# Ferrocene cocatalysis for ruthenium-catalyzed radical miniemulsion polymerization

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## ABSTRACT

In this study we achieved an efficient metal-catalyzed radical "miniemulsion" polymerization with ferrocene ($FeCp_2$) as a cocatalyst in conjunction with a thermoresponsive PEG containing ruthenium catalyst for the polymerization of methacrylate monomers. The iron-cocatalysis worked well even in the miniemulsion similar to homogeneous solution system. The secondary catalytic cycle by ferrocene allows regeneration of Ru(II) activator species through reduction of accumulated Ru(III) deactivator as well as promotion of halogen-capping or deactivation for the active radical species. The effectiveness of this iron cocatalyst in miniemulsion was investigated with both higher polymerization rate and reaching conversion (>90%) than without $FeCp_2$. In this system, the halogen counterion on the cationic surfactant was a major factor in determining the polymerization rate and the end group fidelity. Interestingly, when a non-ionic surfactant was used for the $FeCp_2$-cocatalyzed miniemulsion, a simple addition of salt carrying common halogen ion (e.g., NaCl) in aqueous phase was very effective in terms of polymerization control.

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## 1. Introduction

Metal catalyzed reversible-deactivation radical polymerizations (Mt-RDRP) or living radical polymerizations [1] (Mt-LRP), also know as atom transfer radical polymerizations [2] (ATRP), have found success in various reaction media including organic solvents [3], aqueous media [4], and aqueous dispersions [5−7]. Significant improvements in Mt-LRP in aqueous dispersions have been seen, particularly in miniemulsion, which uses water as the continuous phase with nano-sized hydrophobic droplets prepared by use of a high shear device prior to the polymerization. Miniemulsion Mt-LRP is important for reducing the amount of volatile organic compounds such as solvents in the polymerization and has the added benefits of better heat transfer and lower reaction viscosities [8]. One of the major disadvantages of Mt-LRP in miniemulsion is the residual metal left in the final products due to the hydrophobic

ligands used to keep the metal catalyst in the droplets and particles throughout the polymerization [9]. To solve this problem, we have developed the use of thermoresponsive ruthenium catalyst. At low temperature the catalyst is water-soluble, while at reaction temperatures the catalyst becomes oil-soluble and can enter the particles to catalyze the LRP as seen in Fig. 1 [10]. At the end of the polymerization the reaction can be cooled and the latex washed in methanol leaving a polymer with less than 10 ppm of residual ruthenium. This polymerization successfully showed signs of livingness and reached about 80% conversion at approximately 15 h.

The use of co-catalysts or additives has been shown to increase the rate and the effectiveness of catalysts in ATRP, while also allowing for a reduction in the catalyst concentration as seen in activators regenerated for electron transfer (ARGET) ATRP with the use of reducing agents [11]. During the course of a polymerization there is generally an accumulation of the deactivator form of the catalyst as a result of bimolecular termination. This increase of deactivator changes the equilibrium between the dormant and active species and eventually the polymerization rate slows or even stops at incomplete conversions. Reducing agents can reform the activator and allow higher to complete conversions to be realized. Recently the use of ferrocene ($FeCp_2$) as a co-catalyst for ruthenium
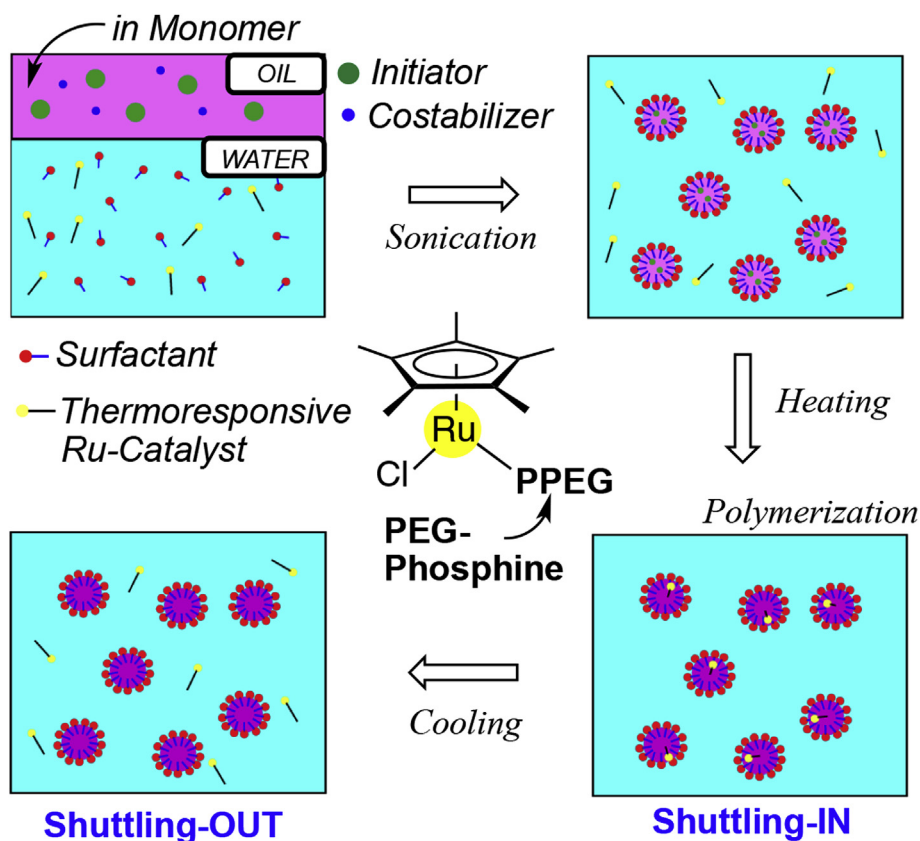
**Fig. 1.** Metal mediated miniemulsion polymerization catalyzed by thermoresponsive catalysts made for easy removal from the final products.

