In situ bidentate to tetradentate ligand exchange reaction in cobalt-mediated radical polymerization

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ABSTRACT

Organometallic-mediated radical polymerization (OMRP) has seen a significant growth in the last years notably due to the development of new metal complexes, especially cobalt derivatives. Despite of this, none of the reported complexes offers optimal control for monomers with very different reactivity, which somewhat limits the synthesis of copolymers. In order to expand the scope of cobalt-mediated radical polymerization (CMRP), we investigated an *in situ* ligand exchange reaction for modulating the properties of the cobalt complex at the polymer chain-end and adjusting the C—Co bond strength involved in the control process. With the aim of improving the synthesis of poly(vinyl acetate)-*b*-poly (n-butyl acrylate) copolymers, bidentate acetylacetonate ligands, which impart high level of control to the polymerization of vinyl acetate (VAc), were replaced *in situ* at the PVAc—cobalt chain-end by tetradentate Salen type ligands that are more suited to acrylates.

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1. Introduction

Controlled radical polymerization CRP has become an important tool for the preparation of well-defined polymer materials [1–9]. The use of organometallic complexes was a significant step towards the development of CRP of various vinylic monomers [1,9–12]. CRP mediated by transition metal complexes can be classified in two families [13], i.e., atom transfer radical polymerization (ATRP) [14–16] and organometallic mediated radical polymerization (OMRP) [11,12,17,18]. The role of the metal center consists in the transformation of the radical species into dormant species through a halogen exchange between the metal center and the radical for the ATRP mechanism (Eq. (1), Scheme 1) [19–21], and in the reversible formation of a metal–carbon covalent bond for the OMRP mechanism (Eq. (2), Scheme 1). In the two cases, the CRP is directed by

the redox M^{n+1}/M^n properties of the metallic center (Scheme 1) which are highly affected by the coordination sphere [18,22].

Numerous transition metals including nickel [23], titanium [24,25], molybdenum [26,27], osmium [28,29] cobalt [30] and rhenium [31] are effective for ATRP [32]. This family is however dominated by ruthenium [33–35], iron [36–39] and copper complexes [10,21,28,40–44].

Until now cobalt complexes remain the most versatile and efficient controlling agents for OMRP process [11,17]. Cobalt mediated radical polymerization (CMRP) [45,46] is extensively studied especially for its high ability to control the polymerization of a large range of monomers including acrylic monomers [47–50] and vinyl esters [12,17,46,51,52]. Depending on the reaction conditions, the CMRP process follows a reversible termination (RT) mechanism (Eq. (2), Scheme 1) [51] or a degenerative transfer (DT) one (Eq. (3), Scheme 1) [53,54]. The latter is observed when the amount of radicals exceeds the amount of cobalt complex. The role of the ligand is crucial and determines the ability of the cobalt complex to control

ATRP	P· + X—M^{n+1}	⇌	P—X + M^n	(1)
OMRP *via RT*	P· + M^n	⇌	P—M^{n+1}	(2)
OMRP *via DT*	P· + P′—M^{n+1}	⇌	P—M^{n+1} + P′·	(3)
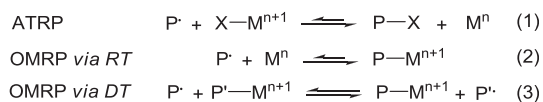
Scheme 1. Radical polymerization controlled via an ATRP or OMRP process.

the polymerization by affecting the stability of the cobalt—carbon bond of the dormant species, and therefore the active/dormant species equilibrium [12]. Cobalt complexes bearing high electron donating ligands such as porphyrin derivatives [49,55], cobaloximes [56] or 1,3-bis(2-pyridilimino)isoindolate ligands [57] (Fig. 1) present high ability to control the radical polymerization of conjugated vinyl monomers such as acrylates. In contrast, low electron donating ligands such as bis(acetylacetonate) (Fig. 1), impart to cobalt an exceptional activity for controlling the radical polymerization of unconjugated vinyl monomers such as vinyl ester, [46,58–60] N-vinyl imidazolium [61], N-vinyl pyrrolidone [62], N-vinyl amides [63–65], and well-defined copolymers of ethylene with vinyl esters and vinyl amides are now accessible [66].

Complex Co(acac)$_2$ presents high abilities to generate reversible dormant species with unconjugated radicals. In

the case of vinyl esters and some vinyl amides, DFT modeling showed that an extra-stabilization of the C—Co bond occurred via an intramolecular chelation of the cobalt atom with the carbonyl function of the last monomer unit and is responsible for the good control observed (Scheme 2) [51,64].

This intramolecular chelation is made possible by the flexible geometry of Co(acac)$_2$ [67,68] that is not possible for cobalt complexes bearing tetradentate ligands with a rigid square-pyramidal geometry (such as cobalt porphyrins) [55,69,70]. Co(acac)$_2$ is however less efficient for acrylates polymerization as the result of the low stability of the C—Co bond of the dormant species [71]. Controlling the radical polymerization of acrylates by Co(acac)$_2$ is feasible but requires specific conditions that allow to shift the active/dormant species equilibrium towards the dormant ones. It can for instance be achieved by decreasing the polymerization temperature to 0 °C and by using an excess of Co(acac)$_2$ to force the reversible deactivation of the chain-end [71]. Using more electron donating bis(chelates) ligands such as ketiminato ligands (Fig. 1) instead of acac ligands led to less efficient control over the VAc polymerization [72].

