

# Metal Complex-Bearing Core-Functionalized Microgel Star Polymers: High Selectivity and Recycles of Catalysts

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## Introduction

Recently we have first achieved the direct introduction of polymerization catalysts into the microgel core of star polymers via Ru(II)-mediated living radical polymerization<sup>1)</sup>. The star polymer catalysts with PMMA and other arms efficiently catalyzed the oxidation of 2-alcohols and the reduction of ketones<sup>2)</sup>, which showed the unique substrate selectivity different from RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>. In particular, the star polymers with PEG-arms have attracted much interesting because of the amphiphilic property. Furthermore, the star polymer catalysts are expected to enable higher stability of the bound Ru(II) complexes encapsulated in the microgel core and thus protected by surrounding arm chains.

In this paper, we report the synthesis of PEGMA-armed star polymers with Ru(II) core to be employed for reduction of ketones. Recycle of the catalysts was also examined.

## Results and Discussion

PEG-armed, amphiphilic, and thermosensitive star polymers (**3**; Scheme 1) with core-bound Ru(II) complexes were synthesized by the linking reaction of PEGMA living polymers with a dimethacrylate (**1**) and a phosphine-bearing styrene (**2**) via Ru-catalyzed living radical polymerization. The obtained star polymers (red-brown; >76% yield) carried 24 μmol core Ru/g-polymer (35 % inclusion of the catalyst); Mw = 772K; 19 arms.

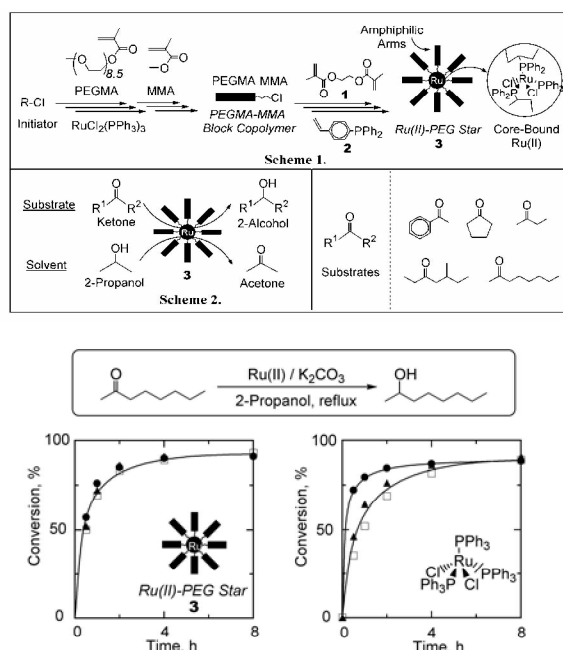
The star polymers (**3**) efficiently catalyzed the reduction of various ketones into *sec*-alcohols in 2-propanol (Scheme 2). Especially, **3** could be reused at least three times in the reduction of 2-octanone without any decline in activity and loss of core-bound Ru(II) (Figure 1). With RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>, however, a gradual decrease of catalytic activity was observed. In aqueous/2-propanol dispersed mixtures at 100 °C, **3** also catalyzed the reduction of 2-octanone, faster than RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> did. This reaction involved a thermoregulated phase-transfer catalysis where **3** moves from the organic reaction phase (100 °C) into the aqueous phase (25 °C; work-up); thus the recycles of **3** could be also achieved.

Furthermore, the removal of the metal complexes from the core and the reintroduction of other metal complexes were also examined.

## Reference

1) Terashima, T. et al. *J. Am. Chem. Soc.* **2003**, *125*, 5288.

2) Terashima, T. et al. *Polym. Prepr. Jpn.* **2003**, *52*, 154; *Polym. Prepr. Jpn.* **2004**, *53*, 2604.



**Figure 1.** Recycle of Ru(II)-PEG star catalysts in reduction of 2-octanone. 2-octanone/Ru<sub>Star</sub>/K<sub>2</sub>CO<sub>3</sub> = 15/0.015/1.5 mmol in 15 mL 2-propanol at 100 °C. Catalyst cycles: 1st (J), 2nd (G), 3rd (H).