

Vinyl Acetate polymerization mediated by 9-oxyphenalenone cobalt(II) complexes: interplay of OMRP and CCT

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1. Experimental details

Materials

Vinyl acetate (VAc, >99 %, Sigma Aldrich) was dried over calcium hydride, distilled under argon at 90 °C, degassed by several freeze/pump/thaw cycles and stored under argon. Pyridine was dried with solid KOH, fractionally distilled and stored under argon. 2,2'-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, Wako Chemicals), 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO, Acros Organics), mesitylene (Mes, >99.9 %, Sigma Aldrich), methanol (>99.9 %, Sigma Aldrich), and anhydrous cobalt(II) acetate (>98 %, Alfa Aesar) were used as received. 9-Hydroxyphenalenone (HOPN) was synthesized according to a published procedure.¹ The bis(pyridine) and bis(aqua) derivative of bis(9-oxyphenalenone)cobalt(II), [Co(OPN)₂(py)₂] (**2**) and [Co(OPN)₂(H₂O)₂] (**3**), were obtained according to previously described procedures.²

The anhydrous complex [Co(OPN)₂] (**1**) is described here for the first time. It was obtained by a procedure similar to that reported for the bis(aqua) derivative **3**, as follows. A solution of anhydrous cobalt acetate (1 mmol, 0.177 g) in absolute methanol (30 mL) was added to a solution of HOPN (2 mmol, 0.392 g) in the same solvent (40 mL). The reaction mixture was heated in an oil bath for 3 hours and the resulting deep-red precipitate of [Co(OPN)₂·nMeOH] was filtered and washed 3 times with methanol. A brown-red powder of the anhydrous **1** was obtained by heating the methanol solvate *in vacuo* at 60 °C for 48 hr. *Anal.* Calcd. for Co(C₁₃H₇O₂)₂: C, 69.50; H, 3.14. Found: C, 69.21; H, 2.93. The previously reported bis(aqua) derivative was obtained by drying the product at room temperature.²

Characterization

¹H NMR spectra were recorded on Bruker Fourier 300 and Bruker AvanceIII 400HD spectrometers. The elemental analysis was carried out by the LCC analytical service on a Perkin Elmer 2400 elemental analyzer. Size exclusion chromatography (SEC) of poly(vinyl acetate) samples was carried out in filtered THF (flow rate: 1 mL·min⁻¹) at 35 °C on a 300×7.5 mm PL gel 5 μm mixed-D column (Polymer laboratories) equipped with multiangle light-scattering (Mini Dawn Wyatt) and refractive index (RI2000, Sopares or Wyatt Optilab Rex) detectors.

General procedures for the radical polymerization of vinyl acetate

All manipulations were carried out under a protective argon atmosphere. All polymerizations carried out at 30°C were conducted by following the same experimental procedures. As a representative example, complex **1** (0.087 mmol, 0.039 g) was introduced in a Schlenk tube and purged by three vacuum-argon cycles, followed by the addition of degassed vinyl acetate (4 mL, 43.4 mmol) and 0.2 mL of mesitylene. The reaction mixture was degassed by two freeze/pump/thaw cycles. V-70 (0.052 mmol, 0.016 g) then was added, followed by immersion in an oil bath at 30 °C. Aliquots were withdrawn periodically for reaction monitoring by ¹H NMR and SEC. The monomer conversion was determined by ¹H NMR in either CDCl₃ or THF-d⁸ using mesitylene as an internal standard. The samples for the SEC characterization were prepared by precipitation of the polymer from the withdrawn solution by addition of a pentane solution containing TEMPO, followed by rinsing with pentane and drying *in vacuo*. The samples used for the end-group analyses by ¹H NMR were prepared, still working under a protective argon atmosphere, by dissolution of the precipitated polymer in toluene, followed by filtration on 45 μm syringe filter (to eliminate the residual toluene-insoluble metal complex), reprecipitation in pentane, triple rinsing of the precipitated polymer with pentane, and drying under vacuum for 2 days. Benzene-d⁶ or CDCl₃ were used as solvents.

Procedure for the radical polymerizations of vinyl acetate at 80°C

The polymerizations were carried out by first preparing the mixture of complex, bulk monomer at the desired molar ratio (VAC/Co = 100:1) and internal standard as described above, then warming to 80°C, then adding pyridine until all complex dissolved (210 equiv.) and finally adding the radical initiator (AIBN, 4 equiv) to start the polymerization. The conversion was monitored as described above for the polymerizations carried out at 30°C. In one experiment, the withdrawn sample was quenched by addition of TEMPO, while in a second one, the quenching was carried out by addition of *n*PrSH.

