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Cobalt-Mediated Radical (Co)polymerization of Vinyl Chloride and Vinyl Acetate

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The Cobalt Mediated Radical Polymerization (CMRP) of vinyl chloride (VC) in the presence of bis(acetylacetonato)cobalt(II) (Co(acac)₂) as controlling agent is presented for the first time. Using an alkyl-Co(III) compound (R₀-(CH₂-CHOAc)_{<4}-Co(acac)₂; R₀ = (H₃C)₂(OCH₃)C-CH₂-C(CH₃)(CN)-) as an initiator, the bulk polymerization under non-isotherm conditions is controlled. ¹H NMR spectra of the resulting PVC show that the CMRP process does not significantly affect the level of defects compared to a PVC prepared by a conventional free radical polymerization at the same temperature. Using the same alkyl-cobalt(III) compound, the copolymerization of VC and VAc is controlled at 40°C provided that enough VAc (about 40 mol%) is present in the polymerization medium to moderate the VC polymerization. In line with reactivity ratios, VC is preferentially incorporated in the polymer at the early stages of the polymerization, leading to copolymers with a high VC content at moderate conversions. This is the first report of a CMRP of VC and of the synthesis of well-defined statistical PVC-co-PVAc copolymers by this technique.

Introduction

Controlling the radical polymerization of vinyl chloride (VC) has long been a challenge because of the high reactivity of the poly(vinyl chloride) (PVC) propagating radical¹⁻³. Besides being a non-activated monomer, vinyl chloride is also characterized by one of the largest transfer constants to monomer (C_M = 22 × 10⁻⁴ at 50°C)^{4,5} among all vinyl monomers (for instance, C_M = 0.35-0.78 × 10⁻⁴, 0.25-4.5 × 10⁻⁴ and 0.2-0.9 × 10⁻⁴ for styrene, vinyl acetate and ethyl acrylate, respectively, at 50°C),⁴ making difficult to control its radical polymerization. Some advances in the development of controlled radical polymerization (CRP) processes have allowed overcoming this problem. Reversible Iodine Transfer Polymerization (RITP),⁶ Nitroxide Mediated Polymerization (NMP)⁷⁻⁸ and *in-situ* NMP⁹⁻¹⁰ demonstrated some moderate activity for VC. More recently, Percec *et al* developed the single-electron transfer – degenerative chain transfer living radical polymerization (SET-DTLRP) of vinyl chloride based on activation and deactivation of the propagating chains by copper species issued from disproportionation.^{3, 11-15} It provides the best level of control ever achieved for the VC polymerization and gives access to novel PVC based block copolymers.¹⁶⁻²¹ Another copper-assisted system able to mediate the control of VC was developed by the same group, *i.e.* the Single-Electron Transfer-

Living Radical Polymerization (SET-LRP), where the degenerative transfer pathway was suppressed.²²⁻²⁵ Reversible Addition Fragmentation chain Transfer polymerization (RAFT) also recently emerged as an efficient technique for controlling the radical polymerization of vinyl chloride.²⁶

Among the controlled radical polymerization (CRP) techniques presently developed,²⁷⁻³¹ Cobalt-Mediated Radical Polymerization (CMRP)³²⁻³⁵ shows good efficiency for various vinyl monomers.³⁵⁻⁴⁰ This system, which belongs to the Organometallic Mediated Radical Polymerization (OMRP) class,⁴¹⁻⁴⁵ involves the formation of a reversible carbon-cobalt bond at the polymer chain-end. CMRP involving bis(acetylacetonato)cobalt (Co(acac)₂) is particularly efficient and has been proven to be the best CRP technique for vinyl acetate (VAc), a non-conjugated vinyl monomer. Similarities between VAc and VC, *i.e.* high reactivity of their propagating radicals and propensity to transfer reactions to monomer and polymer, were strong incentives to test Co(acac)₂ as controlling agent for the CMRP of VC.

In this report, first attempts to mediate the VC homopolymerization and copolymerization with vinyl acetate by CMRP are discussed as well as the impact of the cobalt complex on the level of structural defects of PVC. In case of success, the implementation of CMRP to VC would be of high interest for the production of new PVC based copolymers since this technique can be applied to both non-conjugated vinyl monomers (VAc, N-vinyl pyrrolidone,⁴⁶⁻⁴⁸ N-vinyl caprolactame⁴⁹) and conjugated ones (acrylonitrile,⁵⁰⁻⁵² acrylates⁵³⁻⁵⁴). Moreover, some parameters of the CMRP system can be modulated, such as addition of a neutral ligand, the modulation of the β-diketonate steric requirements,^{40,51,55-56} or an increase of the polymerization temperature,⁵⁷ *via* the fine-tuning of the C-Co bond strength at the polymer chain-end. The tuning of these parameters opens therefore the door to numerous possibilities to influence the CMRP of VC.

Experimental Part

Materials

Vinyl chloride (VC) (≥ 99.9 %, SolVin SA) was used without prerequisite purification. The polymerizations were carried out in 100 ml stainless steel reactors. VC was condensed under nitrogen pressure to be injected into the reactors. Vinyl acetate (VAc) (≥ 99 %, Aldrich) was dried over calcium hydride, degassed by several freeze-pump-thawing cycles before being distilled under reduced pressure and stored under argon at -20°C. Bis(acetylacetonato)cobalt (II) (99 %, Acros), 2,2'-azo-bis-(4-methoxy-2,4-dimethyl valeronitrile) (V-70, t_{1/2} = 10 hours at 30°C) (Wako), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) (98 %, Aldrich) were used as received. Dichloromethane (≥ 99.5 %, VWR, Prolabo) and ethyl acetate (99.8%, Fisher Scientific) were dried over molecular sieves and degassed by bubbling argon for 30 minutes.

Characterizations

The polymer relative molecular weights (M_n SEC) and mass distribution (M_w/M_n) were determined by size exclusion chromatography (SEC) in a dimethylformamide (DMF)/lithium bromide (LiBr; 0.025 M) solution (flow rate: 1 mL min⁻¹) at 55°C

using a Waters 600 liquid chromatograph equipped with a 2414 refractive index detector (RI) and four Styragel HR columns (HR1 (100-500), HR3 (500-30000), HR4 (5000-50000), HR5 (2000-4000000)). Calibration with poly(methyl methacrylate) standards was used to determine the relative molecular weights of poly(vinyl chloride). The absolute molecular weights for the PVC samples were also determined by SEC in DMF-LiBr equipped with a Wyatt multi-angle laser light scattering (MALLS) detector (120mW solid-state laser, $\lambda = 658$ nm, Dawn Heleos S/N 342-H). Data were processed with the Astra V software (Wyatt Technology). ^1H NMR spectra were recorded with a Bruker AM 400 Spectrometer (400 MHz) in deuterated tetrahydrofuran as a solvent. The cobalt concentration of the alkyl-Co(III) compound stock solution in dichloromethane was determined by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS). Atomic Emission Spectroscopy was carried out with a spectrometer (Elan DRC-e Perkin-Elmer SCIEX). Samples were prepared by dissolving 1 ml of the alkyl-Co(III) compound solution (in dichloromethane, previously evaporated under vacuum) in 1 ml of HNO_3 (65 %) at 60°C for 2 hours. These solutions were diluted with 250 ml of bidistilled water at room temperature prior to ICP-MS analysis. DSC curves were recorded with a TA DSC Q 100 thermal analyzer calibrated with indium.

Procedures for polymerizing VC.

PVC syntheses were carried out in 100 ml and 3 liter stainless steel reactors. In both facilities, VC was injected under nitrogen pressure into the reactors *via* stainless steel pipes. The amount of VC injected into the reactor was regulated by weighing the VC cylinder during the VC addition. A vertical agitating axle performed the agitation, which was regulated at about 200 rpm. At the end of the polymerization, the reaction medium was cooled down to room temperature and the residual VC was degassed. When the degassing was over, the polymerization underwent a thermal treatment called “stripping”, which consisted in blowing nitrogen into the polymerization medium in order to remove VC that was not evacuated during degassing. At the end of this thermal treatment, the reactor was opened and the PVC product was recovered.

It is important to note that at the end of each polymerization, after the VC degassing and prior to the stripping, an excess of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (in solution in THF) was added to the reactor in order to irreversibly terminate the polymerization. The nitroxyl radicals irreversibly end-cap the polymer chains, releasing the cobalt complex.³⁸ Therefore, when the stripping is carried out at the polymerization temperature, the polymer chains should not undergo further polymerization or side reactions.

