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## Electronic and Steric Ligand Effects in the Radical Polymerization of Vinyl Acetate Mediated by $\beta$ -Ketoiminate Complexes of Cobalt(II)

Santhosh Kumar K. S.,<sup>[a]</sup> Yugang Li,<sup>[a]</sup> Yves Gnanou\*<sup>[a]</sup>, Ulrich Baisch,<sup>[b]</sup> Yohan Champouret,<sup>[b]</sup> Rinaldo Poli\*<sup>[b],[c]</sup> Kiyoshi C. D. Robson,<sup>[d]</sup> W. Stephen McNeil<sup>[d]</sup>

**Abstract:** Complexes  $\text{Co}[\text{OC}(\text{Ph})\text{CH}-\text{C}(\text{Me})\text{NAr}]_2$  [Ar = Ph, **1**; *o,o'*- $\text{C}_6\text{H}_3\text{Me}_2$  (Xyl), **2**; *p*- $\text{C}_6\text{H}_4\text{CF}_3$ , **3**] were tested in the polymerization of vinyl acetate (VAc) initiated by V-70 (0.8 equiv) at 30°C. Polymerization occurred without any notable induction time yielding PVAc with relatively low polydispersity, but with higher than expected  $M_n$  values, indicating inefficient trapping processes. The apparent polymerization rate constant varies in the order **2** > **1** > **3**. Controlled polymer growth is also

observed when the polymerization is conducted in the presence of a much higher V-70/1 ratio, demonstrating that this system can also function as a transfer agent in a degenerative transfer process. The addition of pyridine does not alter significantly the VAc polymerization rate and the complex controlling ability for compound **1**, whereas a fourfold rate increase is observed for compound **3**. A parallel NMR study indicates no significant interaction between py and compound **1** and a weak interaction between py and compound **3**. Competition between

chain growth and catalyzed chain transfer (CCT) was also observed, the latter prevailing at higher temperatures. Comparison of these results with previous ones obtained with bis( $\beta$ -diketonato) complexes allows a separate assessment of ligand electronic and steric effects in the polymerization controlling ability.

**Keywords:** controlled radical polymerization • OMRP • poly(vinyl acetate) • cobalt •  $\beta$ -ketoiminate ligands

### Introduction

In recent years, increasing attention has been paid to controlled radical polymerization (CRP).<sup>[1-4]</sup> Novel polymeric materials with well-defined molecular parameters such as average molecular weight, molecular-weight distribution, chain-end functions, and topological-structure have been accessible through various strategies. A current challenge of CRP is to control the radical polymerization

of monomers that generate more reactive radicals such as vinyl acetate, vinyl chloride, vinylidene chloride, and ethylene. A variety of methods have been devoted to mediate the polymerization of vinyl acetate with a certain success, such as degenerative chain transfer with alkyl iodides,<sup>[5]</sup> dithiocarbamates and xanthates (RAFT/MADIX),<sup>[6-8]</sup> ATRP,<sup>[9, 10]</sup> and cobalt-mediated radical polymerization (CMRP).<sup>[11, 12]</sup>

It has been argued that the use of metal-mediated CRP may allow controlling difficult monomers.<sup>[13, 14]</sup> The advantage of using metal complexes is the variety of available transition metals and ligands, which can be tailored to mediate the polymerization of the monomer of choice. In recent contributions, it has been shown that the control exerted by acetylacetonatocobalt(II),  $\text{Co}(\text{acac})_2$ , on the VAc polymerization occurs by degenerative transfer (DT) when no additional Lewis bases are present,<sup>[15]</sup> but it switches to reversible deactivation (RD) and more specifically to a process that we have termed “organometallic radical polymerization” (OMRP)<sup>[13]</sup> in the presence of donor ligands such as pyridine,  $\text{NEt}_3$ , or water, see <Scheme 1.<sup>[15, 16]</sup> Indeed, the bond established between  $\text{Co}(\text{acac})_2$  and the growing PVAc chain is too strong to release a sufficient amount of radical chains through homolytic bond cleavage under typical polymerization conditions. However, coordination of Lewis bases stabilizes the  $\text{Co}^{\text{II}}$  radical trapping species by a greater extent, through formation of a bis(adduct)  $\text{Co}(\text{acac})_2(\text{L})_2$ , than the  $\text{Co}^{\text{III}}$  dormant species, through formation of a mono(adduct)  $(\text{L})(\text{acac})_2\text{Co}-\text{PVAc}$ . Thus, the homolytic bond breaking process becomes thermodynamically more favoured. At the same time, coordination by L blocks the open coordination site necessary for the associative radical exchange, shutting down the DT pathway.

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Porphyrin-based cobalt systems have also been shown to function either by the OMRP mechanism<sup>[17-20]</sup> or by degenerative transfer,<sup>[21-25]</sup> depending on conditions and on the nature of the monomer.

