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Bisphosphine Monoxide-Ligated Ruthenium Catalysts: Active, Versatile, Removable, and Cocatalyst-Free in Living Radical Polymerization

Yusuke Fukuzaki, Yusuke Tomita, Takaya Terashima, Makoto Ouchi,* and Mitsuo Sawamoto*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

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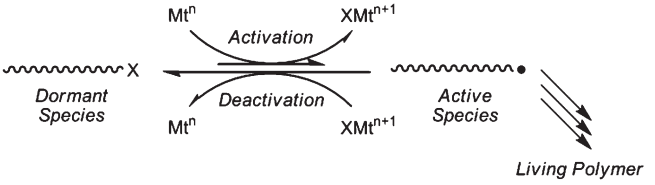
ABSTRACT: As potentially bidentate ligands, bisphosphine monoxides [BPMOs; $Ph_2P(O)(CH_2)_nPPh_2$; $n = 1, 2$; Ph = C_6H_5] were found to be effective for pentamethylcyclopentadiene ruthenium chloride catalysts [$Cp^*Ru^{II}Cl(BPMO)_m$; $m = 1,2$] in living radical polymerization: active, versatile, cocatalyst-free, and removable. The complexes catalyzed living radical polymerizations of a variety of monomers and their functionalized derivatives: methyl acrylate, methyl methacrylate (MMA), styrene, 2-hydroxyethyl methacrylate, and poly(ethylene glycol) methacrylate. The controllability and activity were high enough even with a small amount of catalyst ($[Ru]_0/[initiator]_0 = 1/200$; 50 ppm for monomer), to give high molecular weight PMMA with narrow MWD ($M_n = 103\,000$: $M_w/M_n = 1.19$) and block copolymers. Such an activity and a wide applicability in terms of monomers have been found for few Ru catalysts thus far. Importantly, they did not necessarily need a cocatalyst (aluminum alkoxide, amine, etc.) for their catalysis, in contrast to most of the other ruthenium catalysts that are effective only with a cocatalyst. The cocatalyst-free catalysis is concluded to be derived from the phosphine oxide moiety in BPMO, whose hemilabile coordination promotes the deactivation process [~~~C• (growth active) → —C−Cl (dormant)] and, in turn, accelerates the whole catalytic cycle (radical ↔ dormant; $Ru^{II} \leftrightarrow Ru^{III}$). Furthermore, the high polarity of BPMO ligands effectively helped near perfect removal of the catalyst residue (>99.7% for PMMA) just by single reprecipitation into methanol.

Introduction

Catalytic reactions with transition metal complexes have been attractive since their wide variation allows facile and systematic "on-demand" design and optimization of catalysts. For example, versatility may be enhanced by the combination of a central metal and ligands, which are connected via the d-orbital−σ/π-electrons coordinative interaction. Upon a repetitive association and dissociation of reactants with the central metal, this metal−ligand bond is often so flexible as to activate a particular bond within the complex and/or to develop substrate specificity by opening a particular coordinatively unsaturated, vacant space in the coordination sphere. This is exactly because ligand design plays critical roles in catalysis, indeed bringing about new reactions of hitherto unattained, or at least dramatically improved, activity, selectivity, and specificity.

In this context, transition metal-catalyzed living radical polymerization[1] provides an excellent example that is now among the most versatile, efficient, and user-friendly synthetic tools to control polymer architectures, where transition metal complexes as catalysts govern the precision control of radical propagation (Scheme 1).[1,2] Therein designed metal complexes catalyze the "reversible activation" of a carbon−halogen bond (~~~C−X) at a growing polymer terminal (dormant species), derived from a halide initiator, via the one-electron redox cycle ($Mt^n \leftrightarrow XMt^{n+1}$) and thus generate a growth-active radical species (~~~C•) at a concentration most likely 2 orders of magnitude lower than in conventional free radical polymerization. The reversibility

Scheme 1. Transition Metal-Catalyzed Living Radical Polymerization



[~~~C−X (dormant) ↔ ~~~C• (active)], and the consequently low radical intermediate concentration, is literally essential for this precision control and is also related to the efficiency in catalytic cycle or turnover frequency (TOF) often discussed in organometallc catalysis. Obviously, the more frequently, efficiently, and undisturbedly the redox catalytic cycle proceeds, the finer the precision reaction control, thus allowing a "catalytic" amount of a metal catalyst and the synthesis of high-molecular-weight polymers.

Since the first findings[3] of metal-catalyzed living radical polymerization, metal catalysts have extensively been devised with ruthenium,[4] copper,[2,5] iron,[6] nickel,[1c,7] and other late transition metals (Mt). Among them, ruthenium complexes are active and versatile for a variety of monomers, which advantage stems from their ready and flexible modification with a variety of ligands with carbon- and hetero atoms-based coordinating sites. In contrast to iron counterparts, the tolerance of polar functionality is another advantage inherent to less oxophilic ruthenium complexes in controlling polymerizations of functional monomers, thus allowing the direct synthesis of precision polymer architectures including functionalized random, block, gradient, and star polymers.[1]

*Corresponding authors. E-mail: (M.O.) ouchi@living.polym.kyoto-u.ac.jp; (M.S.)sawamoto@star.polym.kyoto-u.ac.jp.

