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Organometallic Mediated Radical Polymerization of Vinyl Acetate with Fe(acac)₂

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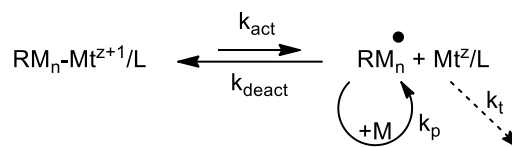
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ABSTRACT

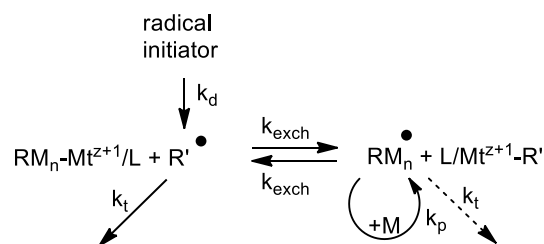
The radical polymerization of vinyl acetate (VAc) is moderated by Fe(acac)₂ by the organometallic route (OMRP), as well as by degenerative transfer polymerization (DTP) when in the presence of excess radicals, through the formation of thermally labile organometallic Fe^{III} dormant species. The PVAc-Fe^{III}(acac)₂ dormant species has been isolated in the form of an oligomer and characterized by ¹H NMR, EPR and IR methods, and then used as a single-component initiator for the OMRP of VAc. The degree of polymerization of this isolated oligomeric species demonstrates the limited ability of Fe(acac)₂, relative to the Co(acac)₂ congener, to rapidly trap the growing PVAc radical chain. Control under OMRP conditions is improved by the presence of Lewis bases, especially PMe₂Ph. On the other hand, iron(II) phthalocyanine inhibits the radical polymerization of vinyl acetate completely.

INTRODUCTION

Organometallic mediated radical polymerization (OMRP),^{1,2} a representative example of controlled radical polymerization, has become a tool in controlling the polymerization of less reactive monomers such as vinyl acetate (VAc). OMRP rests on the use of organometallic dormant species that can easily and reversibly generate the growing radical chain by homolytic cleavage of the metal-carbon bond. This may be possible either by direct dissociative bond breaking, as shown in Scheme 1, or by associative radical exchange (also known as degenerative transfer) if an independent radical source is available and if the metal coordination sphere allows it, Scheme 2. Hence, organometallic chemistry is of great relevance in controlled radical polymerization, but rather than strong metal-carbon bonds that impart thermal stability and robustness to the molecule and allows its manipulation and use under a broad range of experimental conditions, weak metal-carbon bonds leading to thermally fragile systems are necessary here.



Scheme 1. OMRP mechanism by reversible deactivation (Mt = metal, L = ligand, M = monomer, R = initiating radical/chain end).



Scheme 2. OMRP mechanism by associative radical exchange (degenerative transfer). Symbols as in Scheme 1.

The OMRP technique is still rather limited in terms of the choice of the transition metal, with only a handful of complexes having proven successful and each one of them being suited to only one or a few specific monomer(s). The largest number of contributions makes use of

cobalt complexes, after the first reports of the controlled polymerization of acrylates with porphyrin or glyoxime cobalt complexes by Harwood and Wayland^{3,4} and a greater number of recent report for many monomers including vinyl acetate.⁵ Certain complexes of Ti,⁶⁻⁹ Mo,¹⁰ Cr,¹¹⁻¹³ Os,^{14,15} Mn¹⁶ and V,^{17,18} have been successfully employed as OMRP trapping agents, but it would be of interest to develop controlling systems based on iron in light of its low cost and biocompatibility.

Iron-based complexes have attracted particular attention as catalysts in atom transfer radical polymerization (ATRP), the other major controlled polymerization strategy that makes use of transition metal complexes.¹⁹⁻²² Certain FeCl₂ complexes with dimine ligands have been invoked as agents capable of reversibly trapping polymer radical chains, but β -H elimination and atom transfer processes interplay and even dominate the radical polymerization process.²³⁻²⁵ Only one report appears to be available on the use of Fe within a pure OMRP approach, and only for the polymerization of styrene, using various macrocyclic Fe^{II} complexes in AIBN-initiated polymerization.²⁶ Given the application value of iron in polymerization, further development of OMRP using iron complexes as trapping agents seems warranted, particularly for less reactive monomers such as VAc since methods to insure good control for the polymerization of this important monomer are still limited. Herein we report, for the first time, the iron-based organometallic mediated radical polymerization of VAc. A preliminary report of this work has been presented.²⁷

EXPERIMENTAL

Materials. Vinyl acetate (VAc, 99+%, Acros) was passed through a column filled with neutral alumina, dried over CaH₂, distilled under reduced pressure, and stored in a freezer under nitrogen. Pyridine (py, 99.5%, SDS) and triethylamine (TEA, 99%, Acros) were dried over CaH₂ and distilled under reduced pressure. Iron(II) acetylacetonate (Fe(acac)₂, 99.95%,

Aldrich), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, Wako), and dimethylphenylphosphine (DMPP, 97%, Acros) were used without further purification.

Instrumentation. Size-exclusion chromatography (SEC) of PVAc was carried out in THF (flow rate: 1 mL min⁻¹) at 35°C on a 300 x 7.5 mm PL gel 5 micrometer mixed-D column, equipped with multiangle light scattering and refractive index detectors. ¹H (300 MHz) NMR spectra were recorded on a Bruker DPX-300 instrument.

Standard OMRP of VAc initiated by V-70 in the presence of Fe(acac)₂. A Schlenk flask (25 mL) was charged with Fe(acac)₂ (55 mg, 0.216 mmol) and V-70 (53 mg, 0.173 mmol). The flask was sealed with a rubber septum and was cycled three times between vacuum and nitrogen to remove oxygen. Degassed toluene (10 mL) (in solution polymerization), VAc (10 mL, 108.06 mmol) and the ligand (if applicable) were then added to the flask through degassed syringes. The solution was stirred for 20 min at room temperature. After three additional freeze-pump-thaw cycles, the flask was immersed in a thermostated oil bath at 30°C. At timed intervals, samples were withdrawn from the flask with a degassed syringe. The monomer conversion was determined gravimetrically after removal of the unconverted monomer under reduced pressure and the resulting residue was used for SEC characterization.

Synthesis of oligomeric PVAc-Fe(acac)₂. Fe(acac)₂ (2 g, 7.87 mmol) and V-70 (1.942 g, 6.30 mmol) were added to a round-bottomed flask capped by a three-way stopcock and purged by three vacuum-argon cycles. After the addition of degassed VAc (14.6 mL, 157.44 mmol), the mixture was heated at 30°C with stirring for 70 h. The unreacted monomer was removed under reduced pressure, and the resulting residue was dissolved in degassed CH₂Cl₂. The solution was then cannula transferred to the top of a silica-gel column. After the elimination of V-70 residue with CH₂Cl₂, four orange fractions were collected respectively with CH₂Cl₂/EtOAc (3:1), CH₂Cl₂/EtOAc (1:1),

CH₂Cl₂/EtOAc (1:3), and acetone as eluants. The fractions were evaporated to dryness, and the collected orange-red **1** (1.35 g), red **2** (0.20 g), orange-red **3** (0.30 g), and orange **4** (3.0 g) were stored at -20 °C under argon.

Reaction of 3 and 4 with 1-butanethiol. The products **3** (200 mg) and **4** (200 mg) were dissolved in degassed absolute ethanol (20 mL), and degassed 1-butanethiol (2 mL) was then added to each sample with a syringe under an inert atmosphere at room temperature. The mixtures changed from orange to dark green immediately. The mediums were stirred at 50 °C for 24 h. Black precipitates were observed and removed by filtration through Celite. Solvents were removed under reduced pressure, and a small amount of THF was added. The polymers were reprecipitated in heptane before being dried *in vacuo*. The white products **3'** (102 mg) and **4'** (85 mg) were recovered and analyzed by ¹H NMR.

