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Solving the Problem of Bis(acetylacetonato)cobalt(II)-Mediated Radical Polymerization (CMRP) of Acrylic Esters

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ABSTRACT: Recent developments in cobalt-mediated radical polymerization (CMRP) and progress in the mechanistic understanding enabled to optimize the copolymerization of *n*-butyl acrylate (*n*BA) with vinyl acetate (VAc), as well as to control the homopolymerization of *n*BA by means of bis(acetylacetonato)cobalt(II) (Co(acac)$_2$). Critical experimental parameters such as the initiating system, the temperature, and the presence of additives were varied and discussed. Under optimized conditions, an alkylcobalt(III) adduct $R_0-(CH_2-CHOAc)_{<4}-Co(acac)_2$ (R_0 = primary radical from the V-70 decomposition) allowed a better control of the *n*BA/VAc copolymerization than the previously studied V-70/Co(acac)$_2$ pair regarding the molecular weight control and the polydispersities. Importantly, the homopolymerization of *n*BA was controlled by Co(acac)$_2$ for the first time using the alkylcobalt(III) adduct or the lauroyl peroxide (LPO)/Co(acac)$_2$ redox pair as initiating system. Typically, poly(*n*-butyl acrylate) with polydispersity around 1.2 and molar mass as high as 200 000 g/mol was achieved with this cobalt complex.

Introduction

The advent of controlled radical polymerization (CRP) techniques has enabled the synthesis of a diverse array of well-defined polymers with specific functionalities and properties under mild experimental conditions.[1−3] Telechelic, block, gradient, graft, and star (co)polymers are nowadays made available by means of nitroxide-mediated radical polymerization (NMP),[4−6] atom-transfer radical polymerization (ATRP),[7−9] and reversible addition−fragmentation chain transfer (RAFT).[10−12] Other variants of CRP such as single-electron-transfer,[13] organotellurium-, organostilbine-, and organobismuthine-mediated CRPs[14] have also demonstrated high efficiencies.

In addition to these techniques, cobalt-mediated radical polymerization (CMRP) emerged in 1994 when Wayland et al. and Harwood et al. used cobalt porphyrin and cobaloxime complexes **1** and **2** (Figure 1), respectively, to control the radical polymerization of acrylates.[15,16] 1,3-Bis(2-pyridylimino)isoindolatocobalt(II) complex **3** recently described by Gade et al. also proved efficiency for the CMRP of acrylates.[17] These three complexes remained restricted to acrylic monomers for a long time, although recent attempts to mediate the polymerization of vinyl acetate (VAc) with complex **1** succeeded within very low conversion.[18,19] A few years ago, Jérôme et al. used the bis(acetylacetonato)cobalt(II) complex **4** (Co(acac)$_2$) as controlling agent in the polymerization of VAc, which long remained a challenging monomer due to the lack of stabilizing groups resulting in the high reactivity of the propagating radical.[20−23] Recent mechanistic investigations demonstrated that bis(acetylacetonato)cobalt-mediated polymerization follows a degenerative chain-transfer (DT) pathway when the amount of radicals injected in the medium exceeds the one of Co^{II}, whereas a reversible termination process (RT) occurs when the cobalt complex exceeds radicals.[24−26] The reversible-termination process is also predominant when an electron donor ligand saturates the coordination sphere of the ω chain-end cobalt complex. It was also demonstrated that such a metal coordination modifies the cobalt−carbon strength. These developments were notably made possible by the isolation of an alkylcobalt(III) adduct **5** ($R_0-(CH_2-CHOAc)_{<4}-Co(acac)_2$; R_0 = primary radical from the V-70 decomposition) able to generate both the radical initiating and the controlling moieties upon dissociation.[26]

Today, a challenging issue in CMRP still remains to cope with the widest range of vinylic monomers of different reactivity using the same cobalt complex in order to expand the variety of materials achievable by this technique. In this respect, bis(acetylacetonato)cobalt(II) complex appears as the more versatile complex since it can also properly control the polymerization of *N*-vinylpyrrolidone (*N*VP)[27,28] and acrylonitrile (AN).[29,30] However, Co(acac)$_2$ failed to control the homopolymerization of acrylates until now due to the high lability of the cobalt−carbon bond.[31] Satisfying results for *n*-butyl acrylate (*n*BA) were obtained with this complex provided that a significant amount of VAc (9−50 mol %) was added in the reaction medium to moderate the acrylate polymerization, leading to gradient P*n*BA-*grad*-PVAc.[31]

In this paper, the previously reported copolymerization of *n*BA with VAc using Co(acac)$_2$ was optimized by screening the effect of experimental conditions. The influence of key parameters such as the type of initiator, the temperature, and the presence of some additives (DMSO, excess Co(acac)$_2$) was considered. In the second part of this study, the best experimental conditions were implemented to perform the first homopolymerization of *n*BA controlled by Co(acac)$_2$, which considerably increases the potential of CMRP for macromolecular engineering.

Experimental Section

Materials. Vinyl acetate (VAc) (>99%, Acros) and *n*-butyl acrylate (*n*BA) (>99%, Aldrich) were dried over calcium hydride, degassed by several freeze−thawing cycles before being distilled under reduced pressure, and stored under argon at −20 °C. Dimethyl sulfoxide (DMSO) (>99.9%, Merck) was dried over calcium hydride prior to distillation under reduced pressure. Bis(acetylacetonato)cobalt(II) (Co(acac)$_2$) (>98%,

