Polymer Catalysts from Polymerization Catalysts: Direct Encapsulation of Metal Catalyst into Star Polymer Core during Metal-Catalyzed Living Radical Polymerization

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Placing metals into desired sites of organic macromolecules with controlled architecture can afford functional hybrid compounds or materials originating from their controlled micro- or nanostructures. Representatives are a series of dendrimers that have metals on the periphery or in the core, where they might show special reactivity or stability in catalytic reactions.[1] Hyperbranched and star polymers are alternatives with spherically shaped macromolecules, which are more easily accessible, although their sizes have a certain degree of statistical distribution. Encapsulation of metals was recently studied with hyperbranched and star polymers, but it has been done after the synthesis of the polymers.[2–5]

This communication is to present our novel synthetic strategy for star polymers containing metals in the core by direct in situ encapsulation of the catalysts during metal-catalyzed living radical polymerization[6] (Scheme 1). The key is to copolymerize a phosphine-carrying monomer that can serve as a ligand for the metals via ligand exchange in the linking reaction of linear polymers with a divinyl compound.

Scheme 1. Ru-Bearing Core-Functionalized Star Polymers via Metal-Catalyzed Living Radical Polymerization
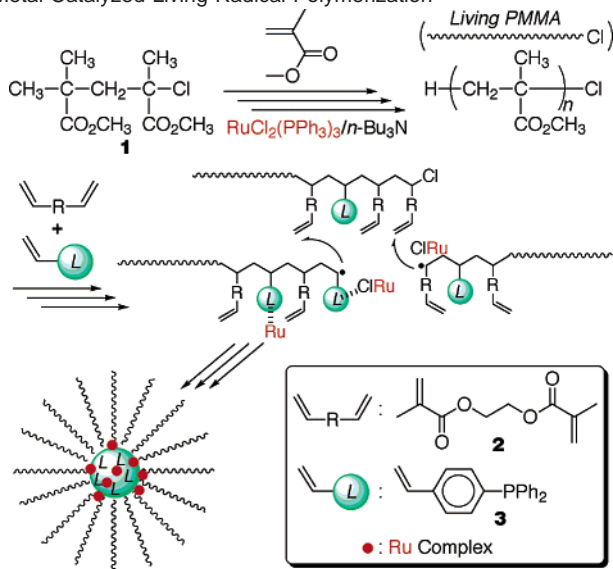
For this purpose, we polymerized methyl methacrylate (MMA) with H-(MMA)$_2$-Cl (**1**) (initiator), RuCl$_2$(PPh$_3$)$_3$ (catalyst),[7] and *n*-Bu$_3$N (additive)[8] in toluene at 80 °C to obtain linear living PMMA with controlled molecular weights (M_n = 11900) and narrow molecular weight distributions (M_w/M_n = 1.19) (Figure 1A), by size-exclusion chromatography (SEC). On addition of a mixture of ethylene glycol dimethacrylate (**2**)[9] and diphenyl-4-styrylphosphine (**3**) into the living polymer when conversion of MMA reached 90%, both were consumed almost simultaneously. As they were
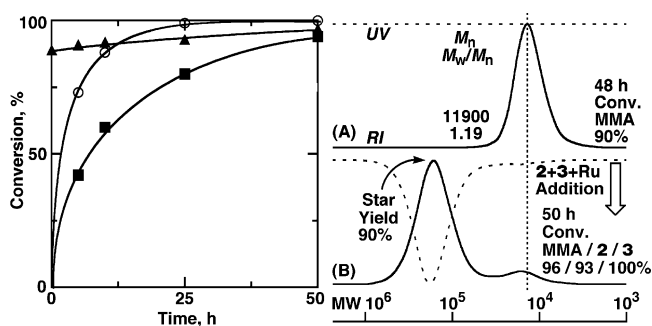

Figure 1. Conversion of MMA (▲), **2** (○), and **3** (■) during linking of PMMA by **1**/RuCl$_2$(PPh$_3$)$_3$/*n*-Bu$_3$N in toluene at 80 °C and SEC of the PMMA and linking products; [MMA]$_0$/[**1**]$_0$/[RuCl$_2$(PPh$_3$)$_3$]$_0$/[*n*-Bu$_3$N]$_0$ = 2000/20/10/40 mM; [**2**]$_{add}$/[**3**]$_{add}$/[RuCl$_2$(PPh$_3$)$_3$]$_{add}$ = 400/100/20 mM; PMMA solution/added solution = 2/1 v/v (The final molar ratio of used compounds MMA/**1**/**2**/**3**/RuCl$_2$(PPh$_3$)$_3$ = 100/1/10/2.5/1).

polymerized, the SEC curves shifted to higher molecular weights to lead to star polymers. Further addition of RuCl$_2$(PPh$_3$)$_3$ along with **2** and **3** accelerated the linking reaction and gave a higher yield of star polymers (90%) (Figure 1B). The resulting higher-molecular weight fraction showed UV absorption at 270 nm, indicating incorporation of **3** into the star polymers. This was also confirmed by ^{1}H NMR analysis of the fraction. The absolute weight-average molecular weight (M_w), the arm number (*f*), and the gyration radius (R_z) were determined by multiangle laser light scattering (MALLS) coupled with SEC: M_w = 3.69 × 10^5; *f* = 22; R_z = 8.9 nm. Another sample obtained with a higher concentration of **3** also had similar values (M_w = 6.17 × 10^5; *f* = 31; R_z = 13.4 nm), comparable to those of star polymers prepared without the phosphine monomer.[10]

Figure 2 shows the atomic force micrograph (AFM) of the latter sample, cast from a 3% DMF solution on a glass plate. It revealed round-shaped images with ∼50 nm diameters and ∼1 nm heights. These are attributed to individual star polymer molecules (globular with a ∼30 nm diameter in solution)[10] rather flattened on the plate on drying.