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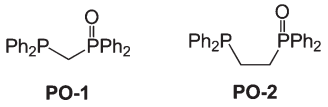
Chart 1. Phenyl BPMO Ligands Employed in This Work



The use of transition metal complexes, however, imposes some issues that should be solved in their actual applications.[1d] Most seriously, metal catalysts and their residues may potentially be toxic and/or detrimental to product performance and should effectively be removed after polymerization, either by a postreaction treatment or by an extreme reduction of catalyst dose. For the latter, the catalytic cycle frequency should be enhanced in the reversible activation process, as recently proposed for copper catalysts.[2c,d,8,9] For ruthenium complexes, designed ligands and cocatalysts (such as metal alkoxide[10] and amines[4h,11]) may offer high catalytic cycle and/or removable catalytic systems, but, to our knowledge, less effort has so far been devoted along this line.

In this work, we have thus targeted more active and smarter ruthenium catalysts for living radical polymerization, primarily by judicious design of phosphine ligands that may also be effective and active enough to free the catalysis from cocatalysis. We specifically focused on bisphosphine monoxides (BPMOs) [$R^1R^2P-Y-P(O)R^3R^4$; Y = divalent spacer such as $-(CH_2)_n-$; n = 1, 2, ...] as potentially asymmetrically bidantate ligands for pentamethylcyclopentadiene ruthenium chloride ($Cp^*Ru^{II}Cl$). With their soft (R^1R^2P-) and hard [$-P(O)R^3R^4$] Lewis-base centers, BPMOs provide unique ligand characteristics, including stabilization of transition metal complexes in *both* low and high oxidation states[12] and coordinate via a labile chelation that readily generates, reversibly, a reactive or coordinatively unsaturated species open to substrate coordination and subsequent intracomplex bond activation. Both factors are expected to enhance the redox catalytic cycle.

This paper is to report that phenyl BPMOs [$Ph_2P-Y-P(O)Ph_2$: $-Y- = -CH_2-$ (**PO-1**), $-C_2H_4-$ (**PO-2**)] (Chart 1) are uniquely effective as ligands for Cp*RuCl catalysts in living radical polymerization. The spacer length turned out to alter coordination pattern (monodantate and bimolecular with **PO-1** versus bidentate and unimolecular with **PO-2**) and thereby affected the catalysis. Especially, the Cp*RuCl/**PO-2** system is particularly active and versatile, leading to living polymerizations of monomers of varying nature, such as methyl methacrylate (MMA), methyl acrylate (MA), styrene (St), 2-hydroxyethyl methacrylate (HEMA), and poly(ethylene glycol) methacrylate (PEGMA). In addition, this system works effectively *without* cocatalyst and actively enough at a low dose ($[Ru]_0/[initiator]_0 \sim$ 0.5−1 mol %), while keeping high controllability. For MMA and other hydrophobic monomers, furthermore, its high solubility in methanol allowed near quantitative removal (>99%) from polymers just by single reprecipitation.

Experimental Section

Materials. MA, MMA, and styrene (all from TCI; purity >99%) were dried overnight over calcium chloride and purified by double distillation from calcium hydride before use. HEMA (Aldrich; > 99%) was singly distilled under reduced pressure before use. PEGMA [$CH_2{=}CMeCO_2-(CH_2CH_2O)_nMe$; Me = CH_3; n = 8.5 on average] (Aldrich) was purified by passing through an inhibitor- removal column (Aldrich) and was subsequently degassed by three-time vacuum-argon bubbling cycles before use. The H−EMA−Br initiator [$(CH_3)_2C(CO_2Et)Br$] (TCI; > 98%) was distilled twice over calcium hydride under reduced pressure before use. The H−$(MMA)_2$−Cl initiator [H−$(CH_2CMeCO_2Me)_2$−Cl]; an MMA dimer chloride] was prepared according to the literature.[13]

All the ligands and materials for ruthenium complexes, listed below, were used as received without further purification and handled in a glovebox (MBraun Labmaster 130, M. Braun Intergas-Systeme GmbH, Garching, Germany) under a moisture- and oxygen-free argon atmosphere (H_2O < 1 ppm; O_2 < 1 ppm): BPMOs, bis(diphenylphosphino)methane monooxide (**PO-1**) and 1,2- bis(diphenylphosphino)-ethane monooxide (**PO-2**) (both from Strem; > 97%); methyldiphenylphosphine ($PMePh_2$) (Aldrich; > 97%); ruthenium(III) chloride hydrate (Wako; > 99.9%); 1,2,3,4,5-pentamethylcyclopentadiene (TCI; > 93%); and lithium triethylhydridoborate (Aldrich, 1.0 M solution in THF).

Toluene (Kishida Kagaku, Osaka, Japan; purity 99.5%) was dried and purified by passing through purification columns (Solvent Dispensing System, SG Water USA, Nashua, NH; Glass Contour) and bubbled with dry nitrogen for more than 15 min immediately before use. *n*-Octane (internal standard for gas chromatography) and 1,2,3,4-tetrahydrousnaphthalene (tetralin; internal standard for ^{1}H NMR) were dried over calcium chloride and distilled twice from calcium hydride.

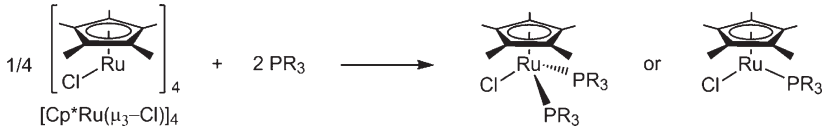
Preparation of [Cp*Ru(μ_3-Cl)]$_4$. Dichloro(pentamethlcyclopentadienyl)ruthenium {$[(Cp^*)RuCl_2]_n$} was prepared by the reaction of $RuCl_3\cdot nH_2O$ (6.0 g, 26.6 mmol) with 1,2,3,4,5-pentamethyl-cyclopentadiene (9.5 mL, 60.7 mmol) in refluxing ethanol (100 mL) for 3 h, according to the literature.[14] The obtained $[(Cp^*)RuCl_2]_n$ (2.03 g, 6.60 mmol for Ru) was reduced to $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ with lithium triethyl-hydridoborate (6.60 mL, 1.0 M solution in THF, 6.0 mmol) at room temperature:[15] Anal. Calcd for $C_{40}H_{60}Ru_4Cl_4$: C, 43.70; H, 5.37; Cl, 12.51. Found: C, 43.49; H, 5.55; Cl, 12.24.

