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Possibility of Living Radical Polymerization of Vinyl Acetate Catalyzed by Iron(I) Complex[1]

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Introduction. Vinyl acetate (VAc) is one of the most representative monomers that can be polymerized only via a radical mechanism. Unlike (meth)acrylates and styrene, VAc lacks a conjugating substituent, and thus its propagating radical is highly reactive, less stable, and tends to undergo, in particular, chain transfer and termination reactions.[2] Thus, the control of VAc polymerization has been considered highly difficult.

Recently, living radical polymerization systems have been reported for a variety of monomers except for VAc and similar nonconjugated analogues.[3] Among various methodologies proposed, transition-metal-catalyzed systems are among the most interesting in terms of controllability and applicability. The key reaction therein is the reversible homolysis of a carbon−halogen bond (R−X; originated from an initiator) by a transition-metal catalyst, which in turn triggers repetitive addition to monomer onto the resulting radical growing species [e.g., $R{-}X + Ru^{II} \rightleftharpoons R^{\bullet}XRu^{III}$]. The catalysts include Ru,[4−11] Cu,[12−24] Fe,[25−33] and Ni[34−37] complexes with phosphine or nitrogen ligands, where the catalytic activity can be tuned by changing their ligands according to monomers. In particular, despite the ample success for conjugated monomers (methacrylates, acrylates, styrenes, etc.), less conjugated counterparts such as VAc and vinyl chloride[38] are still beyond the reach of metal-mediated living radical polymerizations. This is partly due to the difficulty in generating radical species from their dormant carbon−halogen terminals. Specifically for VAc, the acetoxy substituent is weakly electron donating; homolytic cleavage of the carbon−halogen terminal is therefore difficult because the dormant species should receive one electron from a metal complex: Most of the metal catalysts reported thus far seem to be too "mild" for this purpose for VAc.

This work is to develop a transition-metal-catalyzed living radical polymerization of VAc. In contrast to the dearth of effective metal catalysts, some systems can control its radical polymerization, including those based on degenerative chain transfer with iodides[39] and reversible addition−fragmentation chain transfer (RAFT),[40] where the formation of the propagating VAc radical is triggered by conventional radical initiators. Previous attempts using metal catalysis, such as *i*-Bu_3Al/2,2′-bipyridine/TEMPO[41] and carbon tetrachloride/$Fe(OAc)_2$/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine systems,[42] seem to need further clarification.[43] The latter is a redox-initiated radical telomerization apparently based on the irreversible activation of a C−Cl bond, where the polymer molecular weight was independent of monomer conversion but determined by the $[VAc]_0/[CCl_4]_0$ mole ratio.

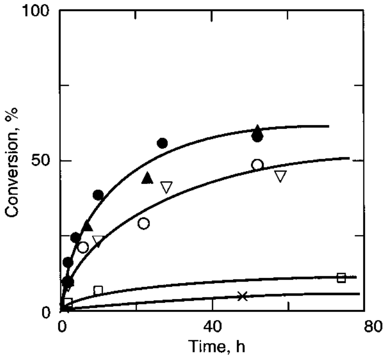

Figure 1. Polymerization of VAc with EMA-I/$[Fe(Cp)(CO)_2]_2$/additive in anisole at 60 °C: $[VAc]_0 = 8.0$ M; $[EMA\text{-}I]_0 = 40$ mM; $[[Fe(Cp)(CO)_2]_2]_0 = 20$ mM; $[additive]_0 = 20$ mM. Additive: $Al(Oi\text{-}Pr)_3$ (●); $Ti(Oi\text{-}Pr)_4$ (▲); *i*-Bu_3Al (○); *n*-Bu_2NH (▽); none (□); ZnI_2 (×).

In this paper, we employed dicarbonylcyclopentadienyliron dimer $[Fe(Cp)(CO)_2]_2$ with an iodo compound as an initiator (Scheme 1). The iron(I) complex is a highly active catalyst for radical addition,[44] partly due to its low redox potential. Noting these features, we have recently found that the dimer catalyst induces fast living radical polymerizations of styrene without additives[28] and of acrylates with iodine as an additive.[45] We wish to report that the iron-based systems induce a possible living radical polymerization of vinyl acetate with an iodo initiator.

Results and Discussion. 1. Polymerization of Vinyl Acetate. In anisole solvent at 60 °C, vinyl acetate was polymerized with the dinuclear iron complex $[Fe(Cp)(CO)_2]_2$ as a catalyst in the presence of an iodo initiator [EMA-I; $(CH_3)_2C(CO_2Et)I$][46] and an additive.[47] The monomer was consumed smoothly up to 60% conversion to produce poly(VAc), when metal alkoxides such as $Al(Oi\text{-}Pr)_3$ and $Ti(Oi\text{-}Pr)_4$ were employed as additives (Figure 1). Isobutylaluminum and di-*n*-butylamine were also effective additives to induce polymerizations slightly slower than those with the two metal alkoxides. In contrast, iodine and zinc iodide were not effective.

