DOI: 10.1002/asia.200800142

VIP

Highly Active and Removable Ruthenium Catalysts for Transition-Metal-Catalyzed Living Radical Polymerization: Design of Ligands and Cocatalysts

Makoto Ouchi,* Makoto Ito, Satoshi Kamemoto, and Mitsuo Sawamoto*[a]

Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

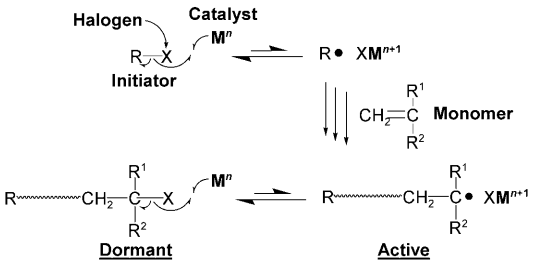
Abstract: The systematic search and design of phosphine ligands (PR_3) and amine cocatalysts resulted in obtaining pentamethyl-cyclopentadienyl (Cp*) ruthenium(II) phosphine complexes [$RuCp^*Cl(PR_3)_2$], which are highly active and removable catalysts, for transition-metal-catalyzed living radical polymerization of methyl methacrylate (MMA). The catalysts are conveniently prepared in situ from a tetrameric precursor [$RuCp^*(\mu_3\text{-}Cl)]_4$ and a selected phosphine (PR_3). The combination of the *meta*-tolyl phosphine [$P(m\text{-}Tol)_3$] ligand and a primary diamine cocatalyst [$NH_2(CH_2)_6NH_2$] provides a highly active catalytic system with precision control of the molecular weight of the polymer. The high activity enables a low catalyst dose and a high turn-over frequency without deteriorating the controllability. A hydrophilic amine cocatalyst (amino alcohol) in place of the diamine, further forms an active and removable catalyst; simple treatment with acidic water gave colorless polymers visually free from metal residues (>97% removal; <64 ppm).

Keywords: amines · phosphine ligands · living radical polymerization · radicals · ruthenium

Introduction

"Transition-metal-catalyzed living radical polymerization"[1] is a family of precisely controlled, chemo- and regioselective, repetitive radical-addition reactions towards alkenes (monomers), mediated by transition-metal catalysts such as ruthenium, copper, iron, and nickel complexes (Scheme 1). A key process therein is the metal-assisted reversible and selective generation of a growth-active carbon radical from an alkyl halide carrying a conjugating, and thus, radical-stabilizing α-substituent; the precursor halide may be a small molecule (initiator) or a polymeric analogue (dormant species) thereof.

In this metal-assisted living process, as its name implies, the metal complex is vital. Its low-valence form catalyzes the homolytic dissociation of the alkyl-halide initiator or the dormant end, whereas the higher-valence form does the back reaction, that is, the regeneration of the halogen-capped dormant species from the growing radical. In summary, the catalysis involves a reversible one-electron redox process, in which the halogen is exchanged between the halide and the metal catalyst by the active carbon radical. The dynamic-fast-exchange process maintains the instantaneous radical concentration much lower than in the conventional radical polymerization, thereby suppressing the bimolecular radical termination and other side-reactions inherent to radicals, whereas ensuring all the dormant ends have a virtually equal probability to dissociate and grow, and ensuring a very narrow molecular-weight distribution (MWD) of the polymer product.



Scheme 1. Transition-metal-catalyzed living radical polymerization.

[a] Dr. M. Ouchi, M. Ito, S. Kamemoto, Prof. M. Sawamoto
Department of Polymer Chemistry
Graduate School of Engineering
Kyoto University
Katsura, Nishikyo-ku, Kyoto 615-8510 (Japan)
Fax: (+81) 75-383-2601
E-mail: ouchi@living.polym.kyoto-u.ac.jp
sawamoto@star.polym.kyoto-u.ac.jp

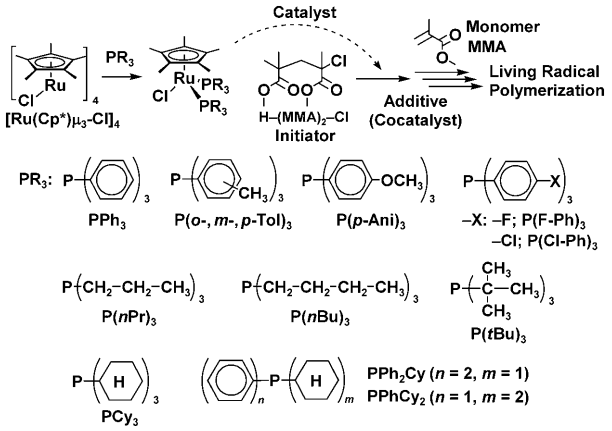
universal "tool" to design and synthesize not only well-defined polymers but also tailored and functionalized polymeric materials. The widespread application of this reaction, in turn, now requires more active and versatile catalysts to enable element-economical processes with a high catalytic turn-over efficiency, and also, that may readily be removed and possibly recycled, so as to obtain cleaner products.

This paper addresses these current requisites for the metal-catalyzed living radical polymerization with ruthenium (Ru^{II}) catalysts. The primary objectives include the development of highly active catalyts, with an additional removability, by the design of phosphine ligands and amine cocatalysts (additives).