Polymerization Procedures. Polymerization was carried out by the syringe technique under dry argon in baked glass tubes equipped with a three-way stopcock or in sealed glass vials. A typical procedure for the MMA polymerization with H−$(MMA)_2$−Cl/$[Cp^*Ru(\mu_3\text{-}Cl)]_4$/**PO-2** is given: In a round-bottom flask (50 mL) was placed $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ (7.6 mg, 0.028 mmol), **PO-2** (22.3 mg, 0.056 mmol), and toluene (3.3 mL). The solution was heated to 80 °C for 1 h, at which point the color changed from black-brown to yellow-brown. After cooling the mixture to room temperature, *n*-octane (0.30 mL), MMA (3.00 mL, 28.0 mmol), and a solution of H−$(MMA)_2$−Cl (0.40 mL, 708.7 mM in toluene) were added; the total volume was 7.00 mL. Immediately after mixing, aliquots (0.50−1.0 mL each) of the solution were injected into baked glass tubes, which were then sealed (except when a stopcock was used) and placed in an oil bath kept at 80 °C. In predominant intervals, the polymerization was terminated by cooling the reaction mixture to −78 °C in dry ice-methanol. Monomer conversion was determined from residual monomer concentration measured by gas chromatography with *n*-octane as an internal standard. The quenched solutions were evaporated to dryness to give the products, which were subsequently dried overnight under vacuum at room temperature.

For HEMA and PEGMA, the same procedures as described above were applied, except that monomer conversion was determined by ^{1}H NMR from the integrated peak area of the olefinic protons of the monomer with tetralin as an internal standard.

Measurements. For poly(MMA), poly(MA), and poly(St), M_n and M_w/M_n were measured by size exclusion chromatography at 40 °C in THF as an eluent on three polystyrene-gel columns (Shodex KF-803; pore size, 20−1000 Å; 8.0 mm i.d. × 30 cm; flow rate, 1.0 mL min^{-1}) connected to a DU-H2000 pump, a 74S-RI refractive-index detector, and a 41-UV ultraviolet detector (all from Shodex). The columns were calibrated against 13 standard poly(MMA) samples (Polymer Laboratories; M_n = 620−1 200 000; M_w/M_n = 1.06−1.22) or 13 standard poly(St) samples (Polymer Laboratories; M_n = 500−3 840 000; M_w/M_n = 1.01−1.14) as well as the monomer. For poly(HEMA) and poly(PEGMA), M_n and M_w/M_n were measured by size exclusion chromatography at 40 °C in DMF containing 10 mM LiBr as an

Scheme 2. Reaction of [Cp*Ru(μ_3-Cl)]$_4$ with Phosphine Ligand (PR_3)



eluent on three polystyrene-gel columns (Shodex KF-805 L; pore size, 20−1000 Å; 8.0 mm i.d. × 30 cm; flow rate, 1.0 mL min^{-1}) connected to a PU-precision pump and a 2031-RI refractive-index detector, and a 2075-UV ultraviolet detector (all from Jasco). The columns were calibrated against 11 standard poly(MMA) samples (Polymer Laboratories; M_n = 630−1 200 000; M_w/M_n = 1.04−1.22) as well as the monomer.

Results and Discussion

1. ^{31}P NMR Analysis for BPMO Ruthenium Complexes: Coordination Pattern. A tetrameric Cp* ruthenium chloride, [Cp*Ru(μ_3-Cl)]$_4$, is known to readily accept a phosphine ligand(s) (PR_3) upon mixing, to form a coordinatively saturated 18e complex [Cp*RuCl(PR_3)$_2$] or a unsaturated 16e complex [Cp*RuCl(PR_3)] (the latter preferred with a bulky phosphine) (Scheme 2).[4h,16] Because BPMO ligands (**PO-1** and **PO-2**) potentially chelate the Cp*RuCl precursor, two mixing ratios were examined: [Ru]$_0$/[ligand]$_0$ = 1/1 and 1/2 mol ratios; [[Cp*Ru(μ_3-Cl)]$_4$]$_0$/[ligand]$_0$ = 1.0/4.0 and 1.0/8.0 mM. The mixtures were analyzed in situ by ^{31}P NMR to characterize the coordination patterns.

With **PO-1** under the equimolar condition, the peaks derived from the free ligand (*a* and *b* at −20 and +30 ppm, respectively) completely disappeared, and two new peaks, alternatively, appeared at 25 ppm (*c*) and 46 ppm (*d*), assignable to the phosphine and the phosphine oxide of **PO-1**, respectively, on the metal. Under the 1:2-mixing conditions, the free-ligand (*a* and *b*) was also observed along with the two coordinating phosphines (*c* and *d*), indicating that monoligated complex formed with an equimolar amount of the ligand remaining free.

On the other hand, **PO-2** led to the same spectra at the two loading ratios, where only two peaks (*g* and *h*), different from those of the free ligand (*e* and *f*). This observation means that, both at the 1:1 and 2:1 ratios, all **PO-2** molecules coordinate ruthenium; no free BPMO remains.

