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$Ru(Cp^*)Cl(PPh_3)_2$: A Versatile Catalyst for Living Radical Polymerization of Methacrylates, Acrylates, and Styrene[1]

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ABSTRACT: $Ru(Cp^*)Cl(PPh_3)_2$ (Cp^* = pentamethylcyclopentadienyl; PPh_3 = triphenylphosphine) has been found to be a versatile catalyst that is applicable to living radical polymerization of methyl methacrylate (MMA), methyl acrylate (MA), and styrene (St) with $Al(O\textit{i}\text{-}Pr)_3$ as an additive. The number-average molecular weights (M_n) of the obtained polymers increased in proportion to monomer conversion, and the molecular weight distributions were very narrow ($M_w/M_n < 1.1$). Effective initiators were all alkyl halides (R−X), where X = Cl for MMA; Cl and Br for St; and Cl, Br, and I for MA. $Ru(Cp^*)Cl(PCy_3)$ (Cy = cyclohexyl) also proved an effective catalyst for living radical polymerization of MMA, faster than that with $Ru(Cp^*)Cl(PPh_3)_2$, to produce polymers with narrow molecular weight distributions ($M_w/M_n <$ 1.2).

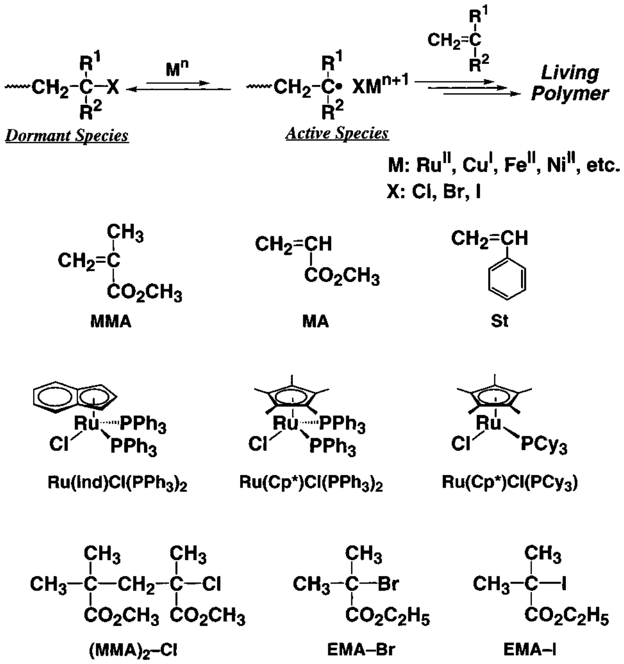
Introduction

In the past several years, extensive efforts have been directed toward developing living radical polymerization, which have changed the hitherto common view that it would be difficult to achieve.[2] Nowadays, one can precisely control radical polymerization of various monomers by using transition-metal complexes of Ru,[3−9] Cu,[10−17] Fe,[18−22] Ni,[23−26] etc., and the metal-based systems are one of the most efficient techniques of living radical polymerization. In most of these systems, the growing radical is transiently capped with halogen X (X = Cl, Br, I) via a covalent bond (C−X) which is reversibly reactivated into the growing radical by a metal complex (Scheme 1). One of the merits of those metal-catalyzed processes is that the catalytic activities of the metal complexes are tunable by their ligands according to monomer structure and reaction conditions. In particular, additives effectively accelerate metal-catalyzed living polymerization.

For example, we have found some ruthenium complexes induce living radical polymerization, and their catalytic activity and the range of applicable monomers depend on the complex's ligands, e.g., $Ru(Cp)Cl(PPh_3)_2$ (Cp = cyclopentadienyl) for methyl methacrylate (MMA)[3] and $Ru(Ind)Cl(PPh_3)_2$ (Ind = indenyl) for MMA and styrene (St).[6] Thus, the Ru(Ind) complex is not only applicable to a wider range of monomers but also effective for faster living polymerization, though it is isoelectronic to the Ru(Cp) complex.

