Radical (Co)polymerization of Vinyl Chloroacetate and *N*-Vinylpyrrolidone Mediated by Bis(acetylacetonate)cobalt Derivatives

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ABSTRACT: The effect of the electron-withdrawing groups on the ligand in a series of bis(acetylacetonate)-cobalt(II) derivatives, $Co(R^1COCH{=}COR^2)_2$ ($R^1 = R^2 = CH_3$ (**1**), $R^1 = CF_3$, $R^2 = CH_3$ (**2**), $R^1 = R^2 = CF_3$ (**3**)), was examined by conducting a controlled radical polymerization of vinyl chloroacetate (VClOAc) and *N*-vinyl-2-pyrrolidone (NVP) under the same reaction conditions. Complex **2** provided better control over the polymerization of VClOAc than complex **1**, resulting in the preparation of a poly(VClOAc) with M_n closer to the theoretical M_n and lower polydispersity at the same monomer conversion. On the other hand, complex **3** was not able to control the radical polymerization of VClOAc. In the case of NVP, only complex **1** produced poly(NVP) with relatively low polydispersity (1.7−2.0). Better control over M_n and polydispersity in the polymerization of VClOAc and NVP was achieved by addition of vinyl acetate (VOAc) to the reaction. The $M_n/M_{n,th}$ and polydispersity of the copolymers became lower as the initial proportion of VOAc in both copolymerization systems was increased. The VOAc content of the poly(VClOAc-*co*-VOAc) and poly(NVP-*co*-VOAc) copolymers calculated from ^1H NMR spectra were in good agreement with the values calculated from monomer reactivity ratios.

Introduction

Recent progress in controlled radical polymerization (CRP)[1,2] processes enables synthesis of various well-defined polymer structures in a controlled fashion. Three different CRP mechanisms have been extensively investigated (Scheme 1).[3] The first mechanism (eq 1) is based on a spontaneous reversible homolytic cleavage of a dormant chain end and is exemplified by nitroxide-mediated polymerization (NMP)[4] or cobalt-mediated radical polymerization (CMRP).[5−10] The second process (eq 2) involves a catalytic reversible homolytic cleavage of a carbon−halogen bond via a redox process, which occurs in atom transfer radical polymerization (ATRP).[11−15] The third (eq 3) is based on a thermodynamically neutral bimolecular exchange between propagating radicals and a dormant species. Degenerative transfer (DT) polymerization with alkyl iodides[16,17] or organostilbene species[18] belongs in this category as well as reversible addition−fragmentation chain transfer (RAFT)[19] polymerization and macromolecular architecture design by interchange of xanthates (MADIX).[20]

The exchange polymerization techniques—DT, RAFT, or MADIX—are the most promising CRP processes for conducting a successful controlled polymerization of unconjugated vinyl monomers, such as vinyl acetate (VOAc) and *N*-vinyl-2-pyrrolidone (NVP). In the case of NMP, it is difficult to control the bond homolysis of VOAc-nitroxide bond because this bond is thermally stable under NMP conditions.[21−23] In the case of ATRP, the application of an iodide system is the best approach to achieve dissociation of the dormant species mediated by a metal complex because the bond strength of the VOAc−iodide bond (35 kcal/mol) is significantly lower than the corresponding chloride (69 kcal/mol) and bromide (60 kcal/mol) in dormant species.[24] However, copper-mediated ATRP of VOAc has not yet been successful due to the small ATRP equilibrium constant ($K_{eq} = k_{act}/k_{deact}$) caused by the poor iodophilicity of copper.

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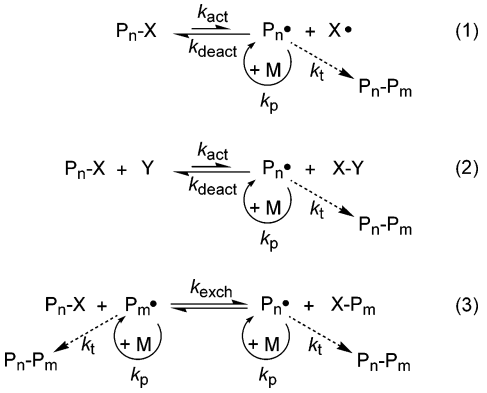
Scheme 1. Three General Mechanisms for Controlled/"Living" Radical Polymerization



Nevertheless, iron-mediated ATRP of VOAc could be carried out; however, the polydispersity of the resulting polymer increased with conversion from 1.3 to 2.1, suggesting inefficient deactivation of the growing polymer radical.[25] In contrast, alkyl iodides,[17] dithiocarbamates,[26] and xanthates[27] can establish an efficient equilibrium between the propagating radical and these compounds. Consequently, poly(VOAc) with molecular weight relatively close to the predicted value and low polydispersity was formed.

A successful CMRP of VOAc was previously reported.[8,9,28] The CMRP was initiated with 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) in the presence of the bis(acetylacetonate)cobalt(II) complex **1**, resulting in the formation of poly(VOAc) with predetermined M_n and low polydispersity. The general scheme for CMRP is illustrated in Scheme 2. In the initiation step, the organic radical created by the decomposition of V-70 reacts with monomer. The generated radical propagates. Meanwhile, the cobalt(II) complex **1** can react with the propagating polymer radical to produce dormant species in the deactivation step. A spontaneous homolytic cleavage of a

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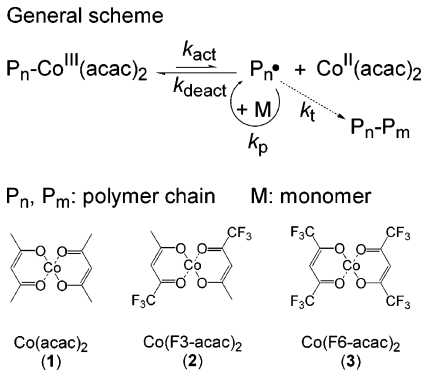
Scheme 2. General Scheme for Cobalt-Mediated Radical Polymerization (CMRP) and Molecular Structures of Bis(acetylacetonate)cobalt(II) Derivatives



dormant chain end reproduces a polymer radical and a complex **1** in the activation step. The overall radical concentration in the polymerization system becomes lower when k_{deact} is much larger than k_{act}. Thus, efficient trapping of the VOAc radical by complex **1** is the main requirement to establish the equilibrium between the cobalt-terminated poly(VOAc) and propagating poly(VOAc) radicals.