OMRP of VAc initiated by PVAc-Fe(acac)₂ adduct 3. The orange-red product **3** (105 mg, 0.013 mmol) was added to a round-bottomed flask capped by a three-way stopcock, purged by three vacuum-argon cycles. VAc (10.0 mL, 108.1 mmol) was then added to the flask by degassed syringes and the mixture was heated at 30°C. At timed intervals, samples were withdrawn from the flask with a degassed syringe. The monomer conversion was determined gravimetrically after removal of the unconverted monomer under reduced pressure and the resulting residue was used for SEC characterization.

RESULTS AND DISCUSSION

Vinyl acetate polymerization under reversible termination conditions

As mentioned in the introduction, iron(II) phthalocyanine was shown to insure the controlled growth of polystyrene by OMRP through the reversible deactivation mechanism.²⁶ We have tested the same system as a controlling agent for the polymerization of VAc initiated by V-70 [V-70 is the trade name of

2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile)], a thermal radical initiator with a half-life of 10 h at 30°C. The bulk polymerization, without additional ligands (30°C, [VAc]:[Fe]:[V-70] = 500:0.8:1) was completely inhibited. No conversion was observed even after raising the temperature to 60 °C. The same irreversible trapping behavior was found for cobalt porphyrins in the polymerization of VAc, whereas the same compound controls the polymerization of acrylates.²⁸ According to DFT calculations, the radicals associated to poly(acrylate) and poly(styrene) chains form much weaker bonds, relative to the radical associated to poly(vinyl acetate), to halogen atoms (in the ATRP dormant species),²⁹ to dithiocarboxyl radicals (in the RAFT dormant species)³⁰ and to transition metal complexes, for instance systems based on Cr^{II} and Co^{II}.^{11,31} On the other hand, the PVAc radical chain was found to be reversibly released from dormant species based on the bis(acetylacetonate) system, PVAc-Co(acac)₂(L) (L = Lewis base such as pyridine, DMF, DMSO, H₂O, ...).³²⁻³⁴ Hence, the oxygen-based coordination sphere on R-Co^{III}(acac)₂ appears to considerably weaken the Co^{III}-C bond compared to a nitrogen-based environment. For this reason, we considered it interesting to test the commercially available Fe(acac)₂ for the radical polymerization of VAc.

To probe for the ability of Fe(acac)₂ to trap and reversibly release the growing PVAc radical chains, initial polymerizations tests were run in bulk with a [Fe(acac)₂]:[V-70] ratio of 1:0.8 and a [VAc]:[Fe(acac)₂] ratio of 500:1. The use of 0.8 equivalents of V-70, generating in principle 1.6 equivalents of primary radicals, effectively affords a nearly stoichiometric amount of initiating chains once the initiator efficiency factor is taken into account. The results are reported in Table 1. Without the iron complex, the polymerization was very fast at 30°C and yielded very high molecular weights and dispersities ($\bar{D} = M_w/M_n$) (Table 1, entries 1 and 2). In the presence of Fe(acac)₂, an induction time was observed (Table 1, entry 3), followed

TABLE 1. Radical Polymerization of VAc mediated by Fe(acac)₂^a

entry	Fe(acac) ₂	medium	time (h)	conv (%) ^b	M _{n,th} (g mol ⁻¹) ^c	M _{n,SEC} (g mol ⁻¹)	Đ
1	No	Bulk	5	48.5		168000	1.70
2	No	Bulk	7	78.2		178000	3.76
3	Yes	Bulk	5	0			
4	Yes	Bulk	14	10.1	4350	61600	1.31
5	Yes	Bulk	22	34.2	14720	152000	1.29
6	Yes	50% ^d	22	8.8	3790	26000	1.46
7	Yes	50% ^d	56	19.4	8340	29830	1.35
8	Yes	50% ^d	312	34.0	14600	34510	1.26

^a Conditions: 30°C, [VAc]:[Fe(acac)₂]:[V-70] = 500:1:0.8. ^b From gravimetry. ^c M_{n,th} = ([VAc]₀/[Fe(acac)₂]₀)M_{VAc} × Conv.(%); M_{VAc} is the molecular weight of the monomer, VAc. ^d 50% v/v in toluene.

by a much slower polymerization relative to the iron-free conditions. This indicates radical trapping by Fe(acac)₂. The molecular weights of the resulting polymer are much higher than the values expected for a well controlled process, indicating that only a small fraction of the iron centers is operating as chain growth moderators. However, the resulting polymer had relatively low dispersity (Đ = 1.29-1.36) and M_n increased more or less proportionally with the conversion. All these results are consistent with a controlled polymerization, although the controllability is far from ideal when compared with that of reported for Co systems.^{32,33,35-41}

When carried out under more diluted conditions (50% v/v in toluene, see Table 1, entries 6-8), the polymerization was expectedly much slower, reaching only a 34% conversion in 312 h. The molecular weights were once again higher than the theoretical ones, but now by a much smaller factor relative to the bulk experiment, indicating improved efficiency of the Fe(acac)₂ trapping agent. Hence, a greater fraction of the iron centers appear to play a role in the moderation of chain growth in the more dilute solution. This phenomenon may be related to solution equilibria involving the Fe(acac)₂ species. Indeed, it is known that this compound adopts a tetranuclear structure in solution,⁴² in equilibrium with less aggregated species that are favored at high dilution.⁴³ This suggests that the polymer dormant chain has a small mixed-valent Fe(acac)₂ oligomer as chain end, PVAc-{Fe(acac)₂}_x with only one Fe^{III} center and (x-1) Fe^{II} centers, the value of x being concentration dependent. Note that the polymer growth was

sustained well beyond the time needed to generate new radicals (7 half-lives or approximately 70 h). This demonstrates the reversible release of the PVAc chains from the PVAc-{Fe(acac)₂}_x dormant species, as expected for a reversible deactivation OMRP mechanism.

It was shown for the Co(acac)₂-mediated VAc polymerization that the addition of coordinating ligands such as pyridine (py), triethylamine (TEA), and H₂O provided faster polymerizations relative to the ligand-free system,^{5,32,34} for which no reversible release of the growing PVAc radicals occurred (the controlled polymerization with ligand-free Co(acac)₂ only occurred by degenerative transfer polymerization in the presence of excess radicals).^{5,32} The Fe/Co comparison shows that the (acac)₂Fe-PVAc bond is homolytically more fragile than the (acac)₂Co-VAc bond. We wondered, however, whether the controlling ability of the Fe(acac)₂ system could be modulated, as for the Co(acac)₂ system, by the addition of Lewis bases (L). An additional reason for using Lewis bases is that these are known to add to Fe(acac)₂ resulting in disaggregation and formation of mononuclear Fe(acac)₂(L)₂ species,⁴⁴ hence perhaps helping to obtain molecular weights in better agreement with the theoretical values for a controlled process. More polymerization experiments were therefore carried out for VAc/Fe(acac)₂/V-70 in the presence of added ligands. The results, shown in Table 2, are again consistent with a certain degree of control for the polymerizations (low dispersity, M_n increasing with conversion in most cases).

TABLE 2. Bulk Polymerization of VAc in the presence of added ligands ^a

Entry	L	[L/Fe]	time (h)	Conv (%)	$M_{n,th}$ (g mol ⁻¹) ^b	$M_{n,GPC}$ (g mol ⁻¹) ^c	\bar{D}
1	py	30	17	14.0	6030	44010	1.16
2	py	30	39	36.0	15480	68280	1.33
3	py	30	116	58.6	25200	93910	1.33
4	TEA	30	20	6.6	2820	30500	1.16
5	TEA	30	112	18.8	8100	33050	1.22
6	TEA	30	209	23.3	10030	30960	1.25
7	H ₂ O	30	20	30.4	13050	120400	1.36
8	DPPE	1	17	13.1	5620	52030	1.29
9	DPPE	1	39	44.9	19340	99930	1.22
10	DMPP	2	17.5	7.1	3070	20860	1.17
11	DMPP	2	44.5	11.7	5030	25490	1.19
12	DMPP	2	374	34.3	14760	39710	1.21

^a Conditions: 30°C; [VAc]:[Fe(acac)₂]:[V-70] = 500:1:0.8. ^b From gravimetry. ^c $M_{n,th} = ([VAc]_0/[Fe(acac)_2]_0)M_{VAc} \times Conv.(\%)$; M_{VAc} is the molecular weight of the monomer, VAc.