catalyzed Mt-LRP showed increased rates of polymerization and better livingness through a concerted co-catalytic mechanism [12]. The rate of activation was increased by reducing the deactivating species, Ru(III), to the activator Ru(II) via a halogen abstraction by the Fe(II)Cp$_2$ to form an unstable ferrocenium salt complex Fe(III) Cp$_2^+$X$^-$ (X: halogen). This complex quickly degrades through a redox process reforming Fe(II)Cp$_2$ with the halogen capping an active radical, thereby increasing the rate of deactivation in FeCp$_2$ co-catalyzed polymerizations (Fig. 2).

Herein we present a study using FeCp$_2$ as an iron cocatalyst in miniemulsion Mt-LRP with a thermoresponsive ruthenium catalyst. The combination allowed for the miniemulsion polymerization of a hydrophobic methacrylate giving >90% conversion in less than 8 h, and after the polymerization the ruthenium catalyst or the residue can be removed from the final product. Furthermore, we explored the effect of the surfactant counter-ion on the rate and the polymer end-group functionality, and demonstrated a surfactant aided Mt-LRP in miniemulsion. This work will ideally lead to improvements in catalysis in miniemulsion for the synthesis of living polymers, reduce the amount of primary catalyst required and move towards an all-iron catalyst system in Mt-LRP emulsions or the use of a removable ferrocene-derived cocatalyst.

## 2. Experimental

### 2.1. Materials

Butyl methacrylate and benzyl methacrylate (BMA and BzMA, Tokyo Kasei; purity > 99%) were dried overnight over calcium chloride and purified by double distillation under reduced pressure over calcium hydride before use. Potassium carbonate (K$_2$CO$_3$, Wako, purity > 99.5%) was degassed by vacuum–argon purge cycles before use. Hexadecyltrimethylammonium bromide (CTAB, Sigma-Aldrich; BioXtra purity $\geq$ 99%), hexadecyltrimethylammonium chloride (CTAC, Sigma-Aldrich; BioXtra purity $\geq$ 99%), Polyoxyethylene (20) oleyl ether (Brij98, Sigma-Aldrich; average M$_n$ 1150 Da), and hexadecane (Sigma Aldrich, purity > 99%) were used without any purification. Ethyl-2-chloro-2-phenylacetate (ECPA, Aldrich; purity > 97%) was distilled under reduced pressure before use. (4-hydroxyphenyl) diphenylphosphine (Sigma-Aldrich; purity > 98%), poly(ethylene glycol) methyl ether tosylate (PEG-tosylate, Sigma-Aldrich; average M$_n$ 5000 Da, PEG$_{113}$, or M$_n$ 2000 Da, PEG$_{45}$) and [RuCp*Cl]$_4$
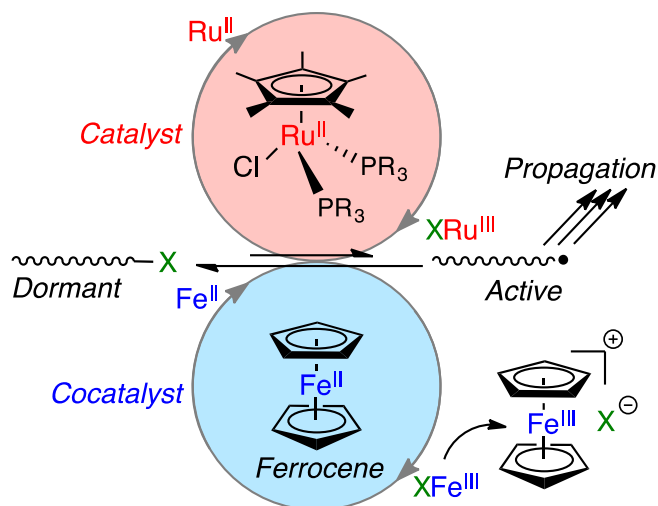


**Fig. 2.** Cocatalysis of FeCp$_2$ in ruthenium-catalyzed Mt-LRP.