All of these polymerizations were not quantitative, where the highest conversions depended on the kind of additives. Without additives, the EMA-I/$[Fe(Cp)(CO)_2]_2$ system led to extremely slow polymerizations. No polymerization proceeded without the iron complex or the iodo initiator. These results show that all three components, EMA-I, $[Fe(Cp)(CO)_2]_2$, and an appropriate additive, are necessary for the efficient polymerization of VAc.

As shown in Figure 2, the number-average molecular weight (M_n) of the poly(VAc) obtained with the $[Fe(Cp)(CO)_2]_2$-based system increased in direct proportion to monomer conversion. Though based on PMMA calibration, the M_n agreed very well with the calculated value assuming that one molecule of EMA-I produces one polymer chain, especially when aluminum additives were employed. EMA-I therefore serves as an initiator that induces a quantitative and relatively fast initiation in the presence of $[Fe(Cp)(CO)_2]_2$ and a suitable additive (see also the next section). The size-exclusion chromatography (SEC) curves of the obtained polymer were unimodal and relatively narrow at low conversions ($M_w/M_n \sim 1.4$) and shifted toward high molecular weight

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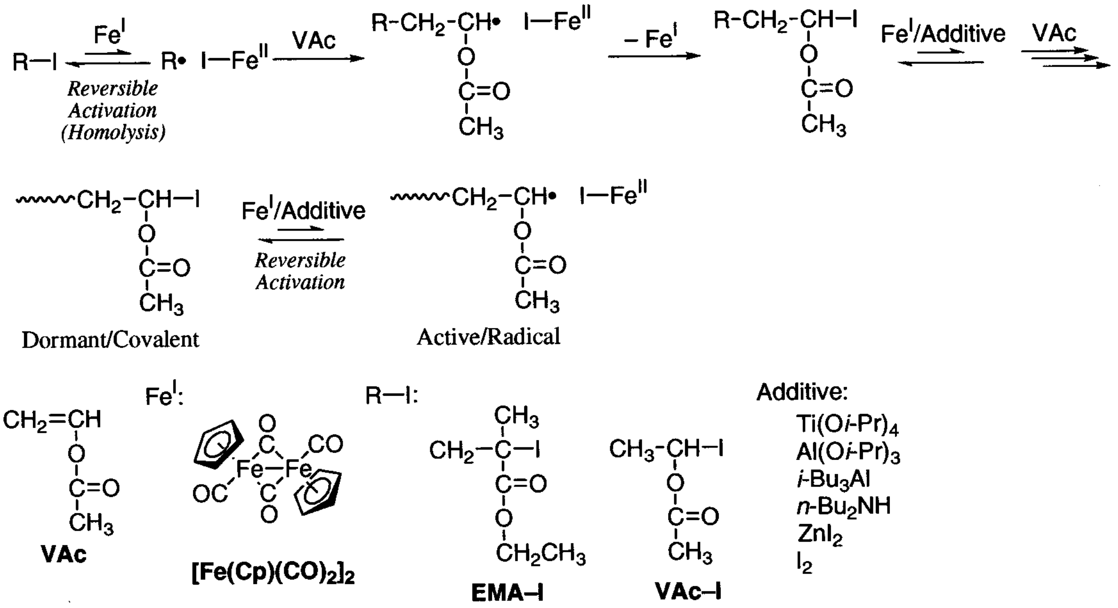
Scheme 1. Living Radical Polymerization of Vinyl Acetate by Iron(I) Complex



with increasing conversion with some broadening. A similar polymerization was also possible with the HI adduct with VAc [VAc-I; $CH_3CH(OCOCH_3)I$][48] in place of EMA-I.

Thus, the polymerization most probably proceeds as illustrated in Scheme 1, i.e., via the metal-catalyzed activation (homolysis) of the C–I terminal originated from the initiator to give polymers with controlled molecular weights. To our knowledge, this is the first example of a radical polymerization of VAc in which a metal-catalyzed system leads to a linear increase of M_n with monomer conversion. Although the contribution of the iodine-transfer process[39] cannot be fully excluded, this polymerization is undoubtedly triggered by the metal catalysts.