Table 1S. Data for the bulk polymerization of VAc at 30 °C mediated by **1** (VAc/1 = 500) with different initiator amounts.

time, h	V-70/1 = 4						V-70/1 = 2						V-70/1 = 0.6					
	Z (%) ^a	10 ⁻⁴ ·M _{n,th.} ^b (g·mol ⁻¹)	10 ⁻⁴ ·M _{n,SEC} (g·mol ⁻¹)	10 ⁻⁴ ·M _{w,SEC} (g·mol ⁻¹)	D	M _{n,th./} M _{n,SEC}	Z (%) ^a	10 ⁻⁴ ·M _{n,th.} ^b (g·mol ⁻¹)	10 ⁻⁴ ·M _{n,SEC} (g·mol ⁻¹)	10 ⁻⁴ ·M _{w,SEC} (g·mol ⁻¹)	D	M _{n,th./} M _{n,SEC}	Z (%) ^a	10 ⁻⁴ ·M _{n,th.} ^b (g·mol ⁻¹)	10 ⁻⁴ ·M _{n,SEC} (g·mol ⁻¹)	10 ⁻⁴ ·M _{w,SEC} (g·mol ⁻¹)	D	M _{n,th./} M _{n,SEC}
6	13.7	0.59	1.33	1.65	1.24	0.4	13.8	0.59	1.29	1.63	1.26	0.5	20.5	0.88	1.67	2.11	1.27	0.5
24	42.9	1.85	1.87	2.74	1.46	1.0	41.4	1.78	2.36	3.32	1.41	0.8						
47	58.2	2.50	2.04	3.17	1.55	1.2	49.5	2.13	2.47	3.76	1.52	0.9						
70	63.0	2.71	2.30	3.39	1.47	1.2	56.7	2.44	2.76	3.98	1.44	0.9	33.2	1.43	2.08	2.94	1.42	0.7
144	78.4	3.37	2.32	3.57	1.54	1.5	74.7	3.21	2.65	4.14	1.56	1.2	38.8	1.67	1.98	2.95	1.49	0.8
220													49.5	2.13	2.04	2.97	1.45	1.0

^a Conversion from NMR. ^b M_{n,th.} = ([VAc]₀/[complex]) × M_{VAc} × conversion where M_{VAc} is the molecular weight of vinyl acetate.

Table 2S. Data for the bulk polymerization of VAc at 30 °C mediated by **2** and **3** (VAc/V-70/Co = 500:4:1).

time, h	2 (no added py)						2 (plus 30 equiv of added py)						3					
	Z (%) ^a	10 ⁻⁴ ·M _{n,th.} ^b (g·mol ⁻¹)	10 ⁻⁴ ·M _{n,SEC} (g·mol ⁻¹)	10 ⁻⁴ ·M _{w,SEC} (g·mol ⁻¹)	D	M _{n,th./} M _{n,SEC}	Z (%) ^a	10 ⁻⁴ ·M _{n,th.} ^b (g·mol ⁻¹)	10 ⁻⁴ ·M _{n,SEC} (g·mol ⁻¹)	10 ⁻⁴ ·M _{w,SEC} (g·mol ⁻¹)	D	M _{n,th./} M _{n,SEC}	Z (%) ^a	10 ⁻⁴ ·M _{n,th.} ^b (g·mol ⁻¹)	10 ⁻⁴ ·M _{n,SEC} (g·mol ⁻¹)	10 ⁻⁴ ·M _{w,SEC} (g·mol ⁻¹)	D	M _{n,th./} M _{n,SEC}
6	19.7	0.84	0.55	0.81	1.47	1.53	18.4	0.79	1.97	3.04	1.55	0.40						
7													11	0.47	0.9	1.21	1.35	0.52
23	49.3	2.12	0.97	1.52	1.56	2.19	51.7	2.23	1.92	3.17	1.65	1.16						
24													25.7	1.1	1.16	1.92	1.66	0.95
30	53.5	2.30	0.96	1.60	1.66	2.40	57.1	2.46	1.91	3.18	1.66	1.23	29.9					
47	75.4	3.24	0.98	1.65	1.67	3.31	68.7	2.95	1.85	3.17	1.72	1.59						
72	81	3.48	0.97	1.65	1.70	3.59	77.8	3.35	1.81	3.14	1.73	1.85						
77													49.1					
149													58.7					

^a Conversion from NMR. ^b M_{n,theor.} = ([VAc]₀/[complex]) × M_{VAc} × conversion where M_{VAc} is the molecular weight of vinyl acetate.