General procedure for the alkyl-cobalt(III) compound synthesis and purification

According to the literature,⁵⁴ 34 g of $\text{Co}(\text{acac})_2$ (1.32×10^{-1} mol) and 20 g of V-70 (6.5×10^{-2} mol) were added in a 1 L round-bottomed flask capped by a three-way stopcock and degassed by three vacuum-argon cycles. 100 ml of vinyl acetate (1.08 mol) were then added and the mixture was stirred and heated at 30°C for about 70 hours. The medium remained pink throughout the reaction, with no increase in viscosity. The unreacted vinyl acetate was evaporated under reduced pressure at room

temperature. The residual mixture was placed under argon and then diluted into dry and degassed dichloromethane, ready for purification by chromatographic separation under an inert atmosphere. The solution was transferred by cannula to a silica-gel column placed under argon and equipped with a three-way stopcock at the bottom and with dry and degassed CH_2Cl_2 as eluent. After the elimination of the V-70 residues (yellow colored) with CH_2Cl_2 , a green fraction was collected with $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ (75:25) as eluent. Finally, the pink fraction corresponding to the alkyl-Co(III) compound ($\text{R}_0-(\text{CH}_2-\text{CHOAc})_4-\text{Co}(\text{acac})_2$; R_0 = primary radical from the V-70 decomposition) was collected with EtOAc as eluent and was dried under vacuum. The alkyl-Co(III) compound was obtained as a pink sticky solid and was conserved under argon at -20°C after dilution with 40 ml of degassed dichloromethane. The cobalt concentration was measured by ICP ($[\text{Co}] = 1.56 \times 10^{-1}$ mol/L).

Typical procedure for the vinyl chloride bulk polymerization mediated by the alkyl-Co(III) compound

The alkyl-Co(III) solution in dichloromethane (2 ml, $\text{Co}(\text{acac})_2 = 3.13 \times 10^{-4}$ mol) were added to a 100 ml stainless steel reactor under a nitrogen flux. The reactor was closed and the dichloromethane evaporated under vacuum for 15 minutes. The reactor was degassed by five vacuum-nitrogen cycles. 60 g of VC (0.96 mol) were then injected in the reactor under nitrogen pressure. The mixture was stirred and heated at the desired temperature, and at the end of the polymerization, the reactor was degassed to eliminate the unreacted vinyl chloride. Then a TEMPO solution in THF (20 ml, $[\text{TEMPO}] = 4.7 \times 10^{-2}$ mol/L) was added to kill the reaction before stripping at 40°C for 2 h. The reactor was opened and the homopolymer was recovered. For the polymerizations carried out in the presence of a ligand, the latter was injected before degassing by five vacuum-nitrogen cycles.

General procedure for the bulk vinyl chloride/vinyl acetate statistical copolymerization initiated by V-70

V-70 (0.0856 g, 2.78×10^{-4} mol) was added in the reactor, and then 24 ml of vinyl acetate (2.6×10^{-1} mol) were added under a nitrogen flux. The reactor was degassed by five vacuum-nitrogen cycles and 8 g of vinyl chloride (1.3×10^{-1} mol) were then injected under nitrogen pressure. The mixture was stirred and heated to 40°C for 1.5 h. At the end of the polymerization, the reactor was degassed to eliminate the unreacted vinyl chloride. Then, a TEMPO solution in THF (20 ml, 4.17×10^{-2} mol/L) was added before stripping at 40°C for two hours. The reactor was opened and the copolymer PVC-*co*-PVAc (table 5, entry 4) was recovered.: M_n (MALLS) = 47500 g/mol; VC conversion = 19 %; VAc conversion = 6 %; VC composition in the copolymer = 60 %; VAc composition in the copolymer = 40 %.

General procedure for the bulk vinyl chloride/vinyl acetate statistical copolymerization in the presence of V-70 and $\text{Co}(\text{acac})_2$

V-70 (0.0856 g, 2.78×10^{-4} mol) and 0.0715 g of $\text{Co}(\text{acac})_2$ (2.78×10^{-4} mol) were added in the reactor, and then 24 ml of vinyl acetate (2.6×10^{-1} mol) were added under a nitrogen flux. The reactor was degassed by five vacuum-nitrogen cycles and 8 g of vinyl chloride (1.3×10^{-1} mol) were then injected under nitrogen

pressure. The mixture was stirred and heated to 40°C. At the end of the polymerization, the reactor was degassed to eliminate the unreacted vinyl chloride. A TEMPO solution in THF (20 ml, 4.17 x 10⁻² mol/L) was added prior to stripping at 40°C for 2 h. The reactor was opened and no copolymer was recovered (table 5, entries 7 and 8).

Conversions of VC and VAc during the statistical copolymerization were determined on the basis of the VC composition (measured by ¹H NMR), the initial VC and VAc masses, the VC and VAc molecular weights, and the final total mass of the obtained copolymer. Conversions were therefore determined by the resolution of a system of two equations with two unknowns, *i.e.* :

$$(1) \text{ VC composition} = ((m_{VC}/MM_{VC}) \times \text{VC conv}) / (((m_{VC}/MM_{VC}) \times \text{VC conv}) + ((m_{VAc}/MM_{VAc}) \times \text{VAc conv}))$$

$$(2) m_{\text{copolymer}} = (m_{VC} \times \text{VC conv}) + (m_{VAc} \times \text{VAc conv})$$

where VC composition = the VC composition in the copolymer; m_{VC} = the initial VC mass, MM_{VC} = VC molecular weight, m_{VAc} = the initial VAc mass, MM_{VAc} = VAc molecular weight, $m_{\text{copolymer}}$ = the final total mass of the obtained copolymer.

The theoretical VC composition in the copolymer shown in figures 4 and 6 were calculated on the basis of the integration of the differential Alfrey, Mayo and Lewis' equation:⁵⁸

$$F_{VC} = ((r_{VC} \times f_{VC}^2) + (f_{VC} \times f_{VAc})) / ((r_{VC} \times f_{VC}^2) + (2f_{VC} \times f_{VAc}) + (r_{VAc} \times f_{VAc}^2))$$

where F_{VC} = the mole fraction of vinyl chloride in the copolymer formed at a particular instant in time, r = the monomer reactivity ratio, f = the mole fraction of a monomer in the comonomer mixture.

General procedure for the bulk vinyl chloride/vinyl acetate statistical copolymerization initiated by the alkylcobalt(III) compound

The alkyl-Co(III) solution in dichloromethane (2 ml, 2.78 x 10⁻⁴ mol of alkyl-Co(III)) was added to a 100 ml stainless reactor under a nitrogen flux. The reactor was closed and the dichloromethane evaporated under vacuum for 15 minutes. Vinyl acetate (24 ml, 2.6 x 10⁻¹ mol) was then added under a nitrogen flux and the reactor was closed before degassing by five vacuum-nitrogen cycles. Vinyl chloride (8 g, 1.3 x 10⁻¹ mol) was injected in the reactor under nitrogen pressure. The mixture was then stirred and heated to 40°C. After 6 h of polymerization, the reactor was degassed to eliminate the unreacted vinyl chloride. A

TEMPO solution in THF (20 ml, 4.17 x 10⁻² mol/L) was added prior to stripping at 40°C for 2 h. The reactor was opened and the copolymer was recovered. The statistical copolymer PVC-co-PVAc was characterized by ¹H NMR (figure 11) and by SEC MALLS (table 5, entry 3): $M_{n,MALLS}$ = 56000 g/mol; VC conversion = 79 %, VAc conversion = 44 %, VC composition in the copolymer = 50 %; VAc composition in the copolymer = 50 %.

Results and Discussion

Bulk VC polymerization initiated by V-70 in the presence of Co(acac)₂.

When using a Co(acac)₂/V-70 molar ratio of 1/1 at 40°C, the monomer conversion evolved from 3 to 6 h of polymerization, with only a slight increase of molar masses (Table 1). However, there was no further conversion when the polymerization time was extended to 8 h. This indicates that the polymerization occurs within the first 6 hours and stops at about 19 % of VC conversion. The overlay of SEC chromatograms clearly evidences that the molecular weight does not increase significantly with the monomer conversion (Figure 1), in contrast to what is expected for a controlled process. Interestingly, when we compare this experiment with the reference experiment carried out under the same conditions but in the absence of Co(acac)₂ (Table 1, entry REF), it clearly appears that adding Co(acac)₂ to the VC polymerization negatively affects the monomer conversion and the molar masses of the resulting polymer. No control of the VC radical polymerization was observed under these conditions, in sharp contrast with the CMRP of VAc that gave access to poly(vinyl acetate) (PVAc) with well-defined molecular parameters (Figure 2a). Under the same experimental conditions, an induction period of about 16 h was observed for the VAc polymerization while some polymer (about 8% monomer conversion; Table 1, entry 1) was already collected after 3 h of VC polymerization. The induction period for the VC polymerization is therefore much shorter than for the VAc polymerization. This suggests that Co(acac)₂ traps the PVC radicals less efficiently than the PVAc radicals, suggesting that the C-Co bond at the polymer chain-end is weaker in PVC than in PVAc.