For living radical polymerization, a variety of transition-metal catalysts have evolved,[1,2] some of which are actually directed towards their enhance catalytic activity and facile removal for more simplified and cost-effective processes. For example, in the copper-catalyzed living radical polymerization (atom-transfer radical polymerization), highly active catalytic systems have been developed with the use of reducing agents,[3] improved ligands,[4] and/or zero-valence metal Cu^0 for a Cu^I catalyst.[5]

As demonstrated in the representative ruthenium-catalyzed organic reactions and polymerizations, including those pioneered by Noyori and Grubbs,[6] ruthenium complexes offer quite attractive catalysts, particularly with regards to the high tolerance to functional groups and facile tunability by a variety of ligands. This is equally the case for living radical polymerization, and Ru^{II}-based catalysts have extensively been developed since our first discovery.[7] For example, half-ruthenocene complexes [e.g., $[Ru(Ind)Cl(PPh_3)_2]$; Ind = η^5-C_9H_7] are active, versatile, and applicable to high-molecular-weight polymers and block copolymers.[8–10] Their catalytic efficiency is thus intrinsically low (typically, $[catalyst]_0/[initiator]_0 = 1:10$) but not low enough, and their removal is not efficient.

This work is more specifically directed to the systematic design of ligands and cocatalysts for ruthenium (Ru^{II}) catalysts, by which new, highly active, and removable complexes are generated in situ, while retaining the advantage of the functionality tolerance of the Ru^{II} catalysts. Herein, we focus on pentamethylcyclopentadiene [Cp*: η^5-$C_5(CH_3)_5$]-based ruthenium complexes ($[Ru(Cp^*)Cl(PR_3)_2]$; PR_3 = alkyl and aryl phosphines; Scheme 2). The Cp* family would be potentially active and versatile, as judged from the low redox potential[11] and our recent studies with the PPh_3 derivative[9,10], demonstrating fast halogen exchange with alkyl halides and applicability to both methacrylate and styrene. Another advantage is that $[Ru(Cp^*)Cl(PR_3)_2]$ can readily be prepared in situ by mixing a tetrameric precursor $[RuCp^*(\mu_3\text{-}Cl)]_4$ and a PR_3 ligand[12].



Scheme 2. In-situ preparation of $[Ru(Cp^*)Cl(PR_3)_2]$ for living radical polymerization of MMA.

Our objectives specifically include the design of more active and removable $[Ru(Cp^*)Cl(PR_3)_2]$ catalysts by systematically examining the electronic and steric effects of the PR_3 on the catalytic activity and controllability, in conjunction with the use of bifunctional amine cocatalysts in the polymerization of methyl methacrylate (MMA).

Results and Discussion

Ligand Design

According to Scheme 2, Cp*-based ruthenium complexes $[Ru(Cp^*)Cl(PR_3)_2]$ were prepared in situ by the reaction of $[RuCp^*(\mu_3\text{-}Cl)]_4$ with two equivalents of a phosphine (PR_3)-bearing different substituent(s) with varying electronic and steric (bulkiness) factors. Without isolation and purification, the prepared complexes were directly employed as catalysts for the MMA polymerization, coupled with a chloride initiator [H-$(MMA)_2$-Cl] and dibutylamine (nBu_2NH; additive or cocatalyst)[13,14] in toluene at 80 °C. Herein, these combinations of a metal catalyst, PR_3, and an amine cocatalyst are coined as catalyst systems. The overall results are summarized in Table 1, along with some physical properties of the ligands.

***para*-Substituted Triphenyl Phosphines: Effects of the Electronic Properties**. First, we compared a series of *para*-substituted triphenyl phosphines [-H: PPh_3; -CH_3: P(*p*-Tol)$_3$; -OCH_3: P(*p*-Ani)$_3$; -F: P(F-Ph)$_3$; -Cl: P(Cl-Ph)$_3$] to examine the electronic effects on living radical polymerization, in terms of the reaction rate (catalytic activity) and molecular-weight control (controllability; Figure 1). The electronic factor was estimated by the pK_a of the phosphine's conjugate acid (PR_3H^+);[15] the larger the pK_a, the higher the ba-

Abstract in Japanese:

ペンタメチルシクロペンタジエン環(Cp*)を有するルテニウム錯体[Ru(Cp*)Cl(PR$_3$)$_2$]を触媒とするリビングラジカル重合に対し、ホスフィン配位子の電子的／立体的因子の影響を調べ、メタ位にメチル基を有するトリフェニルホスフィンが分子量／分子量分布の高制御に有効であることを明らかにした。さらに、アミン助触媒をジアミン、アミノアルコールにすることで、その高い制御性を維持しつつ、仕込み触媒量の低減、重合後の簡易触媒除去を達成した。

Table 1. Effects of Ligands on the Polymerization of MMA Coupled with $[RuCp^*(\mu_3\text{-}Cl)]_4$.[a]

Entry	Ligand	pK_a[b]	Cone angle, θ[c]	t [h]	Conv [%]	M_n (calcd)[d]	M_n (obsd)[e]	M_w/M_n[e]
1	PPh_3	2.73	145	30	90	9300	13000	1.20
2	P(*o*-Tol)$_3$	3.08	194	30	72	7500	61000	2.24
3	P(*m*-Tol)$_3$	3.30	165	34	87	9000	10900	1.07
4	P(*p*-Tol)$_3$	3.84	145	34	88	9100	11000	1.15
5	P(*p*-Ani)$_3$	4.59	145	50	94	9700	10800	1.31
6	P(F-Ph)$_3$	1.97	145	30	91	9400	10900	1.13
7	P(Cl-Ph)$_3$	1.03	145	30	93	9600	13400	1.19
8	P(*n*Pr)$_3$	8.64	132	30	73	7600	10500	1.39
9	P(*n*Bu)$_3$	8.43	132	30	88	9100	10000	1.24
10	P(*t*Bu)$_3$	11.40	182	28	92	9500	73500	1.85
11	PCy_3	9.70	170	22	97	10000	14700	1.74
12	PPh_2Cy	5.05	153	50	95	9800	12000	1.10
13	$PPhCy_2$	-	162	28	88	9100	19000	1.32