Table 3S. Data for the bulk polymerization of VAc at 30 °C mediated by **2** (VAc/V-70/2 = 500:0.6:1) at different pyridine/2 ratios.

time, h	2 (no added py)						2 (plus 30 equiv of added py)					
	Z (%) ^a	10 ⁻⁴ ·M _{n,th.} ^b (g·mol ⁻¹)	10 ⁻⁴ ·M _{n,SEC} (g·mol ⁻¹)	10 ⁻⁴ ·M _{w,SEC} (g·mol ⁻¹)	D	M _{n,th./} M _{n,SEC}	Z (%) ^a	10 ⁻⁴ ·M _{n,th.} ^b (g·mol ⁻¹)	10 ⁻⁴ ·M _{n,SEC} (g·mol ⁻¹)	10 ⁻⁴ ·M _{w,SEC} (g·mol ⁻¹)	D	M _{n,th./} M _{n,SEC}
23	18.6	0.78	1.07	1.69	1.58	0.73	23.3	1.00	2.58	3.78	1.47	0.39
47	28.4	1.22	1.06	1.68	1.55	1.15						
72	36.7	1.58	1.05	1.70	1.62	1.50	37.9	1.58	2.48	3.72	1.50	0.64
95	40.5	1.74	1.09	1.78	1.63	1.60	43.2	1.74	2.41	3.70	1.54	0.72
167	52.3	2.25	1.10	1.71	1.55	2.05	49.4	2.13	2.40	3.63	1.51	0.89
264	63.3	2.72	1.10	1.72	1.55	2.47	62.3	2.68	2.42	3.62	1.50	1.11
365.5	81.3	3.50	1.16	1.80	1.55	3.02	77.9	3.35	2.41	3.64	1.51	1.39

^a Conversion from NMR. ^b M_{n,theor.} = ([VAc]₀/[complex]) × M_{VAc} × conversion where M_{VAc} is the molecular weight of vinyl acetate.

2. VAc polymerization mediated by compound 1 at 30°C

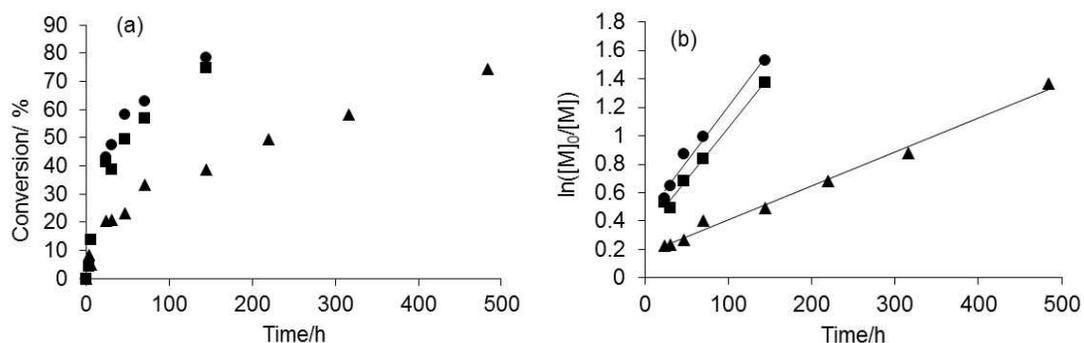


Figure 1S. Conversion of VAc as a function of time (a) and first order plot (b) for the bulk VAc polymerization at 30 °C mediated by compound **1** (VAc/**1** = 500). V-70:**1** = 4 (●), 2 (■), 0.6 (▲). The non-zero intercept of the fitted 1st order straight lines suggests that the polymerization has a poorly controlled initial phase before installment of the persistent radical effect, consistent with the initially high MWs relative to the theoretical values and the not-so-narrow MWD (Figure 1).

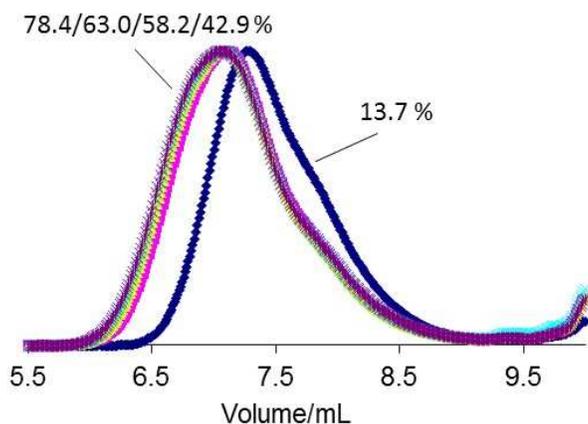


Figure 2S. SEC chromatograms of the isolated polymers from the bulk polymerization of VAc mediated by **1** at 30°C (VAc:V-70:Co = 500:4:1). The bimodal distribution most probably results from the sample work-up, leading to extensive chain-chain coupling by oxidation.

