $M_w/M_n$ was not significantly affected, the initial ATRP equilibrium was apparently so shifted to the active state that the high concentration of radicals resulted in low initiation efficiency (observed $M_n$ was approximately twice higher than theoretical values, Figure 2S).

It was thus demonstrated that **1** could act as an ATRP catalyst by activating alkyl halide initiators and mediating a controlled polymerization in bulk monomer. Reverse ATRP would be employed in an effort to establish the ATRP equilibrium from **2** and a free radical. However, **2** was not fully soluble in bulk monomer. DMF proved suitable to conduct reverse ATRP under homogeneous conditions, so the effect of this solvent was first investigated in direct ATRP. The color of a solution of **1** changed from dark green in bulk monomer to brown when diluted with DMF, likely indicating coordination of the solvent to the catalyst that could potentially affect the ATRP equilibrium. Sty was then initiated by PEB and mediated by **1** in 50% (v/v) DMF (Table 2). Initially, the reaction in DMF was faster than that in bulk monomer, but after 5 h the rate of polymerization slowed significantly. Although observed molecular weights agreed well with theoretical values, $M_w/M_n$ was higher in DMF than in bulk monomer, and linear first-order kinetics were not observed (Figure 1S).

Additionally, the rates of halogen exchange between the catalyst and a polymer chain end can significantly affect control over molecular weight and molecular weight distribution in ATRP. This control could be very different in a direct ATRP experiment initiated by PEB and a reverse ATRP experiment catalyzed by **2** where only chloride-capped polymer chains could be formed. Therefore, the direct ATRP of Sty initiated by 1-phenylethyl chloride (PEC) and mediated by **1** in 50% (v/v) DMF was also studied. The results were very similar to those of the PEB initiated polymerization in DMF; after ~5 h, the rate of polymerization slowed significantly. Although observed molecular weights agreed well with theoretical values, linear first-order kinetics were not observed (Figure 1S). Polymerization could thus be mediated under direct ATRP conditions in DMF, but this solvent had an adverse effect on catalyst performance.

In a reverse ATRP experiment initiated by 2,2′-azobis(isobutyronitrile) (AIBN) at 100 °C, where [Sty]:[**2**]:[AIBN] = 200:1:2/3, virtually all of the AIBN had decomposed when the first sample was taken after 1 h ($t_{1/2}$ of AIBN at 100 °C is ~6–7 min). 15% conversion was reached in the first hour with observed $M_n$ = 3160 g/mol. Thereafter, the rate of polymerization quickly diminished, and after 20 h, conversion had only reached 27% with $M_n$ = 4690 g/mol. No significant polymerization occurred thereafter. These results were comparable to those observed in the direct ATRP experiment in DMF. Even though the rate of polymerization diminished early, it was clearly demonstrated that **2** could deactivate propagating chains, as only low molecular weight polymers were produced.

To investigate whether the coordinatively unsaturated **1** could mediate CRP under SFRP conditions, Sty was initiated by AIBN at 100 °C in the presence of **1** ([Sty]:[**1**]:[AIBN] = 200:1:2/3). A free radical polymerization of styrene under these conditions in the absence of **1** produces polymers with $M_n$ in excess of $1 \times 10^5$ g/mol and reaches >90% conversion before 1 h; interestingly, a linear increase in $M_n$ with conversion was observed between $1.0 \times 10^4$ and $4.4 \times 10^4$ g/mol over 48 h in the presence of **1**, indicative of a controlled polymerization (Figure 4S). However, $M_w/M_n$ was quite high (2.81 at 71% conversion). This was due to the bimodality of the molecular weight distribution caused by a significant number of low molecular weight dead chains present from the beginning of the reaction (Figure 5S). These dead chains may have been generated as a result of the rapid decomposition of AIBN at 100 °C, which would have led to a high concentration of radicals and significant radical termination by coupling. While control was seemingly poor in this experiment in terms of $M_w/M_n$, **1** must be a sufficiently good radical trap to continue mediating the polymerization over 48 h.

Additionally, **1** was investigated for its ability to mediate polymerization under SFRP conditions in DMF, a solvent which can coordinate to **1** and potentially obstruct its ability to trap propagating radicals. If indeed there is an interplay of ATRP and SFRP in these polymerization systems (which has been proposed for Mo complexes capable of mediating polymerization under ATRP and SFRP conditions[30]), the use of an appropriate solvent could potentially influence the contribution from each mechanism. When the polymerization of Sty ([Sty]:[**1**]:[AIBN] = 200:1:2/3) was conducted in 50% (v/v) DMF, similar control over molecular weight with conversion was observed as in the experiment conducted in noncoordinating toluene (Table 2). At similar conversion, the observed $M_n$ of the polymer generated in DMF was slightly lower than that generated in toluene (31 860 g/mol at 76% conversion reached in 48 h), but $M_w/M_n = 3.19$ was higher. The use of a coordinating solvent did not appear to significantly affect the ability of **1** to trap propagating radicals.

Thus, **1** has been shown to control the polymerization of Sty, BA, and MMA under direct ATRP conditions in bulk monomer. The Os-catalyzed polymerizations did not require any additives, nor did the addition of Al(O*i*Pr)$_3$ to Sty and BA polymerizations improve control. ATRP can be conducted in DMF, but this solvent has an adverse effect on catalyst performance. **2** was employed to successfully deactivate chains in reverse ATRP. Additionally, the coordinatively unsaturated **1** could mediate controlled polymerization under SFRP conditions in both coordinating and noncoordinating solvents. Further studies are being conducted to verify the mechanism by which **1** mediates polymerization when initiated by an alkyl halide as opposed to AIBN, including chain-end analysis of the isolated polymer by mass spectrometry and $^1$H NMR. Future work will also seek to investigate the potential interplay of ATRP and SFRP with these and similar osmium complexes using EPR and various other techniques.

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**Supporting Information Available:** Detailed experimental procedures of all polymerizations; plots of $M_n$ vs conversion and $\ln([M]_0/[M])$ vs time for Sty, BA, and MMA polymerizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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