Cobalt-Mediated Radical Polymerization (CMRP) of Vinyl Acetate Initiated by Redox Systems: Toward the Scale-Up of CMRP

Rayna Bryaskova, Christophe Detrembleur, Antoine Debuigne, and Robert Jérôme*

Center for Education and Research on Macromolecules (CERM), University of Liege, Sart-Tilman B6a, 4000 liège, Belgium

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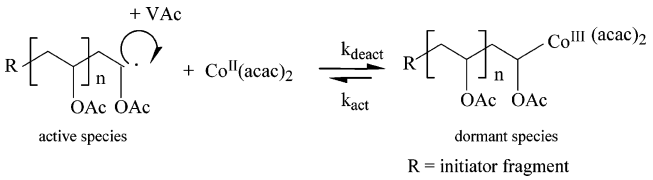
ABSTRACT: A redox initiating system was developed in order to bypass 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V70) as the initiator of the cobalt-mediated radical polymerization (CMRP) of vinyl acetate (VAc) in the presence of cobalt(II) acetylacetonate ($Co(acac)_2$). It is indeed a problem to stock up with V70 because of needed storage at −20 °C during transportation. This paper reports on the controlled CMRP of VAc initiated by ascorbic acid combined with either lauroyl peroxide or benzoyl peroxide at 30 °C. Substitution of citric acid for ascorbic acid results in faster polymerization whereas the polymerization control is maintained. All these improvements facilitate the implementation of the vinyl acetate CMRP and open the door to the scale-up of the process.

Introduction

In the recent past, substantial progress was reported in controlled radical polymerization and contributed to the synthesis of end-functional polymers. Although the radical polymerization of a variety of vinylic monomers is easily mediated by different controlling agents,[1−5] key monomers examplified by vinyl acetate (VAc) are reluctant to control. Special attention has been paid to VAc because the polymer finds many applications, including adhesives, paints, and additives to pharmaceuticals. Moreover, the water-soluble poly(vinyl alcohol) (PVOH) is made commercially available by hydrolysis of poly(vinyl acetate) (PVAc). The very high reactivity of the propagating radicals makes the control of the radical polymerization of VAc challenging. The first attempt to regulate this radical polymerization was based on a ternary iBu$_3$Al/2,2′-bipyridine/TEMPO (TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy) initiator,[6] which proved to be complex and poorly reproducible.[7] Another ternary system, CCl_4/Fe(OAc)$_2$/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine, was also tested, in which CCl_4 has a dual role of initiator and chain-transfer agent. PVAc with a relatively high polydispersity (M_w/M_n = 1.8−2.0) was then collected.[8] Until now, the best control was achieved by RAFT with dithiocarbamate and xanthate agents[9−12] and by degenerative chain transfer in the presence of iodides.[13] Combination of an iodo compound with dicarbonylcyclopentadienyliron dimer $[Fe(Cp)(CO)_2]_2$ was also effective in initiating the controlled radical polymerization of VAc.[14] Very recently, bulk radical polymerization of VAc was successfully controlled by cobalt-mediated radical polymerization (CMRP) using 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) as an initiator in the presence of cobalt acetylacetonate ($Co(acac)_2$) as a regulating agent.[15] In this method, $Co(acac)_2$ reacts reversibly with the growing poly(vinyl acetate) chains, which are accordingly involved in an equilibrium between active and dormant species (Scheme 1).