<Scheme 1 here>

Following the original report of the Co(acac)<sub>2</sub>-mediated polymerization,<sup>[11]</sup> Matyjaszewski has reported the VAc polymerization mediated by fluorinated β-diketonato analogues of Co(acac)<sub>2</sub>, namely Co(CF<sub>3</sub>C(O)CHC(O)CH<sub>3</sub>)<sub>2</sub>, Co(acac-F<sub>3</sub>)<sub>2</sub>, and Co(CF<sub>3</sub>C(O)CHC(O)CF<sub>3</sub>)<sub>2</sub>, Co(acac-F<sub>6</sub>)<sub>2</sub>.<sup>[26]</sup> The study shows that Co(acac-F<sub>3</sub>)<sub>2</sub> can control the polymerization, whereas Co(acac-F<sub>6</sub>)<sub>2</sub> cannot. Diblock copolymers of VAc with N-vinylpyrrolidone,<sup>[27]</sup> styrene,<sup>[28]</sup> and acrylonitrile<sup>[29, 30]</sup> have also been obtained by use of Co(acac)<sub>2</sub>. More recently, we have shown that an increase of steric bulk in the β-diketonate ligand without a major change in the electronic properties, namely going to the 2,2,6,6-tetramethylheptane-2,5-dionato (tmhd) system, Co(*t*BuC(O)CHC(O)*t*Bu)<sub>2</sub>, results in a slight weakening of the Co<sup>III</sup>-PVAc bond and renders this system operational also in the OMRP of VAc, even in the absence of Lewis base additives.<sup>[31]</sup>

<Scheme 2 here>

In this paper, we report the use of Co[OC(Ph)CHC(Me)NAr]<sub>2</sub> [Ar = Ph, **1**; *o,o'*-C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub> (Xyl), **2**; *p*-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>, **3**] (<Scheme 2) in the radical polymerization of vinyl acetate initiated by 2,2'-azobis(4-methoxyl-2,4-dimethylvaleronitrile) (V-70) at 30°C. β-Ketiminato ligands are isoelectronic with β-diketonato ligands, but the metal-bound nitrogen group permits a greater versatility in both steric and electronic changes in close proximity to the metal centre,<sup>[32]</sup> which can lead to dramatic variations in properties such as the geometry, spin state, and metal–ligand bond strengths.<sup>[33]</sup> As will be shown, the polymerization rate is indeed sterically activated by the bulk of the NAr group, although the electronic difference between the NAr group of these ligands and the O atom in the β-diketonate ligand has a more important effect. It will also be demonstrated that the positive effect of steric activation for the dormant Co<sup>III</sup>-PVAc chain is associated with a negative effect of slower trapping for the active PVAc radical chain.

## Results and Discussion

### (a) Polymerization of vinyl acetate in the absence of external base

In order to probe for an OMRP mechanism, polymerization experiments of vinyl acetate (VAc) initiated by V-70 were initially conducted with a small amount (0.8 equiv per Co) of initiator in toluene solution (50% v/v) at 30°C. Under these conditions, the initiator half life is ca. 10 h. With each of the compounds **1-3**, polymerization took place, although rather slowly, and continued well beyond the time needed to completely decompose the initiator, namely ca. 50-60 hours (5-6 half-lives), see Table 1. Without cobalt complex, a more rapid polymerization takes place under these conditions, which stops after all initiator has been consumed and yields higher molecular weights, as also reported in Table 1. This proves that the growing PVAc chains are trapped by the cobalt complex and that they are subsequently released reversibly and continuously into solution according to the OMRP mechanism.

Table 1. Polymerization of VAc initiated by V-70 in the presence of complexes **1-3**.<sup>a</sup>

Complex	Time(h)	Conv(%)	M <sub>n,SEC</sub>	M <sub>n,theo</sub>	PDI
<b>1</b>	64	12.3	15000	5300	1.17
<b>1</b>	96	17.1	18700	7400	1.20
<b>1</b>	160	24.6	21300	10600	1.36
<b>2</b>	25	22.9	31300	9900	1.37
<b>2</b>	49	33.8	33900	14600	1.34
<b>2</b>	72	40.2	35300	17300	1.34
<b>2</b>	114	49.1	37600	21200	1.30
<b>3</b>	16	3.3	-	-	-
<b>3</b>	38.75	4.8	-	-	-
<b>3</b>	63	5.2	-	-	-
<b>3</b>	134.5	12.3	8700	5290	1.15
<b>3</b>	212	18.6	10700	8000	1.19
<b>3</b>	303	22.7	12800	9770	1.22
-	3.25	8.9	33800	-	1.23
-	6	12.8	25300	-	1.22
-	21.5	27.9	25100	-	1.21
-	30.5	38.8	24100	-	1.19
-	46	49	20600	-	1.28
-	117.5	56.8	15600	-	1.47

[a] Conditions: VAc/Co/V-70 = 500:1:0.8 (500:0:6.0 for the experiment without cobalt); VAc/Toluene = 1:1 (v/v); T = 30°C.

The monomer consumption follows first order kinetics reasonably well in all cases after then end of the initiator decomposition (> ca. 60 h), see Figure 1, in agreement with the presence of a persistent radical effect. The effective polymerization rate constant varies in the order **3** ( $9.04 \cdot 10^{-4} \text{ h}^{-1}$ ) < **1** ( $1.56 \cdot 10^{-3} \text{ h}^{-1}$ ) < **2** ( $4.02 \cdot 10^{-3} \text{ h}^{-1}$ ). The rate change on going from **3** to **1** (rate ratio of ca. 1.7) is less important than on going from **1** to **2** (rate ratio of ca. 2.6). The difference between compounds **2** and **1** can be easily rationalized on the basis of the steric effect of the aryl *o*-Me substituents in **2**, which is expected to weaken the Co<sup>III</sup>-PVAc bond. Similar steric effects have previously been noted for Co[OC(R)CHC(R)O]<sub>2</sub> (R = *t*Bu vs. Me)<sup>[31]</sup> and for CpCr[ArNC(Me)CHC(Me)NAr] (Ar = 2,6-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>, 2,6-C<sub>6</sub>H<sub>3</sub>*i*Pr<sub>2</sub>).<sup>[14]</sup> Note that the electronic effect due to the greater electron-donating power of the xylyl group relative to Ph, as confirmed by the easier oxidation of **2** (E<sub>p,c</sub> = +0.91 V) relative to **1** (E<sub>p,c</sub> = +1.02), should make the formation of the Co<sup>III</sup>-PVAc thermodynamically more favorable and thus the radical dissociation less extensive (*i.e.* slow down the polymerization process) for the former complex. Thus, the faster polymerization observed in the presence of **2** relative to **1** shows that the steric effect overrules the electronic one.