In order to directly compare with the Co(acac)₂ system,³² the polymerizations in the presence of py, TEA, and H₂O were conducted with the same ligand excess, namely with [L]:[Fe(acac)₂] = 30. The polymerization rate in the presence of py was slightly slower, relative to the ligand-free conditions (*cf.* 34.2% conversion in 22 h without ligand, run 5 in Table 1, vs. 36% conversion in 39 h in the presence of py, run 2 in Table 2) and it was lower still in the presence of TEA (only 23.3% conversion in 209 h, run 6 in Table 2). The observed M_n values of these polymers were again much greater than expected. The same behavior was observed in the presence of H₂O. Water was immiscible at the beginning of the reaction but then the mixture became clear and the polymerization proceeded at a rate comparable to the ligand-free system. The polymerization was also tested in the presence of bis(diphenylphosphino)ethane (DPPE), and dimethylphenylphosphine, PMe₂Ph (DMPP). Since phosphine ligands and particularly chelating diphosphines bind metals more strongly, a P/Fe ratio of 2 was used in these cases (*i.e.* [DPPE]/[Fe(acac)₂] = 1:1 and [DMPP]/[Fe(acac)₂] = 2:1). A well-defined Fe(acac)₂(DPPE) complex has been described in the literature.^{45,46} Also in these cases, the polymerizations were slower than for the ligand-free system, the M_n were greater than the theoretical values but increased with conversion, and the dispersity was low. Note that the DMPP system gave a much lower rate of

polymerization, a smaller discrepancy between observed and calculated molecular weight, and narrower molecular weight distribution (\bar{D} = 1.16-1.21). The effect of added Lewis bases on the polymerization rate is therefore opposite for Fe(acac)₂ than for Co(acac)₂, where the polymerization was accelerated by the presence of Lewis bases. The reason for the acceleration for the cobalt system is the greater stabilization of Co^{II}(acac)₂, by addition of two L molecules and formation of Co(acac)₂(L)₂, relative to the PVAc-Co^{III}(acac)₂ dormant species, which can also add one L ligand (but not two) to form PVAcCo^{III}(acac)₂(L). For the Fe system, the results indicate that the Lewis base is able to stabilize the Fe^{III} dormant species better than the trapping agent Fe^{II}(acac)₂.

An additional experiment was run in the presence of a [DMPP]/[Fe(acac)₂] ratio of 1:1, while maintaining all other parameters unchanged (bulk, 30°C, [VAc]/[Fe(acac)₂] = 500 and [V-70]/[Fe(acac)₂] = 0.8). The results, shown in Figure 1, indicate that the monomer consumption follows the expected first order rate law, that the M_n values are greater than the calculated ones but now only by a factor of 2 at the highest conversions, growing proportionally with the conversion, and that the \bar{D} values are rather low. The size-exclusion chromatograms (SEC) of PVAc mediated by Fe(acac)₂ are shown in Figure 2. They confirm the monomodal distribution of the molecular weights throughout

the polymerization, with only a small shoulder on the low molecular weights side, visible at low conversions, probably related to a small amount of termination processes at the beginning of the polymerization. Note that also in this case the polymerization was sustained well beyond the time needed to generate new radicals, confirming the reversible release of growing chains from the $[(\text{acac})_2\text{Fe}/\text{DMPP}]$ -PVAc dormant species according to a reversible deactivation OMRP mechanism.

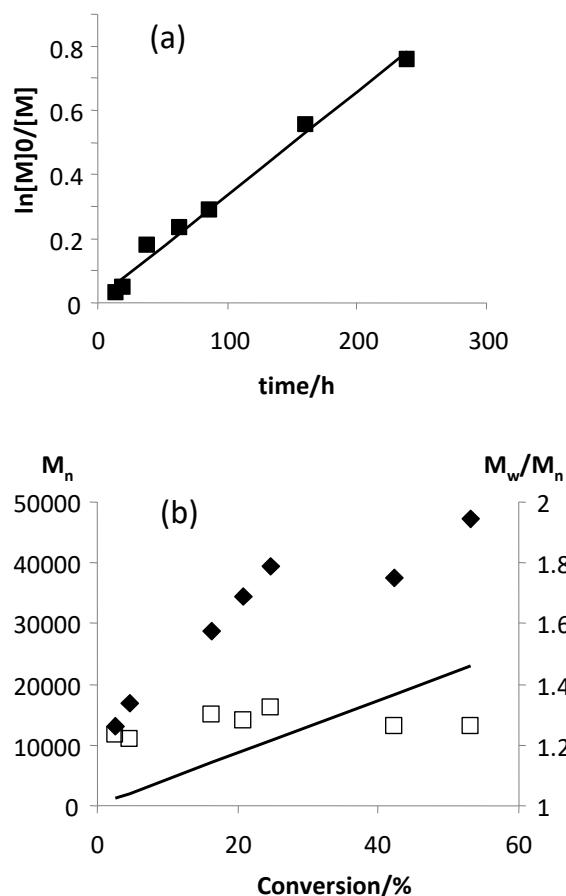


FIGURE 1. Bulk polymerization of VAc at 30°C controlled by $\text{Fe}(\text{acac})_2$ in the presence of DMPP. $[\text{VAc}]:[\text{Fe}(\text{acac})_2]:[\text{DMPP}]:[\text{V-70}] = 500:1:1:0.8$. (a) First order kinetics plot. (b) SEC-determined number-average molecular weight and polydispersity index as a function of monomer conversion. The solid line indicates the molecular weights calculated for one chain per Fe atom.

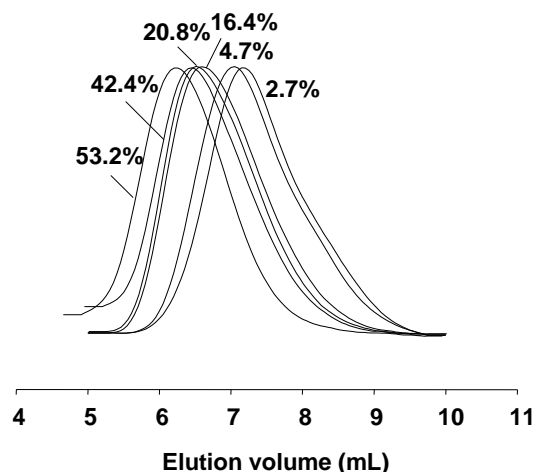


FIGURE 2. SEC chromatograms for PVAc from the OMRP mediated by $\text{Fe}(\text{acac})_2$. Conditions are as shown in Figure 2.

It is also worth pointing out that the monomer conversion in this experiment follows a relatively clean first order behavior without any sign of slowdown (see FIGURE 1 (a)) and that the dispersity is low and does not increase with conversion (see FIGURE 1 (b)), up to a relatively high M_n (~ 50000 , corresponding to a degree of polymerization $X_n \sim 580$). This is consistent with an equally facile reactivation of the dormant chains obtained after a head-to-head and a head-to-tail monomer addition. In fact, it was shown that the VAc polymerization controlled by other mechanisms (ATRP,^{47,48} RAFT,^{49,50} ITP,⁵¹ TERP,⁵² and even OMRP with other metal complexes as controlling agents¹²) suffers from slowdown and/or \bar{M}_n increase with conversion, caused by the more difficult reactivation of the dormant chain obtained after the less frequent (1-2%) head-to-head addition. On the other hand, this problem does not affect the quality of control for the $\text{Co}(\text{acac})_2$ -mediated polymerization.⁵³ It has been suggested that the metal chelation via participation of the ester carbonyl function of the last monomer unit contributes to the stabilization of the dormant species. Since $\text{Fe}(\text{acac})_2$ has the same geometry than $\text{Co}(\text{acac})_2$, it is possible that chelation phenomenon also plays a role here. In any case, it seems that reactivation of the dormant species is equally

possible also after a head-to-head monomer addition.