As a result of the CMRP mechanism, all the chains are end-capped by a $Co(acac)_2$ moiety. Moreover, poly(vinyl acetate) with high molar mass and low polydispersity can be prepared under quite different conditions, i.e., in the bulk,[15] in aqueous suspension,[16] and in miniemulsion.[17] Since then, Matyjasewski et al. observed that the radical copolymerization of VAc and *n*-butyl acrylate was also controlled by $Co(acac)_2$.[18] This CMRP process is however effective when the initiator is V-70, which is difficult to stock up with because transportation at −20 °C is required. This paper aims at reporting for the first time on the initiation of the CMRP of VAc by redox systems in the presence of $Co(acac)_2$. These redox initiators consist of (i) lauroyl peroxide (LPO) or benzoyl peroxide (BPO) as oxidant and $Co(acac)_2$ as a reducing agent and (ii) LPO or BPO as oxidant and ascorbic acid (AA) or citric acid (CA) as reducing agent in the presence of $Co(acac)_2$.

Scheme 1



Experimental Section

Materials. Vinyl acetate (>99%, Aldrich) was dried over calcium hydride, degassed by several freeze−thawing cycles before being distilled under reduced pressure, and stored under argon. Lauroyl peroxide (~97%, Fluka), benzoyl peroxide (>97%, Fluka), ascorbic acid (UCb), citric acid (>99.5, Merck), and cobalt(II) acetylacetonate (>98%, Merck) were used as received.

Characterizations. Size exclusion chromatography (SEC) was carried out in tetrahydrofuran (THF) (flow rate: 1 mL min^{-1}) at 40 °C with a Waters 600 liquid chromatograph equipped with a 410 refractive index detector and Styragel HR columns (5 μm particle size; HR1, molecular weight range = 100−5000; HR2, molecular weight range = 500−20 000; HR4, molecular weight range = 5000−600 000). Polystyrene standards were used for calibration. Inductively coupled plasma (ICP) atomic emission spectroscopy (Perkin-Elmer) was carried out with a charge-coupled device (CCD) and standard cobalt solutions for calibration. Samples were prepared by dissolving 20 mg of poly(vinyl acetate) in 1 mL of HNO_3 (65%) at 60 °C for 2 h. These solutions were diluted with 9 mL of bidistilled water at room temperature.

General Procedure for the Bulk Radical Polymerization of Vinyl Acetate Using the LPO (BPO)/Co(acac)$_2$ Redox System.

* Corresponding author: Fax 0032 43663497; Tel 0032 43663565; e-mail:rjerome@ulg.ac.be.

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Table 1. Bulk Radical Polymerization of Vinyl Acetate Initiated by the LPO/Co(acac)$_2$ Redox System at 30 °C

entry	[VAc]/[LPO]	[LPO]/[Co(acac)$_2$]	time (h)	conv (%)	$M_{n,SEC}$[a] (g/mol)	M_w/M_n
1	255/1	1/1	3	5.0	12 500	1.20
			7	32.5	33 500	1.80
			9	44.0	43 500	1.70
			11	67.0	60 500	1.80
2	255/1	1/1.3	3	5.0	8 500	1.25
			7	31.0	37 000	1.30
			9	42.0	43 000	1.30
			10	56.0	53 000	1.30
3	255/1	1/1.5	3	4.5	6 500	1.20
			7	29.5	28 500	1.60
			9	40.0	33 500	1.65
			23	83.0	48 000	2.60
4	255/1	1/2	5	6.5	7 000	1.35
			7	15.0	12 500	1.45
			9	25	20 500	1.50
			12	42.5	28 000	1.80

[a] Determined by size-exclusion chromatography (SEC) with PS calibration.

Different amounts of Co(acac)$_2$ (0.0437 g, 1.7×10^{-4} mol; 0.0568 g, 2.2×10^{-4} mol; 0.0655 g, 2.5×10^{-4} mol; and 0.087 g, 3.4×10^{-4} mol) mixed with LPO (0.069 g, 1.7×10^{-4} mol) or BPO (0.042 g, 1.7×10^{-4} mol) were added into a glass flask (30 mL) and degassed by three vacuum−argon cycles. Degassed vinyl acetate (4 mL, 430×10^{-4} mol) was then added to each flask. VAc was polymerized at 30 °C. Actually, no polymerization occurred for several hours, followed by a substantial increase in viscosity. Samples were withdrawn from the polymerization medium, and the vinyl acetate conversion was determined by weighing the polymer collected upon removal of the unreacted monomer under reduced pressure at room temperature. The results are reported in Table 1 and Figure 1A for the LPO/Co(acac)$_2$ system and in Table 2 and Figure 1B for the BPO/Co(acac)$_2$ system.