The effect of the type of ligand on the C—Co bond stability was studied by computational calculations of the bond
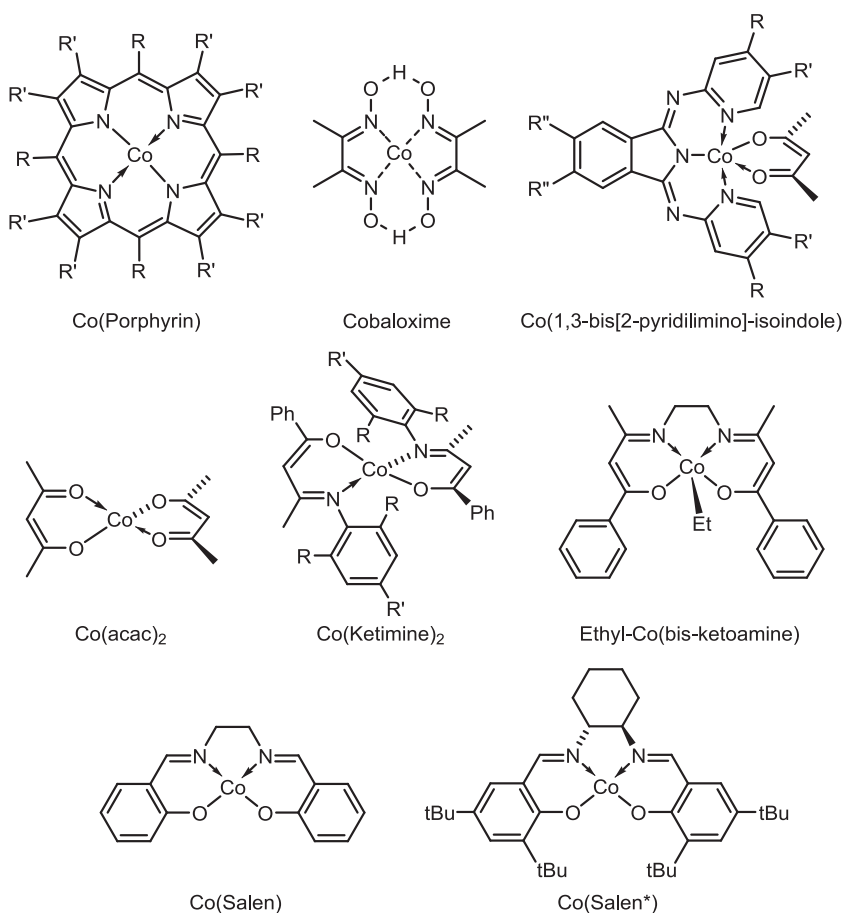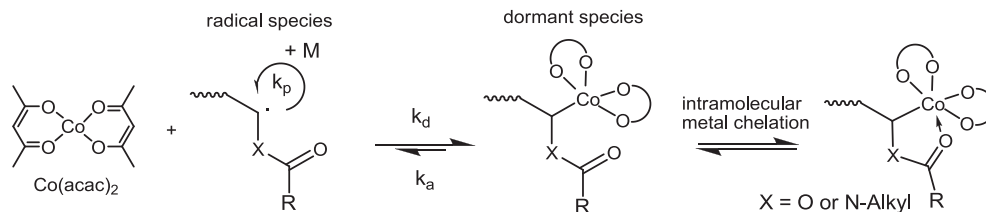

Fig. 1. Cobalt complexes used as controlling agent in CMRP.

Scheme 2. Co(acac)$_2$-based CMRP of vinyl ester or N-vinyl amide monomers.

dissociation energy (BDE) in various models of dormant species. As an illustrative example, the BDE of Co—CH$_3$ was evaluated between 40 and 30 kcal/mol when the cobalt center is coordinated by Salen or dimethylglyoxime ligands [73,74] while this BDE is only 20 kcal/mol for CH$_3$—Co(acac)$_2$ [64]. High electron donating ligands stabilize high oxidation degree of the metal center and so, in OMRP process, stabilize Co(III) dormant species [17]. Considering the BDEs of C—Co bond of alkyl—Co(Salen) in the same range than alkyl—cobaloxime complexes [73], these results support the ability of N,N'-Ethylenebis(salicylimine)-based cobalt complex Co(Salen) to be adapted for the CMRP of acrylates. In addition, a recent article reported the ability of Co(Salen) to mediate the CMRP of VAc in a photo-initiation process at 23 °C but monomer conversions remained low [75]. The same limitation was observed for the VAc polymerization mediated by cobalt porphyrin complexes [76].

In a recent report, Peng and coworkers described the CMRP of both vinyl acetate and methyl acrylate using Cobalt [1,2-Cyclohexanediamino-N,N'-bis(3,5-di-t-butyl-salicylidene)] (Salen*) (Fig. 1) complex as controlling agent. They reported a good control over the two polymerizations with the formation of polymers with low dispersities (between 1.14 and 1.27) [77].

The addition of neutral ligands, such as pyridine, water, THF, DMF, to the CMRP of vinyl monomers is a route to modulate the reactivity of the cobalt complex and to possibly improve the level of control or the kinetics of the polymerization [52,67,78]. This strategy was used to prepare well-defined block copolymers by sequential OMRP of monomers of different reactivity (Scheme 3, route B). For example, the addition of DMF or DMSO to PVAc—Co(acac)$_2$ chains allowed to properly initiate the acrylonitrile polymerization with the formation of well-defined PVAc-b-PAN block copolymers, which is not possible without the addition of the coordinating solvent [68]. It is worth noting that in these above-mentioned cases, these neutral ligands do not substitute the original ones but further coordinate the metal center (Scheme 3, route B).

In the present work, we develop a new approach to modulate in-situ the electronic properties of the cobalt complex at the polymer chain-end in order to adjust the C—Co bond strength involved in the OMRP process. Bidentate acac ligands are substituted for anionic tetradentate ligands, i.e. Salen type ligands, in a one-pot process (Scheme 3, route C) for improving the block copolymerization of vinyl acetate and n-butyl acrylate (Scheme 4). Prior to investigate the block copolymerizations, the performances of Co(Salen) for VAc and nBA polymerizations are

explored and compared to those of Co(acac)$_2$ and Co(Salen*).