Table 1. Conditions and results for the VC polymerization initiated by V70 in the presence of Co(acac)₂ in bulk at 40°C

Entry	Polym time	VC conversion (a)	Mn th (g/mol) (b)	Mn SEC DMF-LiBr (g/mol) (c)	Mw/Mn SEC (e)	Mn MALLS (g/mol) (d)	f (e)
REF (f)	6h00	59 %	/	68 200	2.13	56 000	/
1	3h00	8 %	3200	16 500	2.32	16 900	0.19
2	6h00	19 %	7600	21 600	2.48	23 400	0.32
3	8h00	18 %	7200	20 100	2.24	20 500	0.35

Conditions: VC (500 g, 8 mol) polymerization in bulk at 40°C initiated by V-70 (4 g, 1.29 x 10⁻² mol) in the presence of Co(acac)₂ (3.2 g, 1.25 x 10⁻² mol); [Co(acac)₂]/[V70]/[VC] = 1/1/643.

(a) VC conversion calculated gravimetrically; (b) theoretical Mn calculated on the basis of VC conversion and the cobalt concentration using the following equation: $Mn_{th} = (\text{conversion}) \times (m(\text{VC})/n(\text{Co}(\text{acac})_2))$; (c) SEC DMF-LiBr, calibrated by PMMA; (d) Mn SEC with MALLS detection; (e) initiation efficiency factor $f = Mn_{th}/Mn_{exp}$; (f) VC free-radical polymerization in bulk at 40°C initiated by V-70; $[\text{VC}]/[\text{V-70}] = 643/1$.

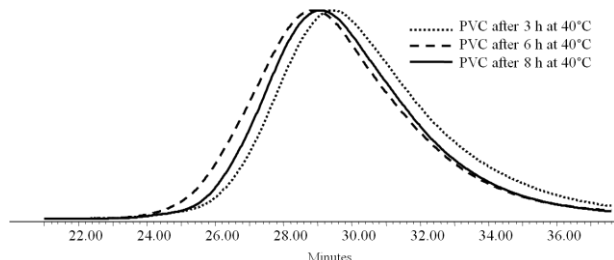


Figure 1. PVC chromatograms obtained for the VC polymerization initiated by V-70 in the presence of $\text{Co}(\text{acac})_2$ in bulk at 40°C $[\text{Co}(\text{acac})_2]/[\text{V70}]/[\text{VC}] = 1/1/643$.

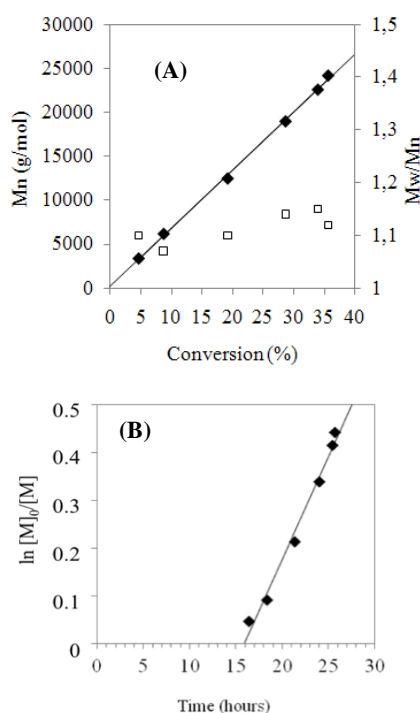
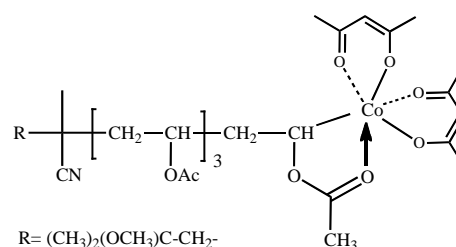


Figure 2. Vinyl acetate CMRP initiated by V-70 in the presence of $\text{Co}(\text{acac})_2$. Conditions: bulk, 40°C with $[\text{Co}(\text{acac})_2]/[\text{V70}]/[\text{VAc}] = 1/1/643$. (a) (◆) Molar mass versus VAc conversion and (□) Mass distribution versus conversion; (b) Time dependence of $\ln([M]_0/[M])$.

VC homopolymerization initiated by alkyl-cobalt(III) in bulk at 40°C. A preformed alkyl-Co(III) adduct ($\text{R}_0-(\text{CH}_2-\text{CHOAc})_4-\text{Co}(\text{acac})_2$; R_0 = primary radical from the V-70 decomposition = $(\text{H}_3\text{C})_2(\text{OCH}_3)\text{C}-\text{CH}_2-\text{C}(\text{CH}_3)(\text{CN})-$; Scheme 1)⁵⁵ that mimics a PVAc-Co(acac)₂ dormant chain demonstrated the best efficiency to initiate and control the polymerization of VAc upon dissociation. Indeed, it was shown that this alkyl-cobalt(III) adduct suppressed the induction period while improving the control on the VAc radical polymerization. More importantly, by suppressing this induction period, it also improved the level of control over the polymerization of conjugated monomers such as acrylonitrile⁵⁰⁻⁵² and *n*-butyl acrylate⁵³ compared to the polymerizations carried out with the V-70/ $\text{Co}(\text{acac})_2$ binary system.



Scheme 1: Structure of the alkyl-Co(III) compound ($\text{R}_0-(\text{CH}_2-\text{CHOAc})_4-\text{Co}(\text{acac})_2$; R_0 = primary radical from the V-70 decomposition) used for the CMRP of vinyl acetate, acrylonitrile and *n*-butyl acrylate.

Because this alkyl-Co(III) adduct proved efficiency for monomers that form a weak C-Co bond at the polymer chain end, it was therefore tested for the polymerization of VC. Different VC/alkyl-cobalt(III) molar ratios were investigated in order to emphasize the possibility for the cobalt to affect the poly(vinyl chloride) (PVC) molar mass. When the vinyl chloride homopolymerization was initiated at 40°C by the alkyl-Co(III) compound, the VC conversion was very low after 1.5 h of polymerization and did not further evolve (*i.e.* after 3 and 6 h) for all VC/alkyl-cobalt(III) molar ratios investigated (Table 2). These observations suggest that the polymerization stops rapidly after the initiation, as observed with the V-70/ $\text{Co}(\text{acac})_2$ system.

Table 2. Bulk VC polymerizations initiated by $R_0-(CH_2-CHOAc)_4-Co(acac)_2$ at 40°C.

Entry	Polym. time	[VC]/[alkyl-Co(III)]	VC conv ^(a)	Mn th (g/mol) ^(b)	Mn SEC DMF-LiBr (g/mol) ^(c)	Mw/Mn SEC DMF-LiBr ^(c)	Mn MALLS (g/mol) ^(d)	f ^(e)
REF ^(f)	6h00	/	59 %	/	68 200	2.13	56 000	/
1	1h30	6500:1	4 %	16 300	32 400	2.56	34 600	0.47
2	3h00	6500:1	3 %	12 200	22 500	2.50	23 500	0.52
3	6h00	6500:1	4 %	16 300	22 800	2.59	23 800	0.68
4	1h30	3250:1	5 %	10 200	18 500	1.90	17 300	0.59
5	3h00	3250:1	4 %	8100	15 000	1.98	15 600	0.52
6	6h00	3250:1	6 %	12 200	20 400	2.48	19 400	0.63
7	1h30	1625:1	8 %	8100	15 000	1.80	13 500	0.60
8	3h00	1625:1	7 %	7100	13 500	1.93	13 500	0.53
9	6h00	1625:1	7 %	7100	13 400	1.92	13 100	0.54

(a) Calculated gravimetrically after precipitation of the sample in cold heptane ; (b) Calculated on the basis of VC conversion and the cobalt concentration using the following equation: $Mn_{th} = (\text{conversion}) \times (m(VC)/n(\text{alkyl-Co(III)}))$; (c) obtained by SEC, in DMF-LiBr, with a PMMA calibration; (d) SEC analysis with MALLS detection, in DMF-LiBr where $dn/dc = 0.0793$; (e) initiator efficiency factor $f = Mn_{th}/Mn_{exp}$; (f) VC free-radical polymerization in bulk at 40°C initiated by V-70; $[VC]/[V-70] = 643/1$.