General Procedure for the Bulk Radical Polymerization of Vinyl Acetate Using the LPO (BPO)/AA Redox System in the Presence of Co(acac)$_2$. The same recipe as above was used, except that ascorbic acid (0.0437 g,1.7×10^{-4} mol) was added to the Co(acac)$_2$ and the peroxide. The results are reported in Figures 2A and 3A for the LPO/AA/Co(acac)$_2$ system and in Figures 2B and 3B for the BPO/AA/Co(acac)$_2$ system.

Procedure for the Removal of the Cobalt from the Polymer. Co(acac)$_2$ (0.142 g, 0.55×10^{-3} mol), LPO (0.1725 g, 0.425×10^{-3} mol), and ascorbic acid (0.109 g, 0.425×10^{-3} mol) were added into a glass flask (100 mL) and degassed by three vacuum−argon cycles. Degassed vinyl acetate (10 mL, 107×10^{-3} mol) was then added to each flask. VAc was polymerized at 30 °C for 16 h. A sample was picked out (21% conversion) and precipitated twice in heptane, dried under vacuum at 60 °C, and analyzed by ICP (17 500 ppm of Co). A solution of TEMPO (0.6875 g of TEMPO (4.4×10^{-3} mol) in 3 mL of degassed toluene) was then added to the flask, and the medium was stirred at 30 °C for 24 h. After this period of time, the polymer was diluted by toluene and filtrated on silica before being precipitated twice in heptane and dried under vacuum at 60 °C. The polymer was analyzed by SEC (M_n = 32 800; M_w/M_n = 1.05) and by ICP (800 ppm of Co).

General Procedure for the Bulk Radical Polymerization of Vinyl Acetate Using the LPO/CA Redox System in the Presence of Co(acac)$_2$. Dispersion of citric acid (0.0357 g, 1.7×10^{-4} mol) within 4 mL of degassed vinyl acetate (3.74 g, 430×10^{-4} mol) was transferred into a flask containing LPO (0.069 g, 1.7×10^{-4} mol) and Co(acac)$_2$ (0.087 g, 3.4×10^{-4} mol), previously degassed by three vacuum−argon cycles. The mixture was stirred and heated at 30 °C. No polymerization occurred for 2−2.5 h, followed by a substantial increase in viscosity for 30 min. Samples were withdrawn from the polymerization medium, and the vinyl acetate conversion was determined as mentioned above. The results are reported in Table 3, entry 1.