<Figure 1 here>

Figure 1. Time dependence of ln([M]<sub>0</sub>/[M]) for the polymerization of vinyl acetate at 30°C (data from Table 1). The dotted line corresponds to the data obtained in the absence of cobalt.

The comparison between compounds **1** and **3** cannot be easily rationalized, because the two systems should be quite similar in terms of steric influence; the *p*-CF<sub>3</sub> substituents in **3** are located far from the Co center. On the other hand, the electronic effect should favour a faster polymerization in the presence of **3**, since this complex is less easily oxidized (E<sub>p,c</sub> = +1.11 V), contrary to the experimental result. However, the apparent rate constant (*k*<sub>app</sub>, <Scheme 3) depends not only on the equilibrium constant of the reversible radical dissociation process (*k*<sub>d</sub>/*k*<sub>a</sub>), which is related to the relative stability of Co<sup>II</sup> and Co<sup>III</sup> species, but also on the concentration ratio of Co<sup>III</sup> and Co<sup>II</sup> species. If the residual amount of Co<sup>II</sup> is greater in the case of **3** (for instance, because of a less efficient radical trapping by this compound), then the apparent polymerization rate constant may become lower even if (*k*<sub>d</sub>/*k*<sub>a</sub>) is higher.

<Scheme 3 here>

The evolution of  $M_n$  for each polymerization in Table 1 is represented graphically in Figure 2. It can be noted that the initial  $M_n$  values are greater than expected (on the basis of one polymer chain per Co atom) and there is an evolution with conversion in each case, but the data deviate from the theoretical line in the order **2** > **1** > **3**, namely the same order as the apparent polymerization rate constants. The polydispersity index is in all cases below 1.4 and as low as 1.15 in the case of **3**. Thus, compounds **1-3** appear to have a certain degree of controlling ability for the VAc radical polymerization by the OMRP mechanism. The larger initial  $M_n$  value is evidence that these  $\text{Co}^{\text{II}}$  complexes are not very efficient free radical scavengers, at least when the radicals are produced in large amounts at the beginning of the polymerization process. This low trapping efficiency, compared for instance with that of  $\text{Co}(\text{acac})_2$ ,<sup>[16]</sup> may be due to the larger steric crowding around the metal for the  $\beta$ -diketiminato system. The slow trapping rate is further confirmed by the results obtained at higher temperatures with compound **3** (*vide infra*).

<Figure 2 here>

Figure 2. Dependence on conversion of  $M_n$  and  $M_w/M_n$  for the VAc polymerization mediated by compounds **1-3** (data from Table 1). The straight line represents the theoretical  $M_n$  evolution.

In comparison with the OMRP mediated by compound  $\text{Co}(\text{tmhd})_2$  the polymerizations mediated by **1-3** are rather slow (a 60% conversion in 91 h was observed in the presence of 0.7 equiv of V-70 under the same experimental conditions of temperature, solvent and monomer dilution).<sup>[31]</sup> This slow rate indicates a rather strong  $\text{Co}^{\text{III}}$ -PVAc bond for the dormant chain and is opposite to the expected trend on steric grounds, since the encumbrance of the NAr group is far larger than that of the carbonyl group. Thus, this bond strengthening must have an electronic origin. The imine N atom of the  $\beta$ -ketiminato ligand is a stronger electron donor than the carbonyl O atom of the  $\beta$ -diketonato ligand, resulting in an electronic stabilization of the higher oxidation state and hence a greater energy cost for the homolytic rupture of the  $\text{Co}^{\text{III}}$ -PVAc bond. This proposition is further confirmed by the comparison of the oxidation potentials. The three  $\beta$ -ketiminato complexes reported here are easier to oxidize than  $\text{Co}(\text{acac})_2$ , for which no oxidation wave was reported in previous electrochemical studies carried out in DME, DMF or MeCN/THF.<sup>[34, 35]</sup> We have reinvestigated the electrochemical behaviour of  $\text{Co}(\text{acac})_2$  in  $\text{CH}_2\text{Cl}_2$ , under identical conditions as those used for the three  $\beta$ -ketiminato complexes, and find an irreversible oxidation at +1.46 V vs. SCE, namely ca. 0.35 mV more positive than the less easily oxidized  $\beta$ -ketiminato complex **3**. Thus, the comparison of the very similar compounds **1** and **2** shows that the steric effect dominates relatively to the (weak) electronic effect, whereas in the comparison between compounds **1-3** with an electronically very different  $\beta$ -diketonato complex,<sup>[31]</sup> the most important effect appears to be the electronic one.

Table 2. Polymerization of VAc in the presence of complex **1** initiated by V-70 (6 equiv).