In line with these observations, the SEC chromatograms of PVC are identical after 1.5, 3 and 6 h of polymerization (Figure 3). It also appears that slightly higher VC conversions are obtained when the VC/initiator molar ratio is decreased, *e.g.* they increase from about 3-4% when $[VC]/[alkyl-Co(III)] = 6500$ to about 7-8% when $[VC]/[alkyl-Co(III)] = 1625$. Importantly, although the monomer conversion is very low, the PVC molecular weight seems to depend on the monomer/initiator molar ratio, as would be expected for a controlled process. The initiator efficiency ($f = Mn_{th}/Mn_{MALLS}$) is in the same range for all VC/alkyl-Co(III) molar ratios, *i.e.* around 0.47-0.68, meaning that only 47 % to 68 % of the alkyl-cobalt(III) initiator contributes to the initiation of PVC chains.

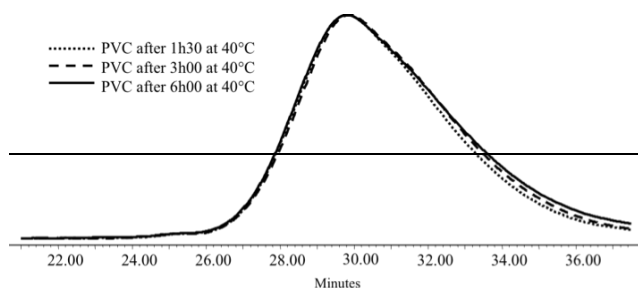


Figure 3. SEC chromatograms obtained for the bulk VC polymerization initiated by alkyl-cobalt(III) at 40°C. Conditions: $[VC]/[initiator] = 1625/1$; Table 2, entries 7–9.

Note that in free radical polymerization, the PVC molecular weight depends only on the polymerization temperature.⁵⁹⁻⁶⁰ However, at the same temperature, *i.e.* 40°C, the molar mass of PVC produced in the presence of cobalt is lower than that obtained without $Co(acac)_2$ (REF, table 2), indicating that the cobalt complex has an influence on the VC polymerization. Moreover, the fact that all VC polymerizations stop at low conversion raises questions. Several hypotheses can be made to explain such observations.

The first hypothesis invokes the occurrence of irreversible H atom transfer reactions. Indeed, it is known that some cobalt(II) complexes, *e.g.* cobaloximes and cobalt porphyrins, are effective chain transfer catalysts responsible for the moderation of the molar mass of polymers prepared by radical polymerization,⁶¹⁻⁶³ particularly poly(alkyl methacrylate)s. According to the commonly accepted mechanism, a cobalt(II) complex can undergo hydrogen atom abstraction with release of a polymer chain with an unsaturated end-group and formation of a cobalt hydride. The catalytic cycle is closed by generation of a primary radical by hydrogen transfer from the cobalt hydride complex to the methacrylate monomer unit, followed by propagation. A similar behavior might therefore be expected for the VC polymerization initiated by the alkyl-Co(III) provided that the cobalt complex at the PVC chain-end is prone to dehydrocobaltation. The VC polymerization might stop at low conversion if the generated cobalt hydride complex

is not able to transfer to VC monomer to reinitiate the polymerization. The formation of this cobalt hydride will therefore result in a termination reaction and is also in line with a decrease of the PVC molecular weight when higher amounts of alkyl-Co(III) are used. The possibility of $\text{Co}(\text{acac})_2$ to favor this β -H elimination was investigated by calculating the energetics of the β -H elimination process from the PVC-Co(acac)₂ dormant chain (corresponding to the process indicated in Figure 3). This was accomplished computationally by modeling the polymer chain (P in Figure 4) by an H atom. Although modelling the polymer chain beyond the metal-bonded monomer unit by a simple H atom may not be the most appropriate choice, this replacement greatly simplifies the computational task and is not expected to introduce a great systematic error. Indeed, the effect on the Co-C bond strength should be negligible since the residue is located on the β -C atom and does not transmit any mesomeric effects to the generated radical. On the other hand, the residue could have an effect on the stabilization of the olefin product, but this should be small and identical for the two types of β -H elimination processes (from the HH and HT chain ends).

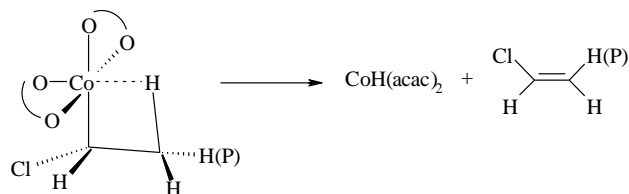


Figure 3. β -H elimination from PVC-Co(acac)₂ dormant chain (head-to-tail addition).

It can be seen from Figure 4 that this dehydrocobaltation is rather difficult from the PVC dormant chain. A costly geometric reorganization of the cobalt complex (~ 13 kcal/mol, Figure 4, blue pathway) has first to occur in order to allow the β -H elimination process to take place from the higher-energy equatorial isomer, because the β -H elimination mechanism requires a vacant coordination site cis to the alkyl ligand. The next intermediate is a 5-coordinate hydride complex at very high energy, with the hydride in the unfavorable equatorial position. Even if this high-energy intermediate may be avoided, depending on the mechanistic details of the β -H elimination process (detailed calculation of transition states were not carried out), the total energy cost for dehydrocobaltation is around 22 kcal/mol, which makes the process difficult. Furthermore, the reverse process is thermodynamically favorable, therefore the H-atom transfer, if occurring at all, would be predicted to serve as a chain transfer process and not as a termination event.

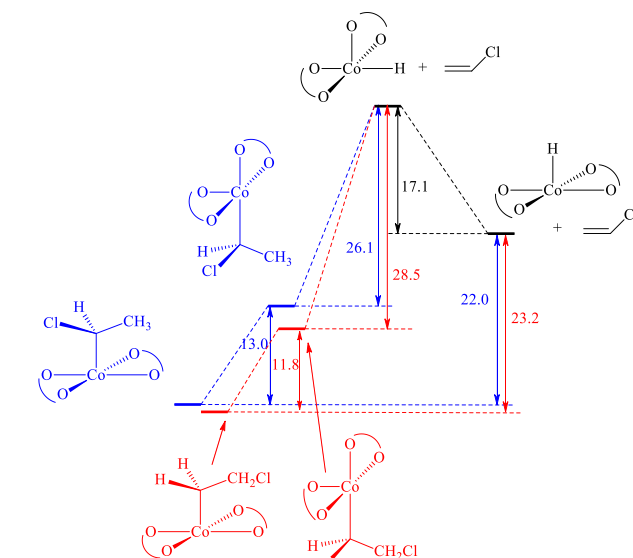


Figure 4. Energetics (in kcal/mol) of the β -H elimination process from a model PVC-Co(acac)₂ dormant chain.

Because VC polymerization is also prone to head-to-head addition, the propensity to dehydrocobaltation of the corresponding PVC-Co(acac)₂ dormant chain (formed by head-to-head addition mode, even if followed by the well-known rearrangement of $\text{P-CHCl-CH}_2^\bullet$ radical in the more stable $\text{P-CH}^\bullet\text{-CH}_2\text{-Cl}$, Figure 5) was also studied. The results are also shown in Figure 4, red pathway. Note that the alkyl-Co(III) compound resulting from the head-to-head coupling (containing a Co-CH₂ bond) is slightly more stable than the isomeric compound resulting from the regular head-to-tail coupling (containing a Co-CHCl bond). This leads to an even slightly greater energy for the β -H elimination process starting from this dormant species (~ 23 kcal/mol, Figure 4). Clearly, a β -H elimination process cannot explain the observed interruption of chain growth.

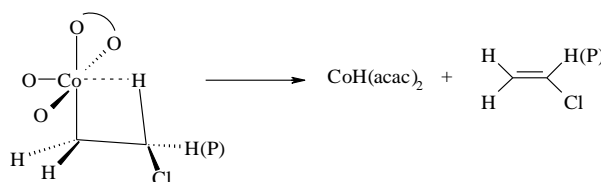


Figure 5. β -H elimination from PVC-Co(acac)₂ dormant chain (head-to-head addition).

A second hypothesis to account for the premature stop of the polymerization invokes the formation of a stronger C-Co bond at the PVC chain-end as a consequence of the head-to-head coupling. Therefore, the homolytic bond dissociation energy (BDE) of the C-Co(acac)₂ bond for the two above mentioned models of the dormant chain has been calculated by DFT. Table 3 shows that the bond made by $\text{Co}(\text{acac})_2$ with the more reactive $\text{CH}_2\text{Cl-CH}_2^\bullet$ radical is ca. 4.8 kcal/mol stronger than that made with the less reactive $\text{CH}_3\text{CHCl}^\bullet$ radical. The $(\text{acac})_2\text{Co-CH}_2\text{CH}_2\text{Cl}$ (BDE = 9.8 kcal/mol, Table 3 entry 1), might be strong enough to prevent further polymerization. This value should be compared with those calculated for the

(acac)₂Co-CH(OOCCH₃)CH₃ bond in the monodentate (5.7 kcal/mol, entry 3) and (κ^2 : C, O)-bidentate (11.9 kcal/mol, entry 4) modes.^{51,55} In the presence of donating ligands such as DMF or DMSO, the first mode is adopted and sustained polymerization is experimentally observed, whereas in the absence of ligands the second mode is adopted and this system is not able to generate radical at room temperature (the ligand-free bulk polymerization can only take place by degenerate transfer). The fact that the (acac)₂Co-CH₂CH₂Cl BDE value is only slightly below that estimated for the inert (acac)₂Co-PVAc dormant species could lend some credence to this hypothesis. Head-to-head addition is a reasonable hypothesis to explain the polymerization inhibition when considering the head-to-head additions extent compared to the head-to-tail one (1 %) ⁶⁴ and the degree of polymerization reached (DP = 210-550; Table 2).