[a] Reaction conditions: $[MMA]_0 = 4.0$ M; $[H\text{-}(MMA)_2\text{-}Cl]_0 = 40$ mM; $[[RuCp^*(\mu_3\text{-}Cl)]_4]_0 = 1.0$ mM; $[PR_3]_0 = 8.0$ mM; $[nBu_2NH]_0 = 40$ mM; in toluene at 80 °C. [b] Ref [15], for the conjugate acid (PR_3H^+) of the phosphine ligand (PR_3). [c] Ref [15] and [16]. [d] M_n (calcd) $= m(H) + m(MMA) \times (2 + DP_n) + m(Cl)$; $DP_n = [MMA]_0/[H\text{-}(MMA)_2\text{-}Cl]_0 \times (\%\ conv)/100$; based on the structure $[H\text{-}(MMA)_2\text{-}(MMA)_n\text{-}Cl]$; $m(X)$ is the molecular or atomic weight of X, in which $m(X) = 1$, 100.12, and 35.5 for X = H, MMA, and Cl, respectively. [e] By size-exclusion chromatography calibrated with PMMA standards.

much oxidized Ru^{III} complex at the early stage of the reaction, which in turn, would lead to the termination of some of the incipient radicals, and thereby, to a slower polymerization. The initial polymerization rate was in fact slower with more electron-donating phosphines (Figure 2). However, no significant effects were observed on the MWD (M_w/M_n) of the polymers.

Methyl-Substituted Triphenyl Phosphines with Different Positions: Steric Effects. More visible effects were observed with the three methyl-substituted tri-

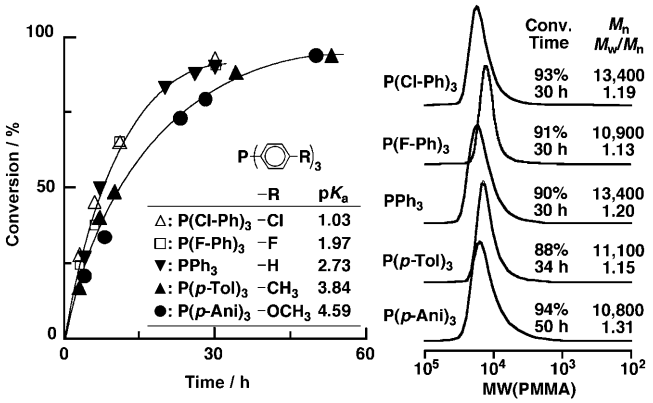


Figure 1. Effects of the electronic properties of ligands (PR_3) on the polymerization of MMA with $H\text{-}(MMA)_2\text{-}Cl/[RuCp^*(\mu_3\text{-}Cl)]_4/PR_3/nBu_2NH$ in toluene at 80 °C: $[MMA]_0 = 4.0$ M; $[H\text{-}(MMA)_2\text{-}Cl]_0 = 40$ mM; $\{[RuCp^*(\mu_3\text{-}Cl)]_4\}_0 = 1.0$ mM; $[PR_3]_0 = 8.0$ mM; $[nBu_2NH]_0 = 40$ mM.

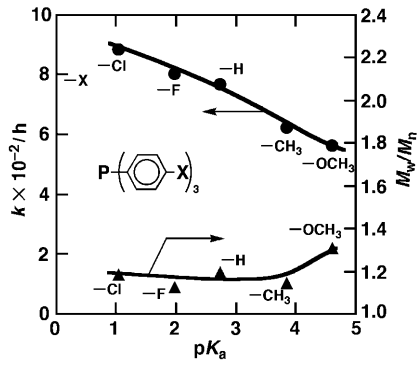


Figure 2. Effects of the electronic properties (pK_a values of R_3PH^+) of ligands (PR_3) on the initial kinetics constant (k, h^{-1}) and the M_w/M_n of PMMAs in the polymerization of MMA with $H\text{-}(MMA)_2\text{-}Cl/[RuCp^*(\mu_3\text{-}Cl)]_4/PR_3/nBu_2NH$ in toluene at 80 °C: $[MMA]_0 = 4.0$ M; $[H\text{-}(MMA)_2\text{-}Cl]_0 = 40$ mM; $[[RuCp^*(\mu_3\text{-}Cl)]_4]_0 = 1.0$ mM; $[PR_3]_0 = 8.0$ mM; $[nBu_2NH]_0 = 40$ mM.

sicity or the stronger the electron donation. *Para*-derivatives were favorably compared because their bulkiness is considered virtually the same (cone angle = 145°).

Figure 1 shows time-conversion curves for the MMA polymerization and size-exclusion chromatography (SEC) curves of PMMAs obtained therein at about 90% conversion. Contrary to our prediction that electron-donating ligands facilitate the generation of radicals by a one-electron transfer from the catalyst, the relevant phosphines [P(*p*-Tol)$_3$ and P(*p*-Ani)$_3$] invariably resulted in slightly slower polymerizations than that observed with the nonsubstituted ligand (PPh_3). The electron-withdrawing counterparts [P(F-Ph)$_3$ and P(Cl-Ph)$_3$] also led to a polymerization rate similar to that observed using PPh_3.

Given the strong electron donation by the Cp* ligand, therefore, the electronic contribution from phosphine ligands may be less influential. Alternatively, the phosphine's strong electron donation occurs and would generate too phenyl phosphines [P(*o*-Tol)$_3$, P(*m*-Tol)$_3$, and P(*p*-Tol)$_3$], in which the bulkiness around the coordinating P-atom, as defined by the cone angle (θ),[15,16] increased in the order: P(*o*-Tol)$_3$ (194°) > P(*m*-Tol)$_3$ (165°) > P(*p*-Tol)$_3$ (145°), while keeping the electron donation ability practically unchanged ($pK_a = 3.08$–3.84; Table 1).