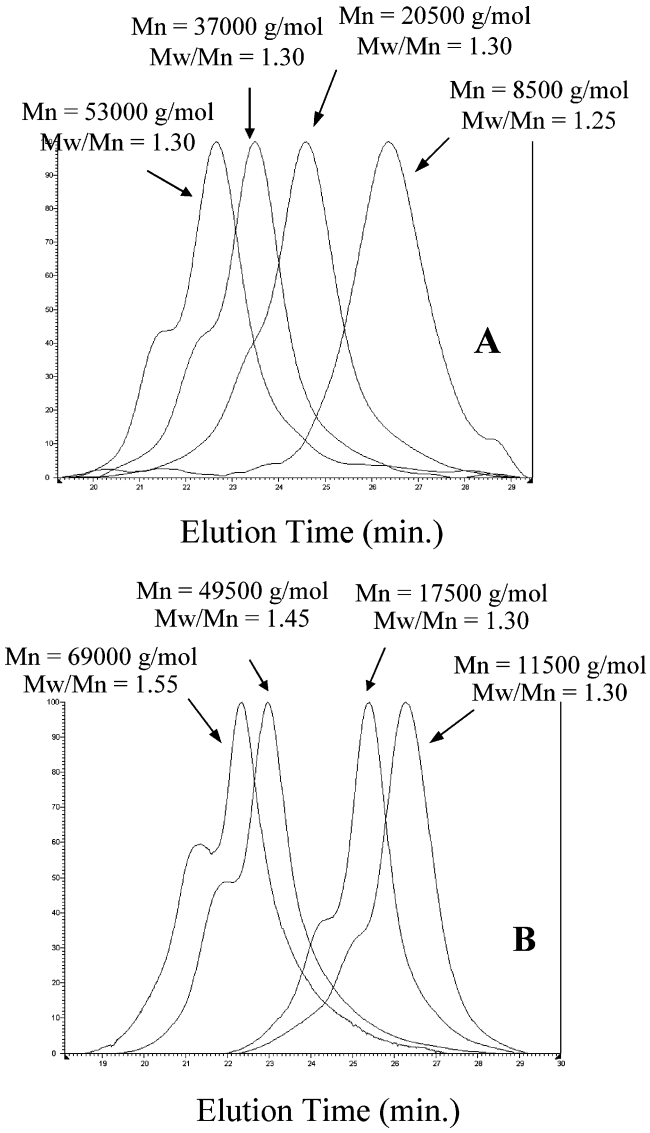

Figure 1. SEC chromatograms for the bulk polymerization of vinyl acetate initiated at 30 °C by (A) lauroyl peroxide (LPO)/Co(acac)$_2$ redox system (Table 1, entry 2) and (B) benzoyl peroxide (BPO)/Co(acac)$_2$ redox (Table 2, entry 2).

Table 2. Bulk Radical Polymerization of Vinyl Acetate Initiated by the BPO/Co(acac)$_2$ Redox System at 30 °C

entry	[VAc]/[BPO]	[BPO]/[Co(acac)$_2$]	time (h)	conv (%)	$M_{n,SEC}$[a] (g/mol)	M_w/M_n
1	255/1	1/1	7	10.5	17 000	1.20
			9	15.6	22 500	1.30
			24	64.2	55 000	1.85
			26	64.8	57 500	1.60
2	255/1	1/1.3	7	7.0	11 500	1.30
			9	12.0	17 500	1.30
			24	23.5	49 500	1.45
			29	79.0	69 000	1.55
3	255/1	1/1.5	9	8.0	11 500	1.35
			24	47.0	35 500	1.75
			26	62.0	36 500	1.85
4	255/1	1/2	5	2.5	3 500	1.15
			9	6.5	9 500	1.15
			26	44.5	32 500	1.65

[a] Determined by size-exclusion chromatography (SEC) with PS calibration.

Synthesis of Poly(vinyl acetate) Macroinitiator End-Capped by a Cobalt Complex Using the LPO/AA Redox System. LPO (0.173 g, 0.4×10^{-3} mol), ascorbic acid (0.075 g, 0.4×10^{-3} mol), and Co(acac)$_2$ (0.165 g, 0.6×10^{-3} mol) were added into a 30 mL

