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Halogen Donors in Metal-Catalyzed Living Radical Polymerization: Control of the Equilibrium between Dormant and Active Species

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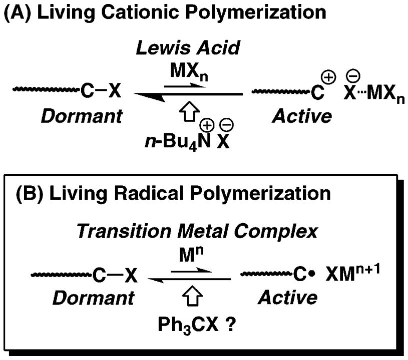
Introduction. Most of the recently developed living or controlled polymerizations involve a dynamic equilibrium between a "dormant" species and an "active" species, favorably shifted to the former so as to retain the instantaneous concentration of the latter unusually low. This feature is believed to be a key for a practically undisturbed propagation,[1] in which the reversible generation of the active end is triggered by such a stimulus as heat and catalysis. In the transition-metal-catalyzed living (or atom transfer) radical polymerization,[2] for example, a metal catalyst is responsible for this stimulation via the homologous dissociation of a terminal carbon−halogen bond into a carbon radical, while the catalyst itself turns into a higher oxidized form by one-electron transfer.

Equally important to this forward process is the regeneration of the dormant species or the reverse process, i.e., the end-capping of the growing radical with the halogen back from the oxidized catalyst to maintain the dynamic reversibility of the dormant-active species equilibrium. Thus, the catalyst must contribute to the two antithetical processes, namely the abstraction (activation) and the return (deactivation) of the halogen, and for this one usually needs the sophisticated and stringent design of ligands in metal catalysts.[3] The design concept of the transition-metal catalysts has so far been focused primarily on the forward process or the efficiency in the terminal halogen abstraction from the dormant species through, for example, the enhancement of electron donation from the ligand.[4] However, the promotion of the halogen return should also be important for the polymerization control, such as the introduction of a "reducing agent" reported by Matyjaszewski et al.[5] or the utilization of "catalyst disproportionation" by Percec et al.,[6] which effectively regenerate the reduced form of a metal catalyst and, in turn, the halogen-capped dormant species.

It occurred to us that the enhancement of the backward process might also be achieved by an externally added "halogen donor" (R−X; X = halogen; R = radical source) that effectively donates its labile halogen X to the growing radical $R^•$, either directly via simple halogen transfer to the radical center or indirectly via reacting with the metal catalyst to give the latter's oxidized form that, in turn, returns its halogen back to the active species. Obviously, the additive R−X should *not* act as a chain transfer agent in the direct pathway *or* as an initiator in the indirect pathway, for this the resulting radical $R^•$ should be thermodynamically stable or sterically hindered enough to be unable to reinitiate radical propagation. In this regard the function of R−X is reminiscent of the "common-ion" salt effect or the "mass-law" effect utilized in living cationic polymerization[7] (Scheme 1A), where the growing carbocation is effectively converted into its formant form (alkyl halide) with an ionic halide additive, typically a tetra-*n*-buthylammonium halide (n-Bu$_4$NX; X = halide).[8]

Scheme 1



In this Communication, we report a "common radical generator" (or an external halogen donor), a novel additive for metal-catalyzed living radical polymerization, which contributes to control of the equilibrium balance between dormant and active species. We herein focused on triphenylmethyl halides (Ph$_3$C−X; X = halogen) because they would promise (1) that the C−X bond might be activated by the transition metal catalyst (M^n) to give the carbon radical ($Ph_3C^•$) and the "common" oxidized catalyst (XM^{n+1} carrying the identical halogen as that in the initiator and (2) the triphenylmethyl radical[9] would be too stable and too bulky to initiate radical propagation, rendering the additive neither an initiator nor a chain transfer agent (Scheme 1B). For demonstrating their expected effects, these halides were deliberately added into an ill-controlled polymerization system or a defective system with low controllability. Consequently, we first demonstrated the contribution of Ph$_3$C−X in controlling the equilibrium balance, which was confirmed by not only the improvement of controllability but also halogen exchange behavior and some comparative experiments. The additives would promise to expand the range of applicable catalysts, however poorly effective in controlling radical propagation they might be, without requiring painstaking development of sophisticated metal catalysts.

