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Synthesis of End-Functional Poly(vinyl acetate) by Cobalt-Mediated Radical Polymerization

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ABSTRACT: Poly(vinyl acetate) (PVAc) chains prepared by cobalt-mediated radical polymerization in the presence of cobalt(II) acetylacetonate ($Co(acac)_2$) were quenched by radical scavengers, such as thiol compounds and nitroxides, to displace the covalently bonded $Co(acac)_2$ moiety and to end-cap them with a reactive group. The cobalt complex was completely removed by filtration, as confirmed by the induction coupled plasma (ICP) analysis of the polymer before and after treatment. Growing poly(vinyl acetate) chains can be end-functionalized either by addition of an appropriately functionalized nonpolymerizable olefin or by displacement of the $Co(acac)_2$ moiety by a functionalized nitroxide. This strategy allows PVAc to be synthesized with a predictable molecular weight, a reasonably low polydispersity ($M_w/M_n \sim 1.1-1.3$), and a functional ω end group, e.g., hydroxyl and epoxy.

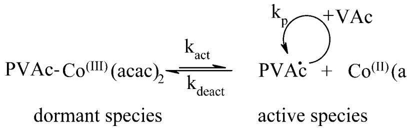
Introduction

Nowadays, a variety of polymers with well-defined molar masses and low polydispersity can be synthesized by the controlled radical polymerization (CRP) processes, mainly by nitroxide-mediated polymerization (NMP),[1] atom transfer radical polymerization (ATRP),[2,3] and radical addition−fragmentation transfer (RAFT).[4] Similarly to living ionic polymerizations, telechelic polymers can be prepared by controlled radical polymerization which has the advantage of being tolerant of many nonprotected functional groups (amine, alcohol, epoxy). The α-end group is controlled by the structure of the initiator, whereas the control agent has a decisive effect on the ω-end group and its possible derivatization into a desired organic function. Examples of chain-end functionalization have been reported by RAFT,[5] by NMP,[6] and more extensively by ATRP.[3,7,8]

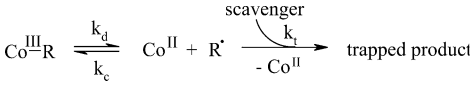
This paper deals with the chain-end functionalization of poly(vinyl acetate) (PVAc) prepared by a recently reported controlled radical polymerization based on a cobalt complex.[9] In this CRP method, cobalt acetylacetonate reacts reversibly with the poly(vinyl acetate) chains, which are accordingly involved in an equilibrium between active and dormant species (Scheme 1). After polymerization, all of the chains are end-capped by a cobalt(II) acetylacetonate ($Co(acac)_2$) moiety. Such a mechanism has already been proposed for the control of acrylate polymerization in the presence of cobalt porphyrin[10] and cobaloxime complexes.[11]

The energy of the cobalt−carbon bond is known to be low enough for homolysis to occur at moderate temperature.[12] Kinetics of homolysis of the Co−C bond has been analyzed by using radical traps, such as thiols[13] and nitroxides,[14] which can scavenge the radicals as soon as they are released by the homolytic cleavage of the cobalt−carbon bond (Scheme 2). The appropriate choice of the scavenger is thus a direct way either to impose the structure of the ω-end groups or, merely, to remove the cobalt complex originally attached to the chains. In this work, three scavengers were tested in the cobalt-mediated radical polymerization of vinyl acetate, i.e., alkanethiol, nitroxide, and nonpolymerizable olefins bearing different reactive groups.

Scheme 1



Scheme 2



Experimental Section

Materials. Vinyl acetate (VAc) (>99%, Acros) was dried over calcium hydride, degassed by several freeze−thawing cycles before being distilled under reduced pressure, and stored under argon. Methanol was degassed by bubbling argon for 30 min. Toluene and THF were distilled from sodium/benzophenone, followed by bubbling with argon for 30 min. Argon was also bubbled through 1-propanethiol (99%, Aldrich), 3-butene-1-ol (96%, Aldrich), 1,2-epoxy-5-hexene (97%, Aldrich), and 3-butenoic acid (97%, Aldrich) for 20 min. Cobalt(II) acetylacetonate ($Co(acac)_2$, >98%, Merck), 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, $t_{1/2} = 10$ h at 30 °C) (Wakko), 2,2,6,6-tetramethylpiperidine 1-oxy (TEMPO) (98%, Aldrich), 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl (>97%, Fluka), sodium hydride (NaH, 60%, dispersion in mineral oil), and epichlorohydrin (99%, Aldrich) were used as received.

Characterization. Size exclusion chromatography (SEC) was carried out in THF (flow rate: 1 mL min^{-1}) at 40 °C using a Waters 600 liquid chromatrograph equipped with a 410 refractive index detector and styragel HR columns (four columns HP PL gel 5 μm 10^5, 10^4, 10^3, 10^2 Å). A calibration curve obtained from polystyrene standards was used to determine the molecular weights. ^{1}H NMR spectra were recorded with a Bruker AM 400 spectrometer (400 MHz) in deuterated chloroform. Induction coupled plasma (ICP) atomic emission spectroscopy was carried out with a spectrometer

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(3510 ICP Bausch & Lomb). Samples were prepared by dissolving a small amount (few milligrams) of poly(vinyl acetate) in 1 mL of HNO_3 (65%) at 60 °C for 2 h. These solutions were diluted with 9 mL of bidistilled water at room temperature. An external calibration was necessary for determining the cobalt content. Infrared spectra (IR) were recorded with a Perkin-Elmer FT-IR instrument (KBr). Elementary analyses (EA) were carried out with a Carlo-Erba elemental analyzer (CHNS-O EA1108).