Vinyl acetate polymerization under degenerative transfer conditions

As already mentioned, the VAc polymerization mediated by $\text{Co}(\text{acac})_2$ in the absence of Lewis bases and in the presence of an excess amount of radicals continuously injected from V-70 proceeds rapidly and in a controlled fashion by a degenerate transfer mechanism (Scheme 2). In other words, the $(\text{acac})_2\text{Co-PVAc}$ dormant species is able to associatively exchange radical chains very rapidly. It was of interest to verify whether a similar associative exchange may occur on $(\text{acac})_2\text{Fe-PVAc}$, since the two complexes should be isostructural. A polymerization carried out in toluene (50% v/v) in the presence of 8 equivalents of V-70 was much faster relative to that with 0.8 equivalents of initiator under the same conditions (see Figure 3a). Conversion reached 46.5% in 72 h, yielding PVAc with a molecular weight of 20000. In this case, the molecular weights matched quite well the theoretical ones, while the dispersity remained relatively low ($\mathcal{D} = 1.36\text{--}1.50$). This observation suggests that the $\text{PVAc-}\{\text{Fe}(\text{acac})_2\}_x$ dormant species are more readily broken down into mononuclear chain ends, $\text{PVAc-Fe}(\text{acac})_2$, in the presence of a greater concentration of radicals, therefore generating one growing chain per Fe center. A mononuclear chain end is also presumably necessary in order to allow the associative radical exchange. Hence, the role of transfer agent in degenerate transfer polymerization seems confirmed for the dormant $\text{PVAc-Fe}(\text{acac})_2$ species.

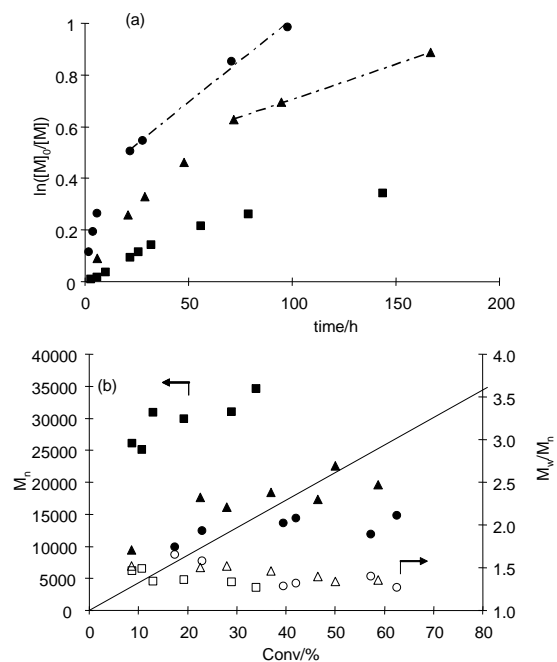


FIGURE 3. (a) Kinetic plots of $\ln([M]_0/[M])$ vs time and (b) dependence of molecular weights, M_n (filled symbols), and molecular weight distributions, M_w/M_n (open symbols), on the monomer conversion for the OMRP of VAc with different ratios of V-70 to Fe in toluene (50% v/v). $[\text{VAc}]:[\text{Fe}(\text{acac})_2] = 500:1$. ■: V-70/Fe = 0.8:1, 30 °C; ▲: V-70/Fe = 8:1, 30 °C; ●: V-70/Fe = 8:1, 40 °C.

As shown in Figure 3, the conversion increased rapidly at the beginning of the polymerization and then slowed down after 72 h (ca. 7 half-lives) but continued at a reduced rate, indicating the installation of control by reversible termination, as described in the previous section. Interplay between associative and dissociative radical exchange processes has already been demonstrated for a few cobalt systems.^{40,54,55} The polymerization was also carried out at 40 °C under the same conditions (50% v/v in toluene, $[\text{V-70}]/[\text{Fe}] = 8:1$), where the half-life of V-70 is about 200 min. Also in this case, there is a break in the polymerization kinetics plot, with a slowdown after ca. 7 half-lives (ca. 25 h). In the OMRP regime, the rate is first order in monomer and the rate constant is greater at the higher temperature, as expected. The measured molecular weights were in agreement with the

theoretical values until the end of the degenerative transfer process, when excess radicals maintain the iron complex in the oxidation state III in the organometallic dormant state. Subsequently, in the reversible termination regime, the M_n values evolve less and become smaller than the calculated ones, presumably because of the formation of additional polymer chains by catalyzed chain transfer reactions, since the inevitable terminations accumulate again $\text{Fe}(\text{acac})_2$, which may act as a chain transfer catalyst.

In conclusion of this polymerization part, we have demonstrated the ability of $\text{Fe}(\text{acac})_2$ to moderate the radical polymerization of VAc, via both the reversible termination and the degenerative transfer mechanisms, with formation of an organometallic dormant species. It is the first report of a controlled polymerization of VAc using an iron complex, and the first report of a controlled radical polymerization by degenerative transfer polymerization with an iron complex for any monomer. Degenerate transfer polymerization with a transition metal complex as a transfer agent has so far been clearly demonstrated only for cobalt, although the intervention of this mechanism in the $\text{Cp}_2\text{TiCl}/\text{epoxide}$ -mediated polymerization of styrene has also been proposed.⁶ While the principles of reversible termination and associative radical exchange have been established for the $\text{Fe}(\text{acac})_2$ -mediated VAc polymerization, the controlling ability of this system is however poor, compared with that of other controlling systems and notably of $\text{Co}(\text{acac})_2/\text{L}$.³⁴

Isolation and investigation of $\text{Fe}(\text{acac})_2$ -terminated oligomers

As shown above, the $\text{Fe}(\text{acac})_2$ -mediated polymerization of VAc initiated by V-70 at 30°C was not well controlled in the absence of ligand (Table 1, entries 3-5), and an induction period was observed. The same behavior was found in the $\text{Co}(\text{acac})_2$ -mediated polymerization of VAc, with an irreversible trapping of the PVAc radicals by $\text{Co}(\text{acac})_2$ in the absence of donor ligands.³²

Low-molecular-weight $\text{Co}(\text{acac})_2$ -terminated oligomers were synthesized by using excess $\text{Co}(\text{acac})_2$ relative to the V-70 initiator.³³ Subsequently, this $R_0\text{-(VAc)}_n\text{-Co}(\text{acac})_2$ product (n was shown to be ~ 4) proved an excellent thermal initiator for the OMRP of VAc with no induction period.³⁴

By analogy with this cobalt study, the thermal decomposition of V-70 in the presence of excess $\text{Fe}(\text{acac})_2$ and VAc gives rise to PVAc- $\text{Fe}(\text{acac})_2$ oligomers. Four fractions (**1**, **2**, **3** and **4**) were eluted through a silica gel column, in that order, using appropriate eluents, the major ones in recovered weight being **1** and **4** (see details in the Experimental Sections). The color varied from red for the more easily eluted fraction **1** to orange for less easily eluted ones **3** and **4**. The color of these samples is clear indication of the presence of the metal complex but does not prove that this is capping the PVAc chains by establishment of $\text{Fe}^{\text{III}}\text{-C}$ σ bonds. The materials appear air stable at room temperature, with no apparent change upon relatively long exposition periods to moist air. However, an EPR analysis (see details below) reveals their thermal deterioration upon long storage even when refrigerated.