Time (h)	Conversion (%)	$M_{n,\text{SEC}}$	$M_{n,\text{theo}}$	PDI
17	27.6	22300	12000	1.21
41	43.3	25400	18800	1.21
65.5	53.7	26800	23300	1.19
88.5	57.5	-	25000	-
161.5	72.8	28700	31600	1.20

At least under the present conditions, the polymerization does not follow the degenerative transfer pathway, which was previously demonstrated for the  $\text{Co}(\text{acac})_2$  and  $\text{Co}(\text{tmhd})_2$ -mediated polymerizations,<sup>[15, 16, 30, 31]</sup> because a DT polymerization needs the continuous injection of new free radicals with respect to the dormant species.<sup>[36, 37]</sup> In order to probe the possible action of this cobalt system as a transfer agent for the DT mechanism, an additional experiment was carried out using compound **1** with a larger V-70 excess (6 equiv relative to Co). The results (Table 2 and Figure 3) show that a faster polymerization occurs relative to the experiment with a smaller amount of V-70, and the resulting polymer has a rather narrow molecular weight distribution (PDI ca. 1.2). Furthermore, the initial  $M_n$  is greater than expected (though only by a factor of less than 2) and then converges to values in closer agreement with theory. Thus, all evidence is in favor of the existence of a relatively efficient control by degenerative transfer, the initial discrepancy between calculated and theoretical molecular weights being related to the initial slow trapping of the PVAc radical chains by the  $\text{Co}^{\text{II}}$  complex. By all evidence, the associative radical exchange appears to be faster than the radical addition to  $\text{Co}^{\text{II}}$  (<Scheme 4). According to our recent study on the  $\text{Co}(\text{tmhd})_2$ -controlled polymerization,<sup>[31]</sup> which was carried out under the same experimental conditions (1:1 in toluene at 30°C), the V-70 initiator is capable to inject new radicals into solution until ca. 60 hours (ca. 6 half-lives), following which time any further polymer growth must be attributed to the OMRP mechanism. The fall of  $M_n$  below the theoretical value at long polymerization times, on the other hand, may be attributed to a catalytic chain transfer (CCT) activity of the  $\text{Co}^{\text{II}}$  complex that can only accumulate in solution when an excess of radicals is no longer present because the irreversible terminations are no longer compensated by an influx of new radicals. Thus, as already demonstrated for the  $\text{Co}(\text{tmhd})_2$ -controlled polymerization,<sup>[31]</sup> three mechanistic pathways (OMRP, DT and CCT) cohabit for the polymerization mediated by compound **1**.

<Figure 3 here>

Figure 3. Time dependence of the conversion for the polymerization of vinyl acetate at 30°C mediated by compound **1**; V-70/Co = 6 (triangles, Table 2), 0.8 (diamonds, Table 1).

<Scheme 4 here>

Next, since compound **3** appeared to afford the best results at 30°C (observed  $M_n$  in closer agreement with theory from the very beginning of the polymerization; linear growth with conversion; lower polydispersities), additional experiments were carried out with this compound at higher temperatures (60 and 80°C). The results are collected in Table 3 and the time evolution of the conversion is graphically shown in Figure 4 in comparison with the 30°C results (Table 1).

Table 3. Polymerization of VAc in the presence of complex **3** at 60 and 80°C.<sup>a</sup>

T	Initiator	Time(h)	Conv(%)	$\ln([M]_0/[M])$	$M_{n,\text{SEC}}$	$M_{n,\text{theo}}$	PDI
60	V-70	0.25	3.5	0.036		1507	
		0.75	4.1	0.042		1765	
		1.5	5.3	0.054	6320	2281	1.11
		6	11	0.117		4735	
		8.75	11.8	0.126	15460	5079	1.32
		32.25	18.6	0.206	17700	8006	1.33
		146	25.1	0.289		10804	
80	AIBN	4	26	0.301	15800	11192	1.29
		22.5	44.2	0.583		19026	
		49	47.5	0.644	18050	20446	1.28
		92.75	51.2	0.717		22039	
		117	55.4	0.807	22900	23847	1.29

<sup>a</sup>Conditions: VAc/Co/Initiator = 500:1:0.8; VAc/Toluene = 1:1 (v/v).

As Figure 4 clearly shows, the conversion increases rather rapidly at the beginning of the polymerization at 60°C and even more at 80°C, but then it slows down to a rate near that observed for the better controlled polymerization at 30°C. This abrupt change of conversion rate coincides approximately with the time necessary to completely consume the initiator. The presence of an initial faster conversion only at the higher temperatures indicates that compound **3** can efficiently trap the growing radical chains only when the release of the primary radicals is sufficiently slow. When the growing radical concentration is too high, irreversible terminations become favoured, which entails a discrepancy between the targeted molar masses and those measured.

<Figure 4 here>

Figure 4. Conversion as a function of time for the polymerization of vinyl acetate in the presence of compound **3**. Temperatures: 30° (triangles), 60°C (diamonds), 80°C (squares). Data are from Table 3 at 60 and 80°C and from Table 1 at 30°C.