Recently, we reported on the effect of electron-withdrawing groups on a series of bis(acetylacetonate)cobalt complexes, Co(R^1COCH═COR^2)$_2$ ($R^1 = R^2 = CH_3$ (**1**), $R^1 = CF_3$, $R^2 = CH_3$ (**2**), $R^1 = R^2 = CF_3$ (**3**)) on a CMRP of VOAc initiated with V-70 (Scheme 2).[28] Cobalt complexes **1** and **3** performed differently in a CMRP of VOAc, indicating that the electronic effect of substituents on the ligand could change the reactivity of the cobalt complex toward the VOAc radical. In this report, we discuss expanding the application of these complexes to the other nonconjugated vinyl monomers such as vinyl chloroacetate (VClOAc) and NVP. The copolymerization of nonconjugated vinyl monomers and VOAc mediated by bis(acetylacetonate)-cobalt(II) derivatives are also discussed in order to investigate the role of a terminal VOAc radical in the copolymerization systems.

Experimental Section

Characterization. Monomer conversion of vinyl chloroacetate (VClOAc), *N*-vinyl-2-pyrrolidone (NVP), and vinyl acetate (VOAc) was determined by gas chromatography (GC) using a Shimadzu GC 14-A gas chromatograph equipped with a FID detector and ValcoBond 30 m VB WAX Megabore column. Toluene or *p*-dimethoxybenzene was used as an internal standard for GC. Molecular weight and molecular weight distribution of the poly-(VClOAc), poly(NVP), and copolymers were measured by gel permeation chromatography (GPC) with PSS columns (styrogel 10^5, 10^3, 10^2 Å) and RI detector. GPC for poly(VClOAc) and poly-(VClOAc-*co*-VOAc) was performed using THF as eluent at a flow rate of 1 mL/min at 35 °C. Molecular weights and polydispersity indices of the poly(VClOAc) and poly(VClOAc-*co*-VOAc) were determined relative to linear polystyrene calibration standards using toluene as an internal standard. GPC for poly(NVP) and poly(NVP-*co*-VOAc) was carried out using 0.05 mol/L LiBr solution of DMF as eluent at a flow rate of 1 mL/min at 50 °C. Molar masses and molecular weight distributions of the poly(NVP) and poly(NVP-*co*-VOAc) were determined relative to linear poly(methyl methacrylate) calibration standards using toluene as an internal standard. The ^{1}H NMR spectrum of the copolymers was examined at 30 °C using a Bruker 300 MHz spectrometer with a delay time of 2 s. Deuterated chloroform was used as the solvent for poly(VClOAc-*co*-VOAc), and *N*,*N*-dimethylformamide-d_7 was used as the solvent for poly(NVP-*co*-VOAc).

Materials. Nitrogen was purified by passing through a column of anhydrous calcium sulfate. Vinyl chloroacetate (Lancaster, >99%) was dried over calcium hydride, distilled under vacuum, and degassed with nitrogen. *N*-Vinyl-2-pyrrolidone (Aldrich, >99%) was deoxygenated by nitrogen prior to use. Vinyl acetate (Aldrich, >99%) was passed through a neutral alumina column to remove stabilizer, dried over calcium hydride, distilled under reduced pressure, and degassed with nitrogen. Toluene (Fisher Scientific, >99%) was distilled over sodium/benzophenone and degassed with nitrogen. Anisole/toluene (9/1 v/v) was stored with molecular sieves after deoxygenation by nitrogen. Bis(acetylacetonate)cobalt(II) (Co-(acac)$_2$; Acros, 99%), bis(trifluoro-2,4-pentanedionato)cobalt(II) (Co(F3-acac)$_2$; TCI), bis(hexafluoro-2,4-pentanedionato)cobalt(II) (Co(F6-acac)$_2$; Alfa Aesar, 97%), 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70; Wako, 96%), and *p*-dimethoxybenzene (Aldrich, 99%) were used as received.

Polymerization of VClOAc with Cobalt Complexes Initiated by V-70. Generally, polymerization was conducted using standard Schlenk techniques. Monomers were deoxygenated by bubbling with nitrogen for 30 min prior to addition to the reaction flask. *p*-Dimethoxybenzene (100 mg), Co(F3-acac)$_2$ (48.2 mg, 1.32×10^{-4} mol), and V-70 (40.6 mg, 1.32×10^{-4} mol) were placed in a Schlenk flask (25 mL) equipped with a magnetic stirring bar at room temperature. This flask was evacuated in a vacuum with cooling in a liquid nitrogen bath and backfilled with nitrogen. This process was repeated three times with cooling. To this flask, VClOAc (4.0 mL, 3.95×10^{-2} mol) was added, and resulting mixture was stirred at room temperature (forming a red solution). After taking an initial sample for GC, the polymerization was started by heating at 30 °C. Samples were taken periodically by a syringe to follow the kinetic of the polymerization process. After 17 h, the stirring bar stopped spinning due to the high viscosity of polymerization medium. The samples were diluted with toluene prior to analysis by GC. After GC measurement, the solvent for the samples was changed to THF for GPC.

Polymerization of NVP in the Presence of Cobalt Complexes Initiated by V-70. Standard Schlenk techniques were used to conduct the polymerization. Solvent and monomers were deoxygenated by bubbling with nitrogen for 30 min prior to the experiments. Co(acac)$_2$ (14.5 mg, 5.61×10^{-5} mol) and V-70 (17.2 mg, 5.61×10^{-5} mol) were placed in a Schlenk flask (25 mL) equipped with a magnetic stirring bar at room temperature. This flask was evacuated under vacuum with cooling in a liquid nitrogen bath and backfilled with nitrogen. This process was repeated three times with cooling. To this flask, the mixed solvent (3.0 mL, anisole/toluene = 9/1 (v/v)) and NVP (3.0 mL, 2.81×10^{-2} mol) were added, and the resulting mixture was stirred at room temperature (purple solution). After taking an initial sample for GC, the reaction was started by heating at 30 °C. Samples were taken periodically by a syringe to follow the kinetic of the polymerization process. After 7 h, the stirring bar stopped spinning due to the high viscosity of polymerization medium. The samples were diluted with 0.05 mol/L LiBr solution of DMF prior to analysis by GC and GPC.