2. End Group Analysis. The terminal structures of the obtained polymers were analyzed by ^{1}H NMR. The samples were obtained with VAc-I and EMA-I as initiators (Figure 3, A and B, respectively) in conjunction with $[Fe(Cp)(CO)_2]_2$ and Al(O*i*-Pr)$_3$ in anisole at 60 °C (reaction time = 2 h, conversion = 15%). Besides the large absorptions of the main-chain repeat units of VAc, there are characteristic signals derived from the initiators. The methyl protons (a) of the initiating end from VAc-I appeared at 1.2 ppm (Figure 3A), whereas the methyl (e and g) and the methylene (f) protons from EMA-I were seen at 1.1–1.3 and 4.1 ppm, respectively (Figure 3B). The ω-terminal methine (c′) and methylene (d′) protons, adjacent to the C–I bond, appeared at 2.7 and 5.3 ppm, respectively. Thus, each iodo compound in fact serves as an initiator for VAc.

The M_n of these poly(VAc) can be determined from the peak intensity ratios of the initiator moiety to the main chain [M_n(NMR; α-end) = 86.09 × 3(b + c + d)/6a + 213.99 for VAc-I and M_n(NMR; α-end) = 86.09 × 11(b + c + d)/6(e + f + g) + 242.06 for EMA-I] or from

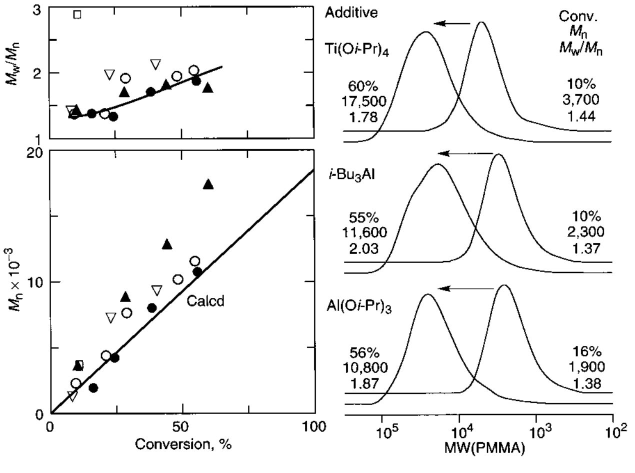


Figure 2. M_n, M_w/M_n, and SEC curves of poly(VAc) obtained with EMA-I/$[Fe(Cp)(CO)_2]_2$/additive in anisole at 60 °C: $[VAc]_0$ = 8.0 M; $[EMA\text{-}I]_0$ = 40 mM; $[[Fe(Cp)(CO)_2]_2]_0$ = 20 mM; $[additive]_0$ = 20 mM. Additive: Al(O*i*-Pr)$_3$ (●); Ti(O*i*-Pr)$_4$ (▲); *i*-Bu$_3$Al (○); *n*-Bu$_2$NH (▽); none (□).

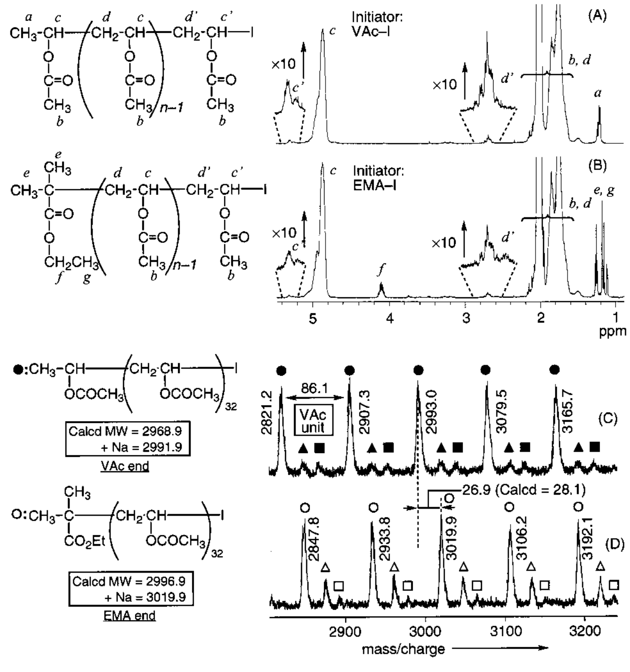


Figure 3. ^{1}H NMR and MALDI-TOF-MS spectra of poly(VAc) obtained with VAc-I (A and C) and EMA-I (B and D). Catalyst system: $[Fe(Cp)(CO)_2]_2$ with Al(O*i*-Pr)$_3$ (20/20 mM) in anisole at 60 °C; $[VAc]_0$ = 8.0 M; $[initiator]_0$ = 40 mM. The two samples were fractionated to remove the catalyst residues; see text for molecular weight data.