These results demonstrate that, with the short one carbon spacer, **PO-1** acts as an asymmetrically bidentate ligand that preferentially undergoes "chelation" via the phosphine (P) and the phosphine oxide (=O) to form a stable five-membered ring. In contrast, with a less bulky two-carbon spacer, **PO-2** would prefer a monodentate ligation, as with PPh_3, into a bisphosphine form.

2. Polymerization of Methyl Acrylate. The in situ obtained BPMO ruthenium complexes were employed for living radical polymerization; no cocatalysts were used. On the basis of the ^{31}P NMR analysis discussed above (Figure 1), **PO-1** was mixed with an equimolar amount of [Cp*Ru(μ_3-Cl)]$_4$ ([Ru]$_0$/[ligand]$_0$ = 1.0), most likely to give the 18e chelate complex [Cp*RuCl(**PO-1**)] without any free ligand remaining, and the resultant complex was directly used for polymerization. On the other hand, **PO-2** was mixed at a 1:2 ratio with the precursor ([Ru]$_0$/[ligand]$_0$ = 0.50), most likely to form the 18e diphosphine complex [Cp*RuCl(**PO-2**)$_2$] without any unligated precursor remaining in the solution. For comparison, a complex with methyldiphenyl phosphine [Cp*RuCl($PMePh_2$)$_2$], without an phosphine oxide moiety in the ligand, was also examined ([Ru]$_0$/[ligand]$_0$ = 0.50).

First, the three complexes [Cp*RuCl(**PO-1**), Cp*RuCl(**PO-2**)$_2$, Cp*RuCl($PMePh_2$)$_2$] were applied for MA in conjunction with a bromine initiator (H−EMA−Br) in toluene at 80 °C ([MA]$_0$/[initiator]$_0$/[catalyst]$_0$ = 4000/40/4.0 mM) (Figure 2). The chelate complex with **PO-1** induced the fastest polymerization, where MA conversion reached 86% in 13 h. The polymerization with **PO-2** was a little slower than with **PO-1**, but faster than with $PMePh_2$.

According to SEC analysis of the products, the polymerizations with both BPMOs were fairly controlled: The molecular weight distributions (MWDs) were narrow; molecular weights (SEC curves) increased with conversion, while unimodal distributions retained. On the other hand, $PMePh_2$ resulted in broader MWDs and less controlled polymerization. Thus, the introduction of a phosphine oxide ligand, either bidentate or monodentate, onto Cp*−ruthenium complexes was effective for polymerization control of MA.

However, the superiority of **PO-1** was not seen with a chloride initiator [H−(MMA)$_2$−Cl], in place of the bromide one, while the **PO-2** monoligated complex was better than $PMePh_2$ (Figure 3). The difference between the initiators is discussed in the following section below.

3. Polymerization of Methyl Methacrylate and Styrene. The BPMO complexes were also applied for MMA and styrene with the chloride initiator [H−(MMA)$_2$−Cl], again without cocatalysts. Difference between **PO-1** and **PO-2** was clearly observed in time−conversion plots for the two monomers: The former gave limited conversions (<30%), while the latter almost quantitative polymerizations (>90%) (Figure 4). The polymers with **PO-2** were fairly controlled, where molecular weights were directly increased with conversion along the theoretical lines, and the MWDs were quite narrow particularly at higher conversion (M_w/M_n < 1.05; >90%) (Figure 5).

Thus, the complex with **PO-2** allowed living radical polymerizatons for MA, MMA, and St without a cocatalyst. Note, however, that these polymerizations of the three monomers can be improved further, especially in rate, by tuning components (initiator and cocatalyst) or reaction temperature (see Supporting Information).

4. Roles of Biphosphine Monoxide Ligands. The superiority of BPMOs over simpler monodentate phosphines like PPh_3 and $PMePh_2$ is discussed here. As described in the Introduction, a basis for metal-catalyzed living radical polymerization is the reversible activation (homolytic dissociation into a growth-active carbon radical) of a carbon−halogen bond [~~~C−X (dormant) ↔ ~~~C• (active)] involving a redox of the catalyst (Mt^n ↔ XMt^{n+1}). As the activation process (→) to generate radical species is accelerated, the reverse deactivation (←) also needs to be promoted to keep the equilibrium balance or the catalytic cycle. Otherwise, a portion of growing chains (or initiator molecules) is "dead" via side reactions (i.e., disproportionation or coupling), and thereby the oxidized complex (XMt^{n+1}) is gradually accumulated, leading to stagnation in propagation.

The typical phenomena indicating such an unfavorable event is that, when applied without a cocatalyst, a PPh_3-based complex Cp*RuCl(PPh_3)$_2$ induces very slow or less quantitative polymerizations, although it may potentially possess a high activity:[14] as indicated by a low redox potential and a fast halogen exchange with a halide initiator. However, once Al(O-*i*-Pr)$_3$ or an amine is combined as a