Another isoelectronic complex, $Ru(Cp^*)Cl(PPh_3)_2$ (Cp^* = pentamethylcyclopentadienyl), can also cleave a C−X bond into a radical.[27] Since the rate of the homolytic C−X bond cleavage increases in the order Ru(Cp) < Ru(Ind) ≪ $Ru(Cp^*)$,[27] $Ru(Cp^*)$ is a potentially effective complex for living radical polymerization. In this paper, we present results demonstrating that $Ru(Cp^*)Cl(PPh_3)_2$ induces living radical polymerizations of MMA, methyl acrylate (MA), and St in the presence of $Al(O\textit{i}\text{-}Pr)_3$, in contrast to $Ru(Ind)Cl(PPh_3)_2$, which is effective for MMA and St but not acrylates. $Ru(Cp^*)Cl(PCy_3)$ (Cy = cyclohexyl) was also examined as a new catalyst for living radical polymerization.

Scheme 1



Results and Discussion

1. Polymerization of Several Monomers. $Ru(Cp^*)Cl(PPh_3)_2$ was employed for polymerizations of three classes of monomers: acrylate, styrene, and methacrylate. They were carried out under the same conditions: $[\text{monomer}]_0$ = 4.0 M, $[(MMA)_2{-}Cl]_0$ = 40 mM, $[Ru(Cp^*)Cl(PPh_3)_2]_0$ = 4.0 mM, and $[Al(O\textit{i}\text{-}Pr)_3]_0$ = 40 mM in toluene at 80 °C; $(MMA)_2{-}Cl$ represents the chlorine-capped MMA dimer: $(CH_3)_2C(CO_2CH_3)CH_2C(CH_3)(CO_2CH_3)Cl$. All polymerizations proceeded smoothly and reached 90% conversion in ca. 150 h for MA, ca. 300 h for MMA, and ca. 500 h for St, respectively (Figure 1).

As shown in Figure 2, the SEC curves of the obtained polymers were unimodal and very narrow and shifted to high molecular weight with monomer conversion. The number-average molecular weights increased in direct proportion to monomer conversion, and in the case of

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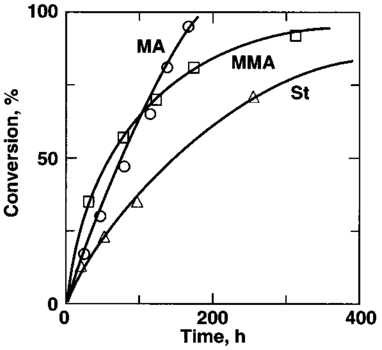

Figure 1. Polymerization of MA, MMA, and St with $(MMA)_2-Cl/Ru(Cp^*)Cl(PPh_3)_2/Al(Oi\text{-}Pr)_3$ in toluene at 80 °C: $[monomer]_0 = 4.0$ M; $[(MMA)_2-Cl]_0 = 40$ mM; $[Ru(Cp^*)Cl(PPh_3)_2]_0 = 4.0$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM. Monomer: MA (○); MMA (□); St (△).

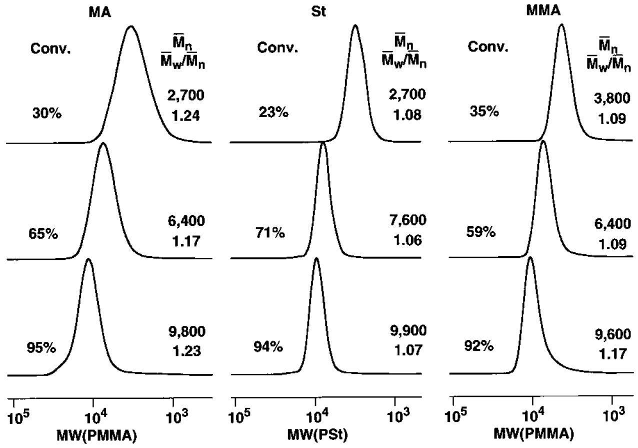

Figure 2. MWD chromatogram curves of poly(MA), poly(St), and poly(MMA) obtained with $(MMA)_2-Cl/Ru(Cp^*)Cl(PPh_3)_2/Al(Oi\text{-}Pr)_3$ in toluene at 80 °C: $[monomer]_0 = 4.0$ M; $[(MMA)_2-Cl]_0 = 40$ mM; $[Ru(Cp^*)Cl(PPh_3)_2]_0 = 4.0$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM.

