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# In Situ Hydrogenation of Terminal Halogen in Poly(methyl methacrylate) by Ruthenium-Catalyzed Living Radical Polymerization: Direct Transformation of "Polymerization Catalyst" into "Hydrogenation Catalyst"

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The so-called "tandem catalysis"[1] is an intriguing sequential or concurrent catalysis where a single catalyst mediates at least two reactions in one-pot, requiring neither recovery of an intermediate of the first step nor an additional use of another catalyst for the subsequent reaction. Especially, in situ direct transformation of a catalyst into another by simple ligand modification is attractive, because sequential multistep reactions are thereby possible with a single catalyst in a single vessel. Certain ruthenium alkylidene complexes[2] can in fact catalyze in tandem such reactions as olefin metathesis and hydrogenation[3] or olefin metathesis and isomerization.[4]

Living radical polymerization[5] is another class of metal-catalyzed reactions of significance, for which a variety of organometallic catalysts, such as ruthenium, iron, copper, and nickel, have been evolving (Scheme 1, upper line). Precision control of propagation has now led to end-functionalized, block, star, and many other designed polymers and materials.

A remaining subject for refinement thereof is the fact that the products by definition carry a halogen terminal, because the catalysis involves a reversible and homolytic cleavage of a carbon−halogen bond in an initiator or a "dormant" polymer terminal originating therefrom. While a requisite for fine reaction control, the terminal halogen is chemically reactive and thermally unstable, possibly resulting in undesirable reactions upon subsequent use of these polymers, and should thus be removed or transformed.[6] Few processes are by now available, however, such as hydrogenation with possible hazardous tin reagents and end-capping with expensive and exotic silyl enolates, none of which seems to be practically versatile.[7]

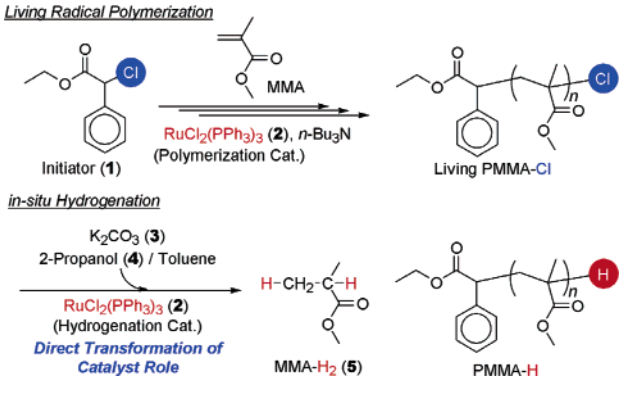
Given these backgrounds, this communication reports a novel tandem Ru(II) catalysis for selective hydrogenation of the terminal halogen in poly(methyl methacrylate) (PMMA) obtained in the ruthenium-catalyzed living radical polymerization, via in-situ transformation of a "polymerization catalyst" into a "hydrogenation catalyst" (Scheme 1). To our knowledge, this is the first example of halogen-hydrogenation in α-haloesters and their polymer analogues with ruthenium complexes.

**In Situ Hydrogenation via Tandem Ru(II) Catalysis.** MMA was polymerized with a ruthenium complex [$RuCl_2(PPh_3)_3$ (**2**)][8] as a catalyst in conjunction with a chloride initiator (**1**: ethyl-2-chloro-2-phenylacetate)[9] and an amine additive ($n$-$Bu_3N$)[10] in toluene at 80 °C (Figure 1). Monomer conversion reached 49% in 5 h to give PMMA of a controlled molecular weight and a narrow molecular weight distribution (MWD) [$M_n = 5000$; $M_w/M_n = 1.37$; by size-exclusion chromatography (SEC); Figure 1a].