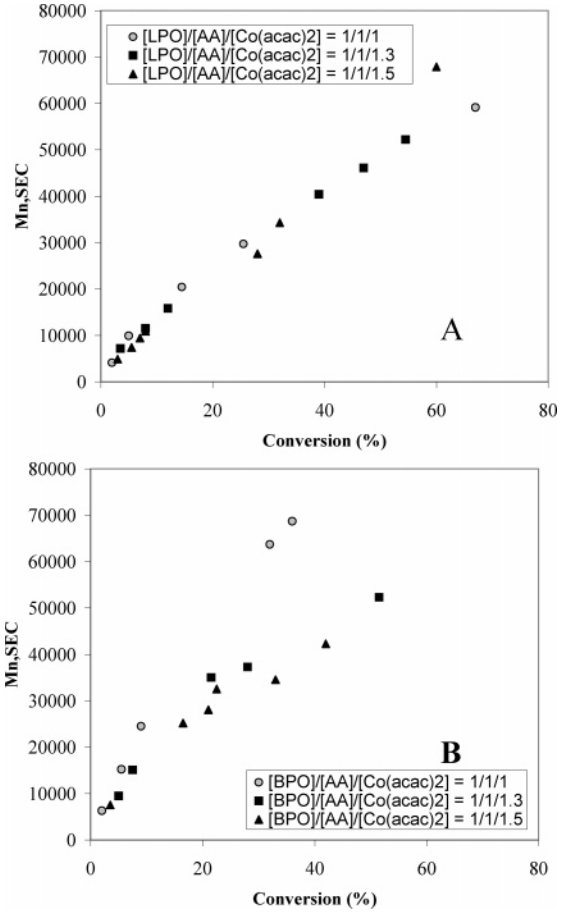

Figure 2. Dependence of the molar mass of poly(vinyl acetate) (PVAc) on the monomer conversion at 30°C for the (A) lauroyl peroxide (LPO)/ascorbic acid (AA)/$Co(acac)_2$ system and (B) benzoyl peroxide (BPO)/ascorbic acid (AA)/$Co(acac)_2$ system.

flask and degassed by three vacuum−argon cycles. Degassed vinyl acetate (10 mL, 108 × 10^{-3} mol) was then added, and VAc polymerization was polymerized at 30 °C for 8 h. The PVAc macroinitiator end-capped by the cobalt complex was collected upon removal of the unreacted monomer under reduced pressure at room temperature (M_n = 8200 g/mol; M_w/M_n = 1.10; ∼10% monomer conversion).

Vinyl Acetate Polymerization Initiated by a Low Molar Mass PVAc Macroinitiator. The poly(vinyl acetate) macroinitiator (0.157 g, 0.2 × 10^{-4} mol) was dissolved in degassed vinyl acetate (2 mL, 217 × 10^{-4} mol) under argon. The dark-brown mixture solution was stirred and heated at 30 °C. After few minutes, a substantial increase in viscosity was observed. Samples were withdrawn from the polymerization medium, and the vinyl acetate conversion was determined as mentioned above. The results are reported in Figure 6.

Results and Discussion

A series of VAc polymerizations were initiated by the LPO-(BPO)/$Co(acac)_2$ redox systems. $Co(acac)_2$ has a dual role. First, it reduces the peroxide with release of lauroyloxy (or benzoyloxy) radicals. Then, it regulates the radical polymerization of VAc if available in a large enough excess. To optimize the amount of $Co(acac)_2$, the peroxide/$Co(acac)_2$ molar ratio was changed from 1/1 to 1/2 by changing the amount of $Co(acac)_2$ at constant concentration of all the other constituents. As a rule, an induction period of time (2−7 h) is observed, which is the time required for the in situ formed radicals to be converted into dormant species by reaction with the cobalt(II) complex left unreacted in the medium (Tables 1 and 2).