2. Results and discussion

### 2.1. Controlled radical polymerization of VAc and nBA using Co(acac)$_2$ and Co(Salen): comparison of the system reactivity

The radical polymerization of VAc is initiated by 2,2'-azo-bis(4-methoxy-2,4-dimethyl valeronitrile (V-70) at 30 °C in the presence of Co(acac)$_2$ or Co(Salen) with a VAc/V-70/Co molar ratio of 542/3/1, thus under DT conditions. The monomer conversion and the molecular parameters of the polymers are determined by ^{1}H NMR and SEC, respectively, for samples withdrawn during the polymerization. Whatever the cobalt complex used, an induction period of about 19 h is observed, suggesting that transformation of the Co^{II} in R-Co^{III} occurs roughly in the same extent with both complexes. Afterwards, the polymerization was faster with Co(acac)$_2$ compared to Co(Salen) (Fig. 2a), indicating a higher tendency of the latter to deactivate the growing PVAc chains. For both complexes, a linear increase of M_n with monomer conversion was observed as expected for a controlled radical polymerization (Fig. 2b).

The molar mass distribution (M_w/M_n) of the resulting PVAc was lower when using Co(acac)$_2$ (between 1.07 and 1.12, Table S1) rather than Co(Salen) (1.09–1.23, Table S1). In contrast to PVAc produced in the presence of Co(acac)$_2$, size exclusion chromatograms (SEC) of those produced by Co(Salen)-mediated polymerization present a tailing on the low molar mass side which contributes to higher dispersity (Fig. S1). This tailing can be characteristic of fast propagation rate compared to a slow initiation by activation of Co dormant species [71] due to a stable polymer-Co(Salen) bond or to the formation of terminated polymer chains during the reaction. However taking into account the efficiency factors ($f = M_{n,theor}/M_{n,SEC}$) with Co(Salen) close to 1 (Table S1), irreversible termination reactions of polymer chains seem to be negligible, if any.

Next, we tested Co(Salen) as controlling agent in the radical polymerization of nBA (nBA/Co molar ratio of 350/1) at 30 °C. In this case, 0.4 equivalent of V-70 compared to the cobalt complex is used in order to avoid any excess of radical and to ensure a RT pathway. After a short induction period of time (about 1 h), nBA polymerized, leading to PnBA with a molar mass between 70,900 and 141,100 g/mol, and dispersities between 1.15 and 1.38 (Table 1, Entry 2; Fig. S2). Although the molar masses
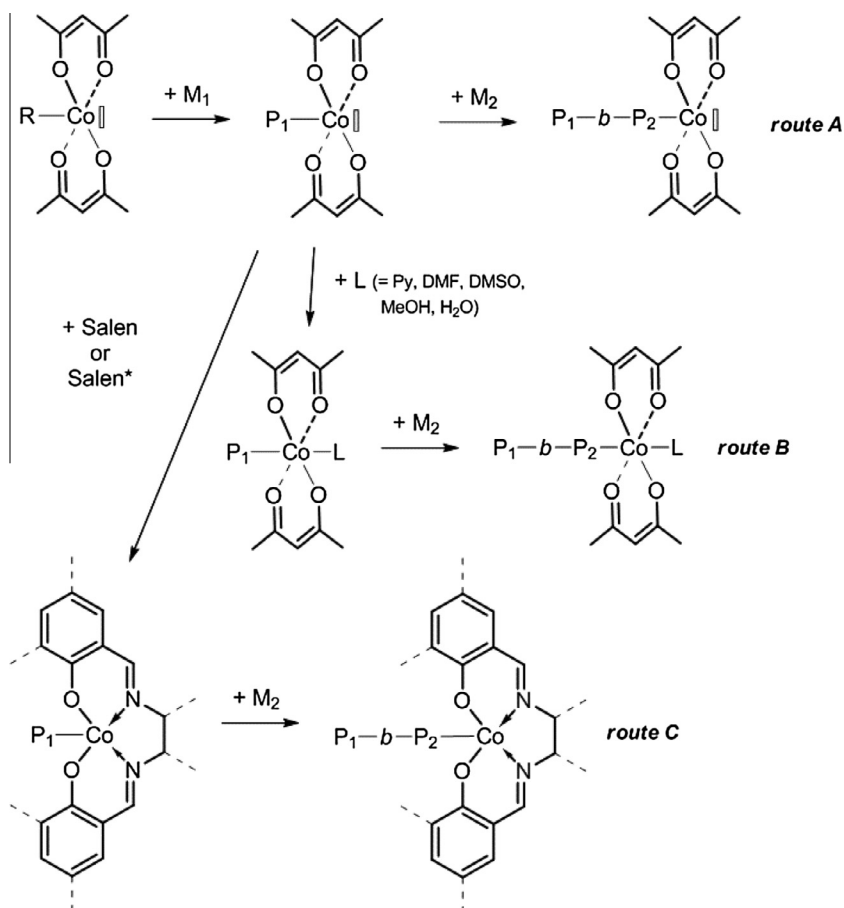
Scheme 3. Sequential CMRP polymerization (route A) as well as addition of neutral ligands (route B) and substitution of the original ligands (route C) of Co to tune the metal center reactivity.
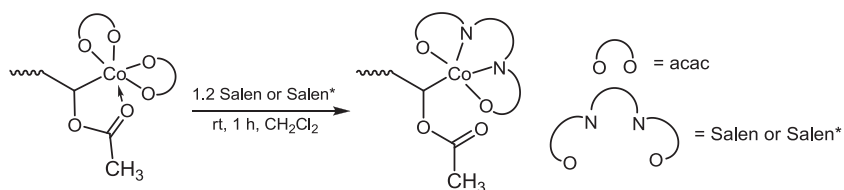
Scheme 4. *In-situ* ligand exchange to form alkyl—Co(Salen) or alkyl—Co(Salen∗) complexes.

increase with the monomer conversion, this evolution is not linear (Fig. S2) and the initiator efficiency factor is low ($f < 0.06$) and is slightly increasing with the reaction time ($f < 0.2$ after 4.5 h; Table 1). The control is far to be optimal. Again, dispersity increases with the reaction time due to the presence of a tailing on SEC-curves (Fig. S3). Under the same experimental conditions, Co(acac)$_2$ provides a very fast and uncontrolled polymerization (Table 1, Entry 1).