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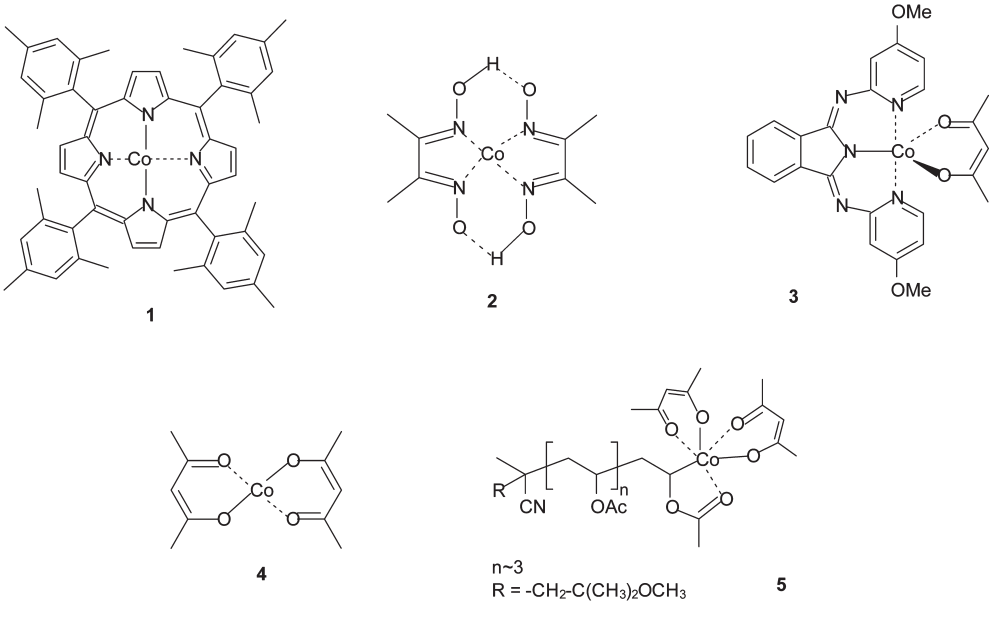

Figure 1. Structures of some cobalt complexes effective as cobalt-mediated radical polymerization mediators.

Acros), 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) (96%, Wako), 2,2,6,6-tetramethylpiperidine 1-oxy (TEMPO) (98%, Aldrich), lauroyl peroxide (LPO) (97%, Fluka), and deuterated chloroform ($CDCl_3$) (99.8%, Eurisotop) were used as received. Toluene (P.A., Prolabo) was distilled over sodium/benzophenone and degassed by argon bubbling.

Characterization. Monomer conversions were determined by ^{1}H NMR spectroscopy at 298 K with a Bruker spectrometer operating at 250 MHz in $CDCl_3$. The relative molecular weights ($M_{n,\ SEC}$) and polydispersity indices (M_w/M_n) of the polymers were determined by size-exclusion chromatography (SEC) in tetrahydrofuran (THF) (flow rate: 1 mL min^{-1}) at 40 °C with 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, and 10^2 Å). Polystyrene (PS) and poly(methyl methacrylate) (PMMA) standards were used to determine the relative molecular weights of the P*n*BA and P*n*BA-*co*-PVAc samples, respectively. The absolute molecular weights of the P*n*BA samples were determined by transformation of the PS molecular weight using the Mark−Houwink parameters for PS and P*n*BA in THF taken from the literature.[32] The absolute molecular weight for the P*n*BA-*grad*-PVAc copolymers was determined using SEC in dimethylformamide (DMF) with lithium bromide LiBr (0.025 M) equipped with a Wyatt multiangle laser light scattering (MALLS) detector (120 mW solid-state laser, λ = 658 nm, Dawn Heleos S/N 342-H). Specific refractive index increment (d*n*/d*c*) for the P*n*BA-*grad*-PVAc copolymers was determined by using a Wyatt Optilab rEX refractive index detector (λ = 658 nm). Data were processed with the Astra V software (Wyatt Technology). The MALLS detector measures the excess Rayleigh ratio R_θ (related to the scattered intensity) at different angles θ for each slice of the chromatogram, which allows the software to solve the light scattering equation:[33]

$$R_\theta = KMcP(\theta)[1 - 2A_2MP(\theta)c]$$

where M is the molecular weight of the polymer, c is the polymer concentration, A_2 is the second virial coefficient, and K is the optical constant related to λ_0, the laser wavelength in the vacuum, n_0, the solvent refractive index, d*n*/d*c*, the refractive index increment in the polymer solution, and N_A, Avogadro's number:

$$K = 4\pi^2(dn/dc)^2 n_0^2/N_A\lambda_0^4$$

$P(\theta)$ is the normalized intensity distribution function, and its expansion to the first order gives

$$P(\theta) = 1 - 16\pi^2 n_0^2 \sin^2(\theta/2)\langle r_g^2\rangle/3\lambda_0^2 + ...$$

where $\langle r_g^2\rangle$ is the mean-square radius.

The cobalt concentration of the alkylcobalt(III) adduct stock solution in CH_2Cl_2 was determined by inductively coupled plasma-mass spectrometry (ICP-MS), carried out with a spectrometer (Elan DRC-e Perkin-Elmer SCIEX). Samples were prepared by evaporating 0.5 mL of the cobalt adduct stock solution and reacting with 0.5 mL of HNO_3 (65%) at 60 °C for 2 h. The solution was then diluted to 250 mL with bidistilled water prior to ICP-MS analysis.

Copolymerization of *n*-Butyl Acrylate with Vinyl Acetate Initiated by V-70 in the Presence of Co(acac)$_2$. All polymerizations were performed by classical Schlenk techniques under argon. Liquids were transferred with syringes and stainless steel capillaries. This copolymerization was carried out according to the previously reported procedure.[31] Co(acac)$_2$ (0.1364 g, 4.422×10^{-4} mol) and V-70 (0.1146 g, 4.422×10^{-4} mol) were added into a round-bottom flask capped by a three-way stopcock and purged by three vacuum−argon cycles. After addition of degassed VAc (3.9 mL, 4.25×10^{-2} mol) and *n*BA (6.0 mL, 4.25×10^{-2} mol), the reaction mixture was heated at 30 °C under stirring. Samples were periodically withdrawn from the medium via a syringe during the whole polymerization procedure and added with few milligrams of TEMPO in order to quench the polymerization. Monomer conversions of each sample were determined by ^{1}H NMR spectroscopy, and macromolecular parameters (M_n, M_w/M_n) were measured by SEC after evaporation of the residual monomers under reduced pressure. Results are shown in Table 1 (entry 1) and Figure 3 (circles).