3. VAc polymerization mediated by compounds 2 and 3 at 30°C

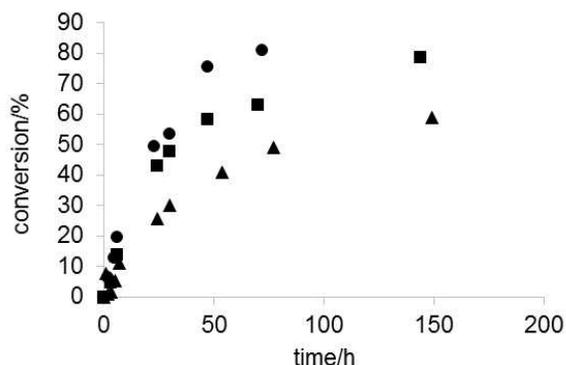


Figure 3S. Comparison of VAc polymerizations mediated by 1 (■), 2 (●) and 3 (▲) (bulk, 30 °C, VAc:V-70:Co = 500:4:1).

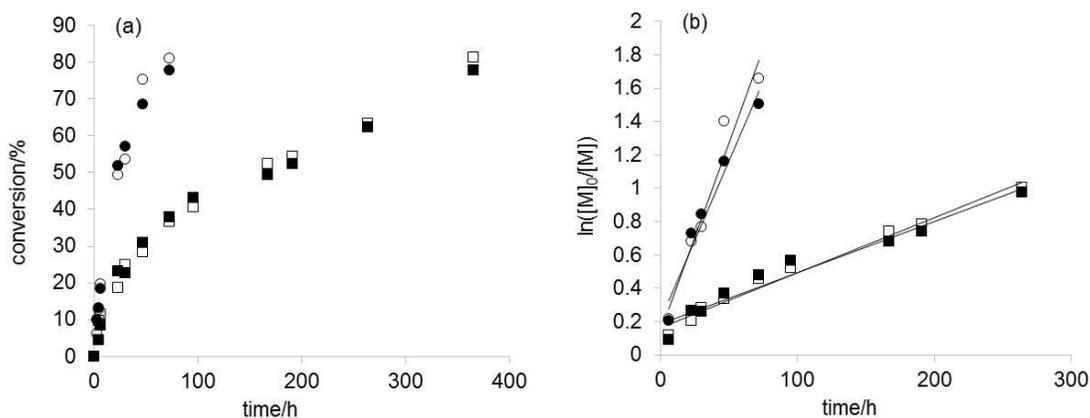


Figure 4S. Conversion of VAc as a function of time (a) and first order plot (b) for the bulk VAc polymerization at 30°C mediated by complex 2 (VAc/2 = 500) in the absence (open symbols) and presence (30 equiv, black symbols) of excess py. V-70/2 = 0.6 (□, ■), 4 (○, ●).

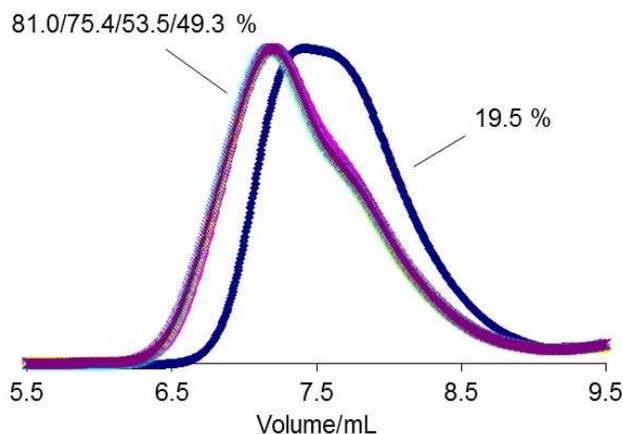


Figure 5S. SEC chromatograms of the isolated polymers from the bulk polymerization of VAc mediated by 2 at 30°C (VAc:V-70:Co = 500:4:1) at various conversions. The bimodal distribution most probably results from the sample work-up, leading to extensive chain-chain coupling by oxidation.