P(*m*-Tol)$_3$ and P(*p*-Tol)$_3$ induced smooth polymerizations reaching >90% MMA conversion without losing the activity (Figure 3). In sharp contrast, the *ortho*-counterpart [P(*o*-Tol)$_3$] resulted in the deceleration beyond 70% conversion. Molecular-weight control was clearly dependent on the position of the methyl group: the *meta*-derivative gave quite a narrow MWD ($M_w/M_n < 1.10$), whereas the *ortho*-counterpart gave broad distributions. These results demonstrate that the ligand bulkiness is more important in determining the controllability, as further discussed in the following section.

CHEMISTRY
AN ASIAN JOURNAL

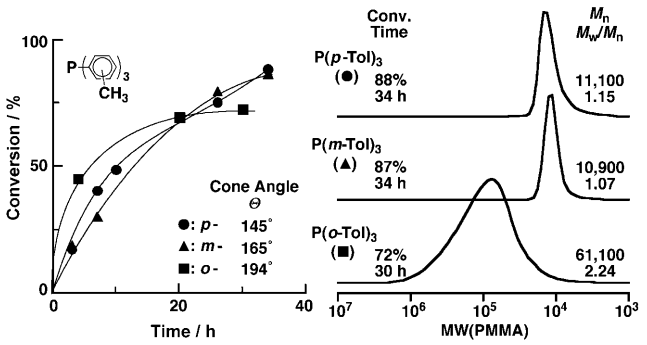


Figure 3. Effects of the steric properties (cone angle, θ) of tritolylphosphine on the polymerization of MMA with H-$(MMA)_2$-Cl/$[RuCp^*(\mu_3\text{-}Cl)]_4$/$PR_3$/$n$-$Bu_2NH$ in toluene at 80 °C: $[MMA]_0 = 4.0$ M; $[H\text{-}(MMA)_2\text{-}Cl]_0 = 40$ mM; $[[RuCp^*(\mu_3\text{-}Cl)]_4]_0 = 1.0$ mM; $[PR_3]_0 = 8.0$ mM; $[n\text{-}Bu_2NH]_0 = 40$ mM.

Effects of Phosphine Ligands on Polymerization. Table 1 summarizes the polymerization results obtained with various phosphine ligands. It is observed that the electronic factor (pK_a) seems less influential to either polymerization rate or controllability (M_w/M_n). Even with basic ligands such as PCy_3 and P(tBu)$_3$ ($pK_a = 170$ and 182, respectively), the rate still did not show a considerable increase (entry 10 and 11).

In contrast, ligand bulkiness appears to be correlated with the MWD of the polymer. Figure 4 plots M_w/M_n against the cone angle (θ). In the range of $\theta = 135$–$165°$, the MWD becomes increasingly narrower with bulkier ligands, but abruptly broadens beyond $\theta > 170°$. Such trends suggest that a moderate bulky ligand may be best for [Ru(Cp*)Cl-$(PR_3)_2$]. With their 18-electron configuration, these complexes must release one of the two ligands, before or upon radical formation, from the dormant end by accepting the terminal halogen,[17] and the released phosphine would sooner or later re-coordinate to the Ru center. The enhanced repetition of ligand release and re-coordination would consequently facilitate the dormant-active species (Scheme 1), and would in turn narrow the MWD of the polymer. For such a dynamic contribution, moderately bulky ligands may be best suited, both for release by some steric repulsion and for re-coordination that would be difficult for too bulky phosphines.

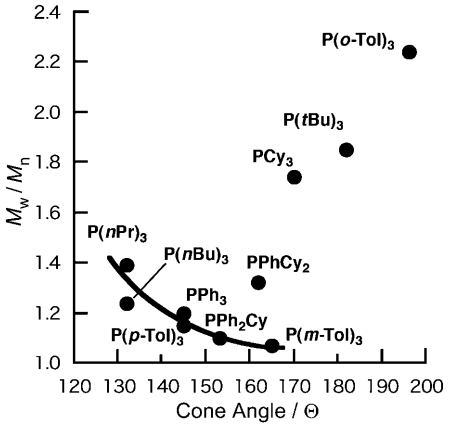


Figure 4. Dependence of M_w/M_n of the prepared PMMAs on the cone angle (θ) of ligands (PR_3) for the polymerization of MMA with H-$(MMA)_2$-Cl/$[RuCp^*(\mu_3\text{-}Cl)]_4$/$PR_3$/$n$-$Bu_2NH$ in toluene at 80 °C: $[MMA]_0 = 4.0$ M; $[H\text{-}(MMA)_2\text{-}Cl]_0 = 40$ mM; $[[RuCp^*(\mu_3\text{-}Cl)]_4]_0 = 1.0$ mM; $[PR_3]_0 = 8.0$ mM; $[n\text{-}Bu_2NH]_0 = 40$ mM.

Cocatalyst Design

Although controllability or the control of the MWD was improved with the moderately bulky phosphines, catalytic activity was not dramatically enhanced. Thus, we turn our attention to another component, that is, the amine cocatalysts in place of n-Bu_2NH, for the P(m-Tol)$_3$-based Cp* ruthenium catalyzed system.

Amine Cocatalysts for Activity Enhancement. We have already reported that the addition of butyl amine (n-$BuNH_2$) considerably accelerates the MMA polymerization with $[RuCl_2(PPh_3)_3]$[13] or $[Ru(Ind)Cl(PPh_3)_3]$,[14] but the strongly basic cocatalyst also deteriorates the controllability, probably by generating a very active catalyst in situ that forms too many radicals. In contrast, when coupled with [RuCl-(Cp*){P(m-Tol)$_3$}$_2$], the same amine induced a fast polymerization without a loss of controllability ($M_w/M_n = 1.10$) (Figure 5). The polymerization rate was further enhanced at a higher temperature (100 °C), at which the MMA conversion reached 86 % in 5 h ($M_w/M_n = 1.09$).