General Procedure for Polymerizations Initiated by the Alkylcobalt(III) Adduct 5. The synthesis and the complete characterization of the low molecular weight alkylcobalt(III) adduct **5** have been described elsewhere.[26] The cobalt complex was stored as a CH_2Cl_2 solution at −20 °C under argon. The cobalt concentration of the stock solution was determined by ICP-MS. Both homo- and copolymerizations were carried out under different experimental conditions (i.e., variation of the temperature, presence of DMSO or Co(acac)$_2$). A typical example for the copolymerization of *n*BA with VAc in presence of Co(acac)$_2$ is given below. Co(acac)$_2$ (0.017 g, 6.6×10^{-5} mol)

Table 1. Effect of Initiator and Temperature on the Copolymerization of *n*BA with VAc[a]

entry	initiator	T (°C)	time	*n*BA conv (%)	VAc conv (%)	$M_{n,SEC}$[b] (g/mol)	M_w/M_n
1[c]	V-70	30	6 h	26	2	16 800	1.37
			10 h	54	6	24 200	1.35
			17 h	82	11	27 200	1.36
2	**5**	30	10 min	75	13	23 200	1.63
			2 h	77	17	22 800	1.64
			50 h	77	17	22 900	1.66
3	**5**	0	30 min	25	2	75 400	2.14
			2 h	49	4	60 000	2.17
			6 h	66	6	53 100	2.23

[a] Conditions: [*n*BA]/[VAc]/[initiator] = 96/96/1. [b] $M_{n,SEC}$ determined by SEC in THF with a PMMA calibration. [c] [V-70]/[Co(acac)$_2$] = 1/1.

Table 2. Use of DMSO and Complex 4 as Additives for the Copolymerization of *n*BA with VAc Initiated by the Alkylcobalt(III) Adduct 5[a]

entry	T (°C)	[**4**]/[DMSO]/[**5**]	time	*n*BA conv (%)	VAc conv (%)	$M_{n,SEC}$[b] (g/mol)	M_w/M_n
1	0	0/32/1	10 min	57	6	21 800	1.89
			1 h	76	10	20 200	1.90
			2 h	89	16	19 000	1.86
2	0	0.3/0/1	3 h	9	1		
			44 h	44	5	12 000	1.60
			71 h	62	5	13 100	1.56
3	30	0.3/0/1	2 h 30 min	69	5	10 900	1.27
			5 h	81	11	13 200	1.22
			9 h	90	19	15 300	1.18
			23 h	96	27	17 200	1.16

[a] Conditions: [*n*BA]/[VAc]/[**5**] = 96/96/1. [b] $M_{n,SEC}$ determined by SEC in THF with a PMMA calibration.

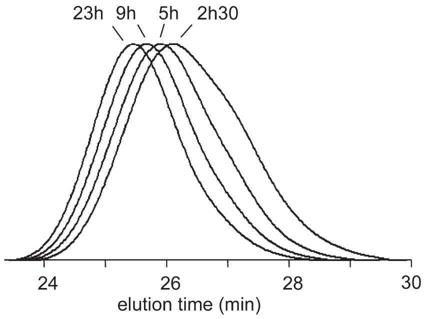

Figure 2. SEC chromatograms for the copolymerization of *n*BA with VAc initiated by the alkylcobalt(III) adduct **5** in presence of complex **4** at 30 °C. Conditions: [*n*BA]/[VAc]/[**4**]/[**5**] = 96/96/0.3/1; Table 2, entry 3.

was added in a round-bottomed flask capped by a three-way stopcock and purged by three vacuum−argon cycles. The alkylcobalt(III) adduct **5** (1.6 mL of the CH$_2$Cl$_2$ stock solution, 2.2 × 10^{-4} mol of cobalt) was introduced under an argon atmosphere and then evaporated to dryness under reduced pressure at room temperature. VAc (1.9 mL, 2.1 × 10^{-2} mol) and *n*BA (3 mL, 2.1 × 10^{-2} mol) were then added under argon. The reaction mixture was stirred at 30 °C, and samples were regularly withdrawn with a syringe prior to quenching by TEMPO. Monomer conversions and macromolecular parameters were determined by ^{1}H NMR spectroscopy and SEC, respectively, as described above. Results are shown in Table 2 (entry 3) and Figures 2 and 3 (triangles).

Synthesis of a Poly(vinyl acetate)-*b*-poly(*n*-butyl acrylate) (PVAc-*b*-P*n*BuA) Block Copolymer Starting from PVAc-Co(acac)$_2$. The block copolymerization of *n*BA initiated by a PVAc-Co macroinitiator was carried out as follows. The alkylcobalt(III) adduct **5** (1.4 mL, 1.93 × 10^{-4} mol) was added in a round-bottomed flask and evaporated to dryness. VAc (10 mL, 0.108 mol) was added, and the medium was stirred at 40 °C for 4 h. A sample was picked out for the conversion (25%) and for the determination of the PVAc molecular weight and polydispersity by SEC in THF (M_n = 14 000 g/mol; M_w/M_n = 1.05). Residual VAc was then evaporated under reduced pressure at room temperature, and a solution of Co(acac)$_2$ (0.047 g, 1.93 × 10^{-4} mol) in *n*BA (20 mL, 0.140 mol) was finally added at 0 °C under argon. Polymerization then occurs at 0 °C under stirring. Monomer conversions and macromolecular parameters were determined by ^{1}H NMR spectroscopy and SEC in THF, respectively. Results are shown in Figure 9.

General Procedure for Polymerizations Initiated by the LPO/Co(acac)$_2$ Redox System. A typical example is given for the copolymerization of *n*BA with VAc. Co(acac)$_2$ (0.617 g, 2.4 × 10^{-3} mol) was added in a round-bottomed flask capped by a three-way stopcock and purged by three vacuum−argon cycles. VAc (6 mL, 6.5 × 10^{-2} mol), *n*BA (9.3 mL, 6.5 × 10^{-2} mol), and LPO in toluene solution (2 mL, 0.318 g, 8.0 × 10^{-4} mol) were added at 0 °C under an argon atmosphere. The mixture was stirred at 0 or 30 °C. Samples were regularly withdrawn and characterized as described above. Results are shown in Figures 4 and 5.

Results and Discussion

Copolymerization of *n*BA with VAc Mediated by Co(acac)$_2$. The previous attempt to control the polymerization of *n*BA with complex **4** resulted in a rapid gelation.[31] The difficulty to mediate the acrylate polymerization was consistent with DFT calculations which predicted a less stable C−Co(acac)$_2$ bond for the *n*BA than for the VAc chain end.[26] These grounds made the CMRP of acrylates with Co(acac)$_2$ very challenging and thus led to use VAc as a comonomer for the CMRP of *n*BA,[31] given the higher trapping efficiency of the VAc radical by **4**. It was demonstrated that increasing the VAc/*n*BA ratio improved the control of the copolymerization. In agreement with the monomers reactivity ratios (r_{nBA} = 10.7, r_{VAc} = 0.02)[34] and the controlled character of the polymerization, well-defined gradient copolymers (P*n*BA-*grad*-PVAc) with high acrylate content were obtained. For an initial [*n*BA]/[VAc] ratio of 50/50, a polydispersity of 1.3 was achieved for a molecular weight of 35 000 g/mol. These results constitute the starting point for our research.