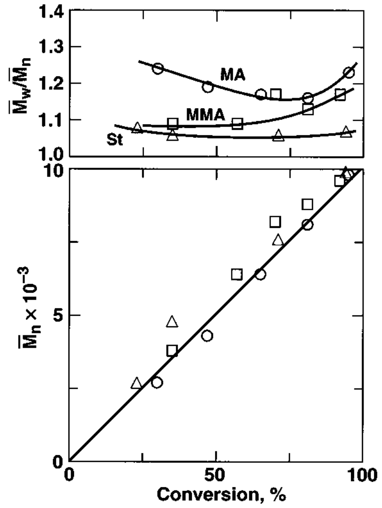

Figure 3. M_n and M_w/M_n curves of poly(MA), poly(St), and poly(MMA) obtained with $(MMA)_2-Cl/Ru(Cp^*)Cl(PPh_3)_2/Al(Oi\text{-}Pr)_3$ in toluene at 80 °C: $[monomer]_0 = 4.0$ M; $[(MMA)_2-Cl]_0 = 40$ mM; $[Ru(Cp^*)Cl(PPh_3)_2]_0 = 4.0$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM. Monomer: MA (○); MMA (□); St (△).

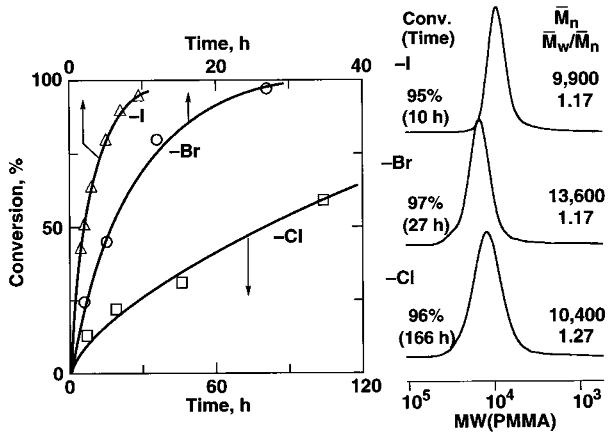

Figure 4. Time–conversion curves for the polymerization of MA with $R-X/Ru(Cp^*)Cl(PPh_3)_2/Al(Oi\text{-}Pr)_3$ and MWD chromatogram curves of poly(MA) in toluene at 80 °C: $[MA]_0 = 4.0$ M; $[R-X]_0 = 40$ mM; $[Ru(Cp^*)Cl(PPh_3)_2]_0 = 2.0$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM. R–X: EMA–I (△); EMA–Br (○); $(MMA)_2-Cl$ (□).

St and MMA, they agreed well with the calculated value assuming that one initiator produces one polymer chain (Figure 3). Molecular weight distributions were narrow throughout the polymerization. Another metal-catalyzed system, sulfonyl chloride/CuCl/4,4′-dinonyl-2,2′-bipyridine,[15] can also produce controlled polymers of these three class of monomers in the same ingredients but requires tuning of conditions such as concentration and/or temperature. On the other hand, $Ru(Cp^*)Cl(PPh_3)_2$ leads to the living radical polymerizations under the same conditions.

2. Effects of the Halogen in Initiators. (a) Methyl Acrylate. We examined effects of the halogen in initiators. As initiators, $(MMA)_2-Cl$, EMA–Br $[(CH_3)_2C(CO_2C_2H_5)Br]$, and EMA–I $[(CH_3)_2C(CO_2C_2H_5)I]$ were employed for methyl acrylate (Figure 4). We chose $(MMA)_2-Cl$ as a chloride initiator because the initiation from MMA–Cl $[(CH_3)_2C(CO_2CH_3)Cl]$ proved very slow in the polymerization of MMA with $RuCl_2(PPh_3)_3$.[28] Though the polymerization proceeded smoothly for all initiators, the rate increased in the order $Cl \ll Br < I$, which is probably due to different carbon–halogen bond strength at the dormant end. For example, the C–I bond strength is weakest in the series, which leads the highest radical concentration to induce the fastest polymerization. The SEC curves of the obtained polymers were unimodal and narrow, especially with the iodide initiator. These results indicate that the iodo initiator leads to not only a high concentration of the growing radical (faster polymerization) but also fast exchange between the dormant and the active species (narrower MWD).