An ^1H NMR study (see Figure 4) confirms the nature of fractions **2**, **3** and **4** as R_0 -terminated PVAc, R_0 being the primary radical generated by V-70 ($R_0 = \text{Me}_2(\text{MeO})\text{CCH}_2\text{C}(\text{CN})(\text{CH}_3)$). In addition to the signals characteristic of the PVAc protons (a, b, c), the R_0 signals at the α -chain end were observed as resonances d, e, f, and g. Figure 4 clearly shows how the PVAc signals increase their importance relative to those of the V-70 initiator fragment as the product residence time in the column increases.

Resonance integration should allow, in principle, to calculate the VAc/ R_0 ratio (degree of polymerization, X_n) for each isolated fraction. After population correction for the number of protons of each type, X_n can be conveniently obtained from either the a/d ratio or from the $(b+c)/d$ ratio. The $(e+f+g)/d$ and the $(b+c)/a$ ratios provide internal checks. A first important

observation is that, while the $(e+f+g)/d$ ratio is always correct, the $(b+c)/a$ ratio is higher than the expected value of 5 (5.5 for **4**, 5.8 for **3**, 6.4 for **2**, 25 for **1**). We believe that this phenomenon is caused by the presence of the paramagnetic Fe^{III} center (presumably $S = \frac{1}{2}$) at the chain end, shifting and broadening the resonances of protons of type a to a greater extent than those of type b and c .

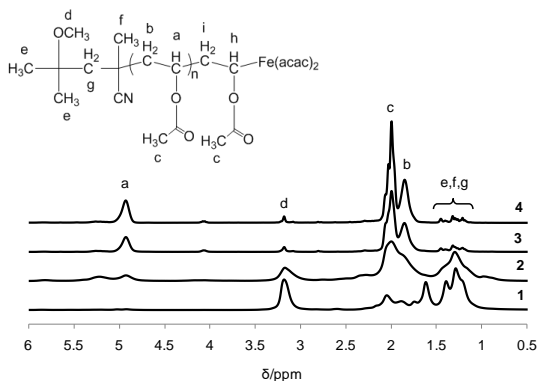


FIGURE 4. ¹H NMR spectra for iron adducts **1**, **2**, **3**, and **4**. Solvent: (CD₃)₂CO.

It is to be noted that the a resonance at δ 4.9 is clearly accompanied by other broad resonances at lower field (δ 5.2 and 5.8), probably associated to the a type protons of VAc units closer to the paramagnetic metal center, which decrease in relative intensity in the longer oligomers. It is impossible to predict the chemical shift of the CH proton of the metal-bonded VAc unit (h) and how many further VAc units are undetected. The same situation (though less dramatic according to the integration) holds for the methylene protons b , with those of the metal-bonded monomer unit (i) remaining unassigned. One possibility for this group may be the broad resonance at δ ca. 4.0. Note that this resonance is not attributable to a hydrolyzed (metal-free) chain, which would be observed at δ ca. 3.7 (*vide infra*). Taking the $(b+c)/d$ ratio as a more reliable indication of X_n , the calculated values increase with the chromatographic residence time of the isolated fraction: **2** (3) < **3** (26) < **4** (28). The same calculation for **1**, which shows very weak resonances in the δ 5-6 region for a and in the δ

2.2-1.8 region for b and c , affords a value of 0.5, which is absurd for an oligomer. This indicates that the majority of this fraction contains no VAc unit. It is worth mentioning here that first eluted fraction of the material from the analogous Co(acac)₂/V-70/VAc reaction was also devoid of VAc and was identified as the product of direct trapping of the primary radical generated from V-70, Me₂C(OMe)CH₂C*(Me)(CN), via the N atom to yield a dinuclear ketiminato-bridged derivative

$$\text{Co(acac)}_2\{\mu\text{-N=C=C(Me)CH}_2\text{C(OMe)Me}_2\}.$$
³³

The resonances of the acac ligands on the Fe^{III} center, like those of the metal bonded CH group (i), could not be identified. The spin state of Fe^{III} in the isolated **1-4** fractions is probably $\frac{1}{2}$, since the strong field alkyl ligand is known to favor a low-spin configuration for Fe^{III} (see also the EPR analysis below). This is the case for a family of aryl(porphyrinato)iron(III) complexes, which adopt a square-pyramidal structure with the organic ligand occupying the apical position.⁵⁶⁻⁶³ The ¹H NMR spectra of $S = \frac{1}{2}$ complexes are notoriously very broad and difficult to detect. For a high-spin Fe^{III} complex ($S = 5/2$), on the other hand, the ¹H spectrum is more easily observable. Indeed, Fe(acac)₃ is high-spin and its ¹H NMR spectrum has been reported in the literature.^{46,64} Upon widening the data collection window for the ¹H NMR spectra of **1-4**, we do find small resonances due to Fe(acac)₃ (broad resonances at δ ca. 21 (6H) and -25 (1H)), especially in the spectrum of **2**. This compound is known to be a contaminant in the commercial Fe(acac)₂ product, being formed from Fe(acac)₂ by air oxidation and ligand redistribution processes.⁴⁶ Most importantly, we do not observe any other broad and paramagnetically shifted band that could be assigned either to the PVAc-Fe(acac)₂ ω -chain end (because of its low spin state) or to residual Fe(acac)₂ ($S = 2$), which also gives rise to visible ¹H NMR bands.^{46,64} Although this may be considered as negative evidence for the presence of the Fe(acac)₂ chain end, positive evidence was provided by the use of these isolated oligomers as thermal macroinitiators (*vide infra*).

Additional and more convincing evidence was obtained by chemical modification of the oligomeric fractions **3** and **4**, in order to remove the metallic chain end, followed by analysis of the metal-free polymers. The treatment was not carried out on fractions **1** and **2** because the first one is mostly not a PVAc oligomer (*vide supra*) and the second one was only available in small quantities. This treatment is also of interest for the post-modification of the isolated polymer, which always remains as a pale yellow material, even after elution through alumina or dissolution and reprecipitation in heptane. An efficient technique for eliminating the iron moiety consisted of treatment with 1-butanethiol. The same treatment was previously shown to demetallate the related PVAc-Co(acac)₂, replacing the Co(acac)₂ moiety by a H atom.⁶⁵ The reaction took place smoothly at 50°C in EtOH to yield white materials (**3'**, **4'**), giving clear indication of the successful quantitative metal removal. The ¹H NMR spectra of the resulting isolated products are shown in Figure 5.

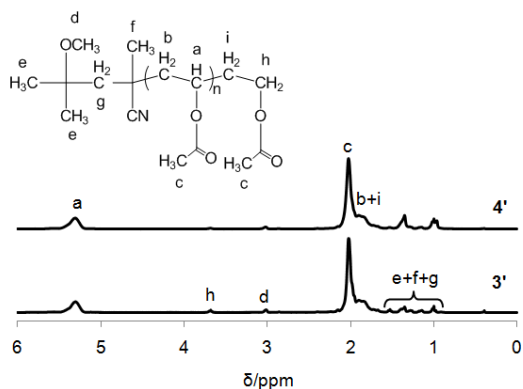


FIGURE 5. ¹H NMR spectra in C₆D₆ of products **1'**, **3'**, and **4'**, obtained respectively from **1**, **3**, and **4** after addition of 1-butanethiol.

The cleavage of Fe-C bond is confirmed by the presence of the methylene protons at the PVAc ω -chain end (3.7 ppm), identical to the material obtained by the same method from the Co(acac)₂ capped polymer.⁶⁵ The characteristic signals of the V-70 fragment at the α -end and of the PVAc chain are also observed. From the

intensity ratio of the methoxy proton (*d*) of the initiating radical and the main-chain repeat units (*a*), the degree of polymerization in the two samples is respectively 41.6 and 47.6 (note that these numbers, now unaffected by paramagnetic broadening effects, are indeed higher than those estimated from the spectra of the Fe-containing oligomers), yielding calculated molar masses ($M_{n,NMR(\alpha\text{-end})}$) of 3722 (**3'**) and 4239 (**4'**).