Copolymerization of VClOAc and VOAc Mediated by Co(F3-acac)$_2$ with V-70. The general procedure was similar to that employed for the polymerization of VClOAc. In the case of the copolymerization with 20% VOAc in the initial feed, Co(F3-acac)$_2$ (52.6 mg, 1.44×10^{-4} mol) and V-70 (44.5 mg, 1.44×10^{-4} mol) were placed in a Schlenk flask (25 mL). After the deoxygenation by the vacuum/nitrogen exchange process, toluene (0.2 mL), VOAc (0.8 mL, 8.68×10^{-3} mol), and VClOAc (3.5 mL, 3.46×10^{-2} mol) were added to the flask. The samples were diluted with acetone prior to the analysis by GC. Then the solvent for the samples was changed to THF for GPC. After 17 h, the reaction mixture was poured into hexane (300 mL), and the precipitate was filtrated, washed with hexane, and dried under reduced pressure at 60 °C.

Copolymerization of NVP and VOAc Mediated by Co(acac)$_2$ with V-70. The general procedure was similar to that of the polymerization of NVP. In the case of the copolymerization with 20% VOAc in the initial feed, Co(acac)$_2$ (15.0 mg, 5.83×10^{-5} mol) and V-70 (18.4 mg, 5.97×10^{-5} mol) were placed in a 25 mL Schlenk flask. After the deoxygenation by the vacuum/nitrogen exchange process, the mixed solvent (3.0 mL, anisole/toluene =

Table 1. Results for Bulk Polymerization of VClOAc Initiated with V-70 in the Presence of Cobalt Complex at 30 °C[a]

cobalt complex	time [h]	conv[b] [%]	$M_n \times 10^{-3}$ (GPC)[c]	$M_{n,th} \times 10^{-3}$[d]	$M_n/M_{n,th}$	M_w/M_n[c]
1	1	4.8				
	2	5.9				
	3	18.1	19.2	6.7	2.87	1.74
	4.4	26.4	23.4	9.7	2.41	1.90
	6	39.1	25.7	14.3	1.80	2.11
	7.5	49.2	27.8	17.9	1.55	2.17
2	1	5.1				
	3	5.5				
	5	5.7				
	7	14.3	8.9	5.3	1.68	1.71
	9	22.0	12.1	8.1	1.49	1.75
	13	38.3	16.4	14.0	1.17	1.87
	17	55.1	22.2	20.1	1.10	1.95
3	0.5	10.7	37.7	4.0	9.43	1.88
	1	28.4	39.4	10.4	3.79	2.03
	1.5	41.7	35.8	15.2	2.36	2.15

[a] Polymerization conditions; VClOAc = 4.0 [mL], *p*-Ph(OMe)$_2$ = 100 [mg] was used as an internal standard for GC, $[VClOAc]_0/[Co]_0/[V\text{-}70]_0 = 300/1/1$. [b] Conversion was measured by GC. [c] M_n and M_w/M_n were determined on the basis of polystyrene standard calibration. [d] $M_{n,th}$ was calculated by the following equation: $M_{n,th} = 140.2 + (\text{conv}) \times 300 \times 120.54$.

9/1 (v/v)), VOAc (0.54 mL, 5.86×10^{-3} mol), and NVP (2.5 mL, 2.34×10^{-2} mol) were added to the flask. The samples were diluted with 0.05 mol/L LiBr solution in DMF prior to analysis by GC and GPC. After 24 h, the reaction mixture was poured into diethyl ether (200 mL), and the precipitate was filtrated, washed with ether, and dried under reduced pressure at room temperature.

Results and Discussion

Effect of Electron-Withdrawing Groups on CMRP of VClOAc Initiated with V-70. As reported recently, the CMRP of VOAc with complexes **1** and **2** proceeded in controlled manner, whereas complex **3** could not mediate the radical polymerization of VOAc presumably due to the much lower trapping efficiency of a VOAc radical by complex **3**.[28] This inefficient deactivation of the VOAc radical by complex **3** was caused by electron-withdrawing groups on the ligand. Therefore, the deactivation efficiency of a complex is related to the affinity between the propagating radical and the specific cobalt complex. VClOAc was employed instead of VOAc in order to examine changes in the electronic affinity of monomer radical. Indeed, the electron-withdrawing effect of chloromethyl acetate group in VClOAc changes the reactivity of VClOAc radical to cobalt complexes relative to that of VOAc radical. Therefore, the deactivation efficiency of cobalt complexes **1**−**3** in the presence of a VClOAc radical was systematically investigated under the same reaction conditions. It should be noted that chloromethyl acetate groups of VClOAc can act as a chain transfer agent in a radical polymerization. Therefore, a bulk polymerization of VClOAc, without cobalt complex, initiated with V-70 ($[VClOAc]_0/[V\text{-}70]_0 = 1000$) was initially performed. The M_n of resulting polymer was in the range 30 000−40 000, suggesting that 40 000 is the maximum M_n from a standard radical polymerization of VClOAc presumably due to chain transfer to chloromethyl groups in monomer and/or polymer. This result demonstrated that these reactions are less important for the targeted molecular weight less than 40 000. Accordingly, the initial molar ratio of VClOAc to cobalt was set at 300, and 1 equiv of V-70 to cobalt was employed as the initiator. The results obtained are presented in Table 1.

Figure 1 shows the semilogarithmic kinetic plots for bulk polymerization of VClOAc initiated with V-70 in the presence of cobalt complex. One of the main differences between VOAc and VClOAc polymerization systems is the length of the induction period. Radicals are constantly forming by the decomposition of V-70 during the induction period. If the radicals efficiently react with complex **2** and k_{act} is much smaller than k_{deact}, the concentration of radicals should be small, resulting in both the efficient formation of dormant species and the induction period. The concentration of radicals depends on the k_{act}/k_{deact} ratio: the lower the k_{act}/k_{deact} ratio, the longer induction period. Accordingly, the longer induction period indicates the better control over polymerization.

