Reversible Activation of Carbon–Halogen Bonds by RuCl₂(PPh₃)₃: Halogen Exchange Reactions in Living Radical Polymerization¹

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ABSTRACT: Influences of the structures of the initiating radical species and terminal halogens of their precursors were examined in the RuCl₂(PPh₃)₃-mediated living radical polymerization of methyl methacrylate (MMA) with the use of model compounds of the polymer terminal, which include four authentic unimer and dimer halides (R–X: (CH₃)₂C(CO₂Me)Cl (1a); (CH₃)₂C(CO₂Et)Br (1b); (CH₃)₂C(CO₂Me)CH₂C(CH₃)(CO₂Me)X, X = Cl (2a) or Br (2b)). These halides induced smooth polymerizations of MMA in conjunction with RuCl₂(PPh₃)₃ and Al(O-i-Pr)₃ in toluene at 80 °C, where the rates were almost independent of R–X while the molecular weight distributions were broader in the order: 2b < 2a < 1b < 1a. This shows that initiation is faster with the dimer and with the bromide than with the unimer and with the chloride, respectively. ¹H NMR analysis of the halogen exchange between the brominated initiator 1b or 2b and RuCl₂(PPh₃)₃ shows that the carbon–halogen bond of the dimer is more reactive than that of the unimer. Added Al(O-i-Pr)₃ led to faster polymerizations and narrower MWDs but had no effects on the halogen exchange reactions.

Introduction

Precision control of radical polymerization has been considered difficult, because neutral radical propagating species undergo side reactions such as disproportionation and coupling. However, recently developed systems now permit the control of molecular weights and molecular weight distributions (MWDs) of polymers,² close to that in classical living anionic polymerization. The common features of these modern living systems are that there is a fast interconversion between the radical species and the dormant covalent species and that the equilibrium is shifted to the latter to effectively suppress bimolecular termination reactions. Also, interconversion faster than propagation warrants narrow MWDs of polymers. Thus, the existence of the dormant species as well as the kinetics related to these species are considered crucial in living radical polymerization. The dormant species thus far effective involve, for example, C–X (X = halogen) bonds for transition metal-catalyzed living radical polymerization,²¹,²² C–ON bonds for nitroxide-mediated polymerization,²³,²⁴ and C–SC(S) bonds for the RAFT processes,²⁵ all of which are transiently converted into radical species by stimuli such as metal catalysts, heat, light, or coexisting radical species.²⁶

In the metal-catalyzed living radical polymerizations, the effective transition metal complexes are metal halides of Ru(II),⁴–¹⁰ Cu(I),¹¹–¹⁶ Fe(II),¹⁷–²⁰ Ni(II),²¹–²³ Rh(II),²⁴–²⁶ Pd(II),²⁷ and Re(V)²⁸ except for some zerovalent metals such as Ni(0)²⁹ and Pd(0).³⁰ These living radical polymerizations proceed via the metal-mediated homolytic and reversible activation of the dormant carbon–halogen bonds at polymer terminal originated from a halide as an initiator (Scheme 1). Because of the reversible formation of the halide dormant species from the growing radicals during the polymerizations, there are two different halogens at polymer terminal, if the halogen on the hybrid metal complex is different from that of the halide initiator. We have already shown that the polymers obtained with R–Br/RuCl₂(PPh₃)₃ had two ω-terminals, chlorides and bromides.²⁹ Similar results were also obtained in the polymerization with R–Br/CuCl.³⁰,³¹ Such halogen exchange reactions indeed affect the polymerizations, especially molecular weights and MWDs, because the reactivity of the C–halogen bonds depends on the halogens therein.

The occurrence of halogen exchange reaction also provides evidence for the proposed reversible activation of C–halogen bonds by metal complexes in metal-catalyzed living radical polymerizations. The exchange reaction most probably proceeds via the same radical species with that for the polymerizations, however, it has not been fully investigated yet. Recently, effects of the halogen exchange reaction on the Cu(I)-mediated polymerization were investigated in model reactions with some organic halides, which indicates that the exchange reaction occurs rapidly and that the terminal chloride is more preferred than the bromide.³² Detailed examination of the halogen exchange reaction will give an insight into the mechanism of metal-catalyzed living radical polymerization.