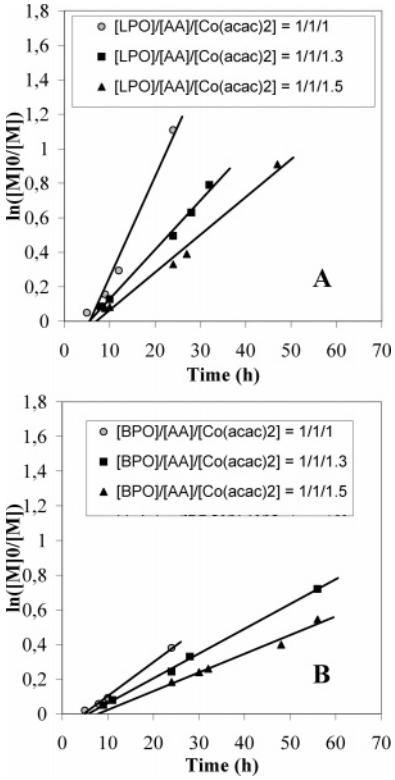

Figure 3. Plots of $\ln([M]_0/[M])$ vs time for the vinyl acetate polymerization at 30 °C initiated by the (A) lauroyl peroxide (LPO)/ascorbic acid (AA)/$Co(acac)_2$ system and (B) benzoyl peroxide (BPO)/ascorbic acid (AA)/$Co(acac)_2$ system.

Table 3. Bulk Radical Polymerization of Vinyl Acetate Initiated by the LPO/CA/$Co(acac)_2$ Redox System at 30 °C

entry	[VAc]/[LPO]	[LPO]/[CA]/[$Co(acac)_2$]	time (h)	conv (%)	$M_{n,SEC}$[a] (g/mol)	M_w/M_n	*f*
1	250/1	1/1/2	2.5	3	2 900	1.15	0.11
			3.0	62	49 000	1.20	0.14
			3.25	79	79 000	1.40	0.11
2	430/1	1/1/2	2.5	14.5	41 500	1.50	0.07
			2.75	31	83 500	1.40	0.07
			3.0	60.5	125 000	1.80	0.09
3	868/1	1/1/2	2.5	16	67 000	1.35	0.09
			2.75	30	109 000	1.30	0.10
			3.0	48.5	154 000	1.55	0.12
4	430/1	1/1/3	4.15	21	38 500	1.35	0.07
			4.25	63.5	90 500	1.25	0.09

[a] Determined by size-exclusion chromatography (SEC) with PS calibration.

Because of reaction with the peroxide, Co^{II} is oxidized into Co^{III} as testified by an intense green color that appears in the reaction medium. When the cobalt complex is used in large excess ($[peroxide]_0/[Co(acac)_2]_0$ = 1/2), the induction period increases and the polymerization rate significantly decreases because it takes more time for a larger amount of $Co(acac)_2$ to be transformed into the dormant species (PVAc−Co(III) complex). Moreover, the induction period of time is shorter when LPO is used (3−4 h, Table 1) rather than BPO (5−7 h, Table 2), which suggests a higher reactivity.

In all the cases, the molar mass of poly(vinyl acetate) increases with the monomer conversion, as listed in Tables 1 and 2. The molar mass distribution, which is relatively narrow at very low monomer conversion (M_w/M_n = 1.2), becomes broader beyond 20% of conversion (Tables 1 and 2). The polydispersity remains however quite narrow when the polymerization is carried out with the LPO/$Co(acac)_2$ system with a 1.3 molar excess of $Co(acac)_2$ with respect to LPO (Table 1,