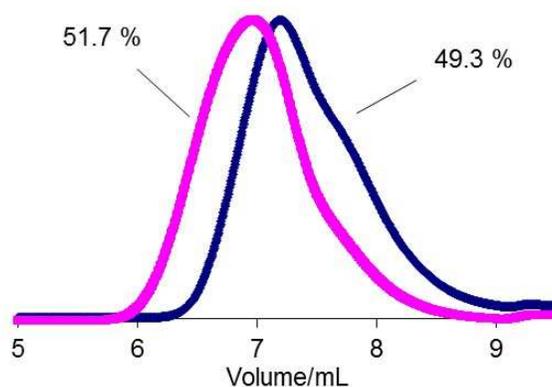
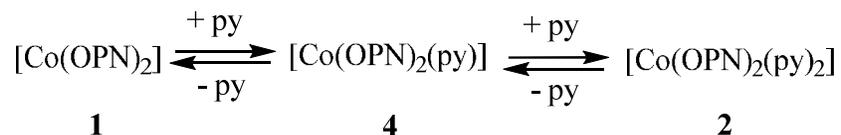


Figure 6S. Comparison of the SEC chromatograms of the isolated polymers, at approximately the same conversion, obtained from the bulk polymerization of VAc mediated by **2** at 30°C (VAc:V-70:**2** = 500:4:1) in the absence of added pyridine (dark blue, right) and in the presence of added pyridine (py/**2** = 30, purple, left).

4. ^1H NMR investigation of $[\text{Co}(\text{OPN})_2(\text{py})_2]$ in the presence of excess py

The lability of the py-Co^{II} bond was probed by a qualitative ^1H NMR study. Cobalt(II) complexes are labile systems leading, under the fast exchange limit for the pyridine addition/dissociation equilibria (Scheme 1S), to the observation of only a single average resonance for each type of nucleus. The chemical shift observed for the resonance of each nucleus is determined by its value in each species and by their relative proportion. More specifically, the chemical shifts observed for the OPN ligand resonances are weighted averages of the **1**, **2** and **4** resonances, whereas those observed for the pyridine nuclei are averages of the **2**, **4** and free pyridine resonances.



Scheme 1S. Equilibria of pyridine addition to compound $[\text{Co}^{\text{II}}(\text{OPN})_2]$.

Figure 5S(a) collects the ^1H NMR spectra of CDCl_3 solutions generated from compound **2** and different amounts of additional pyridine. Upon increasing the py/**2** ratio, three resonances increase in relative intensity while always maintaining a relative 2:2:1 ratio and their chemical shift changes significantly, converging toward the positions expected for the free pyridine resonances (solid arrows). The other resonances corresponding to the dotted arrows exhibit smaller chemical shift changes, approximately constant intensities in a relative

2:2:2:1 ratio, and converge toward paramagnetically shifted positions. They are consequently assigned to the OPN ligand. The chemical shift dependence of all resonances as a function of $\text{py}/2$ ratio is plotted in Figure 5S(b). Among the pyridine resonances, the *p*-H can be readily assigned on the basis of integration to the peak at δ ca. -2.7 ppm in the spectrum of **2**, while the *o*-H resonance is unobserved because of extensive broadening caused by proximity to the paramagnetic cobalt center, but becomes observable at higher py/Co ratios. Therefore, the *m*-H resonance is assigned to the peak at δ ca. 13.4 ppm in the spectrum of **2**. Concerning the OPN resonances, the assignment of the unique 5-H proton to the peak at δ ca. 2.1 ppm is again straightforward on the basis of integration. The assignment of the other three resonances to the (2,8), (3,7) and (4,6) protons is more ambiguous, but we suppose that the (2,8) protons, because of their closer proximity to the Co center, are responsible for the most paramagnetically shifted resonance at δ ca. 50.7 ppm. If pyridine binding to Co had been very strong, the only species present in solution would be **2** independently on the py excess amount and the OPN resonances would not change position. Therefore, the observed chemical shift change for the OPN resonance reflects the py dissociation equilibrium with species **4** and **1**. In order to obtain quantitative equilibrium data it would be necessary to measure a much greater number of spectra for different py/Co ratios, because of the large numbers of variables and unknown parameters to fit in the system (two equilibrium constants, chemical shifts of each nucleus in each paramagnetic species), which is outside of the scope of the present study.