This study is focused on effects of not only the halogens but also the structures of initiating radicals

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of halide initiators, with the use of authentic unimer and dimer models of polymethacrylates that contain chlorine or bromine (1a, 1b, 2a, and 2b) for the RuCl2-(PPh3)3-mediated living radical polymerization of methyl methacrylate (MMA). We also examined effects of added aluminum compounds [Al(O-i-Pr)3] on the polymerization as well as on the halogen exchange reaction with use of the R-Br/RuCl2(PPh3)3 system. This paper shows that more controlled polymerizations can be achieved with initiators that have higher reactivity of C–halogen bonds and that the rate enhancement by the added aluminum compound is absent in the halogen exchange reaction but present in the polymerization.

Results and Discussion

1. Polymerization. (a) Effects of Initiators. A series of halogenated esters (1a, 1b, 2a, and 2b), model compounds of dormant ends for the transition metal-mediated living radical polymerization, were employed as initiators for the polymerization of MMA coupled with RuCl2(PPh3)3 and Al(O-i-Pr)3 in toluene at 80 °C. Herein, the numerical symbols (1 and 2) of the compounds represent unimer and dimer models, respectively, and the attached letter, a or b, is for chloride or bromide, respectively (e.g., 2a means the dimer with a chloride end). As shown in Figure 1, smooth polymerizations occurred in the almost same rate with these initiators, which suggests similarity in the concentrations of the active (radical) species in these polymerizations.

Figure 2 shows the \( M_n \) and MWD curves of the polymers obtained with the unimer or dimer halide/RuCl2(PPh3)3/Al(O-i-Pr)3 initiating system. Specifically with 2b, the \( M_n \) increased in direct proportion to monomer conversion and agreed very well with the calculated value assuming that one initiator produces one polymer chain. The MWD was narrow throughout the reaction \( (M_w/M_n \leq 1.2) \). With 1b and 2a, the \( M_n \) values were very close to the calculated values, though slightly higher than those at low conversions, and the MWDs became narrower with increasing conversion, due to slightly slower initiation. These indicate that the rate of initiation decreases in the following order, \( 2b > 2a \approx 1b > 1a \), and that dimer and bromide is superior to unimer and chloride, respectively.

Figure 3 compares the \( ^{13}C \) NMR chemical shifts of the \( \omega \)-carbons attached to the halogens in the initiators. Irrespective of the halogen, the chemical shifts of the dimers appeared at a lower magnetic field than those of unimers. Therefore, the dimer type \( \omega \)-carbons are more electron deficient, which suggests weaker C–halogen bonds in the dimers. Steric hindrance may also affect the reactivity of the C–halogen bonds, and the more crowded \( \omega \)-carbon in the dimer has a larger back strain, which makes the dissociation of the C–halogen bond easier during rehybridization from sp3 to sp2 via the release of the steric hindrance. Similar results were also obtained in living cationic polymerization of isobutylene, where 2-chloro-2,4,4-trimethylpentane (the dimer chloride of the monomer) is more effective as an initiator than tert-butyl chloride (the unimer chloride).

(b) Effects of Added Aluminum Compounds. Coupled with 2b and RuCl2(PPh3)3, MMA was polymerized in toluene at 80 °C in the presence or absence of Al(O-i-Pr)3. Smooth polymerizations proceeded in both cases, while faster with Al(O-i-Pr)3: 48 h, 91% with Al(O-i-Pr)3; 274 h, 96% without Al(O-i-Pr)3 (Figure 4). Al(O-i-Pr)3 indeed accelerated the polymerization with 2b/RuCl2(PPh3)3, as it did in the previously reported Ru(II)-based system.4 However, there were no such effects of the added aluminum compound on the conventional radical polymerization initiated by AIBN.33 Thus, the faster polymerization is not due to the activation of monomer via possible interaction with Al(O-i-Pr)3 but is due to higher concentration of the radical species. This is probably caused by a slight shift of the equilibrium to the radical species.