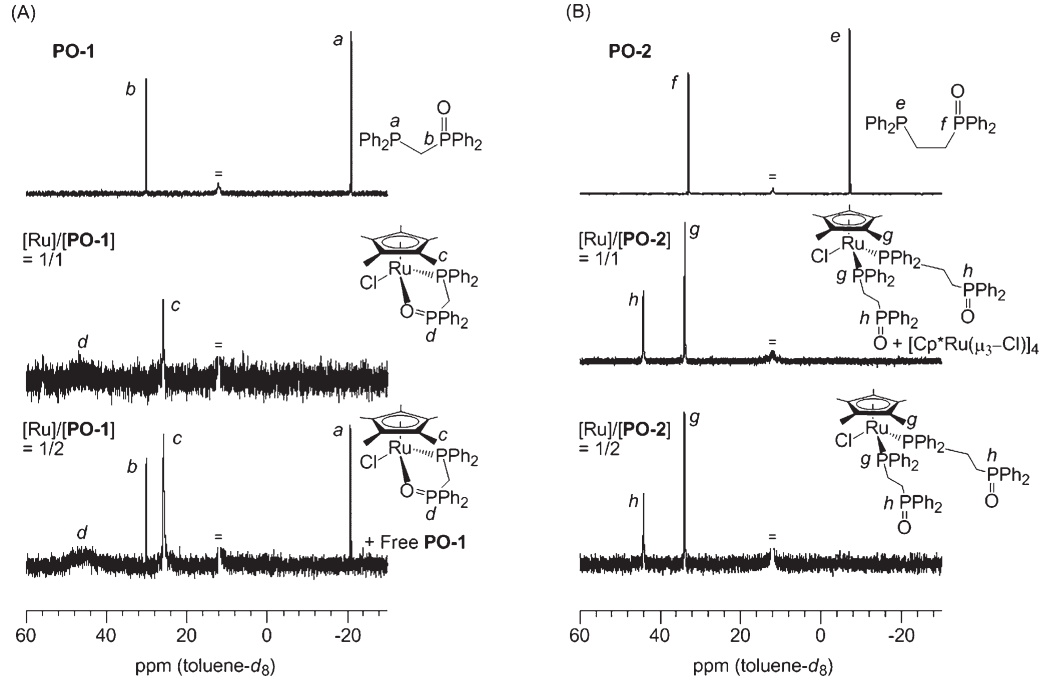


Figure 1. ^{31}P NMR spectra of BPMO ligand (upper), a complex prepared with 1:1 ratio ([Ru]$_0$:[ligand]$_0$) (middle), and a complex with 1:2 ratio (bottom) with **PO-1** (A) and **PO-2** (B) in toluene-d_8 at 25 °C: [BPMO]$_0$ = 8.0 mM (upper); [BPMO]$_0$ = 4.0 mM, [[Cp*Ru(μ_3-Cl)]$_4$]$_0$ = 1.0 mM (middle); [BPMO]$_0$ = 8.0 mM, [[Cp*Ru(μ_3-Cl)]$_4$]$_0$ = 1.0 mM (bottom). The complexes were measured after aging at 80 °C for 1 h. Capillary was used with a toluene-d_8 solution of $(C_2H_5O)_2POH$ as an internal standard for the adjustment of the chemical shift.

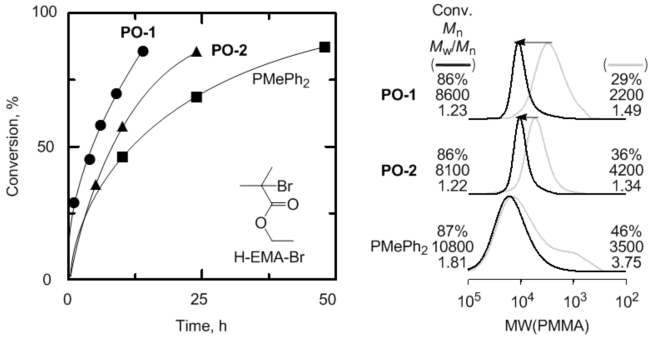


Figure 2. Polymerization of MA with H−EMA−Br/[Cp*Ru(μ_3-Cl)]$_4$/ligand in toluene at 80 °C: [MA]$_0$ = 4.0 M, [H−EMA−Br]$_0$ = 40 mM, [[Cp*Ru(μ_3-Cl)]$_4$]$_0$ = 1.0 mM, [ligand]$_0$ = 4.0 or 8.0 mM ([**PO-1**]$_0$ = 4.0 mM (●); [**PO-2**]$_0$ = 8.0 mM (▲); [PMePh$_2$]$_0$ = 8.0 mM (■)).

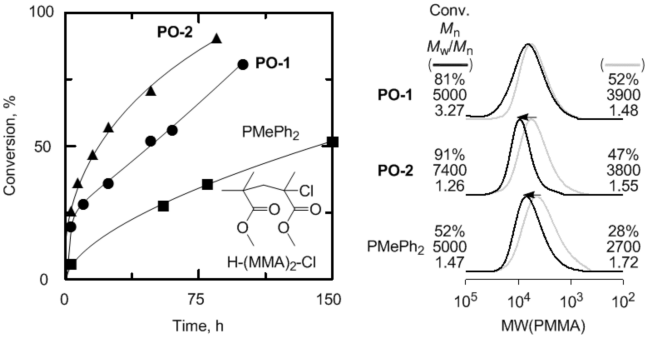


Figure 3. Polymerization of MA with H−(MMA)$_2$−Cl/[Cp*Ru(μ_3-Cl)]$_4$/ligand in toluene at 80 °C: [MA]$_0$ = 4.0 M, [H−(MMA)$_2$−Cl]$_0$ = 40 mM, [[RuCp*(μ_3-Cl)]$_4$]$_0$ = 1.0 mM, [ligand]$_0$ = 4.0 or 8.0 mM ([**PO-1**]$_0$ = 4.0 mM (●); [**PO-2**]$_0$ = 8.0 mM (▲); [PMePh$_2$]$_0$ = 8.0 mM (■)).

cocatalyst, the polymerizations are accelerated without any loss of controllability. These cocatalysts probably contribute to a promotion of the deactivation in some way by which the redox catalytic cycle is facilitated.