At this point, the polymerization solution (unquenched) was added into a $K_2CO_3$ (**3**) solution in a 2-propanol (**4**)/toluene mixture[11] at 80 °C under an inert gas atmosphere. The originally red-brown solution immediately turned red-purple and then yellow upon continuous stirring for ca. 5 min. The color change indicates the formation of a Ru(II) hydride(s), known as a hydrogenation catalyst (Supporting Information, Figure 1; see the discussion below). The polymer, recovered after an additional stirring for 25 h, had a molecular weight and an MWD ($M_n = 5400$, $M_w/M_n = 1.45$, Figure 1c) virtually the same as those of a control sample (a) isolated before the $K_2CO_3$ treatment. Without such quenching, the polymerization proceeded undisturbed to a 85% conversion in 30 h, to give a living PMMA with higher molecular weights ($M_n = 8200$, $M_w/M_n = 1.29$, Figure 1b). In separate runs with addition **3** or **4** alone, the polymerization was not disturbed (Figure 1; see also Support Information, Figure 2 and Table 1), indicating that the combination of **3** and **4** is mandatory.

Direct $^1$H NMR analysis of the polymerization mixture after the treatment with a **3**/**4** pair also showed the in-situ generation of hydrogenated MMA (**5**) from the remaining MMA (44% in 5 h and 47% in 25 h, with $n$-octane as an internal standard). Presumably, such a fast and concurrent hydrogenation of unreacted MMA is one of the essential factors for the efficient quenching of the polymerization.

***Scheme 1.*** In Situ Hydrogenation of Terminal Halogen of Living PMMA-Cl with Ru Catalysts



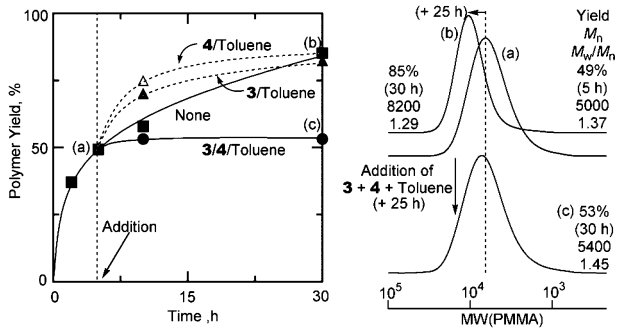




***Figure 1.*** In situ hydrogenation of the terminal halogen of PMMA-Cl with Ru catalysts: polymerization, $[MMA]_0/[\mathbf{1}]_0/[\mathbf{2}]_0/[n\text{-}Bu_3N]_0 = 2000/20/10/40$ mM in toluene at 80 °C; treatment, $[\mathbf{3}]_{add} = 125$ mM in **4**/toluene; polymer solution/added solution = 1/4 v/v; final conditions, $[MMA]/[\mathbf{1}]/[\mathbf{2}]/[n\text{-}Bu_3N]/[\mathbf{3}] = 400/4/2/8/100$ mM in **4**/toluene (1/1, v/v).



10.1021/ja0641507 CCC: $33.50 

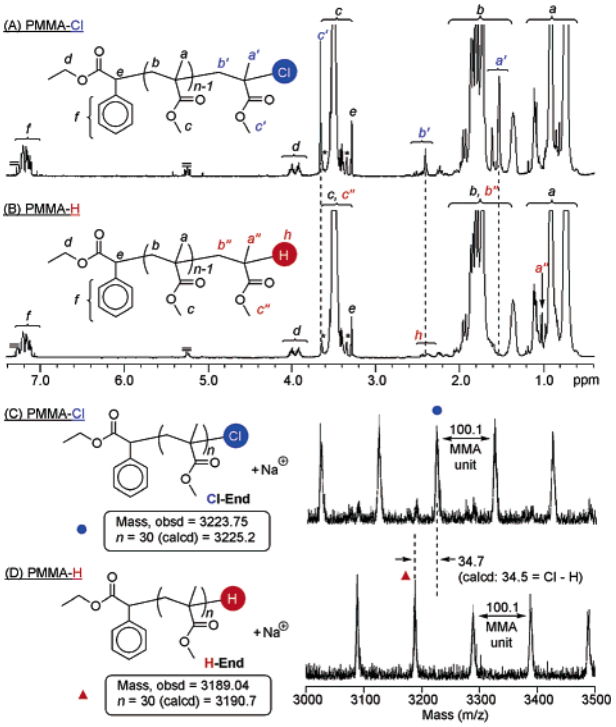



***Figure 2.*** $^1$H NMR (A and B in $CD_2Cl_2$ at 25 °C) and MALDI-TOF-MS (C and D) spectra of PMMA-Cl and PMMA-H. The asterisks (*) indicate satellite peaks. The two samples (A/C and B/D) were fractionated to remove the catalyst residues; see main text and Supporting Information for molecular weight data.