This demetallation and NMR study therefore confirms that the oligomeric species **3** and **4** contain a paramagnetic metal complex as chain end and show that the isolated material is an oligomer with a substantial degree of polymerization (> 40). This situation is in sharp contrast with the analogous Co(acac)₂ oligomer prepared under the same operating conditions, for which the degree of polymerization was much smaller (ca. 4). This difference shows that Fe(acac)₂ is a much poorer trap for the growing PVAc radical chain relative to Co(acac)₂, in line with the observed poorer control of the Fe(acac)₂-mediated polymerization. This different trapping ability was not anticipated and its reason is not currently understood. Indeed, the Fe(acac)₂ and Co(acac)₂ complexes exhibit very similar coordination chemistry. They are both tetranuclear in the solid state and in concentrated solutions, equilibrating with the tetrahedral monomer at high dilution, and form weakly bonded bis(ligand) adducts with a variety of standard Lewis bases. They can both form alkyl adducts in the oxidation state III, either in a square pyramidal coordination environment as mentioned above, or as 6-coordinate pseudo-octahedral Lewis base adducts. Furthermore, both radical trapping processes involve pairing of two electrons, going from $d^7 S = 3/2$ to $d^6 S = 0$ in the case of cobalt and from $d^6 S = 2$ to $d^5 S = 1/2$ in the case of Fe. Therefore, the spin state change cannot be blamed *a priori* as a source of extra energy barrier in the case of Fe.

In order to find more positive evidence for the presence of low spin Fe^{III} on the isolated oligomeric species, an EPR study was carried out

on fraction **4**. The X-band EPR spectrum in a frozen toluene solution is shown in Figure 6 (trace *a*). After keeping the solid sample in storage for several months at -20°C , the spectrum of a new solution (trace *b*) showed a similar general shape, except for the absence of the small and sharp resonances in the 3300-3400 G region, better visible in the figure inset. The rest of the spectrum corresponds to $\text{Fe}(\text{acac})_3$, as confirmed by the EPR of a genuine sample (trace *c*). The sharp features in the 3300-3400 G ($g \approx 2$) are typical of low-spin Fe^{III} ($S = \frac{1}{2}$), similar features being reported for low spin alkyliron(III) porphyrin derivatives.⁵⁷⁻⁵⁹ The presence of $\text{Fe}(\text{acac})_3$ in the sample can be easily explained as resulting from homolytic cleavage of the thermally labile $\text{PVAc-Fe}^{\text{III}}(\text{acac})_2$ bond, yielding $\text{Fe}(\text{acac})_2$, which is known to transform to $\text{Fe}(\text{acac})_3$ in moist air,⁴⁶ as already mentioned above. Thus, the EPR study confirms the presence of thermally labile slow-spin Fe^{III} centers and it indirectly points to the presence of the $\text{Fe}^{\text{III}}(\text{acac})_2$ unit σ bonded to the PVAc chain at the ω end, although this cannot be considered as definite and unambiguous proof.

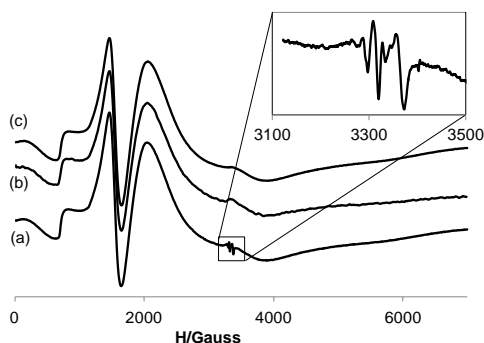


FIGURE 6. X-band EPR spectra in frozen toluene solution at 115K. (a) $\text{PVAc-Fe}(\text{acac})_2$ oligomer **4**; (b) same as (a), after storage of the solid **4** for several months at -20°C . (c) $\text{Fe}(\text{acac})_3$.

Additional characterization was provided by an IR study. The IR spectra of isolated **2-4** (see Figure 7) show the expected bands of PVAc and also those of the acac ligands, with the relative intensity of the PVAc carbonyl band at 1730 cm^{-1} increasing relative to those of the acac ligand at 1570 and 1525 cm^{-1} . The latter have significantly

different frequency relative to those of both $\text{Fe}(\text{acac})_2$ ($1569, 1556, 1518\text{ cm}^{-1}$) and $\text{Fe}(\text{acac})_3$ ($1565, 1518\text{ cm}^{-1}$), particularly the lower frequency one which is significantly blue-shifted. The spectrum of product **1** shows acac bands at 1568 and 1522 cm^{-1} and the typical bands of PVAc are barely perceptible, in agreement with the NMR results discussed above. A sharp band at 2233 cm^{-1} (not visible for samples **2-4**) is typical of the CN group and an even weaker band is also observed at 2015 cm^{-1} , suggesting the presence of a ketimino function analogous to that revealed for the product obtained with $\text{Co}(\text{acac})_2$ (2017 cm^{-1}).³³ Thus, the IR study confirms the presence of $\text{Fe}(\text{acac})$ units in all fractions but, like the EPR study, it does not provide positive evidence for the existence of a $\text{Fe}^{\text{III}}\text{-PVAc}$ σ bond.

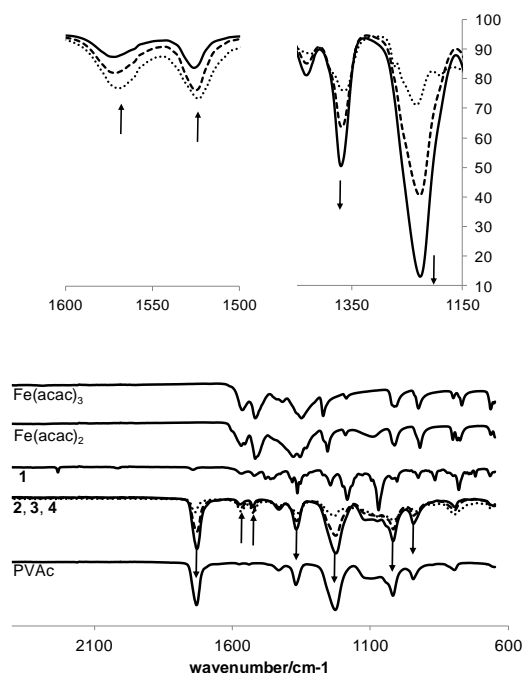


FIGURE 7. IR spectra of the isolated products **1-4**. For comparison, the spectra of $\text{Fe}(\text{acac})_2$, $\text{Fe}(\text{acac})_3$ and a PVAc made by free radical polymerization (V-70 initiator) are also shown. The two upper figures are details of the $1600\text{-}1500$ and $1450\text{-}1150\text{ cm}^{-1}$ regions of the spectra of products **2** (dotted line), **3** (dashed line) and **4** (plain line).

OMRP of vinyl acetate from the PVAc-Fe(acac)₂ macroinitiator

By analogy with the OMRP of VAc initiated by the PVAc-Co(acac)₂ oligomers in the absence of any external radical source,^{31,33,34} we have tested the above described PVAc-Fe(acac)₂ materials (**3** and **4**), and also product **1** that presumably consists mostly of a R₀-Fe(acac)₂ species with no VAc incorporation, as thermal initiators for the VAc polymerization. The bulk polymerization of VAc initiated by **1** was carried out at 30 °C and the results are shown in Figure 8.