Table 3. DFT calculated bond dissociation enthalpies (BDE) at 298K for different R-Co(acac)₂ complexes

Entry	R	BDE (kcal/mol)	References
1	CH ₂ ClCH ₂ -	9.8	This work
2	CH ₃ CHCl-	5.0	This work
3	CH ₃ (CH ₃ COO)CH-	5.7	50,54
4	CH ₃ (CH ₃ COO)CH- (κ^2 : C, O) -	11.9	50,54

Calculations carried out using the B3LYP basis

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The last reasonable hypothesis to explain why the VC polymerization stops at low monomer conversion is the occurrence of extensive irreversible termination reactions at the early stages of the polymerization, accumulating Co(acac)₂ in the medium. Provided that this Co(acac)₂ excess is high enough, the equilibrium between active and dormant chains would be strongly shifted towards the dormant species, leading to a strong slowing down of the polymerization and, eventually, to its inhibition. Incidentally, this hypothesis would also rationalize the low initiator efficiency factors, in the 0.47-0.68 range (see Table 2).

To tentatively control the VC polymerization by the alkyl-Co(III) compound, we decided to work under non-isotherm conditions with a temperature ramp of 0.12°C min⁻¹ from 40 to 80°C (Table 4). Surprisingly, the molar masses increase with time and thus with the temperature (Table 4 and Figure 6). From about 65°C (5 h of polymerization), the experimental molecular weight becomes lower than the theoretical one (Table 4, entries 3 and 4), namely $f > 1$. This is rationalized by the occurrence of a greater degree of chain transfer reactions at higher temperature. At that point, we observed an overheat phenomenon into the reactor, where the temperature was about 10°C higher than the temperature set. This phenomenon is explained by a smooth loss of polymerization control due to the weakness of the C-Co bond at the PVC chain-end at this temperature. The excess calories generated by the exothermic polymerization are the source of this overheating, because they are not efficiently dissipated in bulk polymerizations. This phenomenon certainly contributes to the occurrence of chain transfer reactions (transfer to monomer and to polymer), which are temperature dependent.

Table 4. VC bulk polymerization initiated by the alkyl-Co(III) compound under non-isotherm conditions using a temperature ramp of 0.12°C min⁻¹.

Entry	Polym time & temperature	VC conv (a)	Mn th (g/mol) (b)	Mn SEC DMF-LiBr (g/mol) (c)	Mw/Mn SEC DMF- LiBr (c)	Mn MALLS (g/mol) (d)	f (e)
REF (f)	6h00 at 40°C	59 %	/	68 200	2.13	56 000	/
1	1.5 h = stop at 40°C	7 %	13 400	23 700	2.51	23 500	0.57
2	3 h = stop at 51°C	8 %	15 400	28 600	2.62	29 400	0.52
3	5 h = stop at 65°C	22 %	42 200	37 000	2.21	38 300	1.10
4	7 h = stop at 80°C	34 %	65 200	44 000	2.27	47 100	1.38

Conditions: bulk polymerization of VC initiated by 2 ml of 1.5633 x 10⁻¹ mol/L alkyl-Co (III) solution under non-isotherm conditions with [VC]/ [alkyl-Co (III)] = 3250/1 with a temperature ramp of 0.12°C min⁻¹.

(a) Calculated gravimetrically after precipitation of the sample in cold heptane; (b) Calculated on the basis of VC conversion and the cobalt concentration; (c) obtained by SEC in DMF-LiBr, with a PMMA calibration; (d) SEC analysis with MALLS detection, in DMF-LiBr where dn/dc = 0.0793; (e) efficiency factor $f = \text{Mn th} / \text{Mn exp}$; (f) VC free-radical polymerization in bulk at 40°C initiated by V-70; [VC]/[V-70] = 643/1.

60

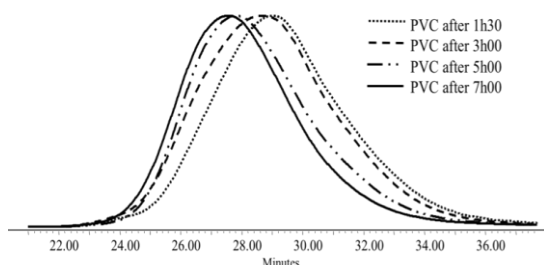


Figure 6. SEC chromatograms obtained during the bulk VC polymerization initiated by the alkyl-Co(III) adduct under non-isotherm conditions (temperature ramp : 0.12°C/minute) with [VC]/ [alkyl-Co (III)] = 3250/1.

In conclusion, our preliminary studies show that the VC polymerization presents some characteristic features of a controlled process when initiated by the alkyl-Co(III) compound under non-isotherm conditions that were never tested before for CMRP. The PVC molecular weight increases with the monomer conversion when the polymerization temperature is gently increased. This observation is in sharp contrast with the conventional VC polymerization in which Mn decreases with the temperature,⁵⁹⁻⁶⁰ due to the occurrence of transfer reactions that are more greatly favored at higher temperatures (Figure 7).

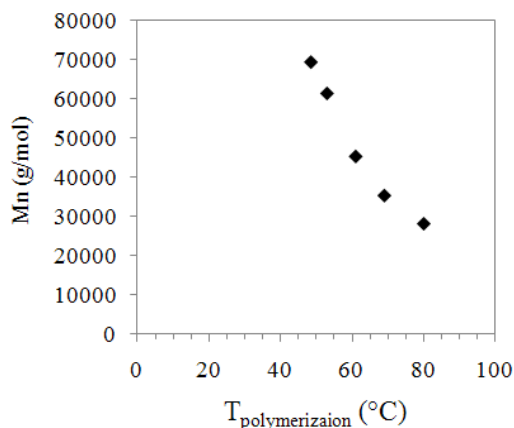
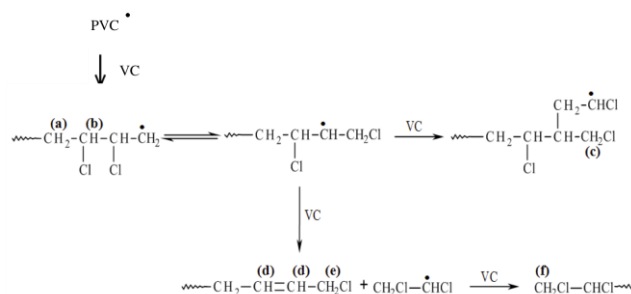


Figure 7. Evolution of the absolute molecular weight of PVC synthesized by free radical polymerization of VC versus the polymerization temperature. Confidential polymerization conditions, SolVin data.

An hypothesis to explain the above-mentioned observation could be to consider a chain-reactivation approach. Increasing the polymerization temperature should not only reactivate the dormant chains favoured by the accumulation of the cobalt complex, but also reactivate the C-Co bond of the stronger CH₂Cl-CH₂-Co(acac)₂ chain-end resulting from the head-to-head addition discussed above. Therefore, by increasing the temperature, the dormant/active species equilibrium should be slightly shifted towards the active ones, with the excess of cobalt complex that should allow the regulation of the polymerization at this temperature.

PVC microstructure investigation. As discussed in the introduction, VC is characterized by one of the largest transfer constant to monomer (C_M) among all the conventional

monomers (*i.e.* 22 x 10⁻⁴ at 50°C).⁴ This limits the PVC maximum molecular weight that can be obtained by free radical polymerization of VC at a given temperature⁶⁵, the chain transfer to monomer being temperature dependent and practically independent of the initiator concentration.^{59,60,65} This large C_M affects the PVC microstructure, since transfer reactions occur during the polymerization and cause the formation of defects. The structural defects can be determined and estimated by NMR spectroscopy, this method allowing characterizing and quantifying the anomalous units along the polymer chain.⁶⁶⁻⁷⁵ A head-to-head addition is believed to be at the origin of the transfer reactions (Scheme 2).⁵⁹⁻⁶⁰ Transfer to monomer is the main transfer reaction observed during VC polymerization and results in the formation of -CH=CH-CH₂Cl chain ends as the major structural defect.