In contrast, the BPMO-ligated Cp*RuCl complexes catalyzed living radical polymerizations even without a cocatalyst (see above). These results most likely indicate that, unlike to PPh_3, the BPMO ligands themselves are responsible not only for stabilization of the Cp*RuCl framework but for the control over the equilibrium balance, especially for promotion of the "deactivation" process.

From these considerations, the catalytic processes with the Cp*RuCl/BPMO systems are proposed as shown in Scheme 3: With **PO-1** (monomolecular bidatate/chelate ligation), the starting 18e complex [**Ru-1(II)**] would turn into a trivalent 17e form [**Ru-1(III)**] in the activation for an initiator or a dormant carbon−halogen terminal, where the initially chelating **PO-1** releases the phosphine oxide moiety, while still coordinating via the arylphosphine end, to generate a vacant site for halogen acceptance franked by the phosphine oxide

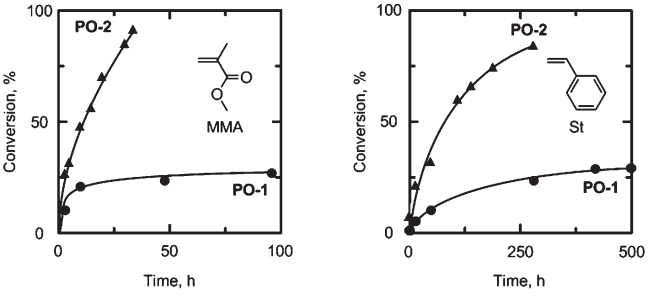


Figure 4. Comparison of **PO-1** and **PO-2** for polymerization rate on living radical polymerization of MMA and St with H−(MMA)$_2$−Cl/[Cp*Ru(μ_3-Cl)]$_4$/BPMO ligand in toluene at 80 °C: [monomer]$_0$ = 4.0 M, [H−(MMA)$_2$−Cl]$_0$ = 40 mM, [[Cp*Ru(μ_3-Cl)]$_4$]$_0$ = 1.0 mM, [ligand]$_0$ = 4.0 or 8.0 mM ([**PO-1**]$_0$ = 4.0 mM (●); [**PO-2**]$_0$ = 8.0 mM (▲)).

now free and dangling (Scheme 3A). After some propagation steps via **Ru-1(III)**, a "deactivation" process occurs in which

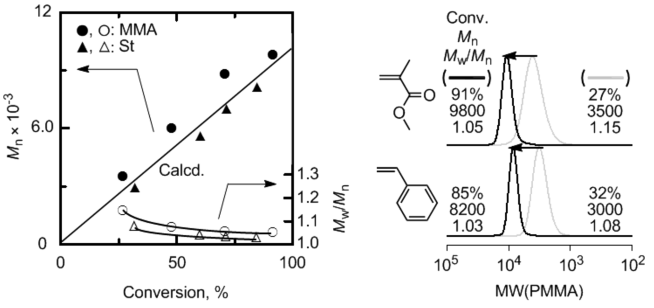
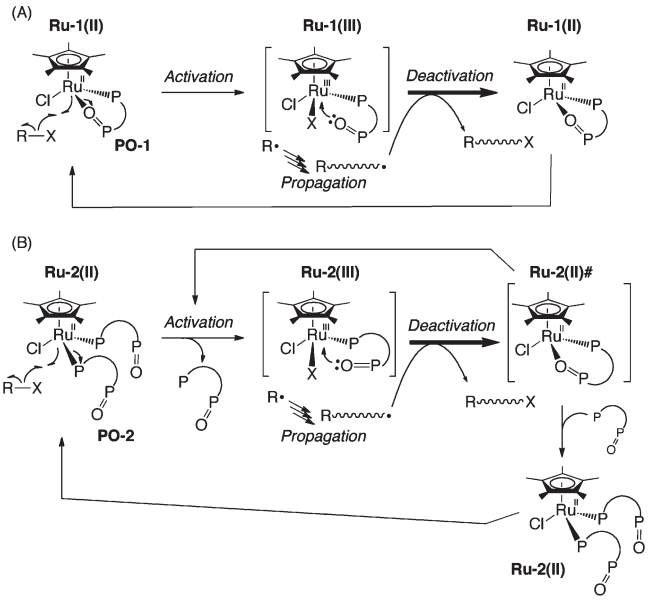


Figure 5. M_n, M_w/M_n, and SEC curves of poly(MMA) and poly(St) obtained with H−(MMA)$_2$−Cl/[Cp*Ru(μ_3-Cl)]$_4$/PO-2 in toluene at 80 °C: [Monomer]$_0$ = 4.0 M, [H−(MMA)$_2$−Cl]$_0$ = 40 mM, [[Cp*Ru(μ_3-Cl)]$_4$]$_0$ = 1.0 mM, [**PO-2**]$_0$ = 8.0 mM. Key: poly(MMA) (●,○), poly(St) (▲,△).

Scheme 3. Proposed Catalysis by BPMO-Ligated Cp* Ruthenium Complexes



the "return" of the dangling oxide onto the Ru^{III} metal center would promote the release of the halogen and in turn the regeneration of the 18e saturated and chelated complex **Ru-1(II)**. Namely, the labile coordination of **PO-1** via the phosphine oxide part is reversible, intramolecular, and thus entropically favored, and this facilitate the redox cycle.