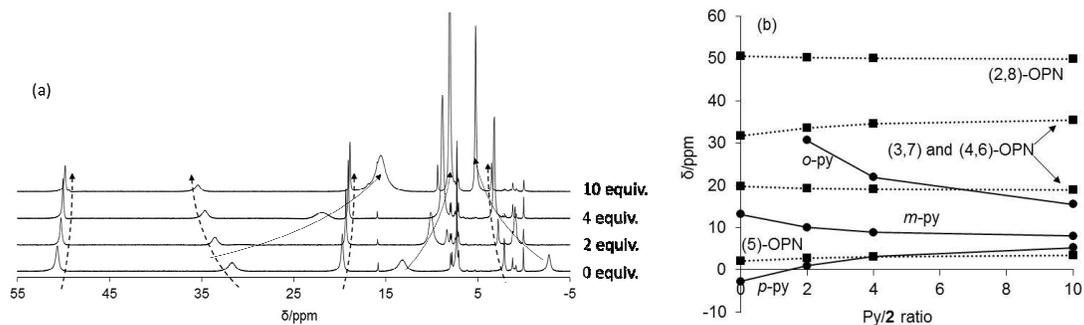


Figure 7S. (a): ¹H NMR spectra of **2** in the presence of different amounts of pyridine in CDCl₃ solution (dotted arrows: resonances of the OPN ligand; solid arrows: resonances of pyridine). (b): dependence of the chemical shifts on the $\text{py}/2$ ratio.

5. NMR investigation of the polymer obtained at 30°C (VAc:V-70:2 = 500:0.6:1)

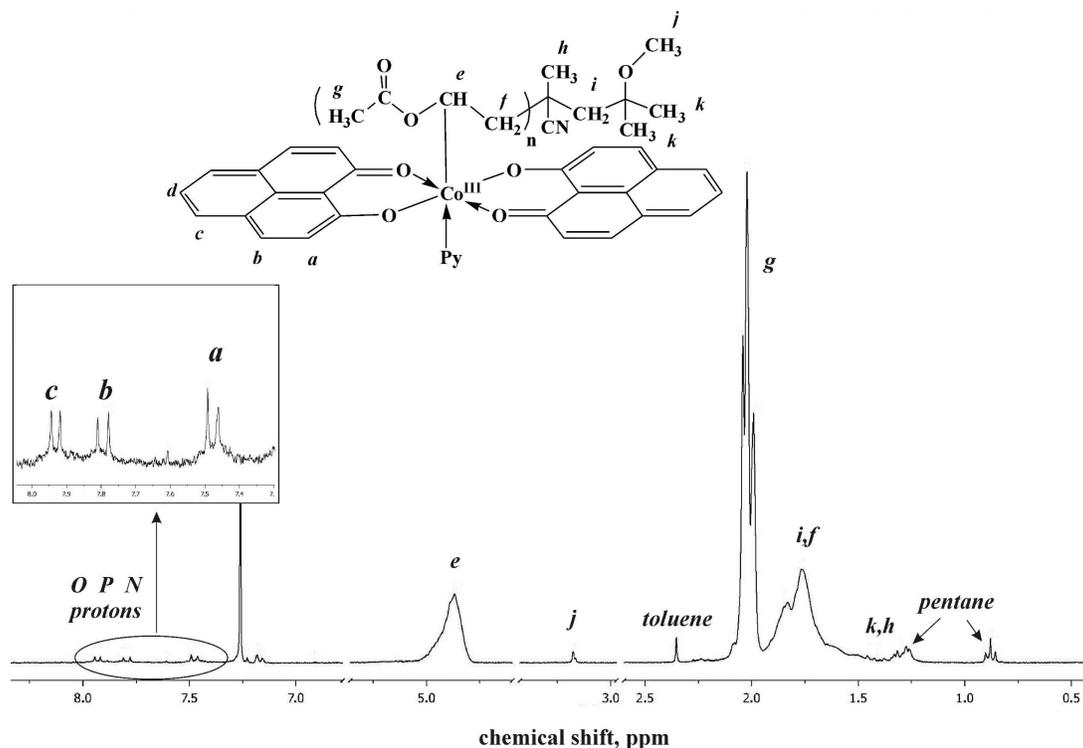


Figure 7S. ^1H NMR spectrum in CDCl_3 of the of PVAc recovered from the bulk polymerization mediated by **2** at 30 °C (VAc:V-70:2 = 500:0.6:1) at 81.3% conversion.