The low efficiency factor observed for Co(Salen) contrasts with the high f values ($\sim$1) reported by Peng et al. for the Co(Salen∗)-mediated radical polymerization of methyl acrylate (MA) and VAc [77]. Salen and Salen∗ present similar metal coordination behavior but the nature of

the substituents on the Salen ligand is known to affect the properties of the metal complex, as observed in ring opening polymerization [79]. Recently Shaver et al. reported that electron donating ortho-substituents in Salen∗-like cobalt complexes enhanced their efficiency in CMRP of VAc but bimodal mass distributions were observed under the hard experimental conditions employed (120 °C) [80]. To ensure a RT mechanism, the authors used a Co complex/radical initiator molar ratio of 1/0.6. However, low VAc conversions were obtained at 65 °C [80]. In contrast Peng et al. conducted the polymerization of VAc and MA under DT conditions using a radical initiator/Co molar ratio of 6.5/1 at 60 °C [77], suggesting a highly stable carbon-Co(Salen∗) bond under these
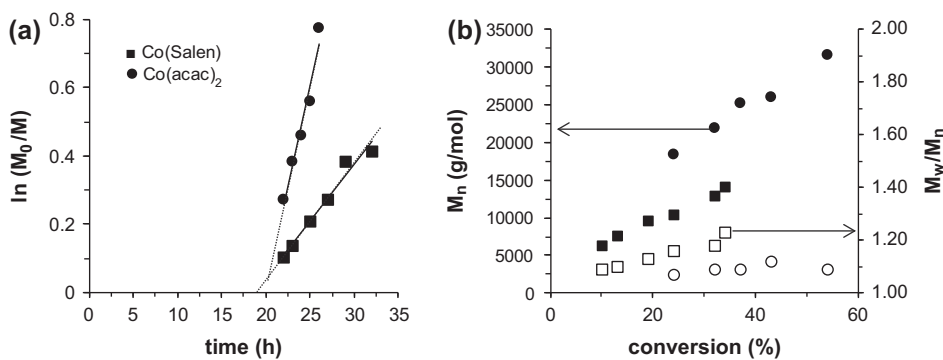
Fig. 2. Plots of $\ln([M]_0/[M])$ with time (a, left) and dependence of PVAc number average molar mass with conversion (b, filled symbols) and dependence of M_w/M_n with conversion (b, open symbols) for the VAc polymerization in the presence of Co(acac)$_2$ (■ or □ symbols) or Co(Salen) (● or ○ symbols). Conditions: $T = 30\,^\circ$C, $V_{VAc} = 5$ mL, Co = 0.10 mmol, V-70 = 0.30 mmol, VAc/Co/V-70 M ratio of 542/1/3, under argon.

Table 1
CMRP of nBA mediated by Co(acac)$_2$ and Co(Salen).[a]

Entry	Co complex	Time (h)	Conv. (%)[b]	M_{nSEC}[c] (g/mol)	$M_{n,theor}$[d] (g/mol)	M_w/M_n[c]	$f = M_{n,theor}/M_{nSEC}$
1	Co(acac)$_2$	0.25	3	157,000	3400	2.14	0.02
		0.5	7	283,400	7800	2.16	0.03
		0.75	13	378,700	14,600	2.07	0.04
		1	82	65,700	91,800	15.70	1.40
2	Co(Salen)	1.5	4	70,900	4500	1.15	0.06
		2	5	92,100	5600	1.15	0.06
		2.5	8	104,500	9000	1.17	0.09
		3	10	112,100	11,200	1.21	0.10
		3.5	13	123,400	14,600	1.28	0.12
		4	19	135,800	21,300	1.29	0.16
		4.5	23	141,100	25,800	1.38	0.18

[a] Conditions: $T = 30\,^\circ$C, $n_{nBA} = 35.20$ mmol (5 mL), Co = 0.10 mmol, V-70 = 0.04 mmol, nBA/Co/V-70 = 350/1/0.4, under argon.
[b] Determined by ^{1}H NMR.
[c] Determined by SEC-THF using PS calibration.
[d] $M_{n,100\% \text{ conv.}} = (350 \times M_{nBA})/0.4 = 112,000$ g/mol, $M_{n,theor} = M_{n,100\% \text{ conv.}} \times$ conv.

conditions. As suggested by Wayland et al., the square planar geometry of cobalt complexes such as Co(Salen*) [80] is well-suited for controlling the radical polymerization via a DT pathway [22,49]. McNeil et al. reported the high efficiency of a square planar bis(β-ketoaminato)cobalt complex (Fig. 1) in controlling MA polymerization via a RT pathway using a V-70/Co ratio of 0.6/1 [70].

Considering the data above, Co(acac)$_2$ appears better suited for VAc than nBA polymerization whereas Co(Salen) type complexes afford a better control to nBA. This observation motivates the *in-situ* exchange of ligands, from bidentate acac to tetradentate Salen type ligands, for the one-pot synthesis of PVAc-*b*-PnBA copolymers (Scheme 4).