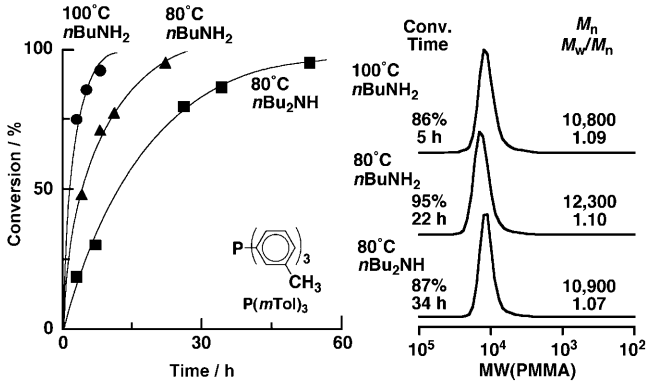


Figure 5. Polymerization of MMA with H-$(MMA)_2$-Cl/$[RuCp^*(\mu_3\text{-}Cl)]_4$/P-($m$-Tol)$_3$/$n$-$Bu_2NH$ or n-$BuNH_2$ in toluene at 80 or 100 °C: $[MMA]_0 = 4.0$ M; $[H\text{-}(MMA)_2\text{-}Cl]_0 = 40$ mM; $[[RuCp^*(\mu_3\text{-}Cl)]_4]_0 = 1.0$ mM; $[P(m\text{-}Tol)_3]_0 = 8.0$ mM; [amine additive]$_0 = 40$ mM.

A similar rate enhancement worked with the primary diamines $[NH_2(CH_2)_nNH_2$, $n = 2, 4, 6]$ (Figure 6). All these bifunctional amines clearly accelerated the polymerization, most notably with the hexayl derivative ($n = 6$), which led to a 92 % conversion in 1.5 h. However, controllability was dependent on the spacer length between the amino groups, with the MWD of the polymer narrowing in the order of $n = 2 < 4 < 6$, most likely because ethylene diamine ($n = 2$)

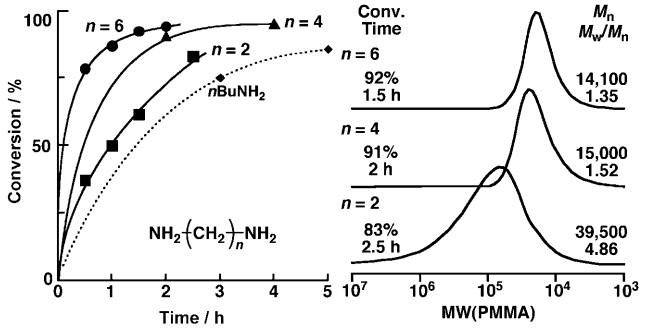


Figure 6. Polymerization of MMA with H-(MMA)$_2$-Cl/[RuCp*(μ_3-Cl)]$_4$/P-(m-Tol)$_3$/NH$_2$(CH$_2$)$_n$NH$_2$ in toluene at 100 °C: [MMA]$_0$ = 4.0 M; [H-(MMA)$_2$-Cl]$_0$ = 40 mM; [[RuCp*(μ_3-Cl)]$_4$]$_0$ = 1.0 mM; [P(m-Tol)$_3$]$_0$ = 8.0 mM; [NH$_2$(CH$_2$)$_n$NH$_2$]$_0$ = 40 mM.

undergoes a chelate coordination to form a too stable complex with a five-membered ring. ^{31}P NMR analysis on the mixture of the ruthenium complex and NH$_2$(CH$_2$)$_6$NH$_2$

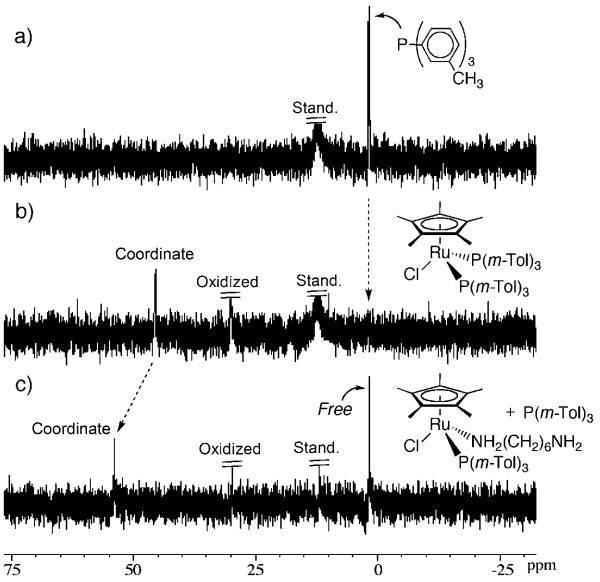


Figure 7. ^{31}P NMR spectra showing the ligand exchange onto the ruthenium complex in toluene at 100 °C: a) P(m-Tol)$_3$ = 2.0 mM, b) [RuCp*(μ_3-Cl)]$_4$/P(m-Tol)$_3$ = 0.25/2.0 mM, c) [RuCp*(μ_3-Cl)]$_4$/P(m-Tol)$_3$/NH$_2$(CH$_2$)$_6$NH$_2$ = 0.25/2.0/80 mM. Capillary tube was used with a [D$_8$]toluene and (C$_2$H$_5$O)$_2$POH as an internal standard for the adjustment of the chemical shift.