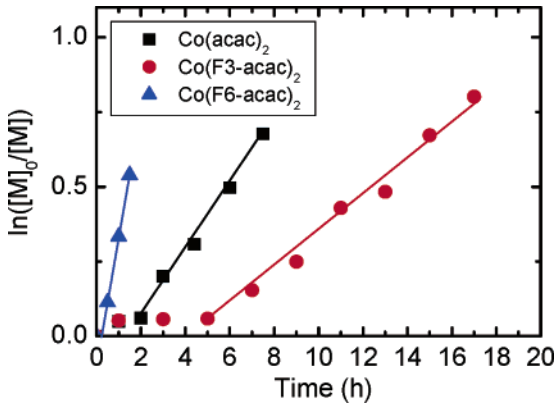


Figure 1. Semilogarithmic kinetic plots for bulk polymerization of VClOAc initiated with V-70 in the presence of cobalt complex at 30 °C: (■) Co(acac)$_2$ (**1**), (●) Co(F3-acac)$_2$ (**2**), (▲) Co(F6-acac)$_2$ (**3**), $[VClOAc]_0/[Co]_0/[V\text{-}70]_0 = 300/1/1$.

In the case of complexes **1** and **2**, the semilogarithmic kinetic plots follow first order after a certain induction period (Figure 1). The induction period for complex **2** (∼5 h) was longer than that with complex **1** (∼2 h), indicating that deactivation efficiency of **2** is higher than of **1**. In addition, the rate of monomer consumption observed for **2** was slower than for **1**, supporting the better deactivation efficiency of **2**. The reaction medium was heterogeneous during the polymerization in the case of polymerizations with complex **1**, whereas complex **2** was completely soluble in VClOAc monomer. Accordingly, the poor solubility of **1** might lead to its less efficient deactivation. However, the induction periods observed for **1** and **2** were shorter than those of VOAc polymerization (>10 h), suggesting that the trapping of VOAc radical was more efficient than that of the VClOAc radical by both complexes. In contrast, no induction period was observed in the case of complex **3**, as was the case of VOAc polymerization, suggesting no deactivation of VClOAc radical. The cobalt(II) radical of complex **3** may be stabilized by the strong electron-withdrawing effect originating from four CF_3 groups. Also, larger steric effects in **3** may destabilize dormant species.

The evolution of M_n and M_w/M_n, as a function of monomer conversion, is shown in Figure 2. A theoretical line ($M_{n,th}$) was calculated on the basis of the assumption that the number of polymer chains corresponds to number of cobalt complexes. The M_n of poly(VClOAc) increased with conversion in the case of **1** and **2**. Moreover, the values of $M_n/M_{n,th}$ and polydispersities of poly(VClOAc) prepared with **2** were lower, relative to those obtained by **1** at the same conversion (∼40%) (Table 1). This result indicates the better performance of **2** at controlling M_n and M_w/M_n. On the other hand, the M_n of poly(VClOAc) formed with **3** remained in the range 35 000−40 000, and polydispersity was higher, similar to those observed in the conventional radical polymerization of VClOAc. Figure 3 shows GPC traces of samples of poly(VClOAc) produced by complex **2** as the reaction progressed. All of the GPC curves display a monomodal

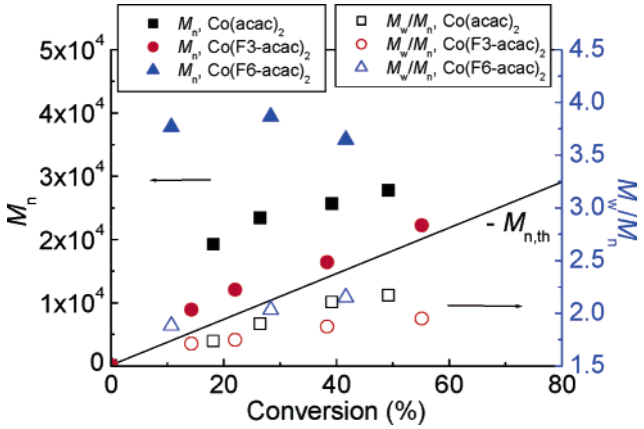


Figure 2. Evolution of M_n and M_w/M_n vs conversion for bulk polymerization of VClOAc initiated with V-70 in the presence of cobalt complex at 30 °C: (■, □) Co(acac)$_2$ (**1**), (●, ○) Co(F3-acac)$_2$ (**2**), (▲, Δ) Co(F6-acac)$_2$ (**3**), $[VClOAc]_0/[Co]_0/[V\text{-}70]_0 = 300/1/1$.

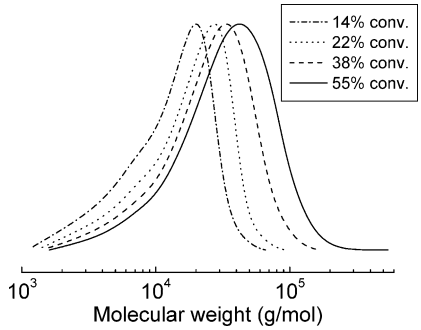


Figure 3. GPC traces of poly(VClOAc) prepared with **2** at 30 °C: $[VClOAc]_0/[\mathbf{2}]_0/[V\text{-}70]_0 = 300/1/1$.

shape, although a small tailing can be observed at the lower molecular weight region. In conclusion, complex **2** was the best complex for mediating the radical polymerization of VClOAc in terms of the lowest $M_n/M_{n,th}$ and lowest polydispersity among the three bis(acetylacetonate)cobalt(II) derivatives examined.