The rate of primary radical production is higher at 60°C (V-70;  $t_{1/2}$  of 10 min) than at 80°C (AIBN;  $t_{1/2}$  of 70 min),<sup>[38]</sup> but the initial rate of monomer consumption is slower at 60°C and in both cases the polymerization is slower than free radical polymerization (i.e. without Co complex) under the same conditions. For instance, only slightly more than 5% conversion is observed in 2 h in the presence of complex **3** vs. 26% without Co complex at 60°C. The observed polymerization rate is obviously a combination of the rate of primary radical generation with ensuing free radical polymerization and the rate of radical trapping with ensuing OMRP. As can be seen in Table 3, the polydispersities are quite low even in this initial period of faster monomer consumption. These data also suggest that a greater number of dead polymer chains are generated during the 60°C experiment, because of the faster primary radical generation. Therefore, a smaller  $[\text{Co}^{\text{III}}\text{-PVAc}]/[\text{Co}^{\text{II}}]$  ratio should result after the end of the initiation phase for the 60°C experiment, giving rise to a slower OMRP according to the equation in <Scheme 3. A smaller  $k_{\text{app}}$  (apparent first order rate constant for monomer consumption) value at 60°C relative to that observed for the 30°C experiment should result. The results shown in Figure 4 are not inconsistent with this proposition.

It is to be noted that the polydispersities remain low throughout the polymerization even though the growing radical chains are slowly trapped. The molar masses are initially higher than the theoretical values for the above mentioned reasons. Note that discrepancy is initially smaller at 80°C, in agreement with the smaller amount of dead chains generated at this temperature (smaller primary radical production). However, the  $M_n$  subsequently drop below the theoretical values for the 80°C experiment. This result is explained, as already mentioned above, by the catalytic activity of the  $\text{Co}^{\text{II}}$  complex for the chain transfer reaction to monomer.

### (b) Polymerization of vinyl acetate in the presence of pyridine

In our previous studies on the VAc polymerization mediated by  $\text{Co}(\text{acac})_2$  or  $\text{Co}(\text{tmhd})_2$ <sup>[15, 16, 31]</sup> we have shown that the addition of external donor ligands, particularly pyridine, facilitates the OMRP process and shuts down the associative exchange (degenerative transfer), see Introduction. We therefore wondered whether the same effect could operate for the  $\beta$ -ketoiminato complexes, particularly those yielding a less active dormant species. Therefore, polymerization experiments were carried out in the presence of

compounds **1** and **3** in the presence of 30 equiv of pyridine. The results are shown in Table 4, while Figure 5 compares the first order kinetics in the presence and absence of pyridine, under the same experimental conditions, for the experiments carried out at 30°C.

Table 4. VAc polymerization in the presence of pyridine.<sup>a</sup>

T	Complex	Initiator	Time (h)	Conv(%)	$M_{n,\text{SEC}}$	$M_{n,\text{theo}}$	PDI
30	<b>1</b>	V-70	18	3.3	-	-	-
			42	8.5	15000	3660	1.19
			68.25	14.3	17500	6160	1.11
			91.25	18.7	-	-	-
			163.5	24.8	20600	10680	1.23
			21.5	8.3	18000	3573	1.14
30	<b>3</b>	V-70	65	22.7	21700	9771	1.27
			90	30.2	-	13000	-
			113.5	31.1	22200	13387	1.34
			24.5	30.5	27200	10000	1.29
60	<b>1</b>	AIBN	33	33.6	30800	11100	1.33
			44	51.3	33700	16900	1.49
			1.5	28.3	23000	9300	1.24
80	<b>1</b>	AIBN	4	45.2	21800	14900	1.27
			1	32.1	16600	10600	1.50
90	<b>1</b>	AIBN	3	45.4	17200	15000	1.44
			7	75.9	19500	24800	1.36
			-	-	-	-	-

<sup>a</sup>VAc/Toluene = 1:1 (v/v). VAc/Co/initiator/py = 500:1:0.8:30.

The monomer consumption follows first order kinetics in all cases. However, the effect of pyridine is strikingly different for the two different compounds. When using compound **1**, the apparent rate constant is essentially unchanged by the presence of pyridine ( $1.92 \cdot 10^{-3} \text{ h}^{-1}$  with py vs.  $1.84 \cdot 10^{-3} \text{ h}^{-1}$  without py), whereas the rate quadruples (from  $9.04 \cdot 10^{-4} \text{ h}^{-1}$  to  $3.63 \cdot 10^{-3} \text{ h}^{-1}$ ) in the presence of pyridine for compound **3**. The polymerization rate for **3** with py becomes even greater than that measured in the presence of compound **1**. The presence of pyridine also decreases the level of control for both compounds, as indicated by the greater discrepancy between observed and calculated  $M_n$  (cf. Table 4 and Table 1). The polydispersities, however, remain low.

<Figure 5 here>

Figure 5. Time dependence of  $\ln([M]_0/[M])$  for the polymerization of vinyl acetate at 30°C in the presence (Table 4) and absence (Table 1) of pyridine (30 equivalents): compound **1** (with py, triangles; without py, diamonds); compound **3** (with py, circles; without py, squares).

These results can be compared with those of the  $\text{Co}(\text{tmhd})_2$ - and  $\text{Co}(\text{acac})_2$ -mediated polymerizations, where OMRP is significantly accelerated by pyridine (as well as by other ligands).<sup>[15, 31]</sup> The acceleration factor is particularly large for  $\text{Co}(\text{acac})_2$  (essentially no OMRP takes place in the absence of added Lewis bases,  $k_{\text{app}} < 1.4 \cdot 10^{-4} \text{ h}^{-1}$  in 50% toluene,<sup>[31]</sup> vs.  $2.25 \cdot 10^{-2} \text{ h}^{-1}$  in the presence of 30 equiv of pyridine in bulk<sup>[15]</sup>) which establishes the stronger interaction with py and this was experimentally indicated by <sup>1</sup>H NMR studies and supported by DFT calculations.<sup>[31]</sup> Thus, the essential equivalence of the polymerization rate in the presence and absence of pyridine for compound **1** shows that this Lewis base does not significantly affect the OMRP equilibrium with this compound. On the other hand, weak pyridine bonding seems to occur for compound **3**. As will be shown in the next section, the NMR investigation confirms these conclusions.