2.2. Acac/Salen and acac/Salen* ligand exchange for conducting CMRP of nBA

Firstly, the possibility to quantitatively exchange acac ligand of cobalt(II) complex by Salen or Salen* ligand is tested by reacting stoichiometric amounts of Co(acac)$_2$ with the Salen type ligand at room temperature in CH$_2$Cl$_2$ for 1 h. The expected cobalt(II)(Salen) complexes are isolated after precipitation in pentane. Indeed, the IR spectra of the collected complexes are identical to Co(II)(Salen)

from commercial sources (Fig. S4) or to those reported in the literature [81,82]. This fast exchange reaction between bidentate and tetradentate ligands most probably consists in an entropy driven process.

Next, this exchange is tentatively carried out on an alkyl—cobalt(III) adduct [Co(acac)$_2$—((CHOCOCH$_3$)—CH$_2$)$_{<4}$-R$_0$; alkyl—Co(acac)$_2$] [51] that mimics a PVAc—Co(acac)$_2$ dormant chain (Scheme 4). The *in-situ* formation of alkyl—Co(Salen) and alkyl—Co(Salen*) is performed according to a similar procedure, i.e. by mixing alkyl—Co(acac)$_2$ with 1.2 equiv. of the corresponding ligand (Salen or Salen*) at room temperature in CH$_2$Cl$_2$. After few minutes, the solutions turn from red to dark green in line with a change in the coordination sphere of the metal.

After solvent elimination, the resulting alkyl—cobalt compounds are used without further purification as CMRP initiator for the bulk nBA polymerization. At 20 °C, no polymerization is observed after 3 h whatever the alkyl—cobalt Salen type used, in sharp contrast to alkyl—Co(acac)$_2$ that leads to a highly exothermic and uncontrolled polymerization in a few minutes [71]. However, increasing the polymerization temperature to 40 °C permits to initiate the nBA polymerization by both alkyl—Co(Salen) and

Table 2
Radical polymerization of nBA initiated by *in-situ* formed alkyl—cobalt adducts R-Co(Salen) and R-Co(Salen*).[a]

Radical initiator	Time (h)	Conv.[b] (%)	M_{nSEC}[c] (g/mol)	$M_{n,theor}$[d] (g/mol)	$f = M_{n,theor}/M_{nSEC}$	M_w/M_n[c]
R-Co(Salen)	0.5	5	8500	2100	0.25	1.10
	1	18	17,700	7400	0.42	1.23
	1.5	35	24,800	14,300	0.58	1.30
	2	44	30,700	18,000	0.59	1.31
	2.5	53	33,100	21,700	0.66	1.38
	3	60	37,900	24,500	0.65	1.41
	4	71	39,600	29,000	0.73	1.46
R-Co(Salen*)	1	11	15,700	4500	0.29	1.12
	2	20	22,000	8200	0.37	1.18
	3	30	27,200	12,300	0.45	1.19
	4	43	29,200	17,600	0.60	1.24
	5	51	32,300	20,900	0.65	1.25
	6	61	32,400	25,000	0.77	1.27

[a] Conditions: $T = 40\,°C$, $n_{nBA} = 35.20$ mmol (5 mL), Co = 0.11 mmol, [nBA]/[Co] = 320/1, under argon.
[b] Determined by ^1H NMR.
[c] Determined by SEC-THF using PS calibration.
[d] $M_{n,100\%\ conv.} = 320 \times M_{nBA} = 41,000$ g/mol, $M_{n,theor} = M_{n,100\%\ conv.} \times$ conv.

alkyl—Co(Salen*) (Table 2). The polymerization is faster with R-Co(Salen) with about 70% monomer conversion after 4 h, compared to about 40% with R-Co(Salen*) after the same period of time (Fig. 3a, Table 2). Molar masses increase almost linearly and similarly with the monomer conversion for the two experiments. Dispersities of PnBAs remain relatively low (Fig. 3b, Table 2) especially for the polymerization conducted by alkyl—Co(Salen*) ($M_w/M_n < 1.3$). Fig. S5 shows that SEC traces are shifted towards the higher molar mass side when the conversion increases although some tailing is observed. The origin of the shoulder observed at the low molar mass side on Fig. S5b after 6 h of reaction is however not understood yet.

The satisfactory efficiency factor obtained with the alkyl—cobalt initiator after the ligand exchange reaction is a strong incentive to apply the same ligand exchange strategy on a PVAc—Co(acac)$_2$ macroinitiator. The main goal is to exploit this ligand exchange for the synthesis of well-defined PVAc-*b*-PnBA block copolymers. Typically, a PVAc—Co(acac)$_2$ with low dispersity ($M_w/M_n \leqslant 1.07$, Table S2) is prepared from the alkyl—Co(acac)$_2$ [51] before the addition of 1.2 equiv. of Salen or Salen* ligand in solution in CH$_2$Cl$_2$ (Scheme 4). After solvent and residual