It was recently shown that the use of the alkylcobalt(III) adduct **5** instead of V-70/Co(acac)$_2$ improved the control on the radical polymerization of VAc.[26] As a rule, this preformed dormant species has a higher initiation efficiency than its nonpurified counterpart formed *in situ* during the induction period preceding the polymerization.[30] Therefore,

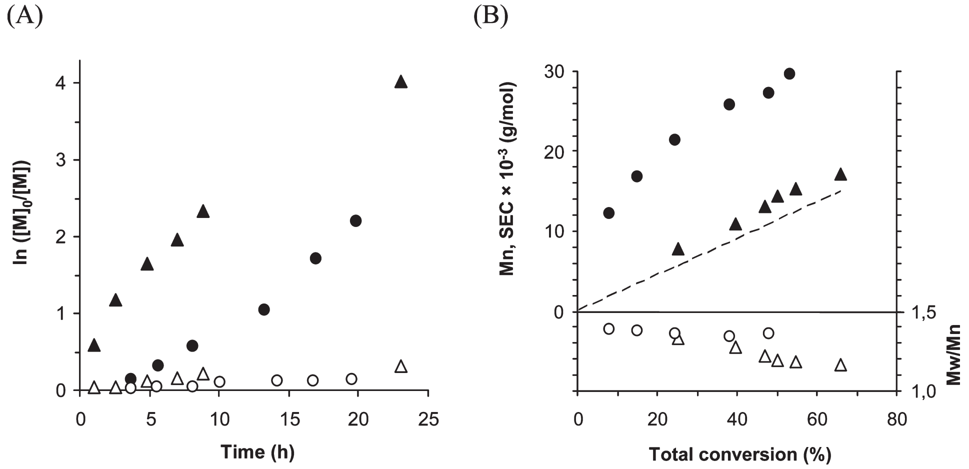

Figure 3. Copolymerization of *n*BA with VAc in presence of complex **4** initiated at 30 °C either by V-70 (circles; [*n*BA]/[VAc]/[**4**]/[V-70] = 96/96/1/1; Table 1, entry 1) or by the alkylcobalt(III) adduct **5** (triangles; [*n*BA]/[VAc]/[**4**]/[**5**] = 96/96/0.3/1; Table 2, entry 3). (A) Semilogarithmic kinetic plot. Initiation by V-70: (●) *n*BA; (○) VAc. Initiation by **5**: (▲) *n*BA; (△) VAc. (B) Evolution of M_n and M_w/M_n as a function of the total conversion. The theoretical molecular weight $M_{n,th}$ is represented by the dotted line and is calculated according to the [monomer]/[initiator] ratio and conversion.

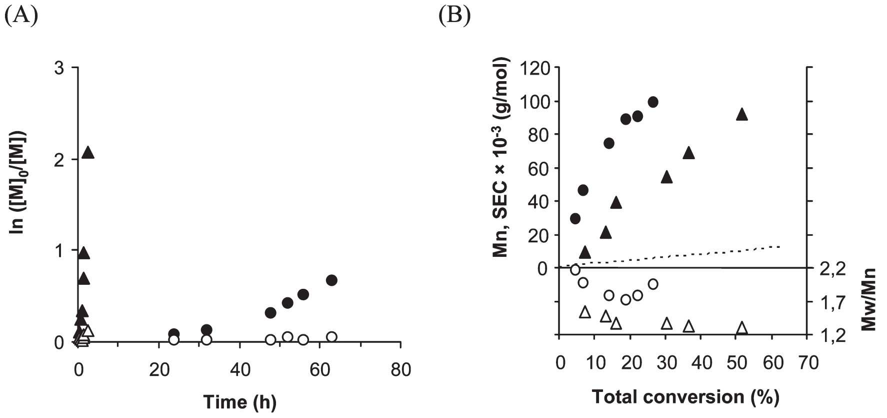

Figure 4. Copolymerization of *n*BA with VAc initiated by the LPO/Co(acac)$_2$ redox system at 0 °C (circles) and 30 °C (triangles). (A) Semilogarithmic kinetic plot. Polymerization at 0 °C: (●) *n*BA; (○) VAc. Polymerization at 30 °C: (▲) *n*BA; (△) VAc. (B) Evolution of M_n and M_w/M_n as a function of the total conversion. The theoretical molecular weight $M_{n,th}$ is represented by the dashed line and is calculated according to the [*n*BA]/[LPO] ratio and conversion. Conditions: [*n*BA]/[VAc]/[Co(acac)$_2$]/[LPO] = 80/80/3/1.

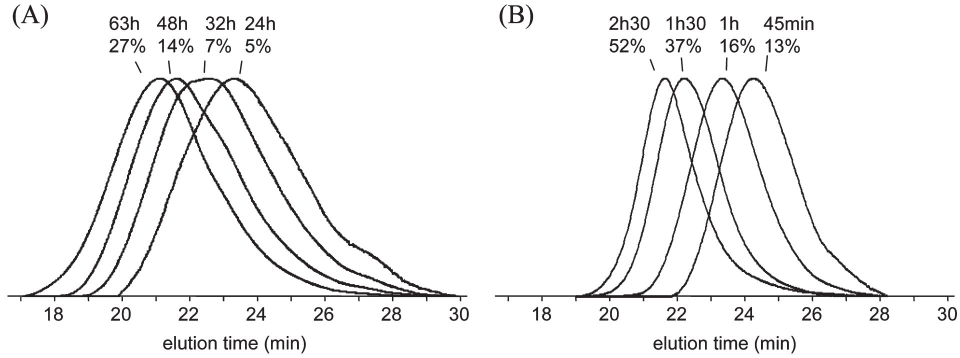

Figure 5. SEC chromatograms with related polymerization time and total conversion for the copolymerization of *n*BA and VAc initiated by the LPO/Co(acac)$_2$ redox system at 0 °C (A) and 30 °C (B). Conditions: [*n*BA]/[VAc]/ [Co(acac)$_2$]/[LPO] = 80/80/3/1.