The initial molar mass, like in the corresponding experiment without pyridine, is greater than  $M_{n,\text{theo}}$ , but increased with monomer conversion in a more pronounced manner. Figure 6 shows the progression of the  $M_n$  measured by SEC.

<Figure 4 here>

<Figure 6 here>

Figure 6. Size-exclusion chromatograms for PVAc initiated at 30°C by V-70 in the presence of 30 equiv of pyridine (the analyzed polymers were those at 8.4, 14.3 and 24.8% conversion in Table 4).

Repeating the experiment at higher temperatures resulted in a faster polymerization (see Table 4). All the higher temperature studies were carried out with 0.8 equiv per Co of the AIBN initiator. At 60°C (initiator  $t_{1/2}$  = ca. 20 h), a 51.3% conversion was reached after 44 h and the initial  $M_n$  was much greater than theory, further increasing very little with conversion (by a factor of 1.24 from 30.5% to 51.3%), but remaining higher than the theoretical value. Note, however, that the polydispersity index is still relatively low (in the 1.3-1.5 range). At 80°C (initiator  $t_{1/2}$  = ca. 70 min), a 45.2% conversion was obtained in only 4 h. Once again, the polydispersity is relatively narrow and  $M_n$  is greater than theory, but less than the  $M_n$  obtained at 60°C. Essentially no increase of  $M_n$  with conversion occurs in this experiment. Finally, at 90°C (initiator  $t_{1/2}$  = ca. 20 min) the polymerization is faster still (45.4% conversion in 3 h, 79.5% in 7 h), and the initial  $M_n$  is smaller than in the lower temperature experiments. In this case, the  $M_n$  value falls below the theoretical value at the highest conversion, suggesting the presence of catalyzed chain transfer, as was the case for the experiment without pyridine (*vide supra*). Comparison of the results at the four different temperatures (especially the two extreme temperatures) shows that the catalyzed chain transfer process becomes more favorable at higher T, as already concluded for the experiments with compound **3** in the absence of pyridine (*vide supra*).

#### (c) NMR study of complexes **1** and **3** in the presence of pyridine

Complexes **1** and **3** were investigated by  $^1\text{H}$  NMR in the absence and presence of up to 3 equivalents of pyridine. The spectrum of **1**, see Figure 7, exhibits relatively broad and shifted resonances, as expected from the compound paramagnetism ( $S = 3/2$ ). Upon addition of pyridine, the resonances due to both compound **1** and pyridine do not change position and do not broaden, while the free pyridine resonance grows in intensity proportionally to the py/Co ratio. This means that binding to the cobalt atom is not sufficiently strong. On the other hand, pyridine addition has a profound effect on the NMR spectrum of compound **3**, see Figure 8, where both the Co complex and pyridine resonances are significantly broadened and slightly shifted. The behavior of compound **3** qualitatively resembles that of complexes  $\text{Co}(\text{acac})_2$ <sup>[15]</sup> and  $\text{Co}(\text{tmhd})_2$ <sup>[31]</sup> where weak metal binding and rapid chemical exchange between coordinated and free pyridine lead to a change of chemical shift and linewidth for the free pyridine resonances as a function of py/Co ratio. Like compound **3**, the two  $\beta$ -diketonato complexes of  $\text{Co}^{\text{II}}$  experience a large accelerating effect on the VAc polymerization rate by the addition of pyridine. This accelerating effect, as detailed in previous contributions,<sup>[12, 15, 16, 30, 31]</sup> is associated with the energetic stabilization of the  $\text{Co}^{\text{II}}$  species by ligand coordination, thereby shifting the OMRP equilibrium toward the active radical chain. The observed difference in pyridine binding affinity for complexes **1** and **3** must be attributed to purely electronic effects associated to the electron withdrawing power of the  $\text{CF}_3$  groups, since the steric control of pyridine coordination should be identical. As a result of this electronic effect, the cobalt center is electron-poorer in complex **3** and thus a greater Lewis acidity is expected.

A semi-quantitative comparison between the behavior of **3**,  $\text{Co}(\text{tmhd})_2$  and  $\text{Co}(\text{acac})_2$  shows that the free pyridine resonance are broadened and shifted to an increasing degree in the order **3** <

$\text{Co}(\text{tmhd})_2$  <  $\text{Co}(\text{acac})_2$ , reflecting an increasing binding affinity in the same order. Conversely, the cobalt ligand resonances are broadened for **3** and not at all for the  $\beta$ -diketonato derivatives. This phenomenon must be related to a faster ligand exchange in the case of **3**, to which the pyridine ligand is less tightly bonded. This is consistent with the expected steric and electronic effects. The above comparisons demonstrate the profound effect that the nature of the anionic bidentate ligand ( $\beta$ -diketonate or  $\beta$ -ketiminate) has on the ability by external Lewis bases to coordinate the  $\text{Co}^{\text{II}}$  complex, which in turn affects the performance of the Co complexes as controlling agents in radical polymerization.

<Figure 7 here>

Figure 7.  $^1\text{H}$  NMR spectrum of compound **1** in the presence of variable amounts of free pyridine in  $\text{CDCl}_3$ .