As shown in Figure 5, the \( M_n \) of the obtained polymers increased with monomer conversion even in the absence
the presence or absence of Al(O-i-Pr)₃ in toluene at 80 °C: [MMA]₀ = 2.0 M; [2b]₀ = 20 mM; [RuCl₂(PPh₃)₃]₀ = 10 mM; [Al(O-i-Pr)₃]₀ = 40 mM. Key: RuCl₂(PPh₃)₃/Al(O-i-Pr)₃ (●); RuCl₂(PPh₃)₃ (○).

2. Halogen Exchange Reactions. (a) Dimer vs Unimer. We then examined the halogen exchange reaction between 2b and RuCl₂(PPh₃)₃ in the absence of MMA, which could occur via the transient radical species as in the corresponding polymerization. As shown in parts A and B of Figure 6, the methylene protons adjacent to the carbon–chlorine bond of 2a appeared as peak c1 at 2.5 ppm, which is clearly different from peak c2 of 2b (2.8 ppm). There were no changes in the spectrum of 2b at room temperature on addition of RuCl₂(PPh₃)₃ and Al(O-i-Pr)₃. When the solution was heated to 80 °C, however, new peaks corresponding to the methylene protons (c1) of 2a appeared besides those of 2b (Figure 6C). This shows the formation of the dimer chlorine via the exchange reaction between the bromine in 2b and the chlorine in RuCl₂(PPh₃)₃, and proves the reversible activation of the C–X bonds with the Ru(II) complex. The halogen exchange reaction also occurred in the absence of Al(O-i-Pr)₃ (Figure 6D).

A similar halogen exchange reaction was examined between 1b and RuCl₂(PPh₃)₃. As shown in parts A and B of Figure 7, the chemical shift of the methyl protons (b1) of 1a is different from that of 1b. Addition of RuCl₂(PPh₃)₃ into a solution of 1b followed by heating to 80 °C led to the formation of the chlorine-unimer (1a) similarly to the reaction for the dimer though the amount of the chloride seemed smaller.

The rates of the halogen exchange process of the unimer and the dimer were thus compared. Figure 8
plots the contents of the chlorides generated via the halogen exchange reaction between R−Br and RuCl2(PPh3)3 in toluene-d8 at 80 °C: [R−Br]/0 = 20 mM; [RuCl2(PPh3)3]0 = 10 mM. R−Br: 2b (○); 1b (∆).

Figure 9. Contents of R−Cl in the halogen exchange reaction between 2b and RuCl2(PPh3)3 in the presence or absence of Al(O-i-Pr)3 in toluene-d8 at 80 °C: [2b]/0 = 20 mM; [RuCl2(PPh3)3]/0 = 10 mM; [Al(O-i-Pr)3]0 = 0 or 40 mM. Key: 2b/RuCl2(PPh3)3 (○); 2b/RuCl2(PPh3)3/Al(O-i-Pr)3 (∆).

plots the contents of the chlorides generated via the exchange reactions. The mole ratios of 2a and 1a were determined from the peak intensity ratios Cl/(C1 + C2) in Figure 6 and b1/(b1 + b2) in Figure 7, respectively. The halogen exchange of 1b was much slower than that of 2b. This comes from the stronger carbon−halogen bond in 1b than in 2b, which agrees with the slower initiation from 1b than from 2b in the polymerizations. The NMR analysis also shows no side reactions such as radical coupling at least within 5 h.

(b) Effects of Al(O-i-Pr)3. The effect of the added Al(O-i-Pr)3 on the halogen exchange was then examined. Figure 9 compares the contents of the chloride-terminal for mixtures of 2b and RuCl2(PPh3)3 in the absence and presence of Al(O-i-Pr)3. In contrast to the acceleration of the polymerization on addition of Al(O-i-Pr)3, there were no effects of Al(O-i-Pr)3 on the halogen exchange reaction. These indicate that the added aluminum compound does not work in the bond-breaking process of the carbon−halogen bond but in the polymerization.