we compared the ability of the V-70/Co(acac)$_2$ system and that of **5** to initiate and control the copolymerization of *n*BA with VAc (Table 1). For sake of comparison, the reference experiment (i.e., initiation by V-70 in the presence of Co-(acac)$_2$ at 30 °C) was repeated in this work with *n*BA/VAc = 50/50 (Table 1, entry 1). When initiated at the same temperature by the alkylcobalt(III) adduct, the polymerization proceeded rapidly and termination reactions occurred after 10 min (Table 1, entry 2). Indeed, the monomer conversion and the molecular weight of the copolymer did not increase further after this period of time. The temperature, known to have a critical effect on the carbon−cobalt bond cleavage,[35] was then lowered to 0 °C (Table 1, entry 3). As expected, the polymerization was slower, but the molecular weight decreased with time. This might be explained by the formation of low molecular weight chains during the whole polymerization process due to a slow initiation by **5** compared to the propagation of *n*BA at 0 °C.

Therefore, experimental conditions had to be adjusted in order to balance the high propagation rate of *n*BA with the high stability of the VAc-terminated initiator at 0 °C. It was recently reported that the presence of DMSO in the polymerization medium of acrylonitrile initiated by **5** at 0 °C could weaken the VAc−Co(acac)$_2$ bond through axial complexation of the cobalt complex.[30] Such an adjustment of the cobalt complex reactivity upon addition of ligands enabled a fast initiation of the AN polymerization without affecting the propagation rate, which resulted in the formation of well-defined PAN. Therefore, adding DMSO in the *n*BA/VAc polymerization medium appeared as a promising strategy to speed up the initiation by the alkylcobalt(III) adduct at 0 °C (Table 2, entry 1). However, the absence of any evolution of M_n vs conversion and the relatively high M_w/M_n values indicated the absence of control in these conditions.

Another parameter which had never been investigated before is the use of additional Co(acac)$_2$ for the copolymerization initiated by complex **5**. As the C−Co(acac)$_2$ bond is very weak in the case of acrylates, adding some control agent should shift the control equilibrium toward the dormant species and enhance the control. This approach is similar to that consisting in adding a slight excess of free nitroxide in some alkoxyamine-initiated NMPs of acrylates in order to decrease their polymerization rate.[4,36,37] The copolymerization of *n*BA with VAc was first conducted at 0 °C in presence of 0.3 equiv of complex **4** with respect to **5** (Table 2, entry 2). As expected, the polymerization was much slower than the same experiment performed in the absence of additional Co(acac)$_2$ (Table 1, entry 3). Although the molecular weight distribution was narrower, the chromatograms (not shown) were bimodal. Finally, by raising the temperature to 30 °C with the same [**4**]/[**5**] ratio (Table 2, entry 3), the copolymerization was nicely controlled as assessed by the molar masses that increased regularly with conversion (Figure 2) and by the polydispersity that remained below 1.2 even at high monomer conversion. It is noteworthy that these polydispersity indices are the lowest ever obtained for this type of copolymerization.

Figure 3A displays the semilogarithmic kinetic plot for the copolymerizations initiated either by V-70 or **5** in the presence of Co(acac)$_2$ at 30 °C. The initiation by V-70 is associated with a several-hour induction period corresponding to the conversion of Co(acac)$_2$ into alkylcobalt(III) derivatives. When initiation by the preformed alkylcobalt(III) compound **5** was concerned, the induction period expectedly disappeared. Regarding the macromolecular parameters (Figure 3B), the copolymerization initiated by **5** appeared better controlled. Indeed, although the experimental molecular weights increased with total conversion in both cases, the molar masses were about 2 times smaller for the copolymer initiated with compound **5** compared to that initiated by V-70 and were clearly closer to the theoretical values (calculated according to the [monomer]/[Co(acac)$_2$] ratio in the case of the V-70/Co(acac)$_2$ system[20] and to the [monomer]/[**5**] ratio when **5** is used to control the polymerization[26,30]). These results underline that the preformed alkylcobalt(III) adduct **5** has a higher initiation efficiency ratio than V-70, in accordance with similar observations drawn for the CMRP of AN.[30] In order to quantify the efficiency ratio, the absolute molecular weight ($M_{n,abs}$) of the last sample (Table 2, entry 3 at 23 h) was determined by SEC equipped with a multiangle laser light scattering (MALLS) detector ($M_{n,abs}$ = 35 100 g/mol; M_w/M_n = 1.06; d*n*/d*c* = 0.0176 mL/g). The initiation efficiency ($f = M_{n,th}/M_{n,abs}$) of the alkylcobalt(III) adduct in these conditions was estimated as 0.4.

From these results, it appears that an optimal control of the *n*BA/VAc copolymerization mediated by Co(acac)$_2$ requires to slow down the *n*BA polymerization compared to the initiation that has to be fast. Another way to rapidly generate radicals is to use redox initiating systems, which can operate at low temperature.[38] Recently, our group developed a redox initiating system for the CMRP of VAc in order to circumvent V-70, which requires transportation at −20 °C.[39] In the basic procedure, lauroyl peroxide (LPO) was used as oxidant with Co(acac)$_2$ acting as both reducing and control agent. Although the initiation at 30 °C suffered from a low efficiency ($0.1 < f < 0.2$), the polymerization was controlled, and the resulting PVAc had a reasonably low polydispersity (M_w/M_n = 1.3).[39] The LPO/Co(acac)$_2$ redox initiating system most probably proceeds similarly to conventional redox systems,[38] since diacyl peroxides (e.g., LPO) are known to initiate radical polymerizations after reaction with various types of reducing agents, such as Co(II) salts.[40−42]