With **PO-2** (bimolecular monodentate ligation), the starting 18e complex [**Ru-2(II)**] would similarly transform into a trivalent analogue [**Ru-2(III)**] for the halogen acceptance and the subsequent radical formation, but in this case one ligand needs to be intermolecularly released for generation of a vacant site (Scheme 3B). As with **PO-1**, **Ru-2(III)** would intramolecularly turn into a divalent [**Ru-2(II)**#] via intramolecular chelation by the remaining **PO-2**, but the chelated form seems too unstable to be observed by ^{31}P NMR (Figure 1). The labile **Ru-2(II)**# complex would immediately activate a dormant terminal or would accept a free **PO-2** to regenerate the starting 18e form [**Ru2-(II)**]. In these ways, both BPMO ligands presumably promote the deactivation processes via the chelate ligation of the oxide portion.

An electron density of the central ruthenium for **Ru-2(II)** (with **PO-2**) should be higher than for **Ru-1(II)** (with **PO-2**), since higher electron donation of phosphine is higher than of phosphine oxide. This difference seemed to be reflected in the

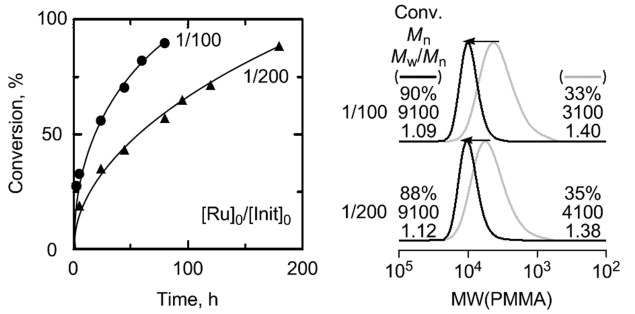


Figure 6. Polymerization of MMA with a low amount of catalyst: H−(MMA)$_2$−Cl/[Cp*Ru(μ_3-Cl)]$_4$/**PO-2** in toluene at 80 °C: [MMA]$_0$ = 6.0 M, [H−(MMA)$_2$−Cl]$_0$ = 60 mM, [[Cp*Ru(μ_3-Cl)]$_4$]$_0$ = 0.15 (●) or 0.075 (▲) mM, [**PO-2**]$_0$ = 2.4 (●) or 1.2 (▲) mM. [Ru]$_0$/[initiator]$_0$ = 1/100 (●) or 1/200 (▲).

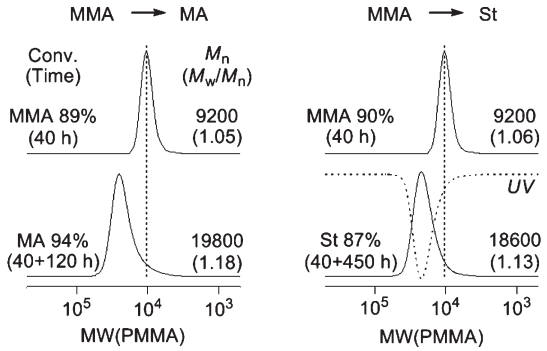


Figure 7. SEC curves on block copolymerization of MMA (first monomer) with MA or St (second monomer) with H−(MMA)$_2$−Cl/[Cp*Ru(μ_3-Cl)]$_4$/**PO-2** in toluene at 80 °C: [MMA]$_0$ = 4.0 M, [H−(MMA)$_2$−Cl]$_0$ = 40 mM, [[Cp*Ru(μ_3-Cl)]$_4$]$_0$ = 1.0 mM, [**PO-2**]$_0$ = 8.0 mM, [second monomer]$_{add}$ = 4.0 M.

polymerization results (see above): a catalytic activity of **Ru-1(II)** was totally less active than that of **Ru-2(II)**, except for MA polymerization with a bromine initiator giving more dissociative leaving group.

5. Demonstrations of the High Catalytic Activity. The high catalytic activity of the Cp*RuCl/BPMO systems were demonstrated by: (1) polymerization control with a low amount of the catalysts; (2) the precision synthesis of high molecular weight polymers; (3) in situ block copolymerization via a direct addition of a second monomer at a high conversion (∼ 90%).

5.1. Reduction of Catalyst Dose. MMA was polymerized under 100-mer conditions ([MMA]$_0$ = 6.0 M; [initiator]$_0$ = 60 mM; initiator: H−(MMA)$_2$−Cl) with a smaller amount of the catalysts ([Ru]$_0$ (as Cp*RuCl/BPMO) = 0.60 or 0.30 mM; i.e., [[Cp*Ru(μ_3-Cl)]$_4$]$_0$ = 0.15 or 0.075 mM and [**PO-2**]$_0$ = 2.4 or 1.2 mM, respectively) (Figure 6). This implies that [Ru]$_0$/[initiator]$_0$ ratio = 1/100 or 1/200, with and that [Ru]$_0$ = 100 or 50 ppm to MMA monomer, respectively. Despite such reduced catalyst concentrations, MMA was almost quantitatively consumed. Furthermore, the obtained polymers were finely controlled, and final MWDs were very narrow (M_w/M_n = 1.09 or 1.12).