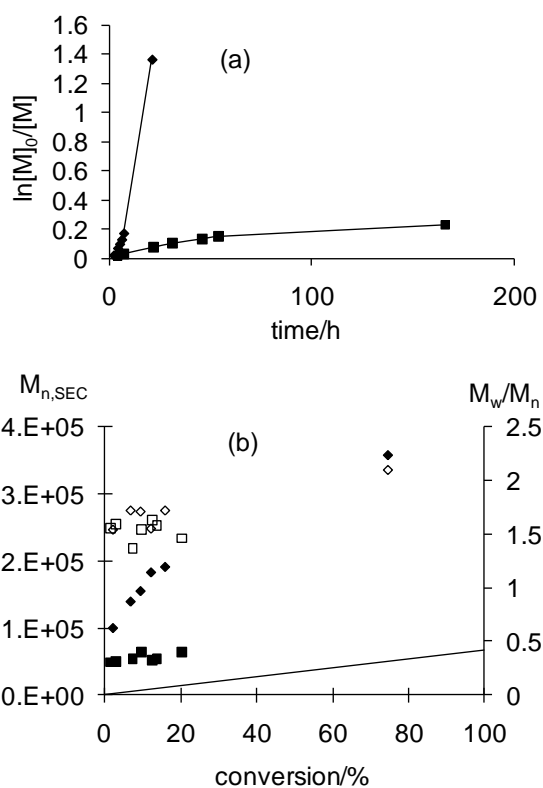


FIGURE 8. Plots of (a) $\ln([M]_0/[M])$ vs. time and (b) molecular weights, M_n (filled symbols), and molecular weight distributions, M_w/M_n (open symbols), vs. monomer conversion for the polymerization of VAc initiated by the iron adduct **1** with (■) and without (◆) DMPP. [VAc]:[Fe]:[DMPP] = 775:1:1.

Polymerization indeed took place, demonstrating the thermal release of radicals from **1**. However, the polymerization was rather

fast when carried out in the absence of ligand (74% conversion in 21 h) and yielded a polymer with very high molecular weight and dispersity ($\mathcal{D} = 1.5$ -2.1). When the same polymerization was carried out in the presence of added ligand (DMPP), the process was much slower and resulted in a polymer with lower M_n (although still greater than the theoretical one) and lower \mathcal{D} (1.35-1.63). These results closely parallel those obtained by the V-70/Fe(acac)₂ initiation method. Note that the molecular weight distributions of these polymers are monomodal.

The iron compounds **3** and **4** were also tested as thermal macroinitiators for the polymerization of VAc at 30 °C. Contrary to the polymer obtained using **1**, the molecular weight distribution is bimodal as shown by the SEC traces of the resulting polymers (Figure 9). Identical results were obtained using the oligoinitiators **3** and **4**. As the polymerization progresses, the low M_n component due to the **3** macroinitiator decreases, while the higher M_n component increases and its distribution is displaced to higher values. This second component has a relatively low \mathcal{D} (1.3-1.6). These results clearly confirm that the isolated systems **3** and **4** are indeed Fe(acac)₂-terminated dormant PVAc chains that are able to be thermally reactivated and serve as single-component macroinitiators for the VAc polymerization. The generation of a bimodal distribution and its evolution as a function of conversion, as shown in Figure 9, demonstrate that the isolated PVAc-Fe(acac)₂ dormant species contains a fraction of chains that can no longer be reactivated, for instance terminated chains obtained by thermal degradation of the Fe(acac)₂-capped chains, as suggested also by the EPR investigation.

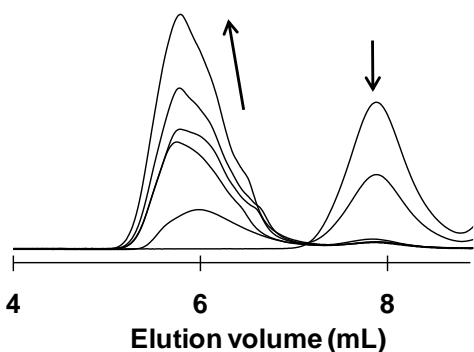


FIGURE 9. SEC chromatograms for PVAc from the bulk polymerization of VAc initiated by compound 3 at 30 °C. [VAc]:[Fe] = 8317:1. The measured fractions are respectively at time/h (conversion/%) of: 0(0), 7(1.1), 22(10.3), 26(13.6), 31(17.9), 46(27.8).

CONCLUSIONS

In summary, we have described the first OMRP of VAc controlled by an iron(II) complex, $\text{Fe}(\text{acac})_2$, by the reversible deactivation strategy as well as by the degenerative transfer strategy. Evidence for the ability of $\text{Fe}(\text{acac})_2$ to act as chain transfer catalyst is also shown by the data. Addition of Lewis bases under reversible termination conditions has the effect of slowing down the polymerization process, indicating a greater stabilization of the dormant $\text{PVAc-Fe}^{\text{III}}(\text{acac})_2$ species relative to the trapping $\text{Fe}^{\text{II}}(\text{acac})_2$ species by Lewis base coordination. The Lewis base, especially PMe_2Ph , slightly improves controllability (molecular weight and molecular weight distribution). An oligomeric $\text{R}_0\text{-(VAc)}_n\text{-Fe}^{\text{III}}(\text{acac})_2$ dormant species with $n > 40$ has been isolated, characterized, and shown to be able to thermally reinitiate the VAc polymerization. The accumulated evidence, however, indicates that this system exerts poor control, much poorer than $\text{Co}(\text{acac})_2$, mainly because of a slower radical trapping rate. The results are, however, encouraging for further exploration of iron complexes as controlling systems within the OMRP approach.

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REFERENCES AND NOTES

- † Current address: Department of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China.
1. R. Poli. *Angew. Chem., Int. Ed.* **2006**, *45*, 5058–5070.
2. K. M. Smith, W. S. Mcneil, A. S. Abd-El-Aziz. *Macromol. Chem. Phys.* **2010**, *211*, 10–16.
3. L. D. Arvanatitopoulos, M. P. Greuel, H. J. Harwood. *Polym. Prep.* **1994**, *35*, 549–550.
4. B. B. Wayland, G. Poszmik, S. Mukerjee. *J. Am. Chem. Soc.* **1994**, *116*, 7943–7944.
5. A. Debuigne, R. Poli, C. Jérôme, R. Jérôme, C. Detrembleur. *Prog. Polym. Sci.* **2009**, *34*, 211–239.
6. A. D. Asandei, I. W. Moran. *J. Am. Chem. Soc.* **2004**, *126*, 15932–15933.
7. A. D. Asandei, I. W. Moran. *J. Polym. Sci., Polym. Chem.* **2005**, *43*, 6039–6047.
8. A. D. Asandei, I. W. Moran. *J. Polym. Sci., Polym. Chem.* **2006**, *44*, 1060–1070.
9. A. D. Asandei, G. Saha. *J. Polym. Sci., Polym. Chem.* **2006**, *44*, 1106–1116.
10. E. Le Grogne, J. Claverie, R. Poli. *J. Am. Chem. Soc.* **2001**, *123*, 9513–9524.
11. Y. Champouret, U. Baisch, R. Poli, L. Tang, J. L. Conway, K. M. Smith. *Angew. Chem., Int. Ed.* **2008**, *47*, 6069–6072.
12. Y. Champouret, K. C. Macleod, U. Baisch, B. O. Patrick, K. M. Smith, R. Poli. *Organometallics* **2010**, *29*, 167–176.
13. Y. Champouret, K. C. Macleod, K. M. Smith, R. Poli. *Organometallics* **2010**, *29*, 3125–3132.
14. W. A. Braunecker, Y. Itami, K. Matyjaszewski. *Macromolecules* **2005**, *38*, 9402–9404.