This CMRP redox system was thus investigated for the controlled polymerization of acrylates. At first, a mixture of *n*BA and VAc (50/50) was polymerized from LPO in presence of Co(acac)$_2$ ([LPO]/[Co(acac)$_2$] = 1/3) at 0 °C. The cobalt complex was used in excess as it is assumed to take part in three main processes, namely (i) generation of the initiating radicals by reaction with LPO, (ii) trapping of the propagating radicals leading to the dormant species, and (iii) adjustment of the control equilibrium toward the dormant species. Similarly to the CMRP of VAc by this redox system, an induction period (ca. 20 h, see circles in Figure 4A) was observed and is attributed to the time required for radicals to react with the cobalt(II) complex and form the alkylcobalt(III) species *in situ*. The subsequent copolymerization was characterized by a regular increase of the molecular weight over conversion (Figure 4B, circles). Nevertheless, the molecular weight distribution remained in the 1.7−2.1 range due to a tailing at the low molecular weight side of the SEC chromatogram (Figure 5A). This tailing might reasonably result from some terminations occurring during the polymerization and/or from a slow and continuous initiation at 0 °C by the VAc-terminated alkylcobalt(III) species formed during the induction period. In order to boost the initiation, the temperature was therefore raised to 30 °C. Under these conditions, not only did the copolymerization proceed much faster than at 0 °C (Figure 4A, triangles) but also in a better controlled manner. Indeed, M_n increased linearly with the total conversion while the polydispersities remained in the 1.2−1.3 range (Figure 4B, triangles). Figure 5B also shows that the SEC chromatograms remained symmetrical during the whole polymerization process and clearly shifted toward higher molecular weights. Noticeably, the molecular weights remained higher than expected. (The theoretical M_n was calculated by the [*n*BA]/[LPO] ratio since Co(acac)$_2$ is used in 3-fold excess compared to LPO. The number of controlled chains can therefore not exceed the amount of radicals generated by LPO.) The initiation efficiency was quantified as f = 0.05 after determination of the absolute molecular weight of the last sample by SEC-MALLS ($M_{n,abs}$ = 181 700 g/mol; M_w/M_n = 1.16; d*n*/d*c* = 0.0218 mL/g). This value of f is slightly smaller than observed for the VAc polymerization using this redox initiating system ($0.1 < f < 0.2$).[39]

Homopolymerization of *n*BA Mediated by Co(acac)$_2$. The attempt to polymerize *n*BA from V-70 in presence of Co(acac)$_2$ resulted in a rapid gel formation.[31] The alkylcobalt(III) adduct **5**, which improved the control of the *n*BA/VAc copolymerization, was therefore tested for the

Table 3. Effect of Temperature and $Co(acac)_2$ on the Homopolymerization of *n*BA Initiated by the Alkylcobalt(III) Adduct 5[a]

entry	T (°C)	$[Co(acac)_2]/[\mathbf{5}]$	time	conv (%)	$M_{n,abs}$[b] (g/mol)	$M_{n,th}$[c] (g/mol)	M_w/M_n
1	30		1 min	76	42 300	6 200	3.90
2	30	10/1	10 min	81	29 700	20 000	2.00
3	0		10 min	80	22 500	19 700	6.68
4	0	1/1	4 h	17	47 800	4 300	1.30
			6 h	32	65 600	7 900	1.33
			8 h	45	86 700	11 100	1.26
			21 h	94	143 900	23 100	1.25
5	0	10/1	7 h	33	66 700	8 100	1.37

[a] Conditions: [*n*BA]/[**5**] = 192/1. [b] $M_{n,abs}$ determined by SEC in THF with a PS calibration and corrected with the Mark−Houwink parameters for PS and P*n*BA. [c] $M_{n,th}$ calculated according to the [*n*BA]/[**5**] ratio and conversion.

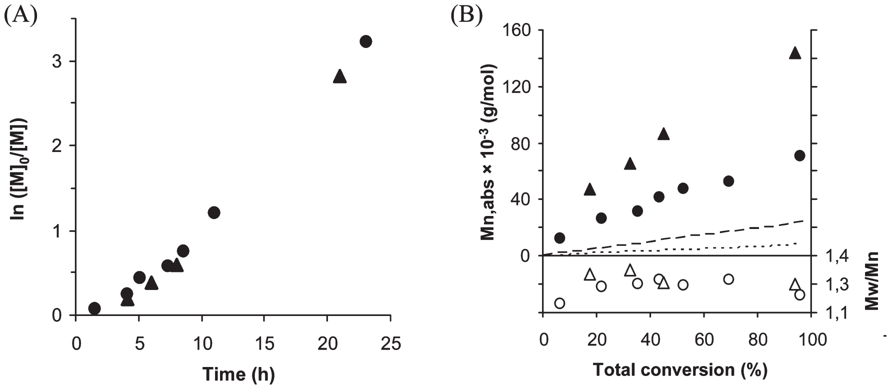

Figure 6. Homopolymerization of *n*BA initiated by the alkylcobalt(III) adduct **5** in presence of additional $Co(acac)_2$ at 0 °C. Triangles; $[nBA]/[Co(acac)_2]/[\mathbf{5}]$ = 192/1/1; Table 3, entry 4. Circles; $[nBA]/[Co(acac)_2]/[\mathbf{5}]$ = 64/1/1. (A) Semilogarithmic kinetic plot. (B) Evolution of $M_{n,abs}$ and M_w/M_n as a function of the total conversion. Theoretical molecular weights $M_{n,th}$ are represented by the dashed and dotted lines for DP_{th} = 192 and 64, respectively.

homopolymerization of *n*BA, and again, other critical parameters were tuned for optimization (Table 3).

At first, the bulk CMRP of *n*BA was carried out from compound **5** at 30 °C without additives as a reference experiment (Table 3, entry 1). As expected, the polymerization was highly exothermic and uncontrolled, even when a 10-fold excess of $Co(acac)_2$ relative to the initiator was added in order to tentatively decrease the polymerization rate (Table 3, entry 2). The polymerization was therefore carried out at 0 °C without additives (Table 3, entry 3) but presented a similar behavior. The addition of 1 equiv of $Co(acac)_2$ with respect to **5** at the same temperature was then considered (Table 3, entry 4). For the first time, the homopolymerization of *n*BA was nicely controlled. Indeed, the semilogarithmic kinetic plot was linear, in line with a constant concentration of active species in the polymerization medium (Figure 6A, triangles). Also, the absolute molecular weight increased linearly with the *n*BA conversion and the polydispersity remained in the 1.20−1.35 range up to high monomer conversion (Figure 6B, triangles). This first control ever observed for the CMRP of *n*BA mediated by $Co(acac)_2$ is best illustrated by the shift of the monomodal GPC trace along the polymerization (Figure 7). The low molecular weight part observed on the SEC chromatograms might reasonably result from some slow initiation at 0 °C, as it will be explained later. An additional evidence for control lies in the dependence of the molecular weight against the initial [*n*BA]/[initiator] ratio. As illustrated in Figure 6A,B (circles), the molar masses decreased with the [*n*BA]/[initiator] ratio without significantly affecting the polymerization rates or the polydispersity. Poly(*n*-butyl acrylate) with molecular weight as high as 150 000 g/mol and low polydispersity (M_w/M_n = 1.25) could be obtained by this process.