Copolymerization of VClOAc and VOAc Mediated by Complex 2 with V-70. Better control over the copolymerization of *n*-butyl acrylate (*n*BA) and VOAc mediated by **1** was accomplished when a higher molar ratio of VOAc was employed.[28] In that case, the k_p/k_{deact} ratio of a CMRP of *n*BA mediated by the complex **1** was much higher than that for VOAc. Therefore, a significantly higher efficiency of deactivation resulting from the reaction of a VOAc chain-end radical with complex **1** allowed better control over the CMRP of *n*BA. Although complex **2** was the best catalyst for radical polymerization of VClOAc among **1**−**3**, the polydispersity of resulting poly(VClOAc) was still in the range 1.7−2.0 (Table 1). Therefore, copolymerizations of VClOAc and VOAc (20% and 50% VOAc in the initial feed) mediated by **2** were conducted in order to achieve the lower polydispersity, as observed in the copolymerization of *n*BA and VOAc.

Figure 4 displays the semilogarithmic kinetic plots of the copolymerizations of VClOAc and VOAc. A longer induction period emerged as the initial proportion of VOAc in the reaction increased, as was the case of copolymerization of *n*BA and VOAc. In addition, the rate of VClOAc consumption in copolymerization was a second order with time, and the rate became slower with increasing the initial molar ratio of VOAc. These data show the higher deactivation efficiency of a VOAc chain-end radical with complex **2**.

The evolution of M_n and M_w/M_n vs total conversion is presented in Figure 5. The theoretical M_n ($M_{n,th}$) was based on

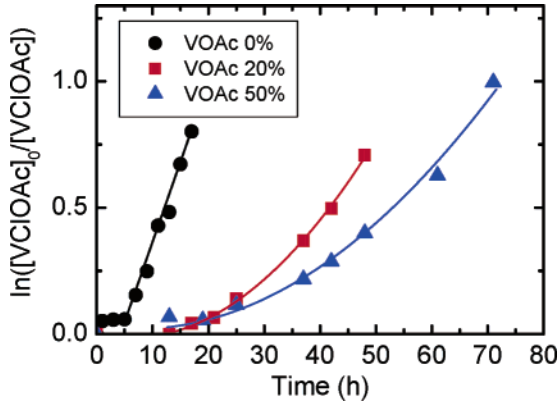


Figure 4. Semilogarithmic kinetic plots of VClOAc in bulk copolymerization of VClOAc and VOAc mediated by **2** with V-70 at 30 °C: (●) $[VClOAc]_0/[Co]_0/[V\text{-}70]_0 = 300/1/1$, (■) $[VClOAc]_0/[VOAc]_0/[Co]_0/[V\text{-}70]_0 = 240/60/1/1$, (▲) $[VClOAc]_0/[VOAc]_0/[Co]_0/[V\text{-}70]_0 = 150/150/1/1$.

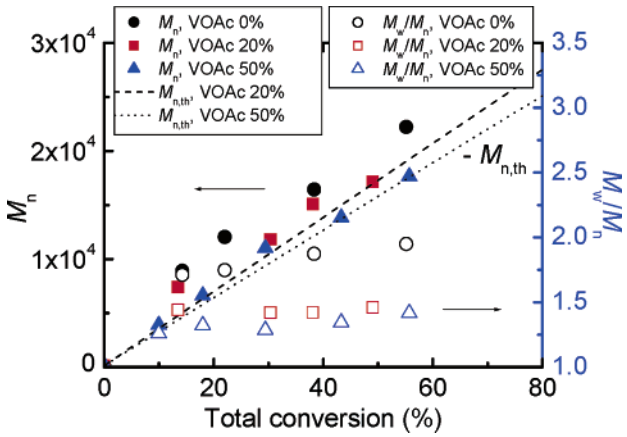


Figure 5. Evolution of M_n and M_w/M_n vs total conversion for bulk copolymerization of VClOAc and VOAc mediated by **2** with V-70 at 30 °C: (●, ○) $[VClOAc]_0/[Co]_0/[V\text{-}70]_0 = 300/1/1$, (■, □) $[VClOAc]_0/[VOAc]_0/[Co]_0/[V\text{-}70]_0 = 240/60/1/1$, (▲, Δ) $[VClOAc]_0/[VOAc]_0/[Co]_0/[V\text{-}70]_0 = 150/150/1/1$.

the assumption that the number of polymer chains corresponds to number of cobalt complexes. Furthermore, $M_{n,th}$ could be simulated on the basis of the monomer reactivity ratios ($r_{VClOAc} = 1.18$ and $r_{VOAc} = 0.80$) reported previously.[29] The M_n of the copolymers increased monotonically with total conversion along the theoretical lines in both cases. Furthermore, the polydispersity of the copolymers decreased to 1.4 as the initial proportion of VOAc in the copolymerization was increased. This indicates that the degree of control over polymerization of VClOAc improved with increasing initial molar ratio of VOAc, as was the case in the copolymerization of *n*BA and VOAc.

The composition of the poly(VClOAc-*co*-VOAc) copolymers was studied by ^{1}H NMR to examine the incorporation and distribution of VOAc in the copolymer. The spectra from the final samples, obtained when initial proportion of VOAc in the copolymerization was 20% or 50%, are displayed in Figure 6. Peaks originating from both VClOAc and VOAc segments are observed in the spectra, indicating a successful copolymerization. The VOAc content of copolymers was calculated by comparison of the integrals of signals labeled $b + e$ and c in Figure 6. The peak c can be assigned to the methylene protons next to the Cl atom, and the peak $b + e$ was assignable to the total of methine protons from the polymer backbone, as depicted in Figure 6. Because the integral of peak c was 2.00, the value of integral 1.00 corresponded to 1 unit of VClOAc ($I_{VClOAc} = 1.00$). The integral of peak $b + e$ composed of sum of VOAc