Results and Discussion. As we have reported, an indenyl ruthenium complex [RuCl(Ind)(PPh$_3$)$_2$, Ind = η^5-C$_9$H$_7$; RuCl(Ind)], coupled with a chlorine initiator, allows a living radical polymerization of methacrylates to give well-controlled polymers with narrow molecular weight distributions ($M_w/M_n \sim 1.1-1.2$).[10] However, the catalyst does not enable control for acrylates, distinguished from the pentamethylcyclopentadienyl couterpart [RuCl(Cp*)(PPh$_3$)$_2$, Cp* = η^5-C$_5$Me$_5$].[11] The uncontrollability would be due to that the tervalent complex [Ru(III)], generated via the activation process, is unfavorable to return the halogen to the acrylate-type active species or a secondary carbon radical.

Thus, we targeted the ill-controlled system of acrylates to examine the effects of Ph$_3$C−Cl. We added it into the polymerization of methyl acrylate (MA) under the RuCl(Ind) catalysis coupled with a chlorine capped dimer of methyl methacrylate (MMA) [(MMA)$_2$−Cl] in toluene at 80 °C, where the concentration of Ph$_3$C−Cl was 0.4, 1.0, 2.0, or 4.0 mM; [MA]$_0$/[(MMA)$_2$−Cl]$_0$/[RuCl(Ind)]$_0$ = 4000/40/4.0 mM. The polymerization rate clearly decreased as increasing amount of Ph$_3$C−Cl, and the polymerization hardly proceeded with higher than 2.0 mM of [Ph$_3$C−Cl]$_0$ (Figure 1A). The number-average

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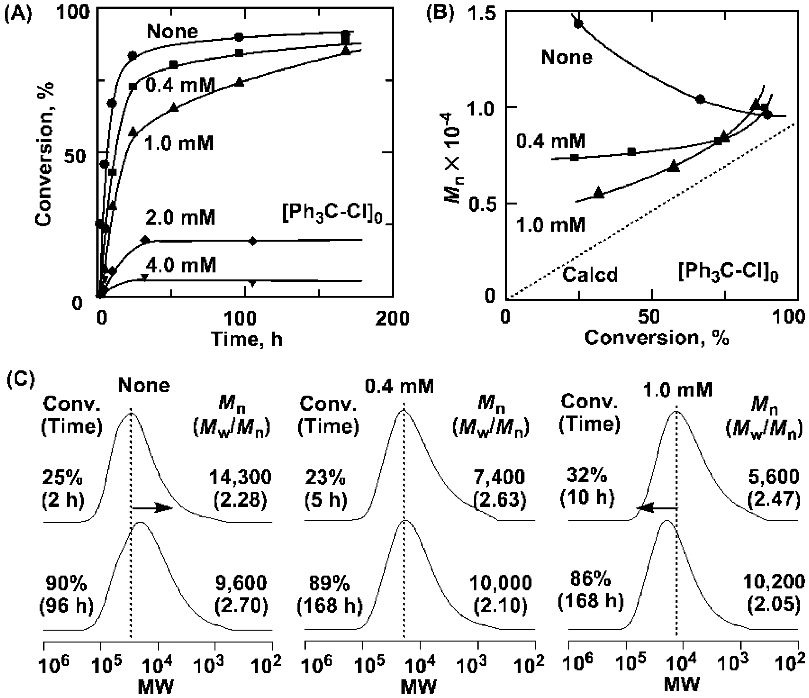

Figure 1. (A) Time−conversion curves, (B) conversion−M_n curves, and (C) MWD chromatogram curves of poly(MA) obtained with $(MMA)_2$−Cl/RuCl(Ind)/Ph_3C−Cl in toluene at 80 °C: $[MA]_0/[(MMA)_2-Cl]_0/[RuCl(Ind)]_0/[Ph_3C-Cl]_0$ = 4000/40/4.0/(0 or 0.4 or 1.0 or 2.0 or 4.0) mM.