5.2. High Molecular Weight Polymers. A 10-times increase in the degree of polymerization (DP$_n$) up to 1000 was targeted in the MMA polymerization with Cp*RuCl/**PO-2** ([MMA]$_0$/[H−(MMA)$_2$−Cl]$_0$/[[Cp*Ru(μ_3-Cl)]$_4$]$_0$/[**PO-2**]$_0$ = 5000/5.0/0.25/2.0 mM). The final conversion reached over 90% in 120 h, and molecular weight linearly increased with conversion and was in agreement with the calculated values based on the monomer/initiator feed ratio (see Supporting

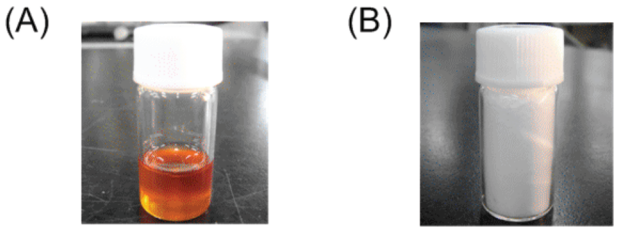


Figure 8. Pictures of polymerization solutions of MMA with the **PO-2** system (A) and isolated PMMA via reprecipitation into methanol (B).

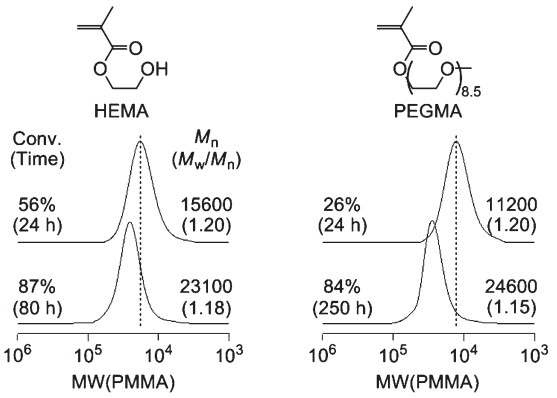


Figure 9. Polymerizations of functional monomers (HEMA and PEGMA) with H−(MMA)$_2$−Cl/[Cp*Ru(μ_3-Cl)]$_4$/**PO-2** in ethanol at 40 °C: [HEMA]$_0$/[H−(MMA)$_2$−Cl]$_0$/[[Cp*Ru(μ_3-Cl)]$_4$]$_0$/[**PO-2**]$_0$ = 2000/20/0.50/4.0 mM, [PEGMA]$_0$/[H−(MMA)$_2$−Cl]$_0$/[[Cp*Ru(μ_3-Cl)]$_0$/[**PO-2**]$_0$ = 500/5.0/0.50/4.0 mM.

Information Figure 1), to reach M_n = 103 000 (DP$_n$ = 1000). MWD was also narrow throughout the polymerization (M_w/M_n = 1.09).

5.3. Block Copolymerizations. Sequential block copolymerizations of MMA with MA or St were also performed with Cp*RuCl/**PO-2** (Figure 7). MMA was first polymerized in conjunction with a chloride initiator [H−(MMA)$_2$−Cl] in toluene at 80 °C, and when conversion reached ~90%, MA or St (neat) was directly added. The added monomer was smoothly consumed to give block polymers with narrow MWDs and without leftover homopolymers as analyzed by SEC. For the MMA−St block polymers, the UV trace at 254 nm agreed with the corresponding RI trace, also supporting an efficient growth of styrene segments from the poly(MMA) prepolymer terminals.

6. Quantitative Removal of Ruthenium Residues. Apart from the high activity and the versatility, another feature of the BPMO ligands is their high polarity and the high solubility of their complexes in methanol and related polar solvents. Thus, after the MMA polymerization with Cp*RuCl/**PO-2** in toluene, the solution was added dropwise into a large amount of methanol to precipitate the produced PMMA (conversion, 91%; M_n = 9800; M_w/M_n = 1.05). The separated polymer was totally colorless and powdery white, while the supernatant was orange, probably due to the catalyst residues (Figure 8). According to the quantitative metal assay by microwave induced plasma mass spectrometry (MIP−MS), the concentration of the ruthenium residue was as low as 3.4 ppm, meaning a 99.7% removal of the initially added catalyst (1000 ppm to MMA).

7. Polymerizations of Functional Monomers. Finally, the Cp*RuCl/**PO-2** system was applied to polymerizations of nonprotected functional monomers, i.e., HEMA (with hydroxyl) and PEGMA (with a polyether pendent chain) (Figure 9). The reaction conditions were as follows: [monomer]$_0$/[H−(MMA)$_2$−Cl]$_0$/[[Cp*Ru(μ_3-Cl)]$_4$]$_0$/[**PO-2**]$_0$ = 2000/20/0.50/4.0 mM (HEMA) or 500/5.0/0.50/4.0 mM (PEGMA). Both monomers were smoothly polymerized, and the polymerizations were fairly controlled, as observed by SEC. The application to other functional monomers is now under investigation.

Conclusions

BPMO ligation on Cp*RuCl complexes remarkably enhanced the catalytic activity for living radical polymerizations and the versatility for a variety of (functional) monomers. The key role of BPMO apparently involves a hemilabile ligation to promote the deactivation of the growing radical species via halogen capping, leading to a frequent catalytic cycle even without a cocatalyst. The high catalytic activity allowed a reduction of catalyst amount ([Ru]$_0$/[initiator]$_0$ = 1/200; 50 ppm to monomer) and controlled syntheses of high molecular weight PMMAs (M_n ~ 100 000) and block copolymers (M_w/M_n < 1.2). Furthermore, a high polarity of the phosphine oxide permitted near quantitative removal (>99.7%) of the catalyst residue via just single reprecipitation into methanol. Thus, BPMOs ligands are useful for various applications with living radical polymerization. Application to other metal complexes is now under investigation.

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Supporting Information Available: A table showing polymerization results under various conditions and a figure for synthesis of high molecular weight polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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