Polymerization of Vinyl Acetate. V-70 (200 mg, 6.5×10^{-4} mol) and $Co(acac)_2$ (52 mg, 2×10^{-4} mol) were added into a 30 mL flask and degassed by three vacuum−argon cycles. Vinyl acetate (10.0 mL, 108×10^{-3} mol) was then added with a syringe under argon. The purple mixture was stirred and heated at 30 °C. After a few hours, the solution changed from purple to dark green. No polymerization occurred for several hours, followed by a substantial increase in the solution viscosity. After 23.5 h at 30 °C, the monomer conversion was determined by weighing the polymer collected upon removal of the unreacted monomer in vacuo at 50 °C (conversion = 20%). The mixture was then diluted in acetone, (re)precipitated in a ice/water mixture, filtered, and dried in vacuo. The green poly(vinyl acetate) (1.6 g) was analyzed by SEC ($M_{n,theor}$ = 9300 g/mol, $M_{n,SEC}$ = 8000 g/mol, M_w/M_n = 1.20).

Treatment of a PVAc End-Capped by Cobalt Complex with 1-Propanethiol. Green poly(vinyl acetate) (1.6 g, $M_{n,SEC}$ = 8000 g/mol, M_w/M_n = 1.20), prepared according to the general procedure, was added to a 50 mL flask under an inert atmosphere and diluted with 10 mL of degassed methanol. Then, degassed 1-propanethiol (4×10^{-3} mol, 0.4 mL) was added with a syringe under an inert atmosphere, and the medium was stirred at 50 °C. After a few hours, the medium changed from green to dark black, and stirring was maintained for 24 h. After elution through celite (removal of a black), the polymer was (re)precipitated in heptane before being dried in vacuo at 40 °C. A slightly yellow poly(vinyl acetate) (1.0 g) was recovered and analyzed by SEC and ICP ($M_{n,SEC}$ = 8000 g/mol, M_w/M_n = 1.20).

Termination of the Vinyl Acetate Polymerization by Radical Scavengers. *1-Propanethiol.* In an example, degassed 1-propanethiol (2×10^{-3} mol, 0.2 mL) was added at 30 °C to the polymerization medium (3.25×10^{-4} mol of V-70, 1.0×10^{-4} mol of $Co(acac)_2$, 54×10^{-3} mol of VAc, 22 h, 14% VAc conversion), which was diluted with methanol 1 h later and eluted through celite in order to remove a black deposit. The polymer was precipitated two times in heptane and dried at 60 °C in vacuo. A very slightly brown polymer was recovered (0.17 g); $M_{n,theor}$ = 6500 g/mol, $M_{n,SEC}$ = 8900 g/mol, M_w/M_n = 1.15, M_n based on the α-end group ($M_{n,NMR,\alpha} = 86.09 \times (3 \times (-C\underline{H}-OCOCH_3$, PVAc)/$(-OC\underline{H}_3$, V-70)) = 7200 g/mol, M_n based on the ω-end group ($M_{n,NMR,\omega}$) = $86.09 \times (2 \times (-C\underline{H}-OCOCH_3$, PVAc)/$(-C\underline{H}_2-OCOCH_3$, ω-end group)) = 8000 g/mol (90% functionalization). ^1H NMR ($CDCl_3$): 4.84 ppm ($-C\underline{H}-OCOCH_3$, backbone); 4.04 ppm ($-C\underline{H}_2-OCOCH_3$, tail); 3.14 ppm ($-OC\underline{H}_3$, V-70); 2.00 ppm ($-OCO-C\underline{H}_3$, backbone); 1.85−1.6 ppm ($-C\underline{H}_2-CH-OCOCH_3$, backbone); 1.5−1.2 ppm ($-C\underline{H}_3$ of V-70).

3-Butene-1-ol. Degassed 3-butene-1-ol (0.34 g, 0.4 mL, 4.6×10^{-3} mol) was added to the polymerization medium (3.25×10^{-4} mol of V-70, 1.0×10^{-4} mol of $Co(acac)_2$, 54×10^{-3} mol of VAc) after 21 h at 30 °C. The monomer conversion (17%) did not change anymore as a result of the polymerization inhibition. After dilution by acetone, PVAc was (re)precipitated two times in ice/water bath. A green polymer (0.20 g) was recovered by filtration and dried in vacuo. $M_{n,theor}$ = 8400 g/mol; $M_{n,SEC}$ = 10 000 g/mol; M_w/M_n = 1.30; $M_{n,NMR,\alpha} = 86.09 \times (3 \times (-C\underline{H}-OCOCH_3$, PVAc)/$(-OC\underline{H}_3$, V-70)) = 10 500 g/mol, $M_{n,NMR,\omega} = 86.09 \times (2 \times (-C\underline{H}-OCOCH_3$, PVAc)/$(-C\underline{H}_2-OH$, ω-end group)) = 8300 g/mol. In this case, functionalization would exceed 100%, which is the consequence of the low intensity of the NMR resonances and the related unaccuracy. ^1H NMR ($CDCl_3$): 3.62 ppm ($-C\underline{H}_2-OH$, ω-chain end).