(b) Styrene. Effects of the halogen in initiators were also investigated for styrene polymerization. In contrast to those of MA, the polymerization of the iodide-initiating system was very slow and gave polymers of broad MWDs (Figure 5). On the other hand, the polymers obtained with the bromo and chloro initiators had well-controlled M_n's with very narrow MWDs. The polymerization rate increased in the order $Cl < Br$.

(c) Methyl Methacrylate. Polymerizations of MMA with the three initiators were similarly studied. The polymerization smoothly proceeded with $(MMA)_2-Cl$ (Figure 6). The M_n agreed well with the calculated value, and the MWD was very narrow ($M_w/M_n < 1.1$). In contrast, the polymerizations with the bromo and iodo initiators almost stopped around 50% and 80%, respectively. The MWDs of the obtained polymers were broad. Thus, the chloro initiator is suitable for MMA polymerization in conjunction with $Ru(Cp^*)Cl(PPh_3)_2$.

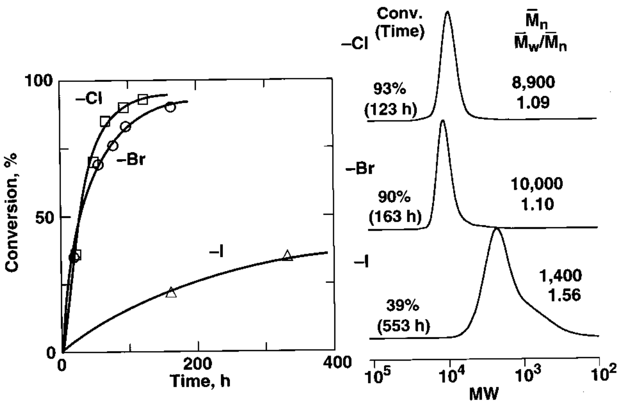

Figure 5. Time–conversion curves for the polymerization of St with R–X/Ru(Cp*)Cl(PPh_3)$_2$/Al(O*i*-Pr)$_3$ and MWD chromatogram curves of poly(St) in toluene at 100 °C: $[St]_0 = 4.0$ M; $[R\text{–}X]_0 = 40$ mM; $[Ru(Cp^*)Cl(PPh_3)_2]_0 = 2.0$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM. R–X: (MMA)$_2$–Cl (□); EMA–Br (○); EMA–I (△).

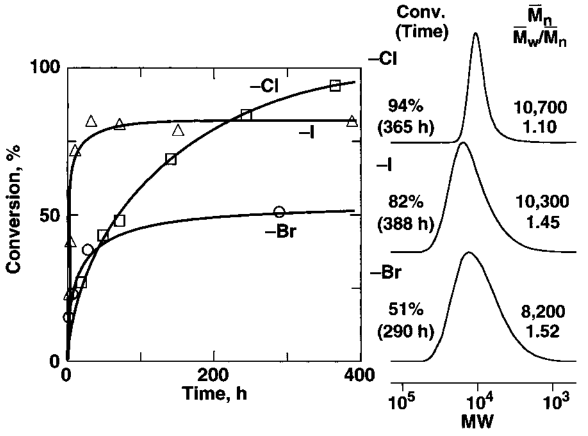

Figure 6. Time–conversion curves for the polymerization of MMA with R–X/Ru(Cp*)Cl(PPh_3)$_2$/Al(O*i*-Pr)$_3$ and MWD chromatogram curves of poly(MMA) in toluene at 80 °C: $[MMA]_0 = 4.0$ M; $[R\text{–}X]_0 = 40$ mM; $[Ru(Cp^*)Cl(PPh_3)_2]_0 = 2.0$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM. R–X: (MMA)$_2$–Cl (□); EMA–I (△); EMA–Br (○).

Such dependence on halogens is due to the difference in reactivity of the chloro-, bromo-, and iodo-capped dormant ends of poly(MA), poly(St), and poly(MMA) to Ru(Cp*)Cl(PPh_3)$_2$, where the C–X bond strength probably decreases in the order of poly(MA), poly(St), and poly(MMA) or with chloride, bromide, and iodide. For example, the reactivities of each halogenated end of poly(MA) are relatively low in contrast to these of poly(St) and poly(MMA) to generate growing radicals at low concentration. In contrast, the bromo- or iodo-dormant ends of poly(MMA) are more reactive and generate a higher concentration of growing radical at a very early stage of the polymerizations. This results in bimolecular termination at the stage, which causes high concentration of Ru(III) species and shifts the equilibrium toward the dormant species to stop the polymerization.