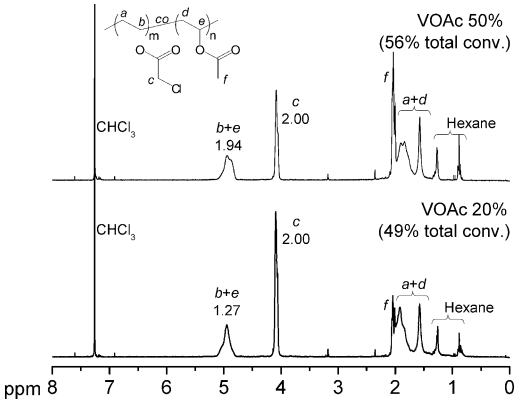


Figure 6. ^{1}H NMR spectra of poly(VClOAc-*co*-VOAc) in $CDCl_3$ at 30 °C (300 MHz): $[VClOAc]_0/[VOAc]_0/[\mathbf{2}]_0/[V\text{-}70]_0 = 240/60/1/1$ (VOAc 20%, overall conversion 49%), $[VClOAc]_0/[VOAc]_0/[\mathbf{2}]_0/[V\text{-}70]_0 = 150/150/1/1$ (VOAc 50%, overall conversion 56%).

and VClOAc units. Therefore, the values of integral corresponding to VOAc units were 0.27 ($I_{VOAc} = 1.27-1.0$, VOAc 20%) and 0.94 ($I_{VOAc} = 1.94-1.0$, VOAc 50%). Consequently, the VOAc contents in the copolymers were 21% (= 0.27/(1 + 0.27), VOAc 20%) and 49% (= 0.94/(1 + 0.94), VOAc 50%), respectively. The VOAc content can be simulated from the monomer reactivity ratios ($r_{VClOAc} = 1.18$, $r_{VOAc} = 0.80$).[29] The values are 18% at 49% overall conversion (VOAc 20%) and 47% at 56% overall conversion (VOAc 50%). These values are close to those calculated from the ^{1}H NMR study. As a result of the monomer reactivity ratios, the monomer sequence distribution of VOAc in the copolymer should be random. The resulting poly(VClOAc-*co*-VOAc) copolymers are suitable for use as multifunctional macroinitiators for a grafting-from ATRP because chloromethyl acetate groups in copolymers can act as initiators for ATRP.

Effect of Electron-Withdrawing Groups on CMRP of NVP Initiated with V-70. Poly(NVP) is hydrophilic in nature and possesses good biocompatibility. Therefore, it is a useful material for several medical applications such as a blood substitute or a drug delivery material. Moreover, only a few results have been reported on CRP of NVP.[18,30] We believe that bis(acetylacetonate)cobalt(II) derivatives are also good candidates to mediate the radical polymerization of NVP because of the success of these complexes to mediate and control the radical polymerization of VOAc. Therefore, radical polymerization of NVP, initiated with V-70 in the presence of complexes **1**−**3**, was performed under the same conditions in order to systematically examine the effect of electron-withdrawing groups on the level of control. Before using cobalt complexes **1**−**3** to mediate the reaction, a standard bulk free radical polymerization of NVP in the presence of V-70 was conducted ($[NVP]_0/[V\text{-}70]_0 = 500$). However, the polymerization medium rapidly became a gel (~30% conversion). Accordingly, 50 vol % of a mixed solvent of anisole and toluene (anisole/toluene = 9/1 (v/v)) was used to continue the polymerization beyond 30% conversion. The results are summarized in Table 2.

The kinetic plots were different from those obtained with VOAc and VClOAc (Figure 7). In the case of complex **1**, after a short induction period (~1 h), the rate of polymerization exhibited a second-order curvature with time. The polymerization was conducted until 55% conversion. The shorter induction period (~1 h) relative to that of VOAc (>10 h) suggests that the deactivation caused by the reaction of NVP radical with **1** was much slower than that for VOAc. In contrast, in the case of both complex **2** and **3** the rate of monomer consumption was

Table 2. Results for Polymerization of NVP Initiated with V-70 in the Presence of Cobalt Complex at 30 °C[a]

cobalt complex	time [h]	conv[b] [%]	$M_n \times 10^{-3}$ (GPC)[c]	$M_{n,th} \times 10^{-3}$[d]	$M_n/M_{n,th}$	M_w/M_n [c]
1	1	1.0				
	2	6.1	22.9	3.5	6.54	1.25
	3	13.5	31.7	7.6	4.17	1.37
	5	32.6	37.8	18.3	2.07	1.73
	7	55.3	59.2	30.8	1.92	1.71
2	1	16.0	35.9	9.0	3.99	2.88
	1.5	24.2	41.1	13.6	3.02	2.43
	2	31.3	37.6	17.5	2.15	2.99
	2.5	37.9	38.8	21.2	1.83	2.94
	3	44.1	50.3	24.6	2.04	2.60
3	0.5	4.6	42.5	2.7	15.7	1.88
	1	15.0	57.0	8.5	6.71	1.81
	1.5	23.4	50.6	13.1	3.86	2.03
	2	31.8	53.1	17.8	2.98	2.13
	3	44.5	57.8	24.9	2.32	2.00

[a] Polymerization conditions; NVP = 3.0 [mL], anisole/toluene (9/1 (v/v)) = 3.0 [mL], $[NVP]_0/[Co]_0/[V\text{-}70]_0 = 500/1/1$. [b] Conversion was measured by GC. [c] M_n and M_w/M_n were determined on the basis of polystyrene standard calibration. [d] $M_{n,th}$ was calculated by the following equation: $M_{n,th} = 140.2 + (conv) \times 500 \times 111.14$.

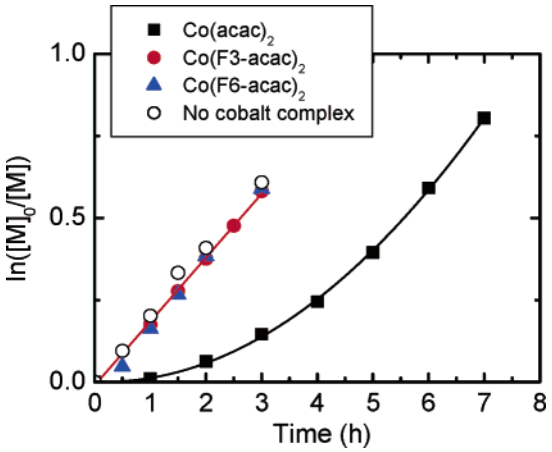


Figure 7. Semilogarithmic kinetic plots for polymerization of NVP initiated with V-70 in the presence or absence of cobalt complex at 30 °C: (■) $Co(acac)_2$ (**1**), (●) $Co(F3\text{-}acac)_2$ (**2**), (▲) $Co(F6\text{-}acac)_2$ (**3**), (○) no cobalt complex, $[NVP]_0/[Co]_0/[V\text{-}70]_0 = 500/(1or\ 0)/1$, NVP/anisole/toluene = 50/45/5 (vol %).

first order with time, with no induction period as well as the result of no cobalt complex. Therefore, these results indicate that the NVP radical is not efficiently trapped by complexes **2** and **3**. This could be due to the stabilization of the cobalt(II) radical caused by the electron-withdrawing effect of CF_3 groups or due to steric effects.