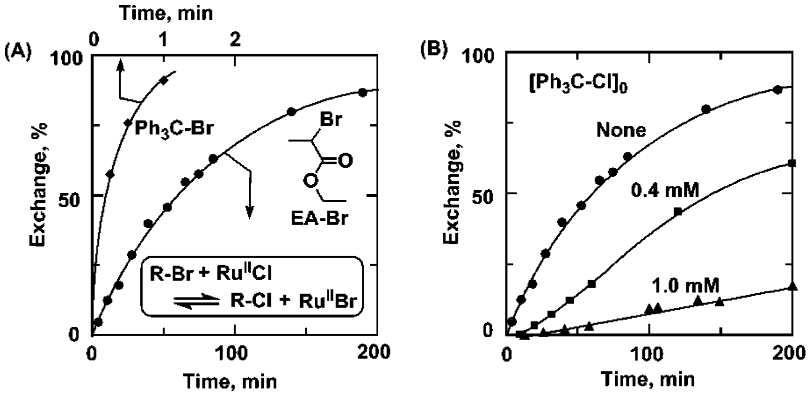

Figure 2. (A) Halogen exchange reaction between (Ph_3C−Br or EA−Br) and RuCl(Ind) in toluene-d_8 at 80 °C: ($[Ph_3C-Br]_0$ or $[EA-Br]_0$)/$[RuCl(Ind)]_0$ = 4.0/4.0 mM. (B) Halogen exchange reaction between EA−Br and RuCl(Ind) in the presence of Ph_3C−Cl in toluene-d_8 at 80 °C: $[(MMA)_2-Cl]_0/[RuCl(Ind)]_0/[Ph_3C-Cl]_0$ = 4.0/4.0/(0 or 0.4 or 1.0) mM.

molecular weights (M_n) of PMMA was also dependent on the amount of Ph_3C−Cl (Figure 1B). In its absence, M_n was higher than the calculated value, assuming that one molecule of initiator generates one living polymer chain, and did decrease as the monomer conversion, indicating ill-controlled character of the system. In contrast, M_n became closer to the calculated value, as Ph_3C−Cl was added. Especially, when $[Ph_3C-Cl]_0$ = 1.0 mM, M_n molecular weight increased against monomer conversion (Figure 1B), and the peak tops of SEC curves shifted to higher molecular weight without broadening the distribution, unlike the Ph_3C−Cl-free system (Figure 1C). These results demonstrated that the added Ph_3C−Cl turned the uncontrolled system into controlled one, although the molecular weight distributions were still broader (M_w/M_n > 2.0).

To examine the contribution of Ph_3C−Cl to control of the equilibrium balance between dormant/active species, we observed the halogen-exchange reaction between a halide compound and RuCl(Ind) by ^{1}H NMR.[12] Thus, the model Br-capped radical generator was reacted with an equimolar amount of RuCl(Ind) ($[R-Br]_0$ = $[RuCl(Ind)]_0$ = 4.0 mM) in toluene-d_8 at 80 °C, and degree of the halogen exchange between the two was monitored.

First, we observed the halogen exchange reaction of Br-capped ethyl acrylate (EA−Br), which is regarded as a model of the growing species in MA polymerization. The peak derived from the methyl proton adjacent to the carbon−halogen bond was shifted according to the halogen (see Supporting Information, Figure S1), and thus the exchange conversion was determined from the integral ratio of the two peaks. The EA−Br was smoothly exchanged at a moderate rate (~50%, 1 h), and finally almost of the EA−Br was exchanged to EA−Cl (Figure 2A). In contrast, the Ph_3C−Br was instantly exchanged to form the Ph_3C−Cl, which was confirmed by the quantitative formation of $RuBr(Ind)(PPh_3)_2$ in the first monitoring (see Supporting Information, Figure S2). These results demonstrate that the ruthenium complex quite rapidly and preferentially activates the Ph_3C−halide compared to the acrylate-type dormant species.