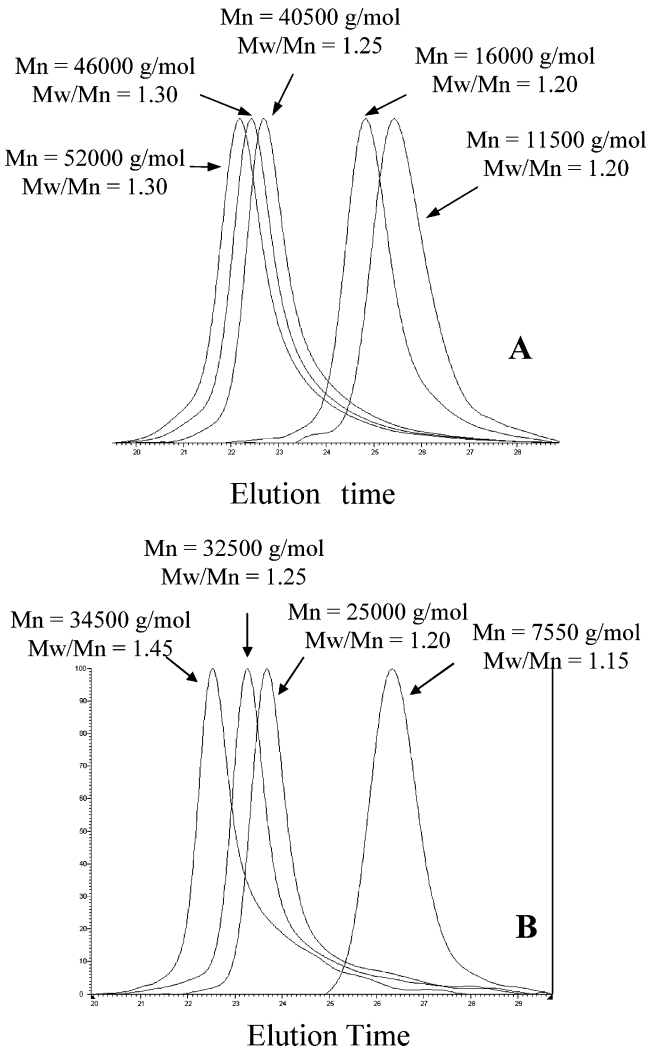

Figure 4. SEC chromatograms for the bulk polymerization of vinyl acetate at 30 °C initiated by the (A) lauroyl peroxide (LPO)/ascorbic acid (AA)/$Co(acac)_2$ system (1/1/1.3) and (B) benzoyl peroxide (BPO)/ ascorbic acid (AA)/$Co(acac)_2$ system (1/1/1.5).

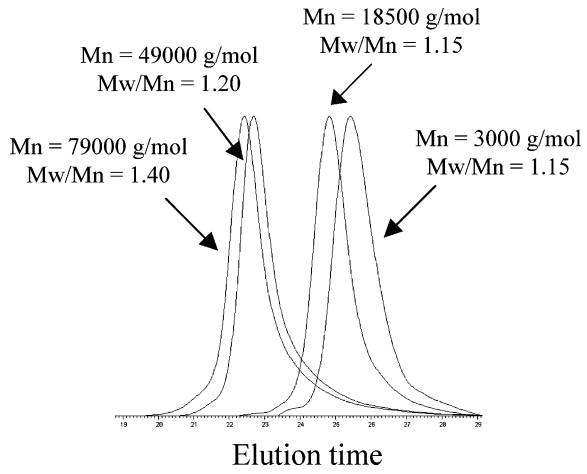

Figure 5. SEC chromatograms for the bulk polymerization of vinyl acetate initiated by the lauroyl peroxide (LPO)/citric acid (CA)/Co-$(acac)_2$ (1/1/2) system at 30 °C.

entry 2). Although the polydispersity is narrow, the SEC chromatograms show a shoulder on the high molar mass side as result of coupling reactions (Figure 1). Indeed, upon deconvolution of the chromatograms into two peaks, the minor chain shows that the chain population has a molar mass which