(Figure 7) indicated that one of the two phosphine ligands exchanged with the amine (52 and 2 ppm are assigned to a singly coordinating and a free P(m-Tol)$_3$, respectively; 44 ppm is assigned to geminally coordinating phosphines without a neighboring amine).[18] The detection of a free amine indicates the in situ generation of a more active catalyst, [Ru(Cp*)Cl{P(m-Tol)$_3$}NH$_2$(CH$_2$)$_6$NH$_2$], whose mixed-ligand structure would enhance the dynamic amine–phosphine exchange between free P(m-Tol)$_3$ and NH$_2$(CH$_2$)$_6$NH$_2$.

Reduction of Catalyst Dose. The fast living polymerization with the diamine enabled us to decrease the RuCp* catalyst concentration (Figure 8). The best system seems to

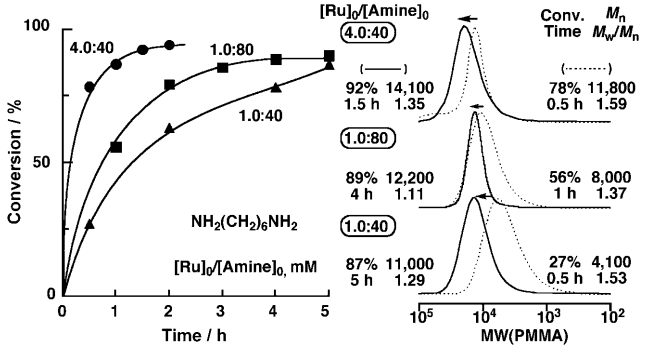


Figure 8. Polymerization of MMA with H-(MMA)$_2$-Cl/[RuCp*(μ_3-Cl)]$_4$/P-(m-Tol)$_3$/NH$_2$(CH$_2$)$_6$NH$_2$ in toluene at 100 °C: [MMA]$_0$ = 4.0 M; [H-(MMA)$_2$-Cl]$_0$ = 40 mM; [[RuCp*(μ_3-Cl)]$_4$]$_0$ = 0.25 or 1.0 mM; [P(m-Tol)$_3$]$_0$ = 2.0 or 8.0 mM; [NH$_2$(CH$_2$)$_n$NH$_2$]$_0$ = 40 or 80 mM. [[RuCp*(μ_3-Cl)]$_4$]$_0$/[P(m-Tol)$_3$]$_0$/[NH$_2$(CH$_2$)$_n$NH$_2$]$_0$: 1.0/8.0/40 mM (●); 0.25/2.0/80 mM (▲); 0.25/2.0/40 mM (■).

be a combination of Ru/amine = 1.0:80 mM (MMA 4.0 M), leading to 89% conversion in 4 h and M_w/M_n = 1.11. Importantly, despite the lower catalyst dose, the MWD is among the narrowest for RuCp*. The excess of amine cocatalyst is apparently needed, and the 1.0:40 mM system in fact slightly decelerated the reaction (87% conversion in 5 h) and broadened the MWD.

Under the best conditions, the products are virtually free of an olefin terminal [~~~~CH$_2$C(CO$_2$CH$_3$)=CH_2, 5.4–6.3 ppm by ^{1}H NMR, <1%], demonstrating the near absence of disproportionation.[13,14] These results indicate the possibility of further reduction of the catalyst dose by designing the cocatalysts and varying their relative amounts.

Hydrophilic Amines for a Removable Catalyst System. The facile in situ ligand exchange of an added amine proved effective, not only in the activity enhancement, but also in the modulation of the catalyst solubility. Thus, a hydrophilic amine, 4-amino-1-butanol [NH$_2$(CH$_2$)$_4$OH], was employed as a cocatalyst for the [RuCl(Cp*){P(m-Tol)$_3$}$_2$] catalyst (Figure 9). The polymerization proceeded as fast as with its hydrophobic analogue NH$_2$(CH$_2$)$_6$NH$_2$, and the molecular weight was well-controlled (being directly proportional to the conversion), though the MWD broadened (M_w/M_n ~ 1.40).

After the polymerization, the reaction mixture (Ru = 1000 ppm to monomer) was washed with a solution of HCl (0.1 N) and then water, three times each, to give a nearly colorless, transparent solution. Also, the solution of the isolated polymers in CHCl$_3$ (3 wt%) was colorless, in contrast to the yellow-brown solution obtained from the nBuNH$_2$ cocatalyst in place of the aminoalcohol, under otherwise the same reaction conditions.

According to the quantitative elemental analysis by inductively coupled plasma-atomic emission spectrometry (ICP-

CHEMISTRY
AN ASIAN JOURNAL

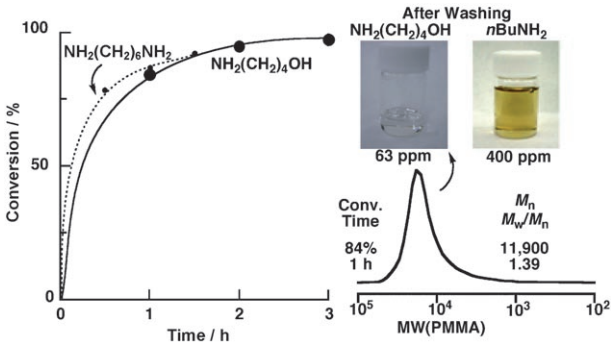


Figure 9. Polymerization of MMA with H-(MMA)$_2$-Cl/[RuCp*(μ_3-Cl)]$_4$/P(*m*-Tol)$_3$/NH$_2$(CH$_2$)$_4$OH in toluene at 100 °C: [MMA]$_0$ = 4.0 M; [H-(MMA)$_2$-Cl]$_0$ = 40 mM; [[RuCp*(μ_3-Cl)]$_4$]$_0$ = 1.0 mM; [P(*m*-Tol)$_3$]$_0$ = 8.0 mM; [NH$_2$(CH$_2$)$_4$OH]$_0$ = 80 mM. Pictures are of PMMA solutions in CHCl$_3$ (3 wt %) after washing with a solution of HCl (0.1 N) and water, three times for each.