The major resonances (*e, f, g, h*) are as expected for PVAc.³⁻⁵ Despite the relatively high MW ($\sim 11600 \text{ g}\cdot\text{mol}^{-1}$ by SEC), the typical signals corresponding to the initiator end groups (*h, i, j, k*)³⁻⁵ and others that can be easily assigned to $[\text{Co}^{\text{III}}(\text{OPN})_2]$ fragments (*a, b, c*) are also clearly observable. The metal fragment, containing $d^6 \text{Co}^{3+}$, is diamagnetic in contrast to the initial paramagnetic Co^{2+} complex and therefore yields sharp ^1H NMR resonances. Three 1:1 doublets having the same intensity at δ 7.47 ($J = 9.4 \text{ Hz}$), 7.79 ($J = 9.4 \text{ Hz}$) and 7.93 ($J = 7.7 \text{ Hz}$) may be attributed to the (2,8)- (3,7)- and (4,6)-H nuclei. The first two signals, having the same value for the coupling constants, must be the mutually coupled (2,8) and (3,7) pairs (*a* and *b*), whereas the latter doublet at 7.93 ppm is assigned to protons *c*. These signals are significantly shifted in comparison with the corresponding ones in the HOPN pro-ligand at δ 7.18 ($J = 9.3 \text{ Hz}$), 8.02 ($J = 7.7 \text{ Hz}$) and 8.09 ($J = 9.3 \text{ Hz}$). The expected triplet of the 5-H nucleus is undetectable, probably hidden under other signals, while other weak resonances in this region are attributable to minor amounts of coordinated or free pyridine.

6. VAc polymerization mediated by compound 2/py at 80°C

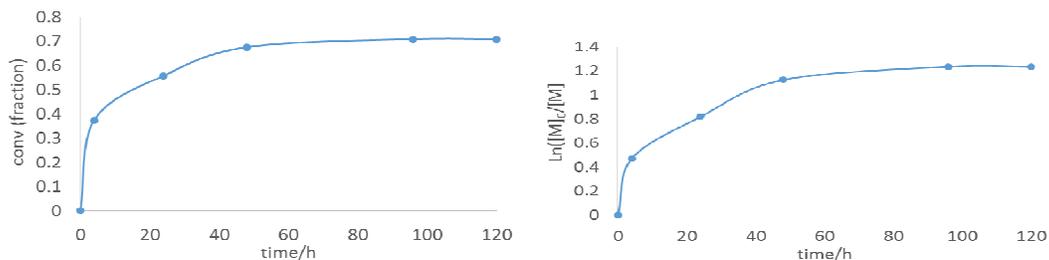


Figure 8S. Kinetics of the bulk polymerization of VAc at 80°C in the presence of $[\text{Co}(\text{OPN})_2(\text{py})_2]$ (VAc/Co = 100) and pyridine (py/Co = 210) initiated by AIBN (AIBN/Co = 4).

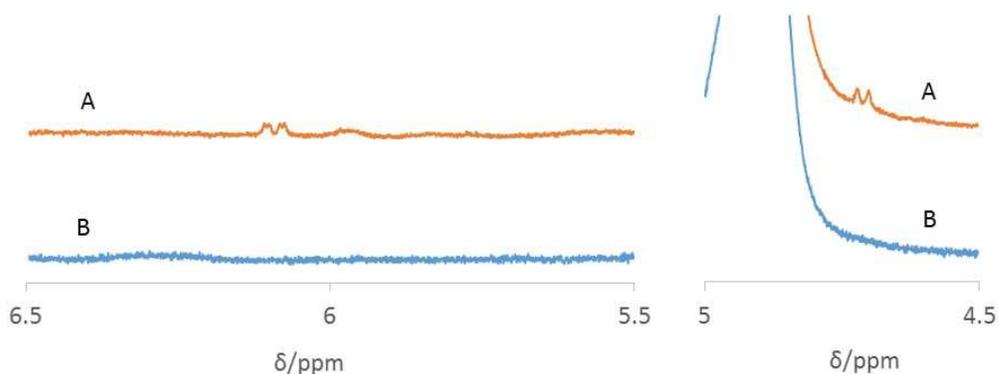


Figure 9S. Expansion of the ^1H NMR spectrum of the polymer from the polymerization at 80°C (VAc/2/py/AIBN = 100:1:210:4). A) 40% conversion and quenching with TEMPO. B) 40% conversion and quenching with *n*PrSH.

The polymer gives rise to observable ^1H NMR resonances for the unsaturated chain ends, PVAc-CH=CHOAc, only after quenching with TEMPO, at δ 6.1 and 4.7 ppm. The quench with PrSH produces a polymer where these unsaturated chain ends are not visible, presumably because of the thiol-ene reaction, producing PVAc-CH(SPr)CH₂OAc chain ends.