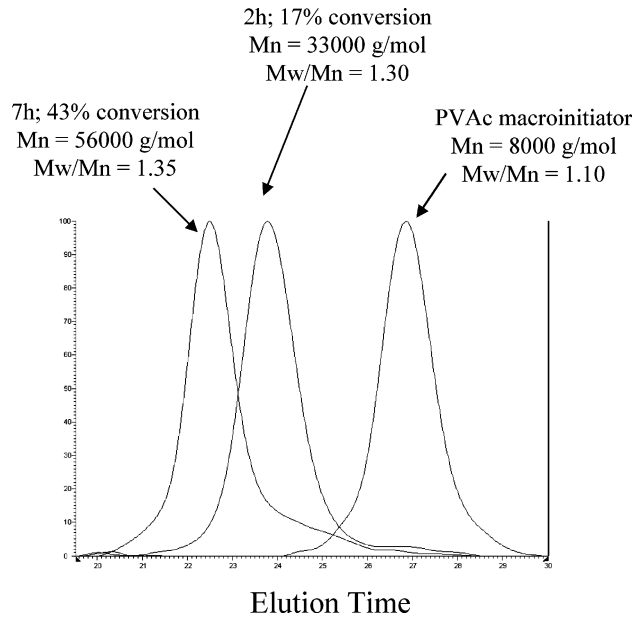

Figure 6. SEC chromatograms for the bulk polymerization of vinyl acetate (VAc) initiated at 30 °C by a poly(vinyl acetate) (PVAc) macroinitiator (M_n = 8200 g/mol; M_w/M_n = 1.10) prepared with the lauroyl peroxide (LPO)/ascorbic acid (AA)/$Co(acac)_2$ redox system [conditions: [VAc]/[PVAc] = 1085; 30 °C].

is twice that one of the main peak. This observation is reported for all the peroxide/$Co(acac)_2$ molar ratios, whatever the peroxide used (LPO or BPO; Figure 1A,B). It must be noted that the ratio of 2 between the molar masses of the two chain populations does not change with the polymerization time, which suggests that the coupling reaction occurs during the polymer recovery rather than all along the polymerization. The underlying mechanism is not understood yet. The polydispersity increases with the amount of $Co(acac)_2$ (peroxide/$Co(acac)_2$ = 1/2), whereas the polymerization rate decreases. The peroxide/Co-$(acac)_2$ redox system with a molar ratio 1/1.3 seems to be optimal despite the shoulder on the SEC chromatogram.

A typical reducing agent was then added to the polymerization medium in order to save the $Co(acac)_2$ complex as a polymerization regulator. Ascorbic acid (AA) was combined with either LPO or BPO in the presence of $Co(acac)_2$, whose concentration was changed. In all the cases, the molar mass (M_n) of PVAc increases quasi-linearly with the monomer conversion (Figure 2). However, experimental M_n's ($M_{n,SEC}$) are much higher than the values predicted ($M_{n,th}$) on the assumption that the cobalt complex is the regulating agent.[15,16] Indeed, the initiation efficiency (f) of this system, calculated from the $M_{n,th}/M_{n,exp}$ ratio, is low ($0.15 \leq f \leq 0.25$ and $0.10 \leq f \leq 0.15$ for the LPO/AA and BPO/AA systems, respectively) compared to polymerization initiated by V70 ($0.85 \leq f \leq 1.0$).[16,17] This observation suggests that part of $Co(acac)_2$ participates to the redox initiation by reducing the peroxide. Interestingly, the molar mass distribution of PVAc initiated by the LPO (BPO)/AA redox system in the presence of $Co(acac)_2$ is narrower compared to the previously discussed LPO (BPO)/$Co(acac)_2$ redox initiating system. The polydispersity remains low ($1.1 \leq M_w/M_n \leq 1.4$) even at higher monomer conversion and relatively high molar mass (50 000−70 000 g/mol), except for the $[LPO]_0/[AA]_0/[Co(acac)_2]_0$ = 1/1/1 system, for which the polydispersity increases with the monomer conversion up to 1.7. The polymerization kinetics is first-order in monomer, as assessed by the linear dependence of $\ln([M]_0/[M])$ vs time (Figure 3), which confirms that irreversible chain termination reactions are quite restricted. Although no important difference in the length of

the induction period is observed for the different peroxide/AA/$Co(acac)_2$ molar ratios, the polymerization rate decreases when the amount of $Co(acac)_2$ is increased (Figure 3), in line with a shift of the dormant/active species equilibrium toward the dormant species (Scheme 1). In contrast to the LPO (BPO)/$Co(acac)_2$ redox system, the color of the medium changes from purple to dark-brown during the induction period when AA is the reducing agent.

When AA is added to $Co(acac)_2$, LPO proves to be more active than BPO because the induction