monomer evaporation, nBA is added and the polymerization occurs in bulk at 40 °C. SEC analysis of the resulting polymer shows the production of a PVAc-*b*-PnBA copolymer with a molar mass that increases with nBA conversion (Fig. 4). However, some PVAc macroinitiator remains unreacted during the whole polymerization process (see below). The nBA polymerization initiated by PVAc—Co(Salen) leads to copolymer with higher molar masses and dispersities compared to the copolymer produced from PVAc—Co(Salen*) (Table S2), which matches the conclusions drawn above for the nBA polymerization initiated from the *in-situ* generated alkyl—Co(Salen) and alkyl—Co(Salen*) complexes (Table 2). Activation of PVAc—Co(Salen*) macroinitiator is also more efficient compared to PVAc—Co(Salen) because only a low amount of unconsumed PVAc is detected with the former complex (Fig. 4). From SEC-chromatogram deconvolution, PVAc-*b*-PnBA prepared from PVAc—Co(Salen*) after 5 h is contaminated by about 10% PVAc macroinitiator (Fig. S6). Since the SEC peak of PVAc-*b*-PnBA copolymer is well resolved and does not overlap with the one of the minor fraction of unreacted chains, the dispersity of the block copolymer can be measured and is equal to 1.32 [77]. This value is
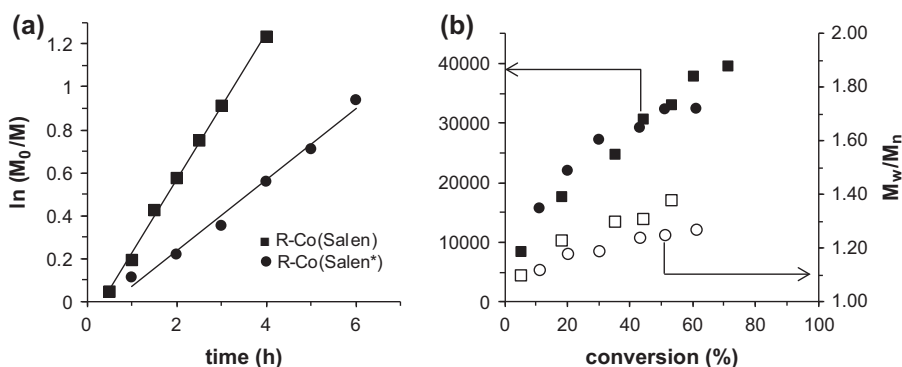

Fig. 3. Plots of $\ln([M]_0/[M])$ with time (a, left) and dependence of PnBA number average molar mass with conversion (b, filled symbols) and dependence of M_w/M_n with conversion (b, open symbols) for the nBA polymerization initiated by R-Co(Salen) (■ or □ symbols) or R-Co(Salen*) (● or ○ symbols). Conditions: $T = 40\,°C$, $n_{nBA} = 35.20$ mmol (5 mL), alkyl—Co = 0.11 mmol, [nBA]/[Co] = 320/1, under argon.
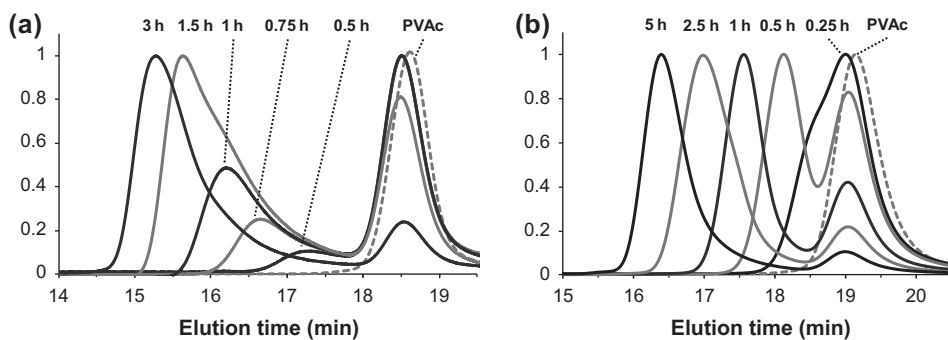
Fig. 4. Selected SEC curves of PVAc-*b*-PnBA copolymers prepared via nBA chain extension initiated by PVAc—Co(Salen) (a, left) or PVAc—Co(Salen∗) (b, right). Conditions: $T = 40$ °C, $n_{nBA} = 35.20$ mmol (5 mL), alkyl—Co = 0.11 mmol, [nBA]/[Co] = 320/1, under argon; PVAc corresponds to initial macro-initiator before chain extension; molecular parameters of the corresponding polymers are presented in *Table* S2. (a) CMRP conducted by PVAc—Co(Salen) (left): PVAc: $M_n = 9900$ g/mol, $M_w/M_n = 1.07$, VAc conv. = 25%; 0.5 h: $M_n = 10,700$ g/mol, $M_w/M_n = 1.18$, nBA conv. = 3%; 0.75 h: $M_n = 12,700$ g/mol, $M_w/M_n = 1.48$, nBA conv. = 5%; 1 h: $M_n = 15,000$ g/mol, $M_w/M_n = 2.05$, nBA conv. = 8%; 1.5 h: $M_n = 21,900$ g/mol, $M_w/M_n = 3.02$, nBA conv. = 15%; 3 h: $M_n = 46,200$ g/mol, $M_w/M_n = 3.40$, nBA conv. = 40%; (b) CMRP conducted by PVAc—Co(Salen∗) (right): PVAc: $M_n = 7900$ g/mol, $M_w/M_n = 1.06$, VAc conv. = 29%; 0.25 h: $M_n = 9100$ g/mol, $M_w/M_n = 1.10$, nBA conv. = 3%; 0.5 h: $M_n = 10,700$ g/mol, $M_w/M_n = 1.16$, nBA conv. = 7%; 1 h: $M_n = 14,100$ g/mol, $M_w/M_n = 1.31$, nBA conv. = 14%; 2.5 h: $M_n = 21,400$ g/mol, $M_w/M_n = 1.43$, nBA conv. = 31%; 5 h: $M_n = 33,000$ g/mol, $M_w/M_n = 1.59$, nBA conv. = 56%.

rather low compared to the dispersity of the PVAc-*b*-PMA copolymer prepared solely by Co(Salen*) ($M_w/M_n = 1.61$) [77] or compared to PVAc-*b*-PnBA obtained by sequential Co(acac)$_2$-mediated copolymerization of VAc and nBA ($M_w/M_n = 1.70$) [71]. In the latter case, the extent of unreacted PVAc macroinitiator was also much higher compared to the exchange ligand strategy presented in this work. A representative ^{1}H NMR spectrum of a PVAc-*b*-PnBA block copolymer prepared by this ligand exchange process is provided in Fig. S7.