Table 1

sample	conv, %	M_n (SEC)	M_n (NMR; α-end)	M_n (NMR; ω-end)
A	14	5500	3200	14400
B	15	4400	3600	7200

those of the C−I bond at ω-terminal to the main chain [M_n(NMR; ω-end) = $86.09 \times 3(b + c + d)/6(c' + d') + 242.06$]; 86.09, 213.99, and 242.06 are the formula weights of the VAc repeat unit, VAc-I, and EMA-I residues, respectively. For the two samples A and B, the values given in Table 1 were obtained. The M_n determined from the α-end were close to, though slightly lower than, those from SEC. On the other hand, the M_n from the ω-end were clearly higher. These indicate that the organic iodide acts as an initiator to produce one polymer chain, while the ω-terminal does not quantitatively produce the expected $-CH(OCOCH_3)-I$ form. This is due to side reactions such as chain transfer and/or termination or due to the formation of the less active $-CH(OCOCH_3)-CH_2-I$ terminal via head-to-head addition: Another cause would be the decomposition of ω-terminal during recovery and purification of the polymer after polymerization (see below). The loss of the secondary C−I terminal is most probably related to the observed incomplete consumption of the monomer and is now under investigation in our group. However, the C−I bond in VAc-I is activated or homolytically cleaved by the transition-metal complex, which supports the similar activation of the C−I dormant terminal of poly(VAc); namely, reversible rather than irreversible activation of the dormant terminal is responsible for the controlled polymerization of VAc with the Fe(I) complex.

Figure 3C also shows MALDI-TOF-MS spectra of the poly(VAc) samples analyzed by ^{1}H NMR (Figure 3A). There was just a single main series (filled circles) of peaks whose interval was regular and separated by 86.1 amu, the molar mass of the monomer. The absolute mass of each peak equals the molecular weight expected for poly(VAc) with one iodine atom at the ω-end, one initiator fragment [H-VAc] at the α-end, and sodium ion from the salt used for the MS analysis: H-(VAc)(VAc)$_n$I/Na$^+$; VAc = $CH_2CH(OCOCH_3)$. Similarly, the MS spectrum of another sample, obtained with EMA-I, shows a single main series (open circles in Figure 3D), with the same peak interval (86.1) as that with VAc-I, but the two series are separated from each other. The mass difference was 26.9, which is close to the calculated mass difference (28.1) between the two initiators, VAc-I and EMA-I. In addition, no peaks are seen for the polymers without the EMA residue. These indicate that EMA-I initiates the polymerization and that no chain-transfer reaction occurs, at least during the initial stages of the polymerization.

However, there were two minor series of peaks (filled triangles and squares in Figure 3C; open triangles and squares in Figure 3D) beside the main series in both spectra. The lower mass series marked by triangles are attributed to the polymers with aldehyde and olefin group ($-CH_2-CH{=}CH-CHO$), caused by decomposition of C−I terminal with water.[49] For example, the peak observed between 3000 and 3100 in Figure 3D has 3046.2 amu, which is very close to the calculated value for the polymer, 3048.2. ^{1}H NMR analysis also showed a trace amount of an aldehyde group. However, this decomposition occurs during recovery and purification of the polymer after the polymerization, as indicated by the increase of the peaks on storage under atmosphere.

The higher mass series (marked by squares) are ascribed to the polymers [$-CH_2-CH_2(OCOCH_3)$ and $-CH{=}CH(OCOCH_3)$] formed via disproportionation of the growing radicals or via elimination of hydrogen iodide during polymerization and/or MS analysis.[50] For example, the peak between 3000 and 3100 in Figure 3D has 3065.9 amu, close to the calculated values for these polymers, 3066.2 [$-CH_2-CH_2(OCOCH_3)$] and 3064.2 [$-CH{=}CH(OCOCH_3)$], respectively. This suggests that, though minor, termination does occur.

In conclusion, the $[Fe(Cp)(CO)_2]_2$ catalyst with an iodide initiator has provided the first example of metal-catalyzed radical polymerization of VAc via reversible activation of the carbon−halogen terminal. This is also the first example where the M_n of poly(VAc) increases in direct proportion to monomer conversion among the metal-catalyzed systems up to 70%. We are now optimizing the reaction conditions, investigating reaction mechanisms such as the role of additives, and developing other metal-catalyzed systems for VAc.

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(48) VAc-I was prepared under dry nitrogen as follows. NaI (15.0 g, 100 mmol) and solutions of HCl (1.0 M in Et_2O; 50 mL, 50 mmol) were placed in a round-bottom 100 mL dry flask. VAc (4.61 mL. 50 mmol) was then added at 0 °C. After stirring for 6 h, the solution was filtered and evapolated under reduced pressure to give crude VAc-I. The crude product was purified by distillation; bp 46 °C at 10 mmHg. ^{1}H NMR (500.16 MHz, $CDCl_3$): δ 1.61 (s, 3H, $COCH_3$), 1.83 (d, 3H, CH_3), 6.60 (q, 1H, CH).

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