AES), the ruthenium residue in the colorless PMMA was 63 ppm (97% removal), much lower than that for the conventional samples (400 ppm) obtained with *n*BuNH$_2$.

These observations have demonstrated that the simple use of a hydrophilic amine as a cocatalyst realizes a near-quantitative facile removal of the metal residue, while retaining a fair catalytic activity of the Ru^{II} catalysts without serious deterioration of the molecular-weight controllability of the polymer.

Conclusions

The systematic search and design of ligands and cocatalysts in the transition-metal-catalyzed living radical polymerization produces highly active and sometimes readily removable Ru^{II} catalysts, that also enables precise molecular-weight control (conv. = 89% for 4 h, M_w/M_n = 1.11). Among the best combinations is the [Ru(Cp*)Cl{P(*m*-Tol)$_3$}$_2$] complex coupled with NH$_2$(CH$_2$)$_6$NH$_2$ as cocatalyst; the catalyst may conveniently and cleanly be prepared in situ from a tetrameric precursor [RuCp*(μ_3-Cl)]$_4$ and a carefully selected phosphine. It is shown that, in the selection of the phosphine ligands, moderate steric bulkiness is the most effective, whereas electron donacity seems unimportant. The highly active catalyst, in fact, works at a low concentration (monomer/Ru^{II} = 4000:1) with a high turn-over efficiency (1:40 relative to the initiator or the dormant end) to give the poly(MMA) with a high and controlled molecular weight.

The use of a hydrophilic amine, NH$_2$(CH$_2$)$_2$OH, provided a simple and efficient way to simultaneously realize both the catalytic activity and controllability with a ready and near quantitative removal of the catalyst residue (>97% removal, 63 ppm). The key to these systems is apparently a facile in situ ligand exchange between the phosphine on the metal and the added amine cocatalyst.

Experimental Section

Materials

MMA (Tokyo Kasei; >99%) was distilled from calcium hydride under reduced pressure after drying overnight over calcium chloride. All the ligands and materials of ruthenium complexes were used as received without further purification and handled in a glovebox under a moisture- and oxygen-free argon atmosphere (H_2O < 1 ppm, O_2 < 1 ppm): triphenylphosphine (Aldrich, 99%), tri-*o*-tolylphosphine (Strem, 99%), tri-*m*-tolylphosphine (Strem, 98%), tri-*p*-tolylphosphine (Strem, 98%), tri-*p*-methoxyphenylphosphine (Strem, 98%), tris(4-fluorophenyl)phosphine (Aldrich, 98%), tris(4-chlorophenyl)phosphine (Aldrich, 95%), tri-*n*-propylphosphine (Strem, >95%), tri-*n*-butylphosphine (Strem, 99%), tri-*tert*-butylphosphine (Strem, 99%), tricyclohexylphosphine (Strem, 97%), cyclohexydiphenylphosphine (Aldrich), dicyclohexyphenylphosphine (Aldrich, 95%), ruthenium(III) chloride hydrate (Wako, 99.9%), 1,2,3,4,5-pentamethylcyclopentadiene (Strem, 98%), lithium triethyl-hydridoborate (Aldrich, 1.0 M solution in THF). The initiator [H-(MMA)$_2$-Cl] was prepared according to the literature.[19] Toluene (Kishida Kagaku; > 99.5%) was purified by passage through a purification column (Seca Solvent System manufactured by Glass Contour Company) before use. An internal standard for gas chromatography, *n*-octane (Wako, >99%), was dried overnight over calcium chloride, distilled twice over calcium hydride, and handled with dry nitrogen for more than 15 min before use. Amine additives were used as received, all from Tokyo Kasei: tributhylamine (>98%), n-butylamine (>99%), ethylenediamine (>98%), 1,4-butanediamine (>98%), 1,6-hexanediamine (99%), 4-amino-1-butanol (>98%).

Preparation of Ruthenium Complexes

Dichloro(pentamethylcyclopentadienyl)-ruthenium, [(Cp*)RuCl$_2$]$_n$, was prepared by the reaction of RuCl$_3$·*n*H$_2$O (6.0 g, 26.6 mmol) with pentamethylcyclopentadiene (9.5 mL, 60.7 mmol) in refluxing ethanol (100 mL) for 3 h according to the literature.[20] The obtained [(Cp*)RuCl$_2$]$_n$ (2.03 g, 6.60 mmol for Ru) was reacted with lithium triethylborohydride (6.60 mL, 1 M solution in THF, 6.0 mmol) at room temperature according to the literature.[12] The formation of [RuCp*(μ_3-Cl)]$_4$ was confirmed by elemental analysis. Calcd (%) for C$_{40}$H$_{60}$Ru$_4$Cl$_4$: C 44.20, H 5.56, Cl 13.05; 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 and sealed glass vials. A typical example for the polymerization of MMA with H-(MMA)$_2$-Cl/[RuCp*(μ_3-Cl)]$_4$/P(*m*-Tol)$_3$/*n*Bu$_2$NH is given. In a round-bottomed flask (50 mL) was placed [RuCp*(μ_3-Cl)]$_4$ (8.7 mg, 0.032 mmol), P(*m*-Tol)$_3$ (19.48 mg, 0.064 mmol), and toluene (2.60 mL). The solution was heated for introduction of phosphine at 80 °C for 12 h, at which point the color changed from black-brown to red-brown. After cooling the flask to room temperature, *n*-octane (0.40 mL), MMA (3.42 mL, 32.0 mmol), a solution of *n*Bu$_2$NH (0.8 mL, 400 mM in toluene), and a solution of H-(MMA)$_2$-Cl (0.40 mL, 809.9 mM in toluene) were added, in which the total volume was 8.00 mL. Immediately after mixing, five aliquots (0.5 mL–1.0 mL each) of the solutions were injected into baked glass tubes. The reaction vials were sealed and placed in an oil bath kept at 80 °C. In predetermined intervals, the polymerization was terminated by cooling the reaction mixtures to −78 °C. Monomer conversion was determined from the residual monomer measured by gas chromatography with *n*-octane as an internal standard. The quenched reaction solutions were diluted with toluene, washed with water, and evaporated to dryness to give the polymers, which were subsequently dried overnight under vacuum at room temperature.