1,2-Epoxy-5-hexene. Degassed 1,2-epoxy-5-hexene (4×10^{-3} mol, 0.5 mL) was added to the polymerization medium (3.25×10^{-4} mol of V-70, 1.0×10^{-4} mol of $Co(acac)_2$, 32×10^{-3} mol of VAc) after 47 h at 30 °C. Before injection of the unsaturated compound, a sample was withdrawn (conversion = 40%, $M_{n,SEC}$ = 13 000 g/mol, M_w/M_n = 1.17). After 2 h, the monomer conversion did not change anymore (42%) as result of the polymerization inhibition. After dilution by acetone, PVAc was (re)precipitated two times in heptane. A green polymer (0.28 g) was collected by filtration and dried in vacuo at 60 °C. $M_{n,theor}$ = 11 800 g/mol, $M_{n,SEC}$ = 14 000 g/mol, M_w/M_n = 1.20, $M_{n,NMR,\alpha} = 86.09 \times (3 \times (-C\underline{H}-OCOCH_3$, PVAc)/$(-OC\underline{H}_3$, V-70)) = 10 500 g/mol, $M_{n,NMR,\omega} = 86.09 \times (3 \times (-C\underline{H}-OCOCH_3$, PVAc)/$(-C\underline{H}-$ and $-C\underline{H}_2$ epoxy, ω-end group)) = 9800 g/mol (functionalization slightly higher than 100%, cf. supra). ^1H NMR: 2.85 ppm ($-C\underline{H}-$ epoxy, ω-chain end); 2.71 and 2.44 ppm ($-C\underline{H}_2$ epoxy, ω-chain end).

3-Butenoic Acid. Degassed 3-butenoic acid (4×10^{-3} mol) was also added to the vinyl acetate polymerization medium (3.25×10^{-4} mol of V-70, 1.0×10^{-4} mol of $Co(acac)_2$, 54×10^{-3} mol of VAc) in order to end-functionalize the PVAc.

TEMPO. A degassed solution of TEMPO (2.0×10^{-4} mol) in toluene (1.0 mL) was added to the polymerization medium (6.5×10^{-4} mol of V-70, 1.0×10^{-4} mol of $Co(acac)_2$, 54×10^{-3} mol of VAc, 16 h, 26% VAc conversion) and reacted for 2 h at 30 °C. After dilution by acetone, the solution was eluted through acidic alumina oxide in order to eliminate a purple deposit of $Co(acac)_2$. PVAc was (re)precipitated two times in heptane and dried at 60 °C in vacuo to yield 0.47 g of a colorless polymer. $M_{n,theor}$ = 12 100 g/mol, $M_{n,SEC}$ = 16 500 g/mol, M_w/M_n = 1.15, $M_{n,NMR,\alpha} = 86.09 \times (3 \times (-C\underline{H}-OCOCH_3$, PVAc)/$(-OC\underline{H}_3$, V-70)) = 12 000 g/mol, $M_{n,NMR,\omega} = 86.09 \times ((-C\underline{H}-OCOC\underline{H}_3$, PVAc)/(AcO$-C\underline{H}-$ON-, ω-end group)) = 18 300 g/mol. (65% functionalization). ^1H NMR: 6.20 ppm (AcO$-C\underline{H}-$ON−), 1.6−1.0 ppm (partially hidden $-C\underline{H}_2-$ and $C\underline{H}_3$ of TEMPO at ω-chain end).

4-(Glycidyloxy)-2,2,6,6-tetramethylpiperidine 1-oxyl was synthesized as follows. NaH (0.75 g, 60% in mineral oil, 19×10^{-3} mol) was added to a solution of 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl, (2.6 g, 15×10^{-3} mol), in THF (15 mL). The mixture was stirred at room temperature for 30 min under argon and evaporated under reduced pressure. Epichlorohydrin (10.0 g, 108×10^{-3} mol) was added to the residue, and the mixture was stirred at 50 °C for 20 h under argon. Excess of epichlorohydrin was distilled off under reduced pressure. The residual red oil was purified by column chromatography (chloroform/silica gel). The collected product (1.3 g) was then purified by distillation under reduced pressure. A vermilion solid was recovered (1.2 g, yield = 35%); mp = 38.3−38.4 °C. IR (KBr) ν_{max}: 3481.63; 3044.65; 2976.37; 2928.58; 2867.13; 1605.36; 1462.48; 1374.03 (·ON); 1360.42; 1241.35 (epoxy); 1217.53; 1176.71; 1091.66; 911.35; 894.34; 850.12; 799.09; 761.66 cm^{-1}. Elementary analysis: Calcd for $C_{12}H_{22}O_3N$: C, 63.13%; H, 6.40%; N, 9.71%. Found: C, 63.09%; H, 6.31%; N, 10.03%.

A degassed solution of 4-(glycidyloxy)-2,2,6,6-tetramethylpiperidine 1-oxyl in toluene (1.0 mL, 3.0×10^{-4} mol/mL) was added to the polymerization medium (6.5×10^{-4} mol of V-70, 1.0×10^{-4} mol of $Co(acac)_2$, 54×10^{-3} mol of VAc, 15.5 h, 12% VAc conversion) and reacted for 1 h at 30 °C. After dilution by acetone, the solution was eluted through acidic alumina oxide. The polymer was (re)precipitated two times in heptane and dried at 60 °C in vacuo to yield 0.25 g of colorless PVAc. $M_{n,theor}$ = 5600 g/mol, $M_{n,SEC}$ = 5700 g/mol, M_w/M_n = 1.16, $M_{n,NMR,\alpha} = 86.09 \times (3 \times (-C\underline{H}-OCOCH_3$, PVAc)/$(-OC\underline{H}_3$, V-70)) = 5800 g/mol, $M_{n,NMR,\omega} = 86.09 \times ((-C\underline{H}-OCOC\underline{H}_3$, PVAc)/(AcO$-C\underline{H}-$ON−, ω-end group)) = 7200 g/mol (80% functionalization). ^1H NMR: 6.18 ppm (AcO$-C\underline{H}-$ON−); 3.6−3.3 ppm ($-C\underline{H}-O-C\underline{H}_2-$, at ω-chain end); 3.09 ppm ($-C\underline{H}-$, epoxy); 2.77 and 2.58 ppm ($-C\underline{H}_2$, epoxy), 1.6−1.0 (partially hidden $-C\underline{H}_2-$ and $C\underline{H}_3$ of the nitroxyl group at ω-chain end).