3. Conclusion

The controlled radical polymerization of VAc and nBA was explored using Co(Salen) or Co(acac)$_2$ as controlling agent in the presence of V70 as free radical initiator, in the bulk at 30 °C. Co(acac)$_2$ was well-suited for the VAc polymerization but was inefficient to control the nBA polymerization. In contrast, Co(Salen) complex proved to be more efficient for the polymerization of nBA than VAc. Therefore, the *in-situ* acac/Salen exchange reaction appeared as a promising approach for expanding the scope of CMRP and particularly for synthesizing well-defined PVAc-*b*-PnBA copolymers. Successful exchange reactions took place when treating a low molar mass alkyl—Co(acac)$_2$ with tetradentate Salen or Salen* ligands. In contrast to alkyl—Co(acac)$_2$ that provides a very fast, exothermic and uncontrolled polymerization of nBA, the *in-situ* formed alkyl—Co(Salen) and alkyl—Co(Salen*) were able to initiate and control the radical polymerization of nBA. By carrying out this ligand exchange reaction on a PVAc—Co(acac)$_2$ prepared by CMRP of VAc initiated by alkyl—Co(acac)$_2$, the resulting PVAc—Co(Salen) and PVAc—Co(Salen*) were successfully used as macro-initiators for the nBA polymerization and provided PVAc-*b*-PnBA block copolymers. Thermal activation of PVAc—Co(Salen*) was more efficient than PVAc—Co(Salen) and led to a PVAc-*b*-PnBA copolymer with a lower dispersity, although a tiny amount of unreacted PVAc chains remained in the final product. Although further optimizations are required,

the modification of the metal center via *in situ* ligand exchange is a convenient and straightforward alternative for the preparation of block copolymers from monomers that are difficult or impossible to control with the same cobalt complex.

4. Experimental section

4.1. General considerations

Vinyl acetate (VAc, >99%, Aldrich) and n-butyl acrylate (nBA, >99%, Aldrich) were dried over calcium hydride, degassed by several freeze–pump–thaw cycles, distilled under reduced pressure and stored at −20 °C under argon. *N,N′*-Bis(salicylidene)ethylenediamine (Salen, 98%, Aldrich), (1R,2R)-(−)-1,2-Cyclohexanediamino-*N,N′*-bis(3,5-di-t-butylsalicylidene) (Salen*, 98%, Aldrich), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO, 98%, Aldrich), *Bis*-(acetylacetonato)cobalt(II) (Co(acac)$_2$, >98%, Acros), [*N,N′*-Bis(salicylidene)-ethylenediamine]cobalt(II) (Co(Salen), >99%, TCI), 2,2′-azo-bis(4-methoxy-2,4-dimethyl valeronitrile) (V-70, Wako) were used as received.

The alkyl—cobalt(III) adduct initiator ([Co(acac)$_2$—((CHOCOCH$_3$)—CH$_2$)$_{<4}$-R$_0$)]; R$_0$ being the primary radical generated by 2,2′-azo-bis(4-methoxy-2,4-dimethyl valeronitrile) (V-70, Wako) was prepared as described previously and stored as a CH$_2$Cl$_2$ solution at −20 °C under argon [51]. All polymerizations and synthesis were performed by classical Schlenk techniques under argon using dry and degassed monomers.

4.2. Characterization

The molar masses (M_n) and molar mass distributions (M_w/M_n) of polymers were determined by size-exclusion chromatography (SEC) in tetrahydrofuran (THF) relative to poly(styrene) (PS) standards at 45 °C (flow rate: 0.7 mL/min) with a Malvern chromatograph equipped with a Viscotek TDA 305 triple detection (refractometer, viscosimeter and low angle laser light scattering (LALLS)) as

well as Agilent columns (three PL-gel 5 μm columns: 10^4, 10^3 and 10^2 Å). ^{1}H NMR spectra of reaction mixtures were recorded in CDCl$_3$ at 298 K with a 250 MHz Bruker spectrometer. IR spectra in the range of 4000–450 cm^{-1} were recorded in KBr pellets on a PerkinElmer Spectrum One FT-IR spectrometer.

4.2.1. CMRP of VAc using Co(acac)$_2$ or Co(Salen) as controlling agent

Radical initiator V-70 (92.5 mg, 0.30 mmol) and Co(acac)$_2$ (25.7 mg, 0.10 mmol) were placed in a 30 mL Schlenk flask and degassed by three vacuum/argon cycles. Vinyl acetate (VAc) (5 mL, 54.20 mmol) was then added by syringe under argon ([VAc]/[V-70]/[Co] = 542/3/1). The purple mixture was stirred and heated at 30 °C. No polymerization occurred for at least 18 h, after which the viscosity of the solution increased substantially. Samples were withdrawn at different reaction times and analyzed by ^{1}H NMR to determine monomer conversion and by SEC-THF for molecular parameters using PS calibration, after addition of TEMPO to neutralize radicals [51]. The same procedure was followed for VAc polymerization using Co(Salen) (32.5 mg, 0.10 mmol) as controlling agent.

4.2.2. CMRP of nBA using Co(acac)$_2$ or Co(Salen) as controlling agent

Radical initiator V-70 (12.3 mg, 0.04 mmol) and Co(acac)$_2$ (25.7 mg, 0.10 mmol) were placed in a 30 mL Schlenk flask and degassed by three vacuum/argon cycles. Pure n-Butyl acrylate (nBA) (5 mL, 35.00 mmol) was then added by syringe under argon ([nBA]/[V-70]/[Co] = 350/0.4/1). The purple mixture was stirred and heated at 30 °C. Samples were withdrawn at different reaction times to determine monomer conversion by ^{1}H NMR and molecular parameters by SEC-THF using PS calibration after addition of TEMPO. The same procedure was followed for nBA polymerization using Co(Salen) (32.5 mg, 0.10 mmol) as controlling agent.