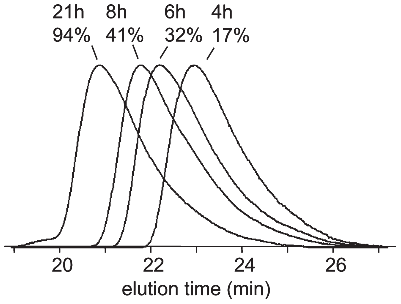

Figure 7. SEC chromatograms with related polymerization time and conversion for the homopolymerization of *n*BA initiated by the alkylcobalt(III) adduct **5** in presence of additional $Co(acac)_2$ at 0 °C. Conditions: $[nBA]/[Co(acac)_2]/[\mathbf{5}]$ = 192/1/1; Table 3, entry 4.

A closer look at the molecular weights points out a marked discrepancy between theoretical and experimental M_n (f = 0.16 at 94% conversion). When the amount of $Co(acac)_2$ was increased from 1 to 10 equiv compared to the initiator **5** (Table 3, entries 4 and 5), the rate of polymerization was similar, and no further increase in the initiator efficiency was observed in these experimental conditions, certainly because $Co(acac)_2$ was already not completely soluble when used in 1 equiv excess. This initiation efficiency for the *n*BA homopolymerization carried out by the alkylcobalt(III) complex is lower compared to that one observed for the VAc homopolymerization ($f \sim 1$) and for the VAc/*n*BA copolymerizations ($f \sim 0.4$) implemented by the same initiator. Significant amounts of initiator are thus lost at the early stages of the polymerization and/or remain dormant in these conditions. The persistent radical effect[43,44] might account for some initiator deactivation but could not reasonably justify that 85% of the alkylcobalt(III) complex **5** are lost at the early stages of the polymerization. We therefore believe that main part of **5** remains dormant in these conditions. In order to confirm this hypothesis, we investigated a polymerization initiation from this hypothetical dormant initiator **5** accumulated in P*n*BA. For that purpose, a well-defined P*n*BA-Co(acac)$_2$ was thus prepared according to our optimal *n*BA polymerization conditions at 0 °C (same conditions as for Table 3, entry 4). After 3 h of polymerization, VAc was added to the reaction medium without removing residual *n*BA in order to reach a [*n*BA]/[VAc] ratio around 1. The temperature was then raised to 30 °C in order to initiate the copolymerization from dormant **5** (that should be now active at this temperature) but also from the P*n*BA-Co(acac)$_2$ chains. The SEC peak associated with P*n*BA-Co(acac)$_2$ (Figure 8a) was shifted toward the higher molecular weight side, in agreement with the chain extension, but remained clearly the minor polymer population. Importantly, new chains were initiated with a molecular weight lower than that of the P*n*BA-Co(acac)$_2$ macroinitiator and shifted with the monomer conversion toward the higher molecular weight side, in agreement with a controlled growth of these chains (Figure 8b−e). This new major population was attributed to novel *n*BA/VAc copolymers initiated from **5** that was activated at 30 °C. Since about 85% of **5** did not contribute to the *n*BA polymerization at 0 °C, when the polymerization medium was heated at 30 °C, the main part of the polymer formed was therefore initiated from this residual initiator. It explains why the amount of P*n*BA-*b*-P(*n*BA-*co*-VAc) copolymer initiated from P*n*BA-Co(acac)$_2$ was very low compared to P*n*BA-*co*-PVAc initiated from **5**. These results unambiguously demonstrate that a non-negligible amount of the alkylcobalt(III) initiator **5** remained dormant during the *n*BA polymerization at 0 °C in the presence of a Co(acac)$_2$ excess. This observation is certainly the result of the important difference of C−Co bond stability in the initiator **5** and in the growing P*n*BuA-Co(acac)$_2$ chains. At 0 °C in the presence of 1 equiv of Co(acac)$_2$ compared to **5**, the C−Co bond in **5** is slowly cleaved while *n*BA rapidly polymerizes once initiating radicals are produced due to the weakness of the C−Co bond at the growing P*n*BA chains. The slow tailing at the low molecular weight side observed on the SEC chromatograms (Figure 7) might be the result of some slow initiation from this alkylcobalt(III) initiator.

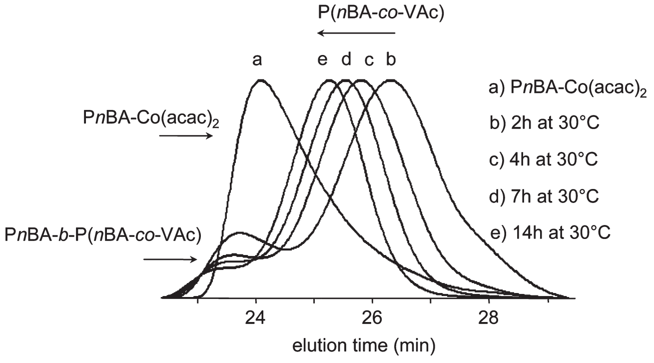

Figure 8. SEC chromatograms with related polymerization time for (a) P*n*BA-Co(acac)$_2$ prepared at 0 °C (conditions: [*n*BA]/[Co(acac)$_2$]/[**5**] = 192/1/1 at 0 °C for 3 h, 10% conversion; $M_{n,abs}$ = 35 300 g/mol; M_w/M_n = 1.30) and for (b−e) the polymerization medium after addition of VAc and heating at 30 °C (conditions: [*n*BA]/[VAc] = 1/1 at 30 °C).