3. Cp* vs Ind Complexes. The two isoelectronic complexes, Ru(Cp*)Cl(PPh_3)$_2$ and Ru(Ind)Cl(PPh_3)$_2$, were then compared in polymerizations of MMA, St, and MA with (MMA)$_2$–Cl as an initiator and with Al(O*i*-Pr)$_3$ as an additive. Although the polymerizations proceeded smoothly with both Ru complexes, their rates were lower with Ru(Cp*) than with Ru(Ind). This suggests that the equilibrium between dormant and active species in the Cp* system inclines to the dormant side more than in the Ind system. This is probably because the Ind complex more easily releases one of the two phosphine ligands or induces easier slipping of the indenyl ligand to be more active. However, the polymers obtained with the Cp* complex were all better controlled (narrower MWD) than those with the Ind complex (Figure 7). Thus, the Ru(Cp*) complex gives better controlled polymerizations of MA, MMA, and St, though they might be slow. Recently, we found that amine additives dramatically accelerate the Ru(Cp*)-catalyzed polymerization.[29]

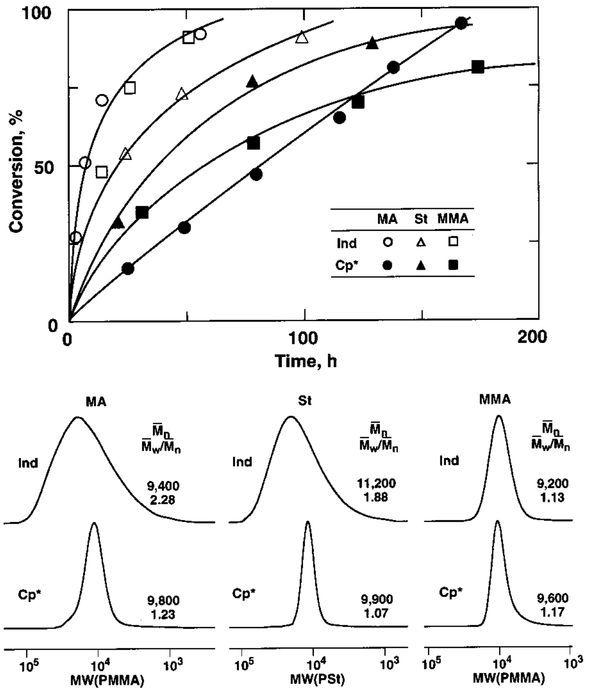

Figure 7. Time–conversion curves for the polymerization of MA, St, and MMA with (MMA)$_2$–Cl/Ru(L)Cl(PPh_3)$_2$/Al(O*i*-Pr)$_3$ (L = Ind, Cp*) and MWD chromatogram curves of poly(MA) in toluene at 80 (MA and MMA) or 100 °C (St): $[monomer]_0 = 4.0$ M; $[(MMA)_2\text{–}Cl]_0 = 40$ mM; $[Ru(L)Cl(PPh_3)_2]_0 = 4.0$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM.

4. Ru(Cp*)Cl(PCy_3): A 16-Electron Complex. This complex resembles Ru(Cp*)Cl(PPh_3)$_2$ but differs in the number of phosphine ligands. Ru(Cp*)Cl(PPh_3)$_2$ is an 18-electron complex and thus might need the release of one of the phosphine ligands or the slipping of the Cp* ring to become an active 16-electron complex.[30] On the other hand, Ru(Cp*)Cl(PCy_3) already lacks one phosphine ligand and might be more active than Ru(Cp*)Cl(PPh_3)$_2$. Polymerization of MMA was thus carried out in the presence of (MMA)$_2$–Cl and Al(O*i*-Pr)$_3$ at 60 or 80 °C. The reactions at 60 °C proceeded much faster than that with Ru(Cp*)Cl(PPh_3)$_2$ at 80 °C (Figure 8). The M_n's of the obtained polymers increased in proportion to monomer conversion and were close to the calculated values assuming that one initiator produces one polymer chain (Figure 9). The MWDs of poly(MMA) became narrower with increasing monomer conversion. As shown in Figure 9, the Ru concentration and the polymerization temperature affected the MWD. The higher the Ru concentration and the lower the polymerization temperature, the narrower the MWD.