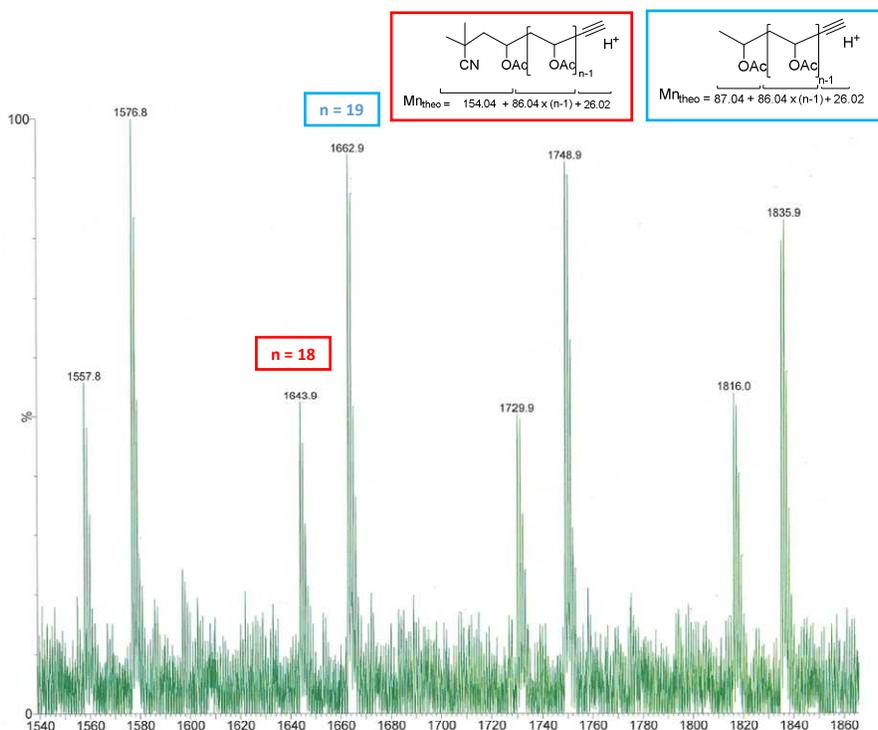
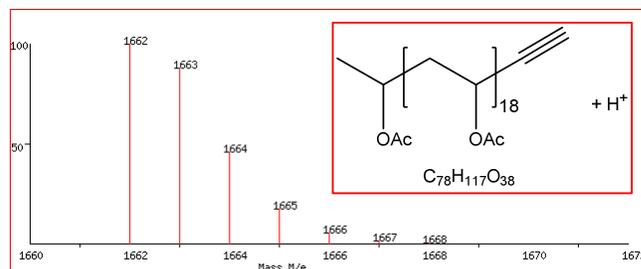
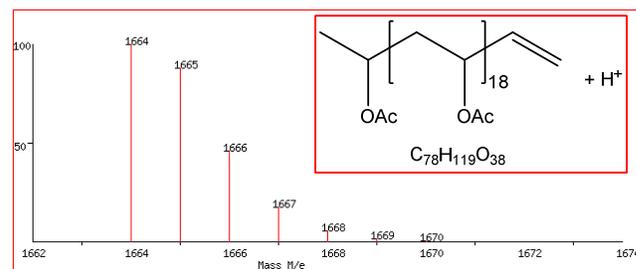
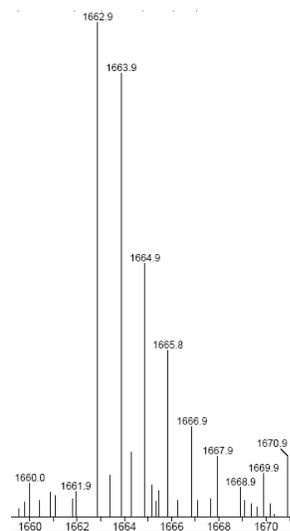


Figure 10S. Excerpt of the MALDI-TOF MS of the polymer from the polymerization at 80°C (VAc/2/py/AIBN = 100:1:210:4) at 40% conversion, after quenching with *n*PrSH.

The *n*PrSH quench of the PVAc-Co(L)₂ terminated chains leads to saturated chain ends, PVAc-CH₂CH₂(OAc),⁶ which give, by a McLafferty rearrangement with loss of acetic acid, PVAc-CH=CH₂ chains in the MALDI MS spectrum.⁶ The two families of isotopic distributions in the above spectrum are one mass unit smaller than those expected for this formula, with the α-chain end being either Me₂(CN)C from AIBN or H from CCT (see simulations below). Note that the H-terminated polymer is the greater fraction. We presume that the dominant species in both families has an unsaturated ω-chain end, resulting from the transfer process, hence the McLafferty rearrangement produces alkyne chain ends.



Simulations



Expansion of experimental spectrum

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