As described above, the added Al(O-i-Pr)3 most likely accelerates the exchange reaction between the dormant and the active species as well as the propagation. On the other hand, the halogen exchange is not affected by the additive. If the two exchange reactions occur via exactly the same process, these two results are contradictory to each other. Therefore, the simple equilibrium shown in Scheme 1 cannot fully explain these results. If it is assumed that the halogen exchange occurs via an inner-sphere activated species or a radical bound in the Ru coordination sphere34 and that the propagation mainly proceeds via a radical species out of the sphere (k p1 ≪ k p2), these two apparently inconsistent results could be explained (Scheme 2). For the proposed mechanism, the halogen exchange rate is only dependent on k p1 and k p2, and the polymerization rate and MWDs are mainly regulated by k p2, k p1, and k k2. The added aluminum compound most probably affects the latter exchange reaction, i.e., that between the inner- and outer-sphere species.

Another possibility is the formation of a new complex from Al(O-i-Pr)3 and RuCl2(PPh3)3, which has larger k p2 and k p1 but similar k p1 and k p2, although it is less plausible in view of the absence of changes in the NMR spectrum on mixing.33 The effects of the added aluminum compound are under further investigation with the use of cyclic voltammetry (CV) as well as NMR.

Conclusions

Four model compounds (1a−2b) for the dormant species of poly(MMA) with C−Cl or C−Br terminal, unimer and dimer halides, were employed for the RuCl2(PPh3)3-mediated living radical MMA polymerization in the presence of Al(O-i-Pr)3. The polymerization rates were almost independent of the initiators, whereas the Mn and MWDs of the obtained polymers were dependent: Narrower MWDs were obtained with the dimer and with the bromide. This is due to the differences in the reactivity of the C−halogen bonds as suggested by the halogen exchange reactions between the initiators and RuCl2(PPh3)3. The added Al(O-i-Pr)3 proved effective in accelerating the polymerization and narrowing the MWDs, however, had no effects on the rate of the halogen exchange reaction.

Experimental Section

Materials. MMA (Tokyo Kasei; purity >99%) was dried overnight over calcium chloride and distilled twice over calcium hydride under reduced pressure before use. RuCl2(PPh3)3 (Merck; purity >99%) and Al(O-i-Pr)3 (Aldrich; purity >99.99%) were used as received and handled in a glovebox under a moisture- and oxygen-free argon atmosphere (H2O < 1 ppm; O2 < 1 ppm). Ethyl 2-bromoisobutyrate (1b) (Tokyo Kasei; >98%) was purified by distillation over calcium hydride under reduced pressure. Toluene (solvent) and n-octane (internal standard for gas chromatography) were dried overnight over calcium chloride, distilled twice over calcium hydride, and bubbled with dry nitrogen for more than 15 min immediately before use.

Synthesis of Initiator 1a. Methyl 2-chloroisobutyrate (2a) was synthesized as follows: Methyl 2-hydroxyisobutyrate (25 mL, 21.6 mmol) was added into a slurry of phosphorus pentachloride (58.6 g, 28.1 mmol) and calcium carbonate (21.7 g, 21.7 mmol) in 100 mL of dry chloroform at 0 °C. The mixture was stirred for 10 min and then filtered. The filtrate was diluted with diethyl ether and washed with distilled water three times and evaporated under reduced pressure to give 1a. The initiator 1a was purified by distillation over calcium hydride under reduced pressure (yield = 2.1%).