Polymerizations of St and MA with Ru(Cp*)Cl(PCy_3) were also investigated. In conjunction with (MMA)$_2$–Cl and Al(O*i*-Pr)$_3$, polymers were in fact obtained but were not controlled. A higher than calculated M_n was

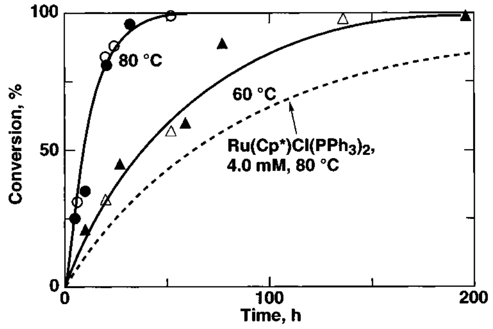

Figure 8. Polymerization of MMAwith $(MMA)_2{-}Cl/Ru(Cp^*)Cl(PCy_3)/Al(O\textit{i}\text{-}Pr)_3$ in toluene at 60 or 80 °C: $[MMA]_0 = 4.0$ M; $[(MMA)_2{-}Cl]_0 = 40$ mM; $[Ru(Cp^*)Cl(PCy_3)]_0 = 2.0$ or 4.0 mM; $[Al(O\textit{i}\text{-}Pr)_3]_0 = 40$ mM. key: $[Ru]_0 = 2.0$ mM at 80 °C (○); $[Ru]_0 = 4.0$ mM at 80 °C (●); $[Ru]_0 = 2.0$ mM at 60 °C (△); $[Ru]_0 = 4.0$ mM at 60 °C (▲).

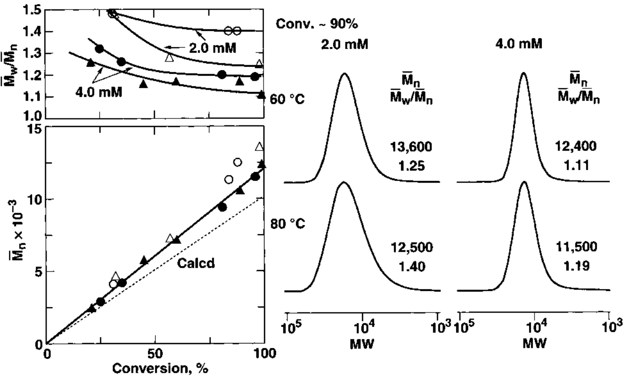

Figure 9. M_n, M_w/M_n, and MWD chromatogram curves of poly(MMA) obtained with $(MMA)_2{-}Cl/Ru(Cp^*)Cl(PCy_3)/Al(O\textit{i}\text{-}Pr)_3$ in toluene at 60 or 80 °C: $[MMA]_0 = 4.0$ M; $[(MMA)_2{-}Cl]_0 = 40$ mM; $[Ru(Cp^*)Cl(PCy_3)]_0 = 2.0$ or 4.0 mM; $[Al(O\textit{i}\text{-}Pr)_3]_0 = 40$ mM. key: $[Ru]_0 = 2.0$ mM at 80 °C (○); $[Ru]_0 = 4.0$ mM at 80 °C (●); $[Ru]_0 = 2.0$ mM at 60 °C (△); $[Ru]_0 = 4.0$ mM at 60 °C (▲).

Table 1. Polymerizations of MA and St with $Ru(Cp^*)Cl(PCy_3)$[a]

entry	monomer	time, h	conv, %	M_n	M_w/M_n
1	St	21	26	4700	3.12
2	St	46	49	9000	2.92
3	St	389	95	12 900	2.44
4	MA	1.25	67	34 700	2.82
5	MA	4.5	85	28 500	3.26
6	MA	19	96	16 000	6.23

[a] Monomer/$(MMA)_2{-}Cl/Ru(Cp^*)Cl(PCy_3)/Al(O\textit{i}\text{-}Pr)_3$ = 4000/40/2.0/40 mM in toluene at 80 °C.

obtained in each case, and the MWD's were quite broad (Table 1). Thus, $Ru(Cp^*)Cl(PCy_3)$ is not suitable for polymerization of St or MA.