Encapsulation of the ruthenium complexes was confirmed by UV−vis spectroscopic analysis of the star polymers, isolated by double precipitation into methanol to remove unloaded catalysts.[11] The isolated polymers are nearly white powders while being reddish brown in solution, similarly to RuCl$_2$(PPh$_3$)$_3$. Both solutions showed a broad absorption at λ_{max} = 475 nm, which is not observed for linear PMMA and **3**, indicating incorporation of the ruthenium complexes into the star polymers. The amount of the loaded complex was calculated to be 58 μmol per 1 g of polymer on the assumption that the complex in the core has the same extinction coefficient as that for RuCl$_2$(PPh$_3$)$_3$. This suggests that 77% of the ruthenium catalysts were encapsulated into the cores. The other sample prepared with a higher **3** concentration had a higher Ru
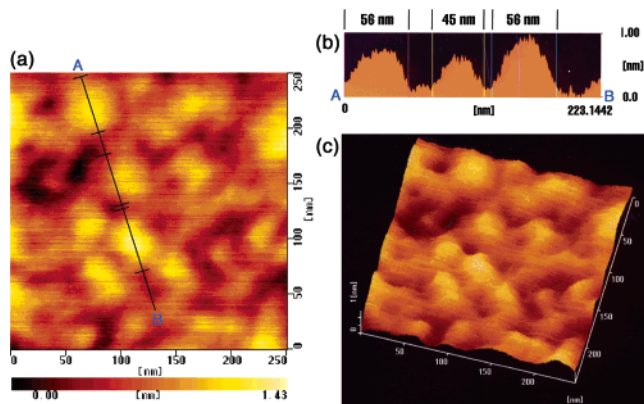
Figure 2. AFM images of the star polymers cast on a glass plate. (a) Height contrast picture; (b) cross sectional view of the line A−B in (a); (c) side view.

content, 74 μmol/g polymer, which means almost 100% of the ruthenium catalysts were encapsulated. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) of the latter indicated 84 μmol Ru/g polymer, similar to that by UV−vis analysis.

Transmission electron micrograph (TEM) analysis of a spin-cast film of the star polymers with a homogeneous thickness ($\leq$50 nm) showed darkened dots with 2−3 nm diameters, attributed to the Ru-containing core of the star polymers; no staining was needed for TEM (Figure 3). The size was slightly smaller than that of the core of similar star polymers in solution, 5.4 nm, measured by small-angle X-ray scattering.[10] This is due to densely packed star polymers in solid state.
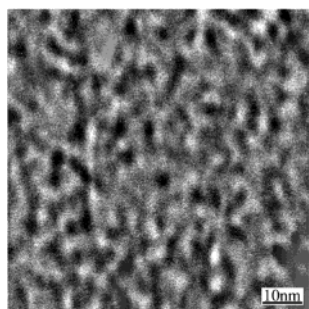

Figure 3. TEM micrograph (unstained) of the spin-casted star polymer film with a homogeneous thickness ($\leq$50 nm).

These star polymers were then employed as catalysts for oxidation of alcohols into ketones.[12] Three samples with different catalyst loads but with almost the same arm length [DP_n(arm) $\approx$ 100] were used at the same ruthenium concentration (Figure 4). They induced the reaction, where the activity increased with a decrease in the loading amount and was lower than that of RuCl$_2$-(PPh$_3$)$_3$ in solution. This suggests that a high catalyst load may adversely affect the activity.[13] Further tuning of the star polymer catalysts should be needed for a higher activity and is now in progress with varying arm chains as well as cross-linking reagents.

In conclusion, this communication describes the first example of in situ direct encapsulation of metal catalysts into star polymer cores thorough metal-catalyzed living radical polymerization, where
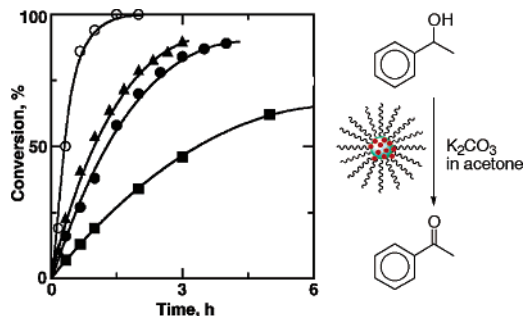

Figure 4. Ruthenium-catalyzed oxidation of 1-phenylethanol to acetophenone in acetone (10 mL) under reflux; [1-phenylethanol]$_0$/[Ru]$_0$/[K$_2$CO$_3$]$_0$ = 10/0.010/1.0 mmol; star polymers with 31 (▲), 58 (●), 74 (■) μmol Ru/g polymer, RuCl$_2$(PPh$_3$)$_3$ (○).

hybrid materials with controlled structures can be prepared in a one-pot procedure.

Supporting Information Available: Experimental details for the polymerization and the characterization, data for star polymers, photograph of star polymer powder and solution, and the UV−vis spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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