Figure 8 displays the development of M_n and M_w/M_n vs monomer conversion. A theoretical line ($M_{n,th}$) was calculated using the same methodology as for VClOAc. Although the M_n of poly(NVP) increased with conversion in all cases, the departure of M_n from $M_{n,th}$ was larger than with VOAc, particularly when the monomer conversion was less than 20%. In addition, the lowest polydispersity for poly(NVP) samples were observed in the polymerizations conducted with complex **1**. The values were in the range 1.3−1.7. These data also support a less efficient deactivation reaction between the NVP radical and **1**. As shown in Figure 9, GPC traces for poly(NVP) formed with **1** were monomodal, and the peaks shifted toward higher molecular weight. In conclusion, complex **1** was the best catalyst for mediating the radical polymerization of NVP because it provided polymers with the lowest polydispersity among **1**−**3** although it is necessary to improve the control of M_n. When

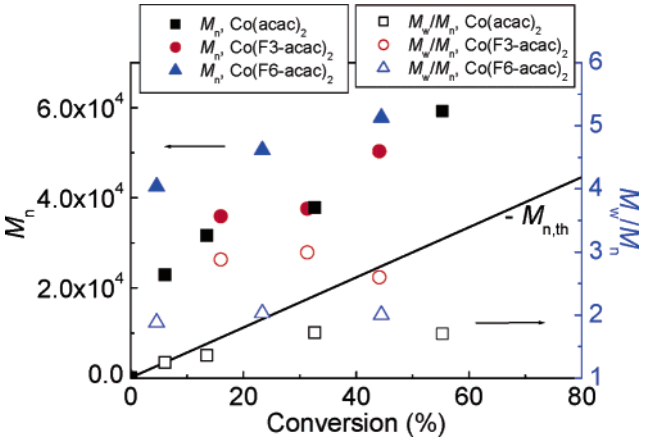


Figure 8. Evolution of M_n and M_w/M_n vs conversion for polymerization of NVP initiated with V-70 in the presence of cobalt complex at 30 °C: (■, □) Co(acac)$_2$ (**1**), (●, ○) Co(F3-acac)$_2$ (**2**), (▲, Δ) Co(F6-acac)$_2$ (**3**), [NVP]$_0$/[Co]$_0$/[V-70]$_0$ = 500/1/1, NVP/anisole/toluene = 50/45/5 (vol %).

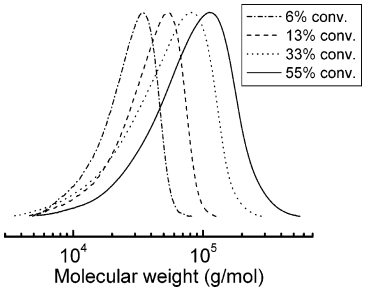


Figure 9. GPC traces of poly(NVP) prepared with **1** at 30 °C: [NVP]$_0$/[**1**]$_0$/[V-70]$_0$ = 500/1/1, NVP/anisole/toluene = 50/45/5 (vol %).

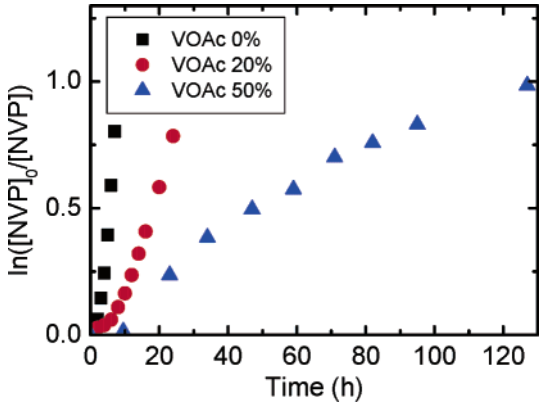


Figure 10. Semilogarithmic kinetic plots of NVP for copolymerization of NVP and VOAc mediated by **1** with V-70 at 30 °C: (●) [NVP]$_0$/[**1**]$_0$/[V-70]$_0$ = 500/1/1, (■) [NVP]$_0$/[VOAc]$_0$/[**1**]$_0$/[V-70]$_0$ = 400/100/1/1, (▲) [NVP]$_0$/[VOAc]$_0$/[**1**]$_0$/[V-70]$_0$ = 250/250/1/1, monomer/anisole/toluene = 50/45/5 (vol %).

0.5 equiv of V-70 to complex **1** was used as the initiator, the same degree of control of M_n as with 1 equiv of V-70 was observed, presumably due to the inefficient deactivation and/or faster propagation of NVP radical as compared to deactivation.

Copolymerization of NVP and VOAc Mediated by Complex 1 with V-70. To obtain better control over M_n in a CMRP of NVP, the copolymerizations of NVP and VOAc mediated by complex **1** and initiated with V-70 were carried out. Kinetic plots for NVP consumption during the copolymerizations of NVP and VOAc are presented in Figure 10. As expected, the rate of NVP consumption was slower, and the induction period became longer as the proportion of VOAc in the copolymerization increased. This is due to the more efficient deactivation resulting from the reaction of VOAc-terminated polymer radical with **1**. Figure 11 shows the evolution of M_n and M_w/M_n for the copolymers vs total conversion. The $M_{n,th}$ was calculated on the basis that the number of polymer chains corresponds to number of cobalt complexes and that the monomer reactivity ratios (r_{NVP} = 3.75, r_{VOAc} = 0.28) were the same as those reported previously.[31] The M_n of the copolymers increased with total conversion, and the departure of M_n from $M_{n,th}$ became much smaller than that seen in the homopolymerization. This indicated 20% of VOAc was sufficient to provide control over the molecular weight of the copolymers. However, the M_w/M_n of the copolymers did not decrease significantly with increasing molar ratio of VOAc. All GPC traces for resulting copolymers showed monomodal shapes.