Conclusions

$Ru(Cp^*)Cl(PPh_3)_2$ was found to be a versatile catalyst in that it induces living radical polymerizations of three monomer classes: methacrylates, acrylates, and styrene. Such a versatility cannot be found for other ruthenium catalysts thus far employed for living radical polymerizations (e.g., $Ru(Ind)Cl(PPh_3)_2$ is not effective for acrylates). $Ru(Cp^*)Cl(PCy_3)$, a 16-electron complex, is also effective for living radical polymerization of MMA. Though those Cp*-type Ru catalysts are versatile and give very narrow MWD, the polymerizations are slow, needing over 100 h for completion, but this drawback may be overcome by using other additives.[29]

Experimental Section

Materials. MMA (Tokyo Kasei, >99%) was dried overnight over calcium chloride and distilled twice over calcium hydride under reduced pressure before use. $Al(O\textit{i}\text{-}Pr)_3$ (Aldrich, >99.99%) was used as received and handled in a glovebox under a moisture- and oxygen-free argon atmosphere (<1 ppm). Toluene used as solvent and *n*-octane used as internal standard for gas chromatography were dried overnight over calcium chloride, distilled twice from sodium benzophenone ketyl (toluene) or calcium hydride (*n*-octane), and bubbled with dry nitrogen for more than 15 min immediately before use. Initiator $(MMA)_2{-}Cl$ was prepared according to the literature.[28]

Preparation of Ru Complexes. $Ru(Cp^*)Cl(PPh_3)_2$[31] and $Ru(Cp^*)Cl(PCy_3)$[32,33] were prepared according to the literature.

Polymerization Procedures. Polymerization was carried out under dry nitrogen in baked and sealed glass tubes. A typical example of the MMA polymerization with $Ru(Cp^*)Cl(PPh_3)_2$ is given below. In a 50 mL round-bottomed flask was placed $Ru(Cp^*)Cl(PPh_3)_2$ (15.3 mg, 0.0192 mmol), toluene (0.81 mL), *n*-octane (0.192 mL), and MMA (2.05 mL, 19.2 mmol), solutions of $Al(O\textit{i}\text{-}Pr)_3$ (1.54 mL of 125 mM in toluene, 0.192 mmol), and solutions of $(MMA)_2{-}Cl$ (0.192 mL of 1.0 M in toluene, 0.192 mmol) were added sequentially in this order at room temperature under dry nitrogen. The total volume of the reaction mixture was 4.80 mL. Immediately after mixing, six aliquots (0.60 mL each) of the solution were injected into baked glass tubes, which were then sealed and placed in an oil bath at 80 °C. In predetermined intervals, the polymerization was terminated by cooling the reaction mixtures to −78 °C. Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography using *n*-octane as the internal standard. The quenched reaction solutions were diluted with toluene (ca. 20 mL) and rigorously shaken with an absorbent [KYOWAAD-2000G-7 ($Mg_{0.7}Al_{0.3}O_{1.15}$); Kyowa Chemical Industry] (ca. 5 g) to remove the metal-containing residues. After the absorbent was separated by filtration (Whatman 113V), the filtrate was washed with water and evaporated to dryness to yield the products, which were subsequently vacuum-dried overnight.

Polymer Characterization. The M_n, M_w/M_n, and MWD curves of the polymers were determined by size-exclusion chromatography in chloroform at 40 °C using three polystyrene gel columns [Shodex K-805L (pore size: 20−1000 Å; 8.0 mm i.d. × 30 cm) × 3; flow rate 1.0 mL/min] that were connected to Jasco PU-980 precision pump and a Jasco RI-930 refractive index detector. The columns were calibrated against 13 standard poly(MMA) samples (Polymer Laboratories; M_n = 202−1 200 000; M_w/M_n = 1.04−1.22) as well as the monomer.

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(1) This work was presented in part at the following meetings: The 49th Annual Meeting of the Society of Polymer Science, Nagoya, Japan, May 2000; paper IPc011: Watanabe, Y.; Tokuchi, K.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **2000**, *49* (2), 276.

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