Measurement

The MWD, M_w, and M_w/M_n ratios of the polymers were measured by SEC in chloroform at 40 °C on three linear-type polystyrene-gel columns (Shodex K-805 L; pore size = 20–1000 Å, 8.0 mm i.d. × 30 cm, flow rate = 1.0 mL min^{-1}) connected to a Jasco PU-980 precision pump and a Jasco 930-RI refractive index detector. The columns were calibrated against 11

standard poly(MMA) samples (Polymer Laboratories, $M_w = 630–220000$, $M_w/M_n = 1.06–1.22$). ^{1}H NMR spectra of the obtained polymers were recorded in $CDCl_3$ at 25 °C on a JEOL JNM-LA500 spectrometer operating at 500.16 MHz. Polymer samples for ^{1}H NMR analysis were fractionated by preparative SEC (column: Shodex K-2002).

Acknowledgements

This research was partially supported by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Creative Scientific Research (18GS0209). We thank Takeshi Niitani (Nippon Soda Co., Ltd.) for the ICP-AES measurements.

[1] a) M. Kamigaito, T. Ando, M. Sawamoto, *Chem. Rev.* **2001**, *101*, 3689–3745; b) M. Kamigaito, T. Ando, M. Sawamoto, *Chem. Rec.* **2004**, *4*, 159–175; c) T. E. Patten, K. Matyjaszewski, *Acc. Chem. Res.* **1999**, *32*, 895–903; d) J. Xia, K. Matyjaszewski, *Chem. Rev.* **2001**, *101*, 2921–2990.

[2] T. Pintauer, K. Matyjaszewski, *Coord. Chem. Rev.* **2005**, *249*, 1155–1184.

[3] a) W. Jakubowski, K. Min, K. Matyjaszewski, *Macromolecules* **2006**, *39*, 39–45; b) W. Jakubowski, K. Matyjaszewski, *Angew. Chem.* **2006**, *118*, 4594–4598; *Angew. Chem. Int. Ed. Engl.* **2006**, *45*, 4482–4486; c) K. Matyjaszewski, W. Jakuboeski, K. Min, W. Tang, J. Huang, W. A. Braunecker, N. V. Tsarevsky, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15309–15314.

[4] H. Tang, N. Arulsamy, M. Radosz, Y. Shen, N. V. Tsarevsky, W. A. Braunecker, W. Tang, K. Matyjaszewski, *J. Am. Chem. Soc.* **2006**, *128*, 16277–16285.

[5] V. Percec, T. Guliashvili, J. S. Ladislaw, A. Wistrand, A. Stjerndahl, M. J. Sienkowska, S. Sahoo, *J. Am. Chem. Soc.* **2006**, *128*, 14156–14165.

[6] a) R. Noyori, S. Hashiguchi, *Acc. Chem. Res.* **1997**, *30*, 97–102; b) R. H. Grubbs, *Tetrahedron* **2004**, *60*, 7117–7140.

[7] M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, *Macromolecules* **1995**, *28*, 1721–1723.

[8] H. Takahashi, T. Ando, M. Kamigaito, M. Sawamoto, *Macromolecules* **1999**, *32*, 3820–3823.

[9] Y. Watanabe, T. Ando, M. Kamigaito, M. Sawamoto, *Macromolecules* **2001**, *34*, 4370–4374.

[10] M. Kamigaito, Y. Watanabe, T. Ando, M. Sawamoto, *J. Am. Chem. Soc.* **2002**, *124*, 9994–9995.

[11] T. Ando, M. Kamigaito, M. Sawamoto, *Macromolecules* **2000**, *33*, 5825–5829.

[12] a) P. J. Fagan, M. D. Ward, J. C. Calabrese, *J. Am. Chem. Soc.* **1989**, *111*, 1698–1719; b) P. J. Fagan, W. S. Mahoney, J. C. Calabrese, I. D. Williams, *Organometallics* **1990**, *9*, 1843–1852.

[13] S. Hamasaki, M. Kamigaito, M. Sawamoto, *Macromolecules* **2002**, *35*, 2934–2940.

[14] S. Hamasaki, C. Sawauchi, M. Kamigaito, M. Sawamoto, *J. Polym. Sci. Part A* **2002**, *40*, 617–623.

[15] a) M. M. Rahman, H. Y. Liu, A. Prock, W. P. Giering, *Organometallics* **1987**, *6*, 650–658; b) M. M. Rahman, H. Y. Liu, K. Eriks, A. Prock, W. P. Giering, *Organometallics* **1989**, *8*, 1–7.

[16] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313–348.

[17] F. Simal, L. Wlodarczak, A. Demonceau, A. F. Noels, *Eur. J. Org. Chem.* **2001**, 2689–2695.

[18] When ruthenium complexes were analyzed with ^{31}P NMR spectroscopy, the unknown peak was observed at around 30 ppm. This peak would be attributed to the oxidized phosphine, caused by ruthenium catalysis.

[19] T. Ando, M. Kamigaito, M. Sawamoto, *Macromolecules* **1998**, *31*, 6708–6711.

[20] P. G. Gassman, C. H. Winter, *J. Am. Chem. Soc.* **1988**, *110*, 6130–6135.

Received: March 31, 2008
Published online: July 9, 2008