4.2.3. Synthesis of Co(Salen) or Co(Salen*)

Co(acac)$_2$ (113.0 mg, 0.44 mmol) was placed in a Schlenk flask and degassed by three vacuum/argon cycles. A volume of 1.5 mL of CH$_2$Cl$_2$ was added under argon and a solution of Salen ligand (118.0 mg, 0.44 mol) in 2 mL of CH$_2$Cl$_2$ was injected into the suspension under argon. The reaction mixture turned to red and was stirred at room temperature for 1 h. Complex Co(Salen) was precipitated with addition of 40 mL of pentane, recovered by centrifugation and dry overnight at 40 °C under vacuum. The complex was analyzed by IR using KBr (Fig. S4a): 3051 (w), 3019 (w), 2920 (w), 1634 (S), 1600 (S), 1532 (m), 1467 (m), 1449 (S), 1347 (S), 1329 (m), 1273 (m), 1198 (m), 1146 (m), 1127 (m), 753 (m), 735 (m) cm^{-1}.

Complex Co(Salen*) was synthesized following the same method than Co(Salen) by reacting Salen* (31.5 mg, 0.06 mmol) and Co(acac)$_2$ (15.0 mg, 0.06 mmol) and characterized by IR in KBr (Fig. S4b): 2949 (VS), 2864 (S), 1634 (m), 1595 (S), 1526 (S), 1461 (m), 1432 (m), 1385 (m), 1359 (m), 1337 (m), 1320 (m), 1253 (S), 1201 (w), 1175 (S), 929 (m), 867 (m), 834 (m), 786 (m), 746 (w), 639 (w) cm^{-1}.

No characteristic signal of Co(acac)$_2$ (1590 (S), 1514 (S), 1396 (S), 1257 (S), 1020 (m), 920 (m) cm^{-1}) was detected by IR (Fig. S4).

4.2.4. Polymerization of nBA initiated by alkyl–Co(Salen) or alkyl–Co(Salen*)

Ligand Salen (39 mg, 0.14 mmol) was placed in a 30 mL Schlenk flask and degassed by three vacuum/argon cycles. A volume of 5 mL of dry and degassed CH$_2$Cl$_2$ was added under argon and then a solution of alkyl–cobalt(III) initiator [51] in CH$_2$Cl$_2$ (1.0 mL of a 0.11 M stock solution, 0.11 mmol) was introduced under argon in the 30 mL Schlenk tube. The red solution was stirred at room temperature and turned to dark green after a couple of minutes. After 1 h, all volatiles were evaporated to dryness under reduced pressure at room temperature. A volume of 5 mL of dry and degassed nBA was added under argon and then the dark green solution was stirred at 40 °C. The viscosity of the solution increased substantially after a couple of minutes and samples were withdrawn at different reaction times to determine monomer conversion by ^{1}H NMR and molecular parameters by SEC using PS calibration after addition of TEMPO.

The same procedure was followed for nBA polymerization initiated by alkyl–Co(Salen*) after reaction of Salen* ligand (72.0 mg, 0.13 mmol) with alkyl–Co(acac)$_2$ adduct (0.11 mmol).

4.2.5. Preparation of PVAc–Co(acac)$_2$

A solution of alkyl–cobalt(III) initiator [51] in CH$_2$Cl$_2$ was introduced under argon in the 30 mL Schlenk flask (1.0 mL of a 0.11 M stock solution, 0.11 mmol) and evaporated to dryness under reduced pressure at room temperature. A volume of 5 mL of VAc was added and the reaction mixture was stirred at 40 °C for 9 h. At the end of the polymerization, an aliquot was withdrawn to determine the monomer conversion by ^{1}H NMR (conversion: 25% and 29% for PVAc–Co(Salen) and PVAc–Co(Salen*), respectively) and the molecular parameters by SEC after addition of TEMPO (M_n = 9900, M_w/M_n = 1.07 for PVAc–Co(Salen); M_n = 7900, M_w/M_n = 1.06 for PVAc–Co(Salen*), Table S2). All volatiles were removed under reduced pressure at room temperature and the resulting PVAc–Co(acac)$_2$ was stored at −20 °C before further manipulations. No residual VAc was detected by ^{1}H NMR during the next experiments using PVAc–Co(acac)$_2$ macroinitiator.

4.2.6. Synthesis of PVAc-b-PnBA using PVAc–Co(Salen) or PVAc–Co(Salen*) macroinitiators

Ligand Salen (39 mg, 0.14 mmol) was placed in a 30 mL Schlenk flask and degassed by three vacuum/argon cycles and then 8 mL of dry and degassed CH$_2$Cl$_2$ was added under argon. The resulting yellow solution was transferred using cannula into a Schlenk flask containing the PVAc–Co(acac)$_2$ previously prepared (0.11 mmol, M_n = 9900 g/mol, M_w/M_n = 1.07, Table S2). The red solution was stirred at room temperature and turned to dark green after a couple of minutes. After 1 h, all volatiles were evaporated to dryness under reduced pressure at room temperature. A volume of 5 mL of nBA was added under argon and then the dark green solution was stirred at 40 °C. Samples

were withdrawn at different reaction times to determine monomer conversion by ^{1}H NMR and molecular parameters by SEC-THF using PS calibration after addition of TEMPO. Polymerization was stopped when the reaction medium was too viscous to withdrawn samples under argon. Results are summarized in Table S2 and Fig. 4.

The same procedure was followed for the synthesis of PVAc-*b*-PnBA initiated by PVAc—Co(Salen*) after reaction of Salen* ligand (72.0 mg, 0.13 mmol) with PVAc—Co(acac)$_2$ adduct (0.11 mmol, M_n = 7900 g/mol, M_w/M_n = 1.06, Table S2). Results are summarized in Table S2 and Fig. 4, and a ^{1}H NMR spectrum of the resulting PVAc-*b*-PnBA copolymer after monomer elimination under reduced pressure is shown in Fig. S7.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.eurpolymj.2014.08.003.

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