**Polymer Characterization.** The terminal structure of the polymers was analyzed by $^1$H NMR (Figure 2A,B) after purification.[6a] The control sample (a), without the **3**/**4** treatment, exhibited the characteristic signals of a PMMA main chain and the terminal MMA unit adjacent to the $\omega$-end C−Cl bond, methyl (a′: 1.6 ppm), methylene (b′: 2.4 ppm), and methoxy (c′: 3.7 ppm), along with the methylene (d: 4.0 ppm) and methine (e: 3.3 ppm) protons derived from the initiator, indicating the formation of a chlorine-capped PMMA-Cl (Figure 2A).

In contrast, PMMA obtained with the **3**/**4** mixture was completely free from these three characteristic signals (a′, b′, and c′) but showed new absorptions indicative of an $\omega$-end hydrogen (Figure 2B): a multiplet (h) at 2.4 ppm for the terminal hydrogen itself, as well as a methine and a doublet (a″) at 1.0 ppm assignable to the methyl protons of the hydrogenated MMA terminal unit. No other signals were observed, such as olefin and those indicative of the ester exchange between MMA and 2-propanol. As calculated from the signal intensity ratio of the α-end methylene (d) to the pendent methoxy (c) of the main chain, the $M_n$ (NMR) of samples (A) and (B) both agreed with those by SEC [$M_n$ (SEC)] (see Supporting Information). The number-average α-end functionality ($F_n$) for the initiator fragment, $M_n$ (SEC)/$M_n$ (NMR), was close to unity, indicating the absence of side reactions during the hydrogenation as well as the preceding polymerization.

The in situ, selective, and quantitative hydrogenation was also confirmed by MALDI-TOF MS[12] (Figure 2D; the same sample for Figure 2B). The end-capped sample gave only a single major series of peaks, regularly separated by the molar mass of MMA monomer (ca 100.1). The absolute mass of each peak is equal to that expected for the PMMA with one hydrogen atom at the $\omega$-end and one initiator fragment at the α-end, plus a sodium ion from the externally added salt for ionization. On the other hand, the control sample (a) without hydrogenation gave an entirely different MS series (Figure 2C: the same sample for Figure 2A), consistent with the chlorine-capped PMMA to be formed in the living polymerization.[6] Accordingly, the mass difference between spectra C and D was 34.7, close to the mass difference (34.5) between chlorine and hydrogen.

**Reaction Mechanism.** The mechanism of the in situ hydrogenation[13] was further investigated by $^1$H NMR model reactions. For example, treatment of the Ru dichloride complex (**2**) with **3** in **4**/toluene gave signals at −7 and −10 ppm characteristic of the hydride $RuH_2(PPh_3)_3$ and also at −18 ppm of $RuHCl(PPh_3)_3$. Simultaneously, the signal due to acetone via reduction of **4** was also observed. When deuterated 2-propanol (*d*8) was used instead of **4** in the polymer treatment, the signal intensity of the $\omega$-end methine proton decreased, which suggests 2-propanol is the hydrogen source (Supporting Information, Figure 4). From these results, the proposed mechanism is as follows: the Ru hydride complexes are first generated directly from the polymerization catalyst **2** by the $K_2CO_3$-mediated hydrogen transfer from 2-propanol (solvent), and these hydride complexes hydrogenate the terminal chlorine of dormant PMMA-Cl and MMA. The details are now under investigation.

In conclusion, a selective, quantitative, and in situ hydrogenation of the chlorine terminals in PMMA-Cl was achieved in the Ru-catalyzed living radical polymerization, via direct transformation of a polymerization catalyst into a hydrogenation catalyst with $K_2CO_3$ and 2-propanol.

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**Supporting Information Available:** Experimental details for the polymerization, hydrogenation, the characterization data, and $^1$H NMR and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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