Results and Discussion

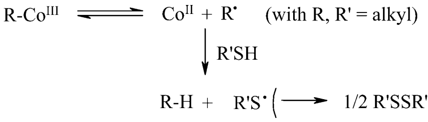
A. 1-Propanethiol as Scavenger. It was previously reported that the radical polymerization is under control (linear dependence of molar mass on monomer conversion, low polydispersity) when initiated by 2,2′-azobis-

Table 1. Induction Coupled Plasma (ICP) Measurement of the Cobalt Content of PVAc before and after Treatment with 1-Propanethiol

	PVAc[a] aspect	PVAc in solution (mg/mL)	cobalt in solution (μg/mL)	cobalt content in PVAc (ppm)	$M_{n,theor}$ (g/mol)
blank		0	0.0033		
before treatment	green	2.32	15.58	6715.5	8800[b]
after treatment	colorless	2.55	≤0.0033	≤1.3	

[a] $M_{n,SEC}$ = 8000 g/mol. [b] Theoretical molar mass ($M_{n,theor}$) of PVAc−Co has been calculated from the weight ratio of PVAc over Co ($M_{n,theor}$ (g/mol) = (M_{PVAc} (g/mL) × 58.93 (g/mol))/M_{Co} (g/mL)).

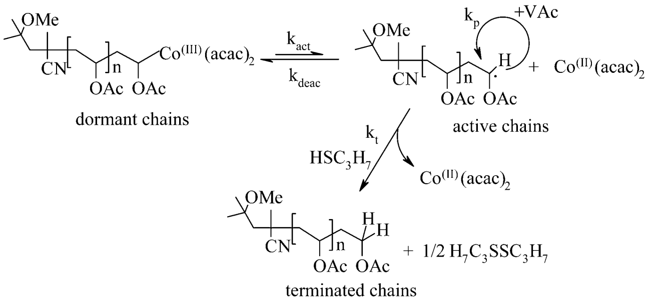
Scheme 3



(4-methoxy-2,4-dimethylvaleronitrile) (V-70) in the presence of Co(acac)$_2$ at 30 °C (Scheme 1).[9] However, the final polymer was collected with a green color, typical of alkyl−cobalt(III) complex, even after precipitation in heptane and water and after elution through alumina oxide and silica gel. The coloration persistency against all these posttreatments is evidence that the cobalt complex is chemically bonded to the polymer chains. Nevertheless, it is essential to eliminate this complex because of the toxicity of cobalt complexes.

In the early 1970s, the chemistry of alkyl−cobalt complexes was actively investigated.[15] The thermal homolytic cleavage of the Co−C bond in the presence of an alkanethiol (R′SH) in methanol resulted in the protonation of the released carbon centered radical, as shown in Scheme 3.[13,16] This potential method of releasing the cobalt derivative from the polymer was tested on a green PVAc end-capped by the Co(acac)$_2$ complex ($M_{n,SEC}$ = 8000 g/mol, M_w/M_n = 1.2), prepared by polymerization of vinyl acetate initiated by V-70 at 30 °C in the presence of Co(acac)$_2$. 1-Propanethiol was added to a green methanol solution of PVAc−Co, followed by filtration through celite and precipitation of polymer from the filtrate in heptane. An almost colorless polymer was recovered, consistent with cleavage of the covalent cobalt−carbon bond. Moreover, SEC chromatograms of PVAc before and after treatment with 1-propanethiol (Figure 1) show that the PVAc radicals, released by homolysis at 30 °C, reacted preferentially with 1-propanethiol rather than by recombination. Indeed, no chain coupling was observed after the posttreatment with the thiol.

Scheme 4



The Co content of PVAc was measured by the induction coupled plasma (ICP) atomic emission spectroscopy before and after treatment with alkanethiol as reported in Table 1. The efficiency of an alkanethiol to eliminate the Co complex of the PVAc chains is highlighted by an ICP signal, which is at the lower limit of detection and leads to the conclusion that there is less than 1.3 ppm of residual Co. Moreover, the experimental molar mass of the untreated poly(vinyl acetate) ($M_{n,SEC}$ = 8000 g/mol) is quite consistent with the molar mass calculated from cobalt content before treatment.

The same reaction was then realized in situ by adding and excess of degassed 1-propanethiol during the course of the vinyl acetate bulk polymerization in the presence of Co(acac)$_2$ (monomer conversion = 14%), the trapping of the growing poly(vinyl acetate) radicals being the expected result (Scheme 4). After stirring for 1 h at 30 °C, the polymerization medium turned from green to dark black. A black insoluble matter was eliminated by filtration, whereas the polymer (re)precipited from the filtrate is quasi-colorless ($M_{n,SEC}$ = 8900 g/mol, M_w/M_n = 1.15). Loss of green coloration is evidence that PVAc free of cobalt complex, which was confirmed by ^{1}H NMR analysis that shows a proton at the PVAc ω-chain end rather than Co(acac)$_2$ (Figure 2). In addition to major resonances of the main-chain repeat units ((**a**) 4.8 ppm,

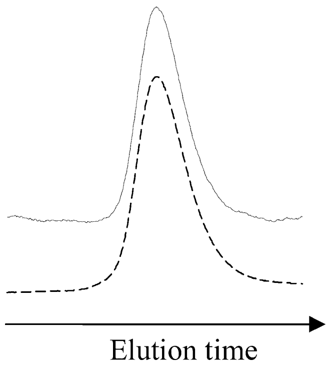


Figure 1. Size exclusion chromatograms of poly(vinyl acetate) (0.2 × 10^{-3} mol, $M_{n,SEC}$ = 8000 g/mol) before (dotted line) and after addition of 1-propanethiol (4 × 10^{-3} mol) (full line).