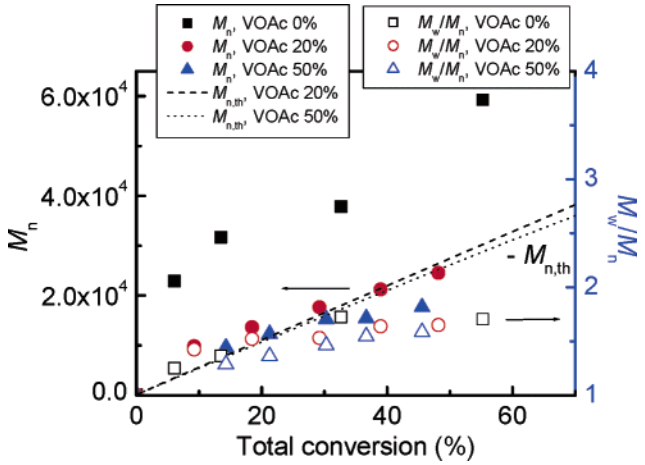


Figure 11. Evolution of M_n and M_w/M_n vs total conversion for copolymerization of NVP and VOAc mediated by **1** with V-70 at 30 °C: (●, ○) [NVP]$_0$/[**1**]$_0$/[V-70]$_0$ = 500/1/1, (■, □) [NVP]$_0$/[VOAc]$_0$/[**1**]$_0$/[V-70]$_0$ = 400/100/1/1, (▲, Δ) [NVP]$_0$/[VOAc]$_0$/[**1**]$_0$/[V-70]$_0$ = 250/250/1/1, monomer/anisole/toluene = 50/45/5 (vol %).

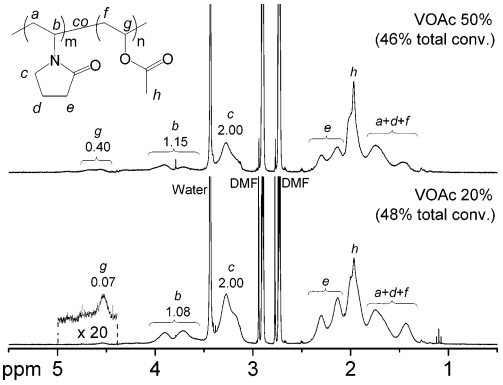


Figure 12. ^{1}H NMR spectra of poly(NVP-*co*-VOAc) in DMF-d_7 at 30 °C (300 MHz): [NVP]$_0$/[VOAc]$_0$/[**1**]$_0$/[V-70]$_0$ = 400/100/1/1 (VOAc 20%, overall conversion 48%), [NVP]$_0$/[VOAc]$_0$/[**1**]$_0$/[V-70]$_0$ = 250/250/1/1 (VOAc 50%, overall conversion 46%).

The molecular structure of the resulting poly(NVP-*co*-VOAc) copolymers was investigated by ^{1}H NMR spectroscopy in DMF-d_7 with a delay time of 2 s. The spectra of final samples, obtained when initial molar ratio of VOAc in the copolymerization was 20% or 50%, are exhibited in Figure 12. These spectra did not clearly prove the incorporation of VOAc into the copolymer because the signals which are assignable to VOAc units (peaks *f* and *h*) overlapped with other signals at 2 ppm. However, the methine proton originating from VOAc units (peak *g*) emerged at 4.6 ppm. The signal was weak due to the low content of VOAc in the copolymer. Therefore, the VOAc

content of the copolymers was estimated by comparison of the integrals of signals labeled *c* and *g* in Figure 12. The peak *c* can be assigned to the methylene protons next to the N atom. When the integral of peak *c* (I_{CH_2} = 2.00) was taken as corresponding to 1 unit of NVP, the integral of peak *g* corresponded to 0.07 and 0.40 units of VOAc in the copolymer when the initial mole ratios of VOAc in the feed was 20% and 50%, respectively. Accordingly, the VOAc content of copolymers were determined to be 6.5% (= 0.07/(1 + 0.07), VOAc 20%) and 29% (= 0.40/(1 + 0.40), VOAc 50%). The VOAc content of copolymers, simulated from the monomer reactivity ratios (r_{NVP} = 3.75, r_{VOAc} = 0.28),[31] were 8% at 48% overall conversion (VOAc 20%) and 28% at 46% overall conversion (VOAc 50%), respectively. These values are in good agreement with that calculated from NMR. The monomer sequence distribution of VOAc units in the copolymer will form gradient because of the large differences in the monomer reactivity ratios. These copolymers were still soluble in water, and therefore poly(NVP-*co*-VOAc) with well-controlled structure may be a good candidate for a novel biomedical material.

Conclusion

Bis(acetylacetonate)cobalt(II) complexes mediate the radical polymerization of VClOAc and NVP, in addition to previously reported VOAc. The Co(F3-acac)$_2$ complex (**2**) provided the best result for mediating the radical polymerization of VClOAc in terms of the M_n and the lowest polydispersity among **1**−**3**. However, only Co(acac)$_2$ complex (**1**) could mediate the radical polymerization of NVP. It formed polymers with the lowest polydispersity among **1**−**3**. The degree of control mediated by complex **1** over polymerization of VClOAc and NVP was inferior to that for VOAc. Control over polymerization of VClOAc and NVP can be improved by the copolymerization with VOAc because of the significantly higher rate of deactivation of a chain-end VOAc radical. The nature of the propagating radical affects the equilibrium constant (k_{act}/k_{deact}) between the dormant species and complex **1**. The stronger electron-withdrawing effect of the ligand decreases the affinity of cobalt(II) radical toward propagating radicals, resulting in the reduced control over polymerization. The effect of electron-withdrawing groups in the ligand on the cobalt(II) metal radical is currently investigated by DFT computations.

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