15. W. A. Braunecker, W. C. Brown, B. Morelli, W. Tang, R. Poli, K. Matyjaszewski. *Macromolecules* **2007**, *40*, 8576-8585.
16. K. Koumura, K. Satoh, M. Kamigaito. *J. Polym. Sci., Polym. Chem.* **2009**, *47*, 1343-1353.
17. M. P. Shaver, M. E. Hanhan, M. R. Jones. *Chem. Commun.* **2010**, *46*, 2127-2129.
18. L. E. N. Allan, E. D. Cross, T. W. Francis-Pranger, M. E. Hanhan, M. R. Jones, J. K. Pearson, M. R. Perry, T. Storr, M. P. Shaver. *Macromolecules* **2011**, *44*, 4072-4081.
19. M. Kamigaito, T. Ando, M. Sawamoto. *Chem. Rev.* **2001**, *101*, 3689-3745.
20. M. Ouchi, T. Terashima, M. Sawamoto. *Acc. Chem. Res.* **2008**, *41*, 1120-1132.
21. M. Ouchi, T. Terashima, M. Sawamoto. *Chem. Rev.* **2009**, *109*, 4963-5050.
22. F. Di Lena, K. Matyjaszewski. *Progr. Polym. Sci.* **2010**, *35*, 959-1021.
23. M. P. Shaver, L. E. N. Allan, H. S. Rzepa, V. C. Gibson. *Angew. Chem., Int. Ed. Eng.* **2006**, *45*, 1241-1244.
24. M. P. Shaver, L. E. N. Allan, V. C. Gibson. *Organometallics* **2007**, *26*, 4725-4730.
25. L. E. N. Allan, M. P. Shaver, A. J. P. White, V. C. Gibson. *Inorg. Chem.* **2007**, *46*, 8963-8970.
26. S. Kanagasabapathy, D. Serero, D. Silie, S. Prost, R. Ruiz-Guerrero, J. Claverie. *Res. Discl.* **1998**, P1595-P1604.
27. Z. Xue, R. Poli. *ACS Symp. Ser.* **2012**, *1100*, 231-242.
28. N. S. Enikolopyan, B. R. Smirnov, G. V. Ponomarev, I. M. Belgovskii. *J. Polym. Sci., Polym. Chem.* **1981**, *19*, 879-889.
29. M. B. Gillies, K. Matyjaszewski, P.-O. Norrby, T. Pintauer, R. Poli, P. Richard. *Macromolecules* **2003**, *36*, 8551-8559.
30. K. Matyjaszewski, R. Poli. *Macromolecules* **2005**, *38*, 8093-8100.
31. A. Debuigne, C. Michaux, C. Jérôme, R. Jérôme, R. Poli, C. Detrembleur. *Chem. Eur. J.* **2008**, *14*, 7623-7637.
32. S. Maria, H. Kaneyoshi, K. Matyjaszewski, R. Poli. *Chem. Eur. J.* **2007**, *13*, 2480-2492.
33. A. Debuigne, Y. Champouret, R. Jérôme, R. Poli, C. Detrembleur. *Chem. Eur. J.* **2008**, *14*, 4046-4059.
34. A. Debuigne, R. Poli, R. Jérôme, C. Jérôme, C. Detrembleur. *ACS Symp. Ser.* **2009**, *1024*, 131-148.
35. A. Debuigne, J. R. Caille, R. Jérôme. *Angew. Chem., Int. Ed.* **2005**, *44*, 1101-1104.
36. A. Debuigne, J. R. Caille, C. Detrembleur, R. Jerome. *Angew. Chem., Int. Ed.* **2005**, *44*, 3439-3442.
37. H. Kaneyoshi, K. Matyjaszewski. *Macromolecules* **2005**, *38*, 8163-8169.
38. H. Kaneyoshi, K. Matyjaszewski. *Macromolecules* **2006**, *39*, 2757-2763.
39. C. H. Peng, J. Scricco, S. Li, M. Fryd, B. B. Wayland. *Macromolecules* **2008**, *41*, 2368-2373.
40. K. S. Santhosh Kumar, Y. Gnanou, Y. Champouret, J.-C. Daran, R. Poli. *Chem. Eur. J.* **2009**, *15*, 4874-4885.
41. K. S. Santhosh Kumar, Y. Li, Y. Gnanou, U. Baisch, Y. Champouret, R. Poli, K. C. D. Robson, W. S. Mcneil. *Chem. Asian J.* **2009**, *4*, 1257-1265.
42. F. A. Cotton, G. W. Rice. *New J. Chem.* **1977**, *1*, 301-305.
43. D. A. Buckingham, R. C. Gorges, J. T. Henry. *Austr. J. Chem.* **1967**, *20*, 281-296.
44. D. A. Buckingham, R. C. Gorges, J. T. Henry. *Austr. J. Chem.* **1967**, *20*, 497-502.
45. S. D. Ittel. *Inorg. Chem.* **1977**, *16*, 1245-1246.
46. Z. Xue, J.-C. Daran, Y. Champouret, R. Poli. *Inorg. Chem.* **2011**, *50*, 11543-11551.
47. J. Xia, H.-J. Paik, K. Matyjaszewski. *Macromolecules* **1999**, *32*, 8310-8314.
48. M. Wakioka, K. Y. Baek, T. Ando, M. Kamigaito, M. Sawamoto. *Macromolecules* **2002**, *35*, 330-333.
49. M. Destarac, D. Charmot, X. Franck, S. Z. Zard. *Macromol. Rapid Comm.* **2000**, *21*, 1035-1039.

50. M. H. Stenzel, L. Cummins, G. E. Roberts, T. P. Davis, P. Vana, C. Barner-Kowollik. *Macromol. Chem. Phys.* **2003**, *204*, 1160-1168.
51. M. C. Iovu, K. Matyjaszewski. *Macromolecules* **2003**, *36*, 9346-9354.
52. Y. Kwak, A. Goto, T. Fukuda, Y. Kobayashi, S. Yamago. *Macromolecules* **2006**, *39*, 4671-4679.
53. A. N. Morin, C. Detrembleur, C. Jérôme, P. D. Tullio, R. Poli, A. Debuigne. *Macromolecules (Washington, DC, United States)* **submitted**.
54. B. B. Wayland, C.-H. Peng, X. Fu, Z. Lu, M. Fryd. *Macromolecules* **2006**, *39*, 8219-8222.
55. C.-H. Peng, M. Fryd, B. B. Wayland. *Macromolecules* **2007**, *40*, 6814-6819.
56. P. Doppelt. *Inorg. Chem.* **1984**, *23*, 4009-4011.
57. R. Guillard, B. Boisselier-Cocolios, A. Tabard, P. Cocolios, B. Simonet, K. M. Kadish. *Inorg. Chem.* **1985**, *24*, 2509-2520.
58. A. Tabard, G. Lagrange, R. Guillard, M. Jouan, N. Q. Dao. *J. Organometal. Chem.* **1986**, *308*, 335-344.
59. A. Tabard, P. Cocolios, G. Lagrange, R. Gerardin, J. Hubsch, C. Lecomte, J. Zarembowitch, R. Guillard. *Inorg. Chem.* **1988**, *27*, 110-117.
60. A. L. Balch, C. R. Cornman, N. Safari, L. Latos-Grazynski. *Organometallics* **1990**, *9*, 2420-2421.
61. K. Kano, M. Takeuchi, S. Hashimoto, Z. Yoshida. *J. Chem. Soc., Chem. Commun.* **1991**, 1728-1729.
62. J. Setsune, Y. Ishimaru, A. Sera. *J. Chem. Soc., Chem. Commun.* **1992**, 328-329.
63. Z. Li, H. M. Goff. *Inorg. Chem.* **1992**, *31*, 1547-1548.
64. D. R. Eaton. *J. Am. Chem. Soc.* **1965**, *87*, 3097-3102.
65. A. Debuigne, J.-R. Caille, R. Jérôme. *Macromolecules* **2005**, *38*, 5452-5458.

GRAPHICAL ABSTRACT

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Organometallic Mediated Radical Polymerization of Vinyl Acetate with $\text{Fe}(\text{acac})_2$

Poly(vinyl acetate) with controlled molecular weight and low dispersity is obtained by $\text{Fe}(\text{acac})_2$ -mediated OMRP. Isolation and characterization of a $\text{PVAc-Fe}^{\text{III}}(\text{acac})_2$ oligomer and chain extension demonstrates the polymerization mechanism, but the controllability is limited by a relatively slow radical trapping rate.