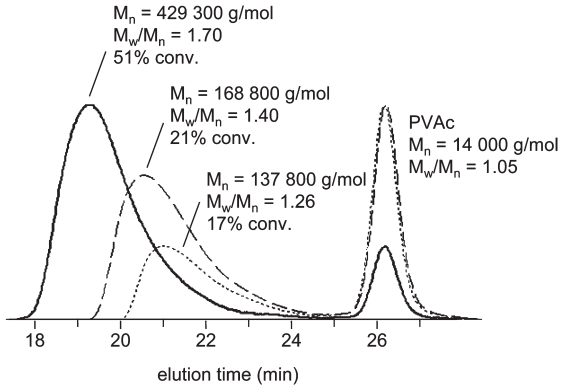

Figure 9. SEC chromatograms for the block copolymerization of *n*BA initiated by a PVAc macroinitiator. Conditions for the preparation of the macroinitiator: [VAc]/[**5**] = 560/1 for 4 h at 40 °C, 25% conversion. Conditions for the block copolymerization: [*n*BA]/[Co(acac)$_2$]/[PVAc-Co] = 723/1/1 at 0 °C.

Since a high proportion of the initiator **5** remained dormant while P*n*BA chains were growing at 0 °C, a similar problem was expected for the block copolymerization experiment, i.e., when a PVAc-Co(acac)$_2$ was used to initiate the *n*BA polymerization at 0 °C in the presence of Co(acac)$_2$ ([PVAc-Co(acac)$_2$]/[Co(acac)$_2$] = 1/1). Figure 9 clearly evidences the formation of the PVAc-*b*-P*n*BA block copolymer with a P*n*BA block that was growing with the monomer conversion, in agreement with a controlled process. As expected, some residual PVAc did not initiate the *n*BA polymerization, in line with the observations made when **5** was used instead of PVAc-Co(acac)$_2$ and with the above conclusions.

Eventually, we implemented the LPO/Co(acac)$_2$ redox initiating system to the homopolymerization of *n*BA in order to take benefit of its practical advantages. When carried out

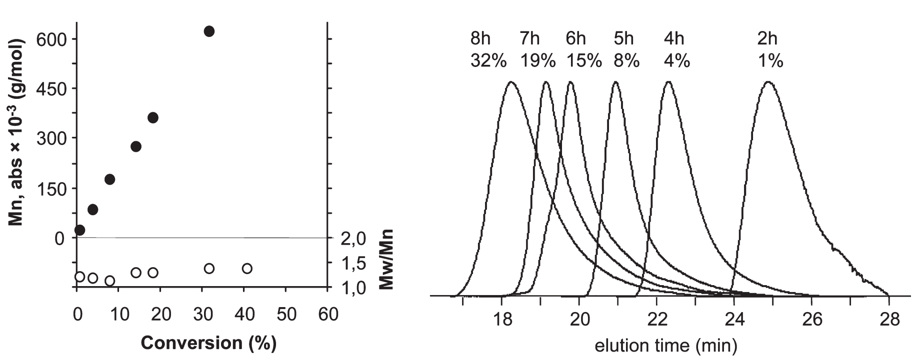

Figure 10. Homopolymerization of *n*BA initiated by the LPO/Co(acac)$_2$ at 0 °C. (A) Evolution of M_n and M_w/M_n as a function of conversion. (B) SEC chromatograms with related polymerization time and conversion. Conditions: [*n*BA]/[Co(acac)$_2$]/[LPO] = 131/3/1.

at 30 °C from an [LPO]/[Co(acac)$_2$] = 1/3 mixture, the polymerization became very exothermic after 10 min (data not shown). It was then carried out at 0 °C (Figure 10). Similarly to the case of VAc, an induction period (3 h) emerged and corresponds to the time required for radicals to react with the cobalt(II) complex and *in situ* form *n*BA-derivated alkylcobalt(III) species. The subsequent polymerization was characterized by a regular increase of the molecular weight up to 40% conversion (Figure 10A). Further sampling was prevented by the high viscosity of the medium, as a result of the very high molecular weight of the P*n*BA ($M_{n,\,abs}$ = 620 000 g/mol). Figure 10B clearly evidence that the SEC chromatograms are relatively narrow (M_w/M_n = 1.36) and shift toward higher M_n upon monomer conversion, as expected for a controlled process. Regarding the initiation efficiency, f was even lower for the redox (f = 0.01) than for the alkylcobalt(III)-initiated experiment ($0.1 < f < 0.2$). A similar tendency was already observed for the CMRP of VAc ($0.1 < f < 0.2$ and $f \sim 1$ for redox[39] and alkylcobalt(III)[26] initiations, respectively) and was explained by the dual role of the cobalt which acts as both controlling and reducing agents for the redox initiation.

Conclusion

In summary, we investigated the bis(acetylacetonato)cobalt(II)-mediated radical polymerization of *n*-butyl acrylate, which was up to now assumed elusive. First, we assessed the ability of an alkylcobalt(III) adduct and that of the LPO/Co(acac)$_2$ redox system to initiate and control the copolymerization of *n*BA with VAc, in place of the previously reported V-70/Co(acac)$_2$ pair. A key parameter for controlling the acrylate polymerization with Co(acac)$_2$ was the presence of a sufficient excess of free cobalt complex compared to the propagating species. The excess of controlling agent was necessary to ensure an efficient trapping of the poly(acrylate) chains because of the weakness of the P*n*BA−Co(acac)$_2$ bond. Typically, the best results for the *n*BA/VAc (50/50) copolymerizations were obtained when the reaction was initiated by the alkylcobalt(III) adduct at 30 °C in presence of additional Co(acac)$_2$ (0.3 equiv compared to the CMRP initiator). In that case, experimental molar masses were closer to the theoretical values and polydispersity lower compared to the ones obtained with the former V-70/Co(acac)$_2$ system. Importantly, Co(acac)$_2$ also revealed as an efficient mediator for the homopolymerization of acrylate for the first time. Indeed, the newly investigated initiating systems, namely the alkylcobalt(III) adduct and LPO/Co(acac)$_2$, succeeded to produce P*n*BA in a controlled manner. For example, under optimized conditions, well-defined homopolyacrylates with molar masses up to 150 000 g/mol and polydispersity indices around 1.25 were obtained using the alkylcobalt(III) adduct, while molar masses around 600 000 g/mol and polydispersity of 1.36 were reached with the redox initiating system. Solving the problem of bis(acetylacetonato)-cobalt(II)-mediated polymerization of acrylates makes Co(acac)$_2$ a versatile mediator for both unconjugated (VAc, *N*VP) and conjugated (AN, *n*BA) vinyl monomers, which could broaden the synthetic possibilities in macromolecular engineering based on CMRP.

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