Scheme 2. Formation of microstructural defects in PVC due to transfer reactions occurring during VC polymerization.

To evaluate the impact of using Co(acac)₂ on the PVC microstructure, some of our PVC samples were analysed by ¹H NMR spectroscopy. It is important to mention that the preparation of samples for the NMR analysis is challenging. Indeed, the free cobalt complex (Co(acac)₂) is paramagnetic and must be eliminated prior to NMR analysis. This is realized by the addition of excess TEMPO at the end of the polymerization, leading to irreversible end-capping of the polymer chain by the nitroxyl radical and to the release of Co(acac)₂.³⁸ Several steps of precipitations and purifications on silica were necessary to remove most of the contaminants and to allow recording satisfactory ¹H NMR spectra.

PVC samples synthesized by free radical polymerization at 40°C in bulk (V70 as initiator) and at 80°C in suspension (confidential initiator) were considered as references. We only investigated the -CH=CH-CH₂Cl structural defect, which is the most representative one for transfer to monomer and is easily detected. Comparison of the signal intensities of the polymer backbone hydrogen atom -CH₂CHCl- (4.2-4.8 ppm) and the hydrogen atoms of the -CH=CH-CH₂Cl defect structure (4.1 ppm for CH₂ (e, scheme 2) and 5.8 ppm for CH=CH (d, scheme 2)) allows quantifying the defect in the PVC sample. The -CH₂CHCl-/ -CH=CH-CH₂Cl molar ratio is 1000/0.56 at 40°C and 1000/2 at 80°C.

The PVC prepared by VC polymerization initiated by the alkyl-Co(III) compound under non-isotherm conditions (Table 4, entry 4) was then analysed and compared to the references. The

polymerization was carried out during 7 hours, after which the temperature reached 80°C. Figure 8 shows that the structural defect at 4.1 ppm and 5.8 ppm is present with a $-\text{CH}_2\text{CHCl}-/\text{CH}=\text{CH}-\text{CH}_2\text{Cl}$ molar ratio of 1000/2. This amount of defects is similar to that of the reference obtained at 80°C. On the basis of this analysis, $\text{Co}(\text{acac})_2$ does not seem to decrease nor increase significantly the level of defects on PVC.

For the sake of comparison, the level of defects that we observe in our PVC produced under these non-isotherm conditions is in the same range as for the PVC produced by SET-DTLRP process at lower temperature (25°C).^{27,69,76}

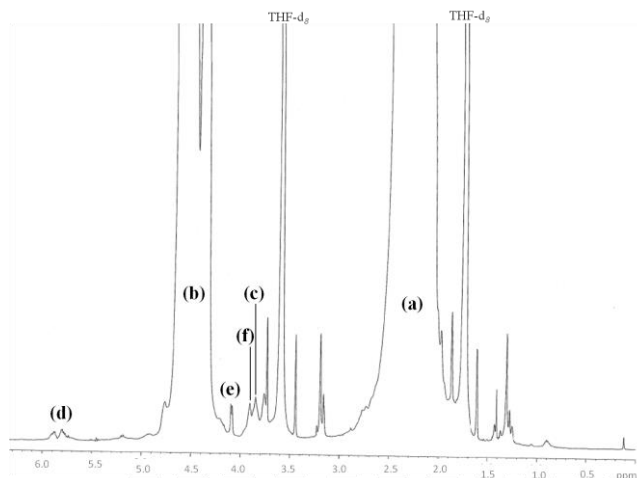


Figure 8. ^1H NMR spectra in THF-d_8 of PVC prepared by CMRP initiated by the alkyl-Co(III) compound under non-isotherm conditions (table 4, entry 4).

Bulk VC/VAc statistical copolymerization by CMRP. The transfer reactions, experienced in the VC homopolymerization at high temperatures might be prevented by copolymerizing VC with VAc, since the latter presents a better coupling efficiency with the cobalt complex. Indeed, the same challenge was already faced in the case of acrylates, where the use of $\text{Co}(\text{acac})_2$ under conditions identical to those of the VAc polymerization did not exert any control. The high lability of the C-Co bond at the polyacrylate chain-end was responsible for this effect.⁷⁷ However, addition of VAc to the acrylate polymerization resulted in a great improvement, provided its presence in significant amounts (at least 25 mol%).⁷⁷

Therefore, we investigated by analogy the effect of VAc addition on the $\text{Co}(\text{acac})_2$ -promoted VC polymerization under various conditions. We first investigated the VC/VAc statistical copolymerization initiated by V-70 in the presence of $\text{Co}(\text{acac})_2$ ([V70]/[$\text{Co}(\text{acac})_2$] = 1/1). A low VC/VAc molar ratio is expected to favor the deactivation by the chain-end VAc radical. However, three VC/VAc molar ratios with increasing VC contents were investigated (33:67, 60:40 and 82:18) and the results compared to those obtained for the conventional free radical copolymerization initiated by V-70 in the absence and in the presence of $\text{Co}(\text{acac})_2$ as the references (Table 5).

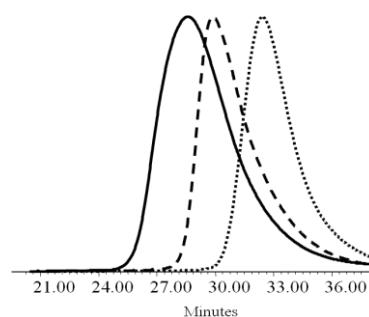
[VC]/[VAc] = 33/67.

In contrast to the copolymerization carried out by the V-70/ $\text{Co}(\text{acac})_2$ mixture, a regular increase of the monomers conversion with the polymerization time (table 5; entries 1-3) was observed when the copolymerization was initiated by the alkyl-cobalt(III) at 40°C. Moreover, a high VC conversion (79 %) was reached after 6 h of reaction. Importantly, the molecular weight of the resulting copolymer increased with the comonomer conversion with a very good agreement between the theoretical and the experimental molecular weights. These data suggest that each alkyl-Co(III) initiates the polymerization of one polymer chain and that the latter continuously grows during the whole polymerization process. The SEC chromatograms of the copolymers are monomodal and clearly shifted towards the higher molecular weight side with the monomer conversion (Figure 9A), in line with a controlled process. The polydispersity is however increasing with the polymerization time due to some tailing observed at the low molecular weight side of the SEC chromatogram. This tailing might be the result of some termination reactions. For the sake of comparison, when the copolymerization was carried out by conventional free radical polymerization using V-70 in the absence of $\text{Co}(\text{acac})_2$, no significant molecular weight evolution was observed (Table 5, entries 4-6; Figure 9B). In the presence of $\text{Co}(\text{acac})_2$, no polymerization was observed after 6 h of reaction (Table 5, entries 7-8), most probably due to a long induction period (> 6 h) as observed in the CMRP of VAc.³⁷

70

..... PVAc-co-PVC after 1h30
- - - PVAc-co-PVC after 3h00
— PVAc-co-PVC after 6h00

(A)



75 (B)

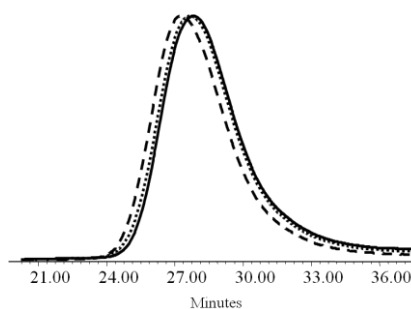


Figure 9. SEC chromatograms obtained for the VC/VAc copolymerization, [VC]/[VAc] = 33/67, bulk, 40°C, initiated by (A)

the alkylcobalt(III) adduct ([alkyl-Co(III)]/([VC]+[VAc]) = 1/1400);

(B) by V-70 ([V70]/([VC]+[VAc]) = 1/1400).