<Figure 8 here>

Figure 8.  $^1\text{H}$  NMR spectrum of compound **3** in the absence and presence of pyridine (5 equiv) in  $\text{CDCl}_3$ .

## Conclusion

The cobalt(II)  $\beta$ -ketiminate complexes  $\text{Co}[\text{OC}(\text{Ph})\text{CH}-\text{C}(\text{CH}_3)\text{N}(\text{Ar})_2]$  (Ar = Ph, Xyl,  $p\text{-C}_6\text{H}_4\text{CF}_3$ ) were tested in the polymerization of vinyl acetate under OMRP conditions (thermal initiation by diazo free-radical initiators). Like previously investigated bis( $\beta$ -diketonato)cobalt(II) complexes, these  $\beta$ -ketiminate complexes are able to reversibly trap the growing PVAc radical chains in a controlled OMRP mechanism and to catalyze chain transfer. The CCT activity of these Co(II) complexes plays a significant role only at high temperatures. The initially high  $M_n$  values indicate a relatively slow radical trapping process by the  $\text{Co}^{\text{II}}$  complexes, slowing down in the order **3** > **1** > **2**. Furthermore, the resulting PVAc-cobalt(III) dormant species are able to function as transfer agents for a controlled polymerization by degenerative transfer. Replacement of a carbonyl function in bis( $\beta$ -diketonato) systems by a bulkier  $\text{C}=\text{NAr}$  function has two effects: the cobalt center becomes electron richer (NAr is less electronegative than O), stabilizing the higher oxidation state complex in the organocobalt(III) dormant chain, but also introduces a greater steric bulk in the metal proximity, weakening the PVAc-Co bond. The relative importance of these two opposing effects depends on the precise nature of the ligand substituents. The NAr group strongly affects the ability of the cobalt(II) system to coordinate Lewis bases (as exemplified by pyridine in this study). Hence, addition of pyridine to system **1** under OMRP conditions results in no significant rate change, whereas a slight accelerating effect results upon addition of pyridine to complex **3**, but the accelerating factor (and the pyridine binding ability as qualitatively indicated by NMR) is lower for **3** than for complexes  $\text{Co}(\text{acac})_2$  and  $\text{Co}(\text{tmhd})_2$ .

## Experimental Section

**Materials.**  $\text{Co}(\text{O}_2\text{CCH}_3)_2 \cdot 4\text{H}_2\text{O}$  (reagent grade), 1-phenyl-1,3-butanedione (99%), aniline (99%), 2,6-dimethylaniline (99%), and 4-(trifluoromethyl)aniline (99%) (all Sigma-Aldrich) were used as received. Vinyl acetate (>99%, Aldrich), N-vinylpyrrolidone (Alfa-Aesar), and anisole (Acros organics) were dried over calcium hydride and freshly distilled under reduced pressure prior to use. Toluene was distilled from sodium benzophenone ketyl. 2,2'-Azobis(4-methoxy-2,4-dimethyl valeronitrile) (V-70; Wako) and azobis(isobutyronitrile) (AIBN; Acros organics) were used as received. The  $\beta$ -ketoimine proligands were prepared by

condensation of 1-phenyl-1,3-butanedione with the appropriate aniline in refluxing toluene, using a catalytic amount of *p*-toluenesulfonic acid and a Dean Stark apparatus.<sup>[39]</sup>

**Characterizations.** <sup>1</sup>H NMR spectra were recorded on a Bruker AC400 NMR spectrometer. Size exclusion chromatography (SEC) of poly(vinyl acetate) was carried out in filtered THF (flow rate: 1 ml/min) at 35°C on a 300x7.5 mm PL gel 5 micrometer mixed-D column (polymer laboratories), equipped with multiangle light scattering (minidawn Tristar, Wyatt Technology Corporation) and refractive index (RI2000, Sopares) detectors or with a waters column pack (300x7.5 mm, ultrastaygel 104,103,100 Å), equipped with multiangle light scattering (miniDawn Tristar, Wyatt Technology Corp.) and refractive index (waters 410) detectors. Cyclic voltammetric measurements of compounds **1-3** were conducted with an EG&G Princeton Applied Research model 263A potentiostat using ~4 mM solutions in anhydrous anaerobic CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M *n*Bu<sub>4</sub>NClO<sub>4</sub>, using glassy carbon disk working, Pt wire auxiliary, and Ag/AgCl pseudoreference electrodes. Potentials at scan rates of 100 mV/s are reported relative to the saturated calomel electrode (SCE), and were measured vs internal ferrocene standard, taken as +480 mV vs SCE under these conditions.<sup>[40]</sup> Complexes **1** and **2** exhibited irreversible oxidations, while that of complex **3** showed some quasi-reversibility. None exhibited any observable reduction features up to ~ -1.2 V.