Synthesis of Initiator 2a. Dimethyl 2-chloro-2,4,4-trimethylglutarate (2a) was synthesized from dimethyl 2,2-dimethyl-4-(methylpentanediolato) [CH3;CO(Me)2]CH2C(CO2Me)=CH2], which was prepared as in the literature.35 MMA (200 mL, 190 mmol), dimethyl 2,2-azobis(isobutyrate)
(2.0 g, 8.7 mmol) and bis(boron difluorodiphenylglyoximato) cobalt(II) (0.50 g, 1.8 mmol) were stirred in 200 mL of 2-butanol at 75 °C for 24 h. The produced unsaturated dimer was purified by distillation. This dimer (180 mL) was then hydrogenated by Palladium-activated carbon (ca 10 g) in 180 mL of ethanol at room temperature for 8 h to give dimethyl 2,2,4,4-trimethylglutarate as a brown oil. The crude product was then concentrated to ca. 60 mL, and recrystallized at 78 °C with stirring overnight. The mixture was allowed rise to ambient temperature with stirring for 2 h. Volatile substances were removed by evaporation and the resultant solution was diluted with ether (100 mL), and treated with water (200 mL). The aqueous layer was extracted with ether (100 mL), and then three times with aqueous solutions of sodium carbonate (100 mL each), and then three times with deionized water (200 mL) and evaporated under reduced pressure to give dimethyl 2-chloro-2,4,4-trimethylglutarate as a brown oil. The crude product was then diluted with 300 mL of n-hexane treated with activated carbon, concentrated to ca. 60 mL, and recrystallized at −30 °C. The pure product was obtained by several recrystallizations from n-hexane as white needles (yield = 33%): λ NMR (500.16 MHz, CDCl3) δ 11.6 (s, 3H, CHi), 1.22 (s, 3H, CH3), 1.71 (s, 3H, CH3) 2.56 (m, 2H, CH2), 3.68 (s, 3H, CO2CH3), 3.78 (s, 3H, CO2CH3); 13C NMR (125 MHz, CDCl3) δ 25.4, 25.6, 28.4, 41.7, 50.3, 51.9, 53.0, 67.1, 171.9, 177.5.

Living Polymerization. The polymerization was carried out under dry nitrogen in baked and sealed glass tubes. All reagents were used after ordinary purifications, and the toluene solvent was bubbled with dry nitrogen for more than 15 min immediately before use. A typical example with 2b is given below. In a 50 mL round-bottomed flask was placed RuCl3(PPh3)3 (92.0 mg), and toluene (3.86 mL), n-octane (0.384 mL), MMA (100 mL), solutions of Al(O-i-Pr)3 (250 mg, toluene, 3.07 mL), and solutions of 2b (800 mM in toluene, 0.240 mL) were added sequentially in this order at room temperature under dry nitrogen. The total volume of the reaction mixture was thus 9.60 mL. Immediately after mixing, aliquots (1.20 mL each) of the solution were injected into baked glass tubes, which were then sealed and placed in an oil bath kept at 80 °C. In predetermined intervals, the polymerization was terminated by cooling the reaction mixture was maintained at 78 °C. The resulting solution was transferred to a test tube, and evaporated to dryness to give the products, which were subsequently vacuum-dried overnight.

Polymer Characterization. The Mn, Mw/Mn, and MWD of the polymers were determined by size-exclusion chromatography in chloroform at 40 °C on the three poly styrene gel columns (Shodex K-805L × 3) that were connected to a J asco PU-980 precision pump and a J asco RI-930 refractive index detector. The columns were calibrated against 11 standard poly(MMA) samples (Polymer Laboratories; Mn = 630–120000, Mw/Mn = 1.04–1.22) as well as the monomer.

Halogen Exchange Reaction. A typical example of a halogen exchange reaction with 2b is given below. Solutions of 2b (0.20 mL of 80 mM, 0.016 mmol), RuCl3(PPh3)3 (0.40 mL of 20 mM, 0.0080 mmol) and Al(O-i-Pr)3 (0.20 mL of 160 mM, 0.032 mmol) in toluene-d8 were mixed in a sample vial under a moisture- and oxygen-free argon atmosphere at room temperature. The mixture was sealed in an NMR tube and then heated to 80 °C in the NMR probe. 1H NMR spectra were recorded on a JEOL JNM-LA500 spectrometer in toluene-d8 at 80 °C, operating at 500.16 MHz. The main parameters were as follows: spectral width = 10000 Hz (19.99 ppm), pulse width = 6.20 μs (45°), acquisition time + pulse delay = 12.0 s, data points = 32768, number of transients = 4 (1.0 min for one spectrum). The probe temperature was regulated with a variable temperature apparatus (temperature fluctuation ≤ 0.1 deg). The spectra were obtained in predetermined intervals, and the halogen-exchange ratios were determined from the peak intensity ratios of the signal of the bromine compound and that of the produced chlorine compound.

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