Table 5. Results of VC/VAc statistical copolymerization with low VC content using alkyl-Co(III) or V70 at 40°C

Entry	Polym time	Initiator	VC/VAc copolymer composition (a)	VC Conv (b)	VAc conv (b)	Mn th. (g/mol) (c)	Mn ¹ H NMR (g/mol) (d)	Mn MALLS (g/mol) (e)	Mn SEC DMF (g/mol) (f)	Mw/Mn SEC DMF	f (g)	Tg th. (°C) (h)	Tg exp. (°C)
1	1.5 h	Alkyl-Co(III)	59 / 41	14 %	5 %	8100	10 200	9600	11 200	1.27	0.84	46	32
2	3 h	Alkyl-Co(III)	62 / 38	32 %	12 %	21 200	22 100	21 500	21 700	1.55	0.99	48	50
3	6 h	Alkyl-Co(III)	50 / 50	79 %	44 %	61 100	/	56 000	39 100	2.18	1.09	43	48
4	1.5 h	V-70	60/40	19 %	6 %	/	/	47 500	46 700	2.15	/	nd	nd
5	3 h	V-70	61/39	53 %	16 %	/	/	68 800	52 100	2.26	/	nd	nd
6	6 h	V-70	63/37	58 %	17 %	/	/	59 100	44 200	2.08	/	nd	nd
7	3 h	V-70+Co(acac) ₂	/	0 %	0 %	/	/	/	/	/	/	nd	nd
8	6 h	V-70+Co(acac) ₂	/	0 %	0 %	/	/	/	/	/	/	nd	nd

5 Conditions : [VC]/[VAc] = 33/67, bulk, 40°C with [alkyl-Co(III)]/([VC]+[VAc]) = 1/1400 for entries 1, 2 and 3; with [V70]/([VC]+[VAc]) = 1/1400 for entries 4, 5 and 6; and with [Co(acac)₂]/[V-70]/([VC]+[VAc]) = 1/1/1400 for entries 7 and 8.

(a) Composition in each monomer in the PVC-co-PVAc copolymer calculated by ¹H NMR; (b) Conversion calculated on the basis of the composition and the total mass of the obtained copolymer, as described in the Experimental section; (c) Mn_{th} calculated for each monomer by : Mn_{th} = ((m_{VC} x VC conv) + (m_{VAc} x VAc conv)) / n(Co), where m_{VC} = initial VC mass, m_{VAc} = initial VAc mass and n(Co) = alkyl-Co(III) mol quantity; (d) Mn_{exp} calculated by ¹H-NMR by comparison of the intensities of signal corresponding to the polymer backbone (CH₂-CH-OCOCH₃ of PVAc (at 4.8-5.5 ppm), CH₂-CH-Cl of PVC (at 3.8-4.7 ppm)) and the α chain-end (-OCH₃) at 3.1 ppm; (e) absolute molecular weight determined by SEC analysis with MALLS detection, in DMF-LiBr and with dn/dc measured for each sample; (f) SEC in DMF-LiBr with RI detection, calibration with PMMA; (g) initiator efficiency factor f = Mn_{th}/Mn_{exp}; (h) Theoretical Tg calculated by 1/Tg_{PVC-co-PVAc} = (W_{PVC}/Tg_{PVC}) + (W_{PVAc}/Tg_{PVAc}), where W = weight fraction of one monomer in the copolymer, measured Tg_{PVC} = 81°C, measure Tg_{PVAc} = 32°C. nd: not determined.

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The ¹H NMR analysis of the copolymer prepared by CMRP evidences the presence of the typical PVAc and PVC signals (Figure 10). The composition of the copolymer was determined by comparison of the intensities of the PVAc CH₂-CH-OCOCH₃ (at 4.8-5.5 ppm) and PVC CH₂-CH-Cl (at 3.8-4.7 ppm) signals. As expected for a statistical copolymer, the peak between 4.3 ppm and 4.7 pm are assigned to the VC moieties adjacent to the VAc moieties.

Table 5 (entries 1-3) clearly shows that the VC incorporation in the polymer is greater than that of VAc, in agreement with the monomer reactivity ratios in favor of VC (r_{VC} = 2 and r_{VAc} = 0.2).⁷⁸⁻⁸⁰

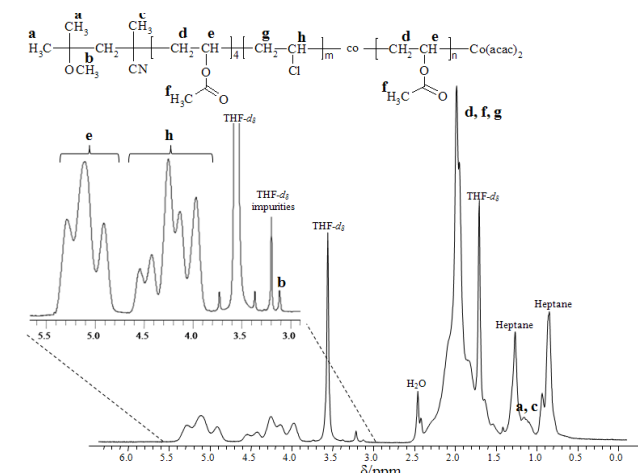


Figure 10. ¹H NMR spectrum in THF-d₈ (400 MHz) of PVC-co-PVAc synthesized from alkyl-Co(III) in bulk at 40°C (table 3, entry 3).

On figure 10, the signal at 3.2 ppm is attributed to the -OCH₃ group of the V-70 fragment and is thus located at the α chain-

end of the polymer. Consequently, comparison of the intensities of this signal with those corresponding to the polymer backbone allows calculating the copolymer molecular weight (Mn NMR, Table 5, entries 1 and 2), which is in very good agreement with that determined by SEC MALLS. This is additional evidence that most of the polymer chains are initiated by alkyl-Co(III) and remain controlled during the whole polymerization process.

Differential scanning calorimetry (DSC) analysis allows measuring the samples glass transition temperature (Tg). These Tg's are compared to the theoretical ones calculated on the basis of the composition of each monomer and the Tg of PVC (81°C) and PVAc (32°C). The good agreement between the experimental Tg values of the copolymer synthesized using alkyl-cobalt(III) with the theoretical one (Table 5, entries 1, 2 and 3) confirms the compositions. Note that the copolymer obtained after 1h30 reaction has an experimental Tg much lower than the theoretical one (32°C vs 46°C). This difference is explained by the molar mass of this sample that is relatively low (less than 10000 g/mol), since the glass transition temperature is affected by the polymer molecular weight.

[VC]/[VAc] = 60/40, and 82/18. The vinyl chloride content was then increased in the polymerization medium in order to determine the maximum amount of VC tolerated by the system. Using a [VC]/[VAc] ratio of 60/40 (table 6, entries 1-3), the comonomers conversion increased with the reaction time and the VC conversion is still higher than that of VAc, in agreement with the reactivity ratios. On the other hand, the conversion after 6 h (Table 6, entry 3) is lower than for the experiment described above with higher VAc content (Table 5, entry 3). Importantly, the molecular weight increases with

monomer conversion, with absolute values in good agreement with the theoretical ones, in line with a controlled process. SEC chromatograms clearly shift towards lower elution volumes (higher molecular weights) as the polymerization progresses (Figure 11a), supporting the controlled growth of the polymer chains until at least 6 h of polymerization.

When the VC/VAc molar ratio was further increased ([VC]/[VAc] = 82/18), the control seems to be (partly) lost as evidenced by absolute molecular weights twice higher than the theoretical values, suggesting that only 50 % of the alkylcobalt(III) adduct initiated polymer chains. Moreover, Figure 11c clearly shows that the SEC chromatograms do not greatly shift with the monomer conversion. The small shoulder

observed on the chromatogram at the higher molecular weight side after 6 h of reaction might be due to the occurrence of some coupling reactions. These side reactions might therefore account for the Mn increase in the last sample (40 800 g/mol). Finally, the monomer conversions are low after 6 h (21 % for VC and 9 % for VAc) and are twice lower than in the previous experiment. Clearly, increasing the VC content in the polymerization medium is not beneficial to the polymerization control. As predicted by the reactivity ratios, VC is preferentially incorporated in the copolymer.

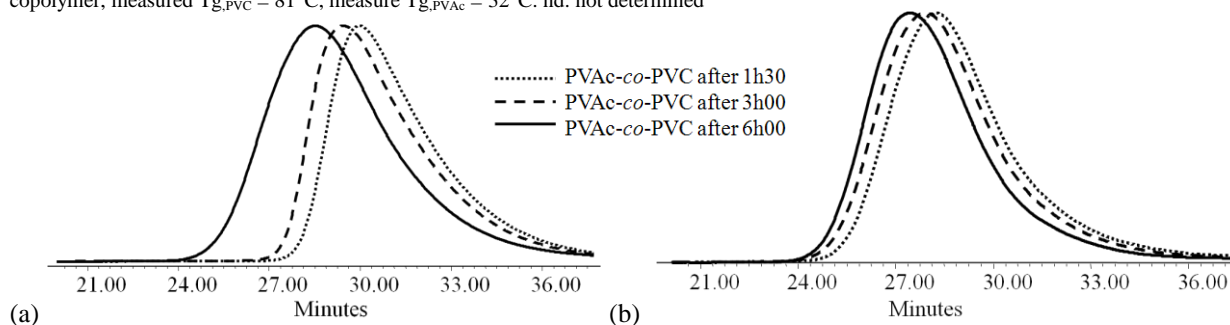
The experimental glass transition temperatures are also in good agreement with the theoretical ones (Table 6), in line with the copolymer composition.