**Syntheses of the cobalt complexes.** Complexes **1-3** were prepared in a modification of the previously published procedure for **2**,<sup>[41]</sup> reported below in detail.

a) *Synthesis of [Co(OC(Ph)CHC(CH<sub>3</sub>)NC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>] (1).* 3.005 g (12.66 mmol) of yellow phenyl proligand HOC(Ph)CHC(CH<sub>3</sub>)NC<sub>6</sub>H<sub>5</sub> was dissolved in 60 mL MeOH in a 125 mL Erlenmeyer flask to yield a yellow solution. The solution was stirred and heated. 0.711 g (12.7 mmol) KOH was dissolved in 5 mL MeOH, and added dropwise over 2 minutes to the reaction flask. 1.566 g (6.287 mmol) of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O was added to the reaction flask, causing an orange solid to precipitate, which was recovered by filtration and washed with 5 mL cold MeOH. The orange solid was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexanes to give deep red block crystals to yield 1.875 g (71.87 %). <sup>1</sup>H NMR (400 MHz, 298K, CDCl<sub>3</sub>): 19.35 (4H), 14.80 (2H), 12.77 (s, 4H), 10.07 (4H), -21.3 (6H), -26.89 (2H), -33.21 (2H), -49.83 (4H). Magnetic moment (Evans' Method, CDCl<sub>3</sub>): 4.1 μB. Anal. Calcd for C<sub>32</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>Co: C, 72.31; H, 5.31; N, 5.27. Found: C, 71.94; H, 5.29; N, 5.28. Cyclic voltammetry: E<sub>p,c</sub> (vs. SCE) = + 1.02 V.

b) *Synthesis of [Co(OC(Ph)CHC(CH<sub>3</sub>)N(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>)] (2).* 2.150 g (8.632 mmol) Co(OAc)<sub>2</sub>·4H<sub>2</sub>O was dissolved in 10 mL MeOH and stirred and heated to give a purple solution. 4.573 g (17.23 mmol) of the yellow xylyl proligand HOC(Ph)CHC(CH<sub>3</sub>)N(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub> was added to the solution to give a suspension. 0.945 g (16.8 mmol) KOH was dissolved in 8 mL MeOH and added dropwise to reaction flask over 8 minutes, causing an orange solid to precipitate. The orange solid was collected by filtration and washed with 5 mL cold MeOH, and recrystallized from CH<sub>2</sub>Cl<sub>2</sub> as deep red needles. Yield: 2.459 g (79.4%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) 17.27 (4H), 14.32 (2H), 11.21 (4H), 9.64 (4H), 3.32 (12H), -16.39 (6H), -25.81 (2H), -34.53 (2H). Magnetic moment (Evans' Method, CDCl<sub>3</sub>): 4.0 μB. Anal. Calcd for C<sub>36</sub>H<sub>36</sub>N<sub>2</sub>O<sub>2</sub>Co: C, 73.58; H, 6.18; N, 4.77. Found: C, 73.20; H, 6.20; N, 4.81. Cyclic voltammetry: E<sub>p,c</sub> (vs. SCE) = + 0.91 V.

c) *Synthesis of [Co(OC(Ph)CHC(CH<sub>3</sub>)N(p-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>)<sub>2</sub>)] (3).* 0.282 g (0.924 mmol) of the yellow *p*-CF<sub>3</sub> proligand HOC(Ph)CHC(CH<sub>3</sub>)N(p-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>)<sub>2</sub> was dissolved in 15 mL MeOH, stirred and heated. 0.051 g (0.91 mmol) KOH was dissolved in 2 mL MeOH and added dropwise to the reaction flask. 0.117 g (0.470 mmol) Co(OAc)<sub>2</sub>·4H<sub>2</sub>O was added to the reaction flask, which caused precipitation of an orange solid, which was collected by filtration and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexanes to give deep red block crystals. Yield: 0.145 g (68.1 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>) 20.10 (4H), 15.25 (2H), 13.48 (4H), 10.27 (s, 4H), -23.65 (6H), -35.24 (2H), -50.23 (4H). Magnetic moment (Evans' Method, CDCl<sub>3</sub>): 4.2 μB. Anal. Calcd for C<sub>34</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>F<sub>3</sub>Co: C, 61.17; H, 3.93; N, 4.20. Found: C, 61.08; H, 4.07; N, 4.53. Cyclic voltammetry: E<sub>p,c</sub> (vs. SCE) = + 1.11 V.

**General procedure for the radical polymerization of vinyl acetate.** The polymerizations were conducted in standard Schlenk glassware. In a typical procedure, VAc (2 mL, 0.014 mol), toluene (2 mL), AIBN (5.1 mg, 0.031 mmol), and compound **1** (21.0 mg,

0.039 mmol) were placed in a Schlenk flask equipped with a magnetic stirring bar. The mixture was degassed by three freeze-vacuum-thaw cycles and then immersed into an oil bath thermostated at 80°C. At the desired time, the Schlenk flask was rapidly cooled to room temperature by immersion into iced water before sample withdrawal. The monomer conversion was determined gravimetrically after removal of the unconverted monomer under reduced pressure and the resulting residue was used for SEC characterization. For the purpose of polymer isolation, the reaction mixture was added to an excess of heptane and the resulting polymer precipitate was collected by vacuum filtration. The product was then vacuum-dried at room temperature for 24 h.

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## Entry for the Table of Contents

### Vinyl acetate polymerization

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Yves Gnanou\*, Ulrich Baisch,  
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Kiyoshi C. D. Robson, W. Stephen  
McNeil ..... Page – Page*

**Electronic and Steric Ligand  
Effects in the Radical  
Polymerization of Vinyl Acetate  
Mediated by  $\beta$ -Ketoiminate  
Complexes of Cobalt(II)**

<ToC figure here>

Bis( $\beta$ -ketoiminate) complexes of cobalt(II) display a controlling ability in the radical polymerization of vinyl acetate; while an increased steric encumbrance of the ligand coordination sphere labilizes the  $\text{Co}^{\text{III}}$ -PVAc bond, it also makes the  $\text{Co}^{\text{II}}$  complex a poorer trap for the active radical chain.