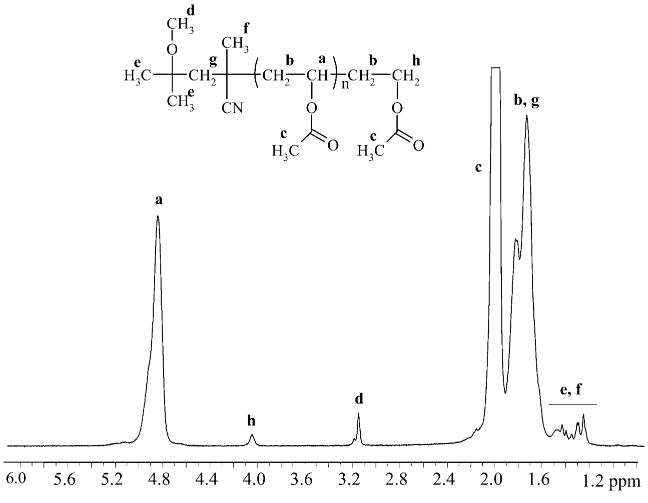
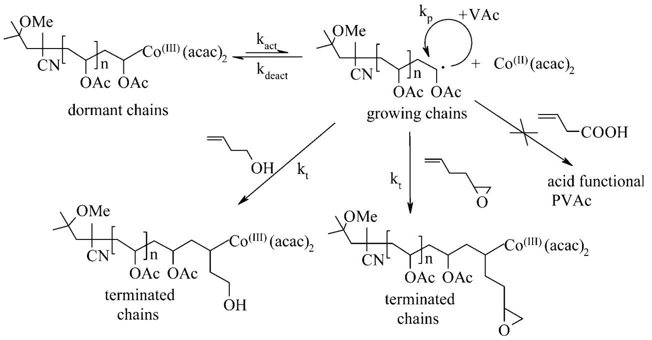


Figure 2. ^{1}H NMR spectrum of poly(vinyl acetate) (M_n = 7200 g/mol) after addition of 1-propanethiol (3.25 × 10^{-4} mol of V-70, 1.0 × 10^{-4} mol of Co(acac)$_2$, and 54 × 10^{-3} mol of VAc at 30 °C, followed by addition of 2 × 10^{-3} mol of propanethiol).

Scheme 5



1H, −C$\underline{H}$−OCOCH$_3$; (**b**) 2.0 ppm, 3H, −OCO−C$\underline{H}_3$; (**c**) 1.85−1.60 ppm, 2H, −C$\underline{H}_2$−CH−OCOCH$_3$), signals characteristic of the initiator fragment are observed. The methoxy protons −OC$\underline{H}_3$ (**d**) and the methyl protons (**e**, **f**) of V-70 are noted respectively at 3.14 and 1.5−1.2 ppm, whereas the signal of the methylene protons (**g**) is more likely hidden by the signal for the methylene protons of the chain (**c**). The molar mass of the chains can be determined from the intensity ratio of the resonance (**d**) (three protons) for the initiator fragment and resonance (**a**) (one proton) for the main chain [$M_{n,NMR(\alpha-end)} = 86.09 \times (3 \times (a/d)) = 7200$ g/mol]. The low intensity signal (**h**), at 4.04 ppm (h/d = 1.8/3), has been assigned to methylene protons of the ω-end group, consistent with the substitution of a proton for the cobalt complex ($M_{n,NMR(\omega-end)} = 86.09 \times (2 \times (a/h))$ = 8000 g/mol, 90% functionalization).

Addition of a radical scavenger, such as an alkanethiol, to growing PVAc chains is not only an efficient technique for eliminating metal contaminants, but it also paves the way to the end-functionalization of the chains as discussed hereafter.

B. Nonpolymerizable Olefins as Scavengers. One technique of chain end-capping in controlled radical polymerization consists of adding nonpolymerizable olefins, such as 1,2-epoxy-5-hexene and allyl alcohol, to the polymerization medium. In the case of ATRP of acrylates, the growing chains were deactivated by these nonpolymerizable olefins. Epoxy and hydroxyl functions were accordingly attached as ω-end groups together with a halogen atom.[8] This strategy has been extended to the cobalt-mediated radical polymerization of VAc. Three nonpolymerizable olefins, i.e., 3-butene-1-ol, 1,2-epoxy-5-hexene, and 3-butenoic acid, have been tested in order to end-functionalize PVAc according to Scheme 5. In the case of success, the chains will be irreversibly capped by Co(acac)$_2$ and could not be reactivated for subsequent monomer addition according to the cobalt-mediated vinylation, largely reported by Giese,[17] Pattenden,[18] and Branchaud.[19]

Addition of 3-Butene-1-ol. An excess of 3-butene-1-ol was added to growing poly(vinyl acetate) chains, initiated by V-70 at 30 °C in the presence of Co(acac)$_2$, at low monomer conversion. The vinyl acetate polymerization was accordingly inhibited, the monomer conversion remaining constant at 17% in this example. Figure 3 shows a sharp deviation of ln([M]$_0$/[M]) vs time from the ideal linear dependence evolution. A polymer with low molar mass and low polydispersity was recovered by repeated precipitation in a ice/water bath ($M_{n,SEC}$ = 10 000 g/mol, M_w/M_n = 1.30). ^{1}H NMR confirmed that 3-butene-1-ol was incorporated as an end group. Indeed, in addition to the signals characteristic of the PVAc protons (**a**, **b**, **c**), signals for the initiator (V-70) fragment at α-chain end (**d**, **e**, **f**, **g**) and a signal (**h**) for the C$\underline{H}_2$−OH protons at ω-chain end (3.62 ppm) were observed (Figure 4) [$M_{n,NMR(\alpha-end)}$ = 10 500 g/mol, $M_{n,NMR(\omega-end)}$ = 8300 g/mol]. Within the limits of the NMR accuracy (very low intensity of the NMR peaks characteristic of the ω-end group), the functionalization is close to completion. No signal corresponding to an unsaturated chain end was detected, which confirms the absence of dehydrocobaltation reaction.

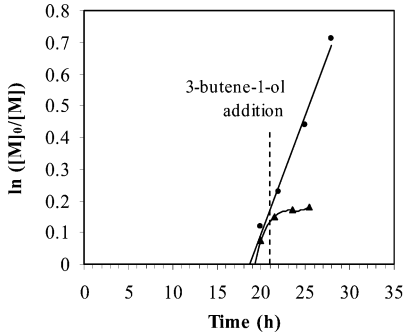


Figure 3. Plot of ln([M]$_0$/[M]) vs time for the vinyl acetate (54×10^{-3} mol) polymerization initiated by V-70 (3.25×10^{-4} mol) at 30 °C in the presence of cobalt(II) acetylacetonate (1.0×10^{-4} mol), with (▲) and without (●) addition of 3-butene-1-ol (4.6×10^{-3} mol).

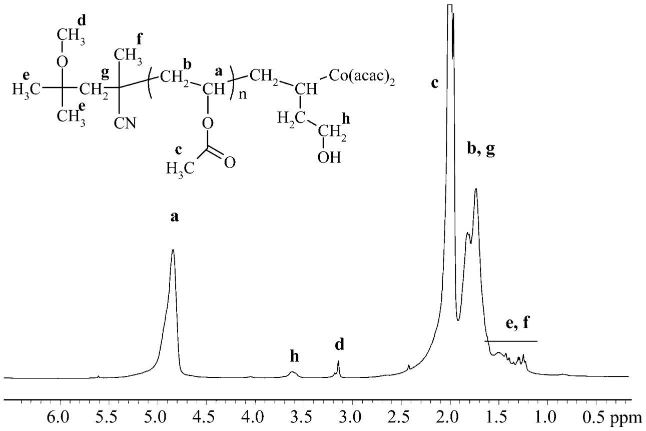


Figure 4. ^{1}H NMR spectrum of poly(vinyl acetate) added with 3-butene-1-ol (3.25×10^{-4} mol of V-70, 1.0×10^{-4} mol of Co(acac)$_2$, and 54×10^{-3} mol of VAc at 30 °C, followed by addition of 4.6×10^{-3} mol of 3-butene-1-ol).

Addition of 1,2-Epoxy-5-hexene. Similarly, 1,2-epoxy-5-hexene has been added to the growing chains. Once again, the polymer chains rapidly lost their capacity to grow further, the monomer conversion leveling off at 42% in this specific example. After purification by (re)-precipitation in heptane, a polymer with $M_{n,SEC}$ = 14 000 g/mol and M_w/M_n = 1.20 was collected and analyzed by ^{1}H NMR spectroscopy. Protons of PVAc (**a**, **b**, **c**) and protons of the initiator V-70 at the α-chain end (**d**, **e**, **f**, **g**) was observed together with C$\underline{H}$ (**h**) and C$\underline{H}_2$ (**i, j**) protons of the epoxy group at 2.85, 2.71, and 2.44 ppm, respectively (Figure 5). The end-capping efficiency has been confirmed by the good agreement between molar masses determined considering the methylene protons at the ω-chain end (9800 g/mol) and the methoxy protons at the α-chain end (10 500 g/mol). Functionalization is also close to 100% (cf. supra).

Addition of 3-Butenoic Acid. 3-Butenoic acid was used as a nonpolymerizable substituted olefin in order to end-

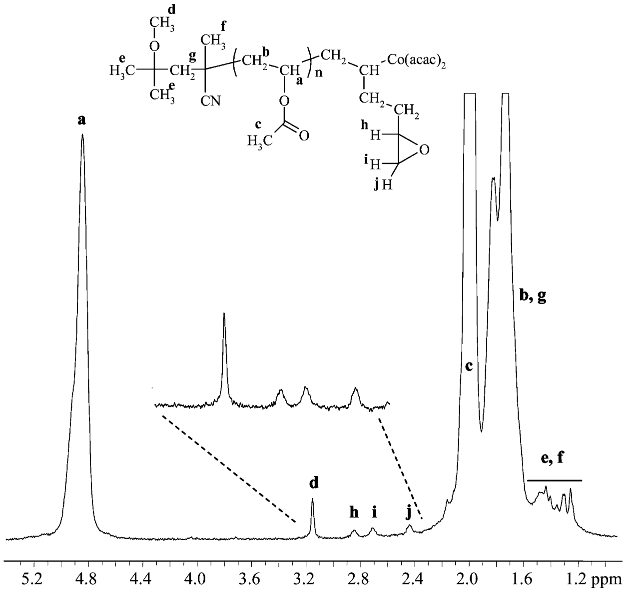


Figure 5. ^{1}H NMR spectrum of poly(vinyl acetate) added with 1,2-epoxy-5-hexene (3.25×10^{-4} mol of V-70, 1.0×10^{-4} mol of Co(acac)$_2$, and 32×10^{-3} mol of VAc at 30 °C, followed by addition of 4×10^{-3} mol of 1,2-epoxy-5-hexene).

Table 2. Addition of 3-Butenoic Acid to the Cobalt-Mediated Radical Polymerization of VAc

time (h)	conv (%)	$M_{n,SEC}$ (g/mol)	$M_{n,theor}$ (g/mol)	M_w/M_n
19[a]	5	3800	2300	1.20
21[b]	15	8400	7000	1.72

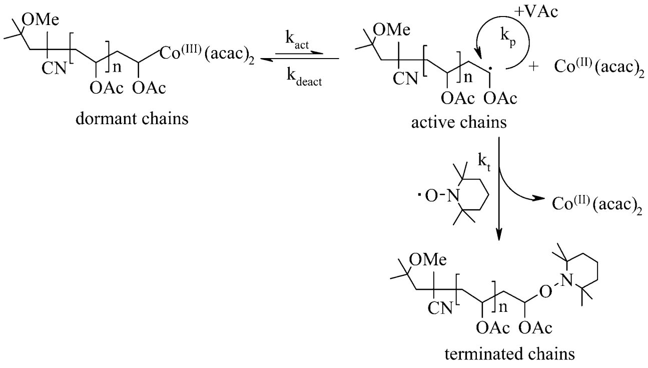
[a] Addition of the acid. [b] 2 h after the addition of 3-butenoic acid.

cap PVAc with a carboxylic acid group. However, addition of this olefin to the polymerization medium does not prevent the chains from growing further, as assessed by the vinyl acetate conversion that increased from 5% to 15%, 2 h after 3-butenoic acid was added. Nevertheless, the control on the vinyl acetate polymerization was perturbed, as shown by the broadening of the molecular weight distribution from 1.20 to 1.72 (Table 2). From the ^{1}H NMR analysis of the end groups of the chains, there is no evidence that the olefin has been added as ω-end group, in contrast to the initiator fragment that can be detected. A too low reactivity might be the reason for lack of addition, whereas interference of the carboxylic acid with the cobalt complex could explain a loss in the polymerization control.

In conclusion, the addition of nonpolymerizable olefins, such as 3-butene-1-ol and 1,2-epoxy-5-hexene, to cobalt-mediated polymerization of vinyl acetate leads to well-defined end-functional poly(vinyl acetate). If not properly chosen, the reactive substituent of the olefin may prevent it from adding and possibly interfere with the polymerization mechanism, as observed in the case of carboxylic acid. Whenever the end-capping is effective, the cobalt catalyst remains attached to the chains, although it could be eliminated by subsequent treatment with 1-propanethiol, if necessary.

C. Nitroxide Scavengers. *Addition of TEMPO.* Nitroxides, including TEMPO, are potential trapping agent of macroradicals. The cobalt-mediated radical polymerization of vinyl acetate has been tentatively quenched by TEMPO with the purpose to displace the cobalt complex from the chain end (Scheme 6). Addition of a degassed toluene solution of TEMPO (two equivalent with respect to Co(acac)$_2$) to the VAc polymerization medium, at low monomer conversion (26%), results in the chain growth termination and formation of a purple deposit characteristic of the Co(acac)$_2$ complex. This insoluble compound was eliminated by elution through alumina column. PVAc was twice precipitated in heptane, and a colorless polymer has been collected ($M_{n,SEC}$ = 16 500 g/mol, M_w/M_n = 1.15). The displacement of the cobalt complex at the chain ends by TEMPO reaction has been confirmed not only by the loss of the green color but also by ^{1}H NMR and ICP analysis.

Scheme 6



The ^{1}H NMR signals characteristic of the C$\underline{H}_2$ (**j**, from 1.5 to 1.2 ppm) and C$\underline{H}_3$ (**i**, from 1.2 to 1.0 ppm) protons of TEMPO are observed although in partial overlap with the signals for the protons of the initiator V-70 (**e**, **f**, **g** from 1.6 to 1.2 ppm) (Figure 6). Moreover, the proton at the junction between PVAc and TEMPO (Ac−O−C$\underline{H}$−ON−, **h**, 6.20 ppm) is clearly detected. However, the intensity ratio of the methoxy protons **d** of V-70 and the proton **h** does fit not exactly prediction based on the chain end-capping by TEMPO (65% functionalization within the limits of the experimental error). Indeed, the intensity of the proton **h** is too low to estimate the molar mass of the polymer with precision.

The completeness of the cobalt complex extraction from the poly(vinyl acetate) has been estimated by the ICP analysis of Co before and after addition of TEMPO to PVAc. Data are listed in Table 3. There is a good agreement between the apparent molar mass of the

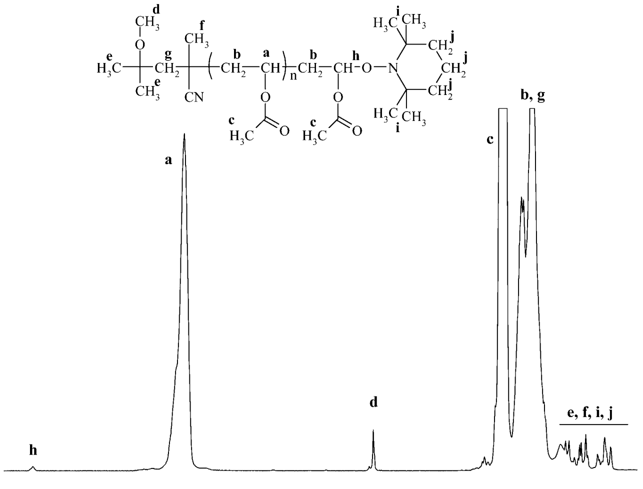


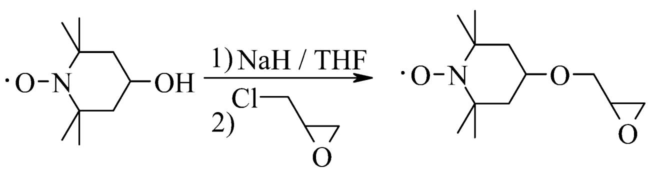
Figure 6. ^{1}H NMR spectrum of poly(vinyl acetate) added with 2,2,6,6-tetramethylpiperidine 1-oxy (TEMPO) (6.5×10^{-4} mol of V-70, 1.0×10^{-4} mol of Co(acac)$_2$, and 54×10^{-3} mol of VAc at 30 °C, followed by addition of 2.0×10^{-4} mol of TEMPO).

Table 3. Induction Coupled Plasma (ICP) Measurement of the Cobalt Content of PVAc before and after Addition of TEMPO

	PVAc[a] aspect	PVAc in solution (mg/mL)	cobalt in solution (μg/mL)	cobalt content in PVAc (ppm)	$M_{n,theor}$ (g/mol)
blank		0	0.0033		
PVAc−Co	green	3.1	9.995	3255.7	18300[b]
PVAc−TEMPO	colorless	3.0	0.0033	<1.1	

[a] $M_{n,SEC}$ = 16 500 g/mol. [b] Theoretical molar mass ($M_{n,theor}$) of PVAc−Co has been calculated from the weight ratio of PVAc over Co ($M_{n,theor}$ (g/mol) = (M_{PVAc} (g/mL) × 58.93 (g/mol))/M_{Co} (g/mL)).

Scheme 7



untreated poly(vinyl acetate) measured by SEC (16 500 g/mol) and the molar mass calculated on the basis of the cobalt content measured by ICP (18 300 g/mol). The efficacy of the substitution by TEMPO has to be found in a residual content of cobalt as low as 1.1 ppm after treatment by TEMPO.

The thermal stability of the covalent bonding of TEMPO to PVAc explains why the radical polymerization of VAc cannot be controlled by nitroxide-mediated polymerization.[20] Advantage of this characteristic feature can be taken for the end-functionalization of cobalt free PVAc.

Addition of 4-(Glycidyloxy)-2,2,6,6-tetramethylpiperidine 1-oxyl. A functional group bearing nitroxide should be an effective end-capping agent. To confirm this expectation, 4-(glycidyloxy)-2,2,6,6-tetramethylpiperidine 1-oxyl was synthesized according to a procedure reported by Endo et al.,[21] i.e., by reaction of 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl with epichlorohydrin (Scheme 7). This epoxy-containing nitroxyl radical was added to the vinyl acetate polymerization medium (actual monomer conversion of 10%), resulting in the termination chains (unchanged VAc conversion). The solution collected after elution through an alumina column was colorless, and PVAc precipitated in heptane was analyzed by SEC ($M_{n,SEC}$ = 5700 g/mol, M_w/M_n = 1.16) and ^{1}H NMR (Figure 7). In addition to the signals for the protons of the PVAc main chain (**a**, **b**, **c**) and for fragment of V-70 (**d**, **e**, **f**, **g**), signal corresponding to the piperidyl group (**i**, **j**) and signals characteristic of the epoxy group (**k**, **l**, **m**) are observed as well as the $-C\underline{H}-O-C\underline{H}_2-$ protons (**n**, **o**) and the proton (**h**) at the junction between PVAc and the nitroxyl group ($AcO-C\underline{H}-ON-$) (Figure 7). End-functionalization efficiency has been calculated by NMR from the ratio of the molar masses determined on the basis of the protons **h** and **d**, respectively (80% efficiency). In this case, a partial opening of the epoxy end groups might contribute to decrease the functionalization efficiency. Therefore, termination of the VAc polymerization by a functional nitroxide turns out to be an effective strategy for the end-capping of cobalt free chains.

Conclusions

This paper has reported on methods for the end-functionalization of poly(vinyl acetate) prepared by cobalt-mediated radical polymerization. Addition of an alkanethiol to the polymerization medium terminates the chains by a proton and releases the cobalt complex as a solid compound which is then easily removed by filtration. Nonpolymerizable olefins substituted by an alcohol or an epoxy group are also terminating agents which are incorporated to the chains as an end group. The cobalt complex remains however covalently bonded to the PVAc chains. More interestingly, nitroxides, e.g. TEMPO, also stop the growth of the chains as result of irreversible substitution of the Co(acac)$_2$. On this basis, the addition of a functional group containing nitroxide to the growing PVAc chains is an efficient strategy to prepare well-defined, end-functional, and cobalt free PVAc by a one-pot technique.

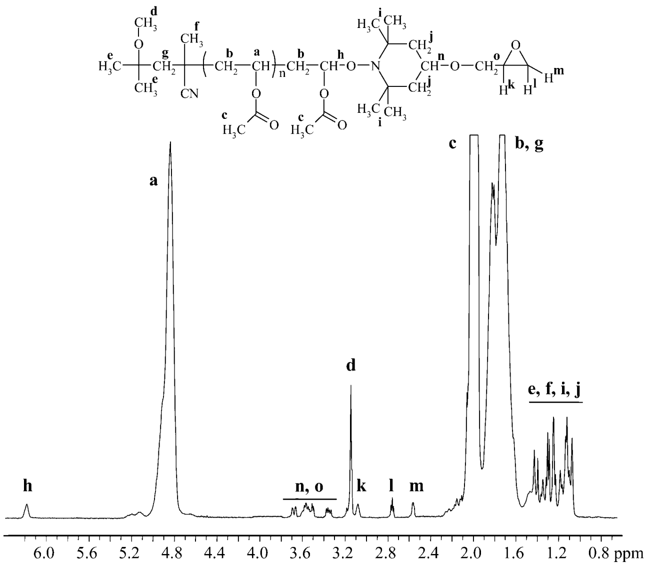


Figure 7. ^{1}H NMR spectrum of poly(vinyl acetate) added with 4-(glycidyloxy)-2,2,6,6-tetramethylpiperidine 1-oxyl (6.5 × 10^{-4} mol of V-70, 1.0 × 10^{-4} mol of Co(acac)$_2$, and 54 × 10^{-3} mol of VAc at 30 °C, followed by addition of 3.0 × 10^{-4} mol of 4-(glycidyloxy)-2,2,6,6-tetramethylpoperidine 1-oxyl).

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