Table 6. Results for the VC/VAc statistical copolymerization with higher vinyl chloride content

Entry	Polym time	Initiator	VC/VAc copolymer composition ^(a)	VC conv ^(b)	VAc conv ^(b)	Mn th. (g/mol) ^(c)	Mn ¹ H NMR (g/mol) ^(d)	Mn MALLS (g/mol) ^(e)	Mn SEC DMF (g/mol) ^(f)	Mw/Mn SEC DMF	f ^(g)	Tg th. (°C) ^(h)	Tg exp. (°C)
1	1.5 h	Alkyl-Co(III)	83 / 17	18 %	5 %	13 100	15 500	19 400	18 000	1.57	0.68	61	66
2	3 h	Alkyl-Co(III)	79 / 21	20 %	8 %	17 200	22 200	20 600	21 800	1.68	0.83	57	58
3	6 h	Alkyl-Co(III)	79 / 21	53 %	21 %	41 800	/	40 100	34 200	2.28	1.04	57	61
4	1.5 h	V-70	81/19	11 %	4 %	/	/	32 000	34 500	2.07	/	nd	nd
5	3 h	V-70	78/22	18 %	7 %	/	/	38 300	40 900	2.12	/	nd	nd
6	6 h	V-70	78/22	74 %	31 %	/	/	55 900	48 600	2.14	/	nd	nd
7	1.5 h	Alkyl-Co(III)	91 / 9	13 %	6 %	12 800	34 400	27 200	24 900	2.01	0.47	68	68
8	3 h	Alkyl-Co(III)	92 / 8	12 %	5 %	11 700	20 700	21 600	20 600	2.23	0.54	70	67
9	6 h	Alkyl-Co(III)	92 / 8	21 %	9 %	20 600	/	40 800	28 800	2.40	0.50	70	74
10	1.5 h	V-70	93/7	20 %	8 %	/	/	46 900	47 600	2.16	/	nd	nd
11	3 h	V-70	92/8	42 %	16 %	/	/	48 100	49 600	2.30	/	nd	nd
12	6 h	V-70	91/9	55 %	24 %	/	/	50 500	49 400	2.06	/	nd	nd

Conditions : [VC]/[VAc] = 60/40, bulk, 40°C, initiated by the alkylcobalt (III) compound with [alkyl-Co(III)]/([VC]+[VAc]) = 1/1545 for entries 1, 2 and 3; [VC]/[VAc] = 60/40, bulk, 40°C, initiated by V-70 with [V70]/([VC]+[VAc]) = 1/1545 for entries 4, 5 and 6; [VC]/[VAc] = 82/18, bulk, 40°C, initiated by the alkylcobalt (III) compound with [alkyl-Co(III)]/([VC]+[VAc]) = 1/1700 for entries 7, 8 and 9; and [VC]/[VAc] = 82/18, bulk, 40°C, initiated by V-70 with [V70]/([VC]+[VAc]) = 1/1700 for entries 10, 11 and 12.

(a) Composition in each monomer in the PVC-co-PVAc copolymer calculated by ¹H NMR; (b) Conversion calculated on the basis of the composition and the total mass of the obtained copolymer, as described in the Experimental section; (c) Mn_{th} calculated for each monomer by : Mn_{th} = ((m_{VC} x VC conv) + (m_{VAc} x VAc conv)) / n(Co), where m_{VC} = initial VC mass, m_{VAc} = initial VAc mass and n(Co) = alkyl-Co(III) mol quantity; (d) Mn_{exp} calculated by ¹H NMR by comparison of the intensities of signal corresponding to the polymer backbone (CH₂-CH-OCOCH₃ of PVAc (at 4.8-5.5 ppm), CH₂-CH-Cl of PVC (at 3.8-4.7 ppm) and the α chain-end (-OCH₃) at 3.1 ppm ; (e) Absolute molecular weight determined by SEC analysis with MALLS detection, in DMF-LiBr and with dn/dc measured for each sample; (f) SEC in DMF-LiBr with RI detection, calibration with PMMA; (g) Initiator efficiency factor f = Mn_{th}/Mn_{exp}; (h) Theoretical Tg calculated by 1/Tg_{PVC-co-PVAc} = (W_{PVC}/Tg_{PVC}) + (W_{PVAc}/Tg_{PVAc}), where W = weight fraction of one monomer in the copolymer, measured Tg_{PVC} = 81°C, measure Tg_{PVAc} = 32°C. nd: not determined



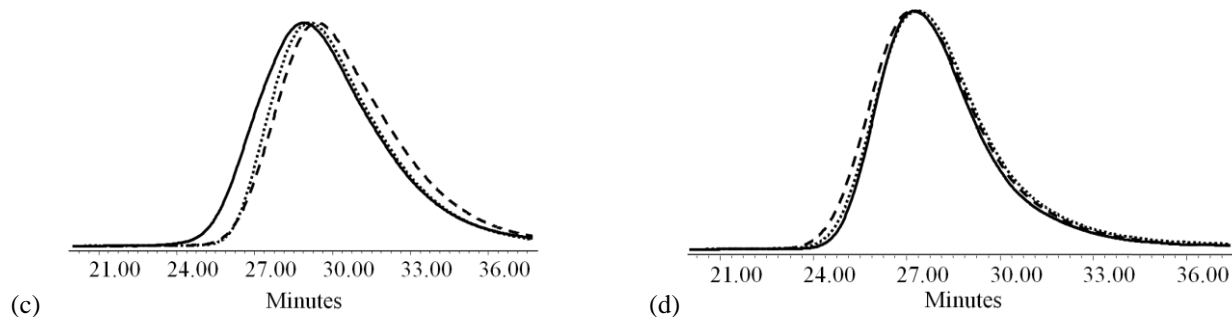


Figure 11. SEC chromatograms obtained during the VC/VAc statistical copolymerization. Conditions: **a.** [VC]/[VAc] = 60/40, bulk, 40°C, initiated by the alkylcobalt(III) compound with [alkyl-Co(III)]/[VC]+[VAc] = 1/1545; **b.** [VC]/[VAc] = 60/40, bulk, 40°C, initiated by V-70 with [V70]/([VC]+[VAc]) = 1/1545; **c.** [VC]/[VAc] = 82/18, bulk, 40°C, initiated by the alkylcobalt(III) compound with [alkyl-Co(III)]/[VC]+[VAc] = 1/1700; **d.** [VC]/[VAc] = 82/18, bulk, 40°C, initiated by V-70 with [V70]/([VC]+[VAc]) = 1/1700.

Conclusions

We have reported herein the first investigation of the CMRP of VC. The polymerization was initially carried out at 40°C with V70 initiation in the presence of Co(acac)₂. On the basis of the polymerization kinetics, Co(acac)₂ appeared to be a less efficient trapping agent for the PVC radicals than for the PVAc ones. The DFT calculations have shown that the PVC-Co bond is marginally more labile than the PVAc-Co one (5.0 kcal/mol versus 5.7 kcal/mol and contrary to the acetate group of the PVAc chain, the Cl atom in the PVC chain cannot stabilize the dormant species by chelation). Under these conditions, the monomer conversion was limited. Then, the VC homopolymerization was initiated by a preformed alkylcobalt(III) in the bulk at 40°C. Again, inhibition of the polymerization was observed at low monomer conversion. Such a limitation was attributed to the occurrence of irreversible termination reactions during the VC polymerization with consequent accumulation of the cobalt(II) deactivator in the medium. Subsequent increase of the temperature medium when carried out under non-isotherm conditions with a positive temperature ramp, allowed the VC homopolymerization to exhibit features of a controlled process, *i.e.* a molar mass increase with monomer conversion, at least below 60°C. A preliminary ¹H NMR study also indicated that the level of defects of the PVC produced by CMRP is similar to that in PVC prepared by conventional free radical polymerization at the same temperature. Finally, the addition of VAc to the VC polymerization medium had a beneficial effect on the course of the CMRP due to the higher coupling efficiency between Co(acac)₂ with the chain end VAc radical. Such copolymerizations were controlled even under isothermal conditions provided that enough VAc (~40 mol %) was present in the comonomer feed. High monomer conversions were reached after 6 h of copolymerization, the experimental molecular weights were in good agreement with the theoretical ones, and the compositions were in line with the reactivity ratios of each monomer, VC being preferentially incorporated. Given the range of monomers (non-conjugated vinyl monomers such as VAc, VC, N-vinylpyrrolidone, and conjugated ones such as acrylonitrile and acrylates) whose polymerization can be controlled by CMRP, and particularly with Co(acac)₂, this

work paves the way to the design of unusual PVC based copolymers.

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‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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