Then, we observed the halogen exchange reaction of the EA−Br in the presence of Ph_3C−Cl ($[EA-Br]_0$ = $[RuCl(Ind)]_0$ =

Table 1. Influence of Ph$_3$C−Cl on Radical Polymerization

entry	monomer	initiator/catalyst	Ph$_3$C−Cl	time, h	conv, %	M_n	M_w/M_n
1[a]	MA	−/Ru(Ind)	40 mM	100	~0		
2[b]	MA	AIBN/−	none	0.25	87	20 300	4.15
3[b]	MA	AIBN/−	100 mM	0.25	83	23 200	4.09
4[b]	MMA	AIBN/−	none	1.5	84	14 900	1.86
5[b]	MMA	AIBN/−	100 mM	1.5	84	13 200	1.93

[a] $[\mathrm{MA}]_0/[\mathrm{Ph_3C{-}Cl}]_0/[\mathrm{RuCl(Ind)(PPh_3)_2}]_0 = 4000/40/4.0$ mM in toluene at 80 °C. [b] $[\mathrm{Monomer}]_0/[\mathrm{AIBN}]_0/[\mathrm{Ph_3C{-}Cl}]_0 = 4000/40/(0$ or $100)$ mM in toluene at 80 °C.

4.0 mM, $[\mathrm{Ph_3C{-}Cl}]_0 = 0.4$ or 1.0 mM), corresponding to a model reaction of the above polymerization. As the amount of Ph$_3$C−Cl was increased, the induction periods were seen and the exchange rates were apparently decreased (Figure 2B). By considering the rapid activation for the Ph$_3$C−halide, the ruthenium complex would predominantly activate the added Ph$_3$C−Cl, despite the smaller amount, rather than the EA−Br. As a result, Ph$_3$C$^\bullet$ and tervalent complex [RuCl$_2$(Ind)] are frequently generated in the system, which would shift the equilibrium in the EA−Br to the dormant species because the tervalent species is "common" for the both halogen compounds. Thus, the addition of Ph$_3$C−Cl would diminish the degree of activation for the EA−Br which appeared in the slower exchange rate. A similar phenomena would also occur in the polymerization, which would lead to the equilibrium shift or the improvement of controllability.

To prove the contribution of Ph$_3$C−Cl only to the equilibrium shift, we confirmed that Ph$_3$C−Cl itself does not serve as an initiator or a chain transfer agent (Table 1). First, we carried out the RuCl(Ind)-catalyzed polymerization of MA with Ph$_3$C−Cl as a potential initiator in place of (MMA)$_2$−Cl in toluene at 80 °C, but the polymerization did not proceed (entry 1). This result suggests the Ph$_3$C−Cl is not responsible for the initiation of MA even under the ruthenium catalysis, although the catalyst affords the activation of the C−Cl bond in the Ph$_3$C−Cl. The resulting radical (Ph$_3$C$^\bullet$) would be too stable and bulky to react with MA monomer under these conditions.[13] Thus, the decrease in M_n by the addition of Ph$_3$C−Cl should not be due to the additional initiation from Ph$_3$C−Cl.

Further, we added a larger amount of Ph$_3$C−Cl into the conventional radical polymerization of MA or MMA with AIBN in toluene at 80 °C to investigate the possibility of a chain transfer agent. Polymerization rate and the M_n and M_w/M_n of obtained polymers were almost the same as those without Ph$_3$C−Cl (entries 2−5), which indicates that the propagating MA or MMA radical does not react with Ph$_3$C−Cl for chain transfer reaction at the temperature. These results support that neither initiation nor chain transfer reaction is induced with the added chloride.

Previously, Otsu et al. reported that a triphenylmethane-based azo compound (Ph−N═N−CPh$_3$) worked as an "iniferter" (initiator chain transfer agent terminator) that induces a controlled radical polymerization of MMA.[14] It was proposed that the control was brought about by the homolytic capping of the growing radical with the triphenylmethyl group from the iniferter. In our system, in contrast, the improvement of controllability was not due to such a capping because any terminal triphenylmethyl group was not found in the obtained polymers (by ^{1}H NMR; see the Supporting Information, Figure S3).

In conclusion, we have demonstrated that Ph$_3$C−Cl is effective as an additive (halogen donor) for metal-catalyzed living radical polymerization, where it is responsible for the "shift" of the equilibrium balance to dormant species. Possibly, the additive can be applied to a variety of originally uncontrolled systems and would expand the range of applicable catalysts where the ligand is not artfully designed. The evolution to other metal-catalyzed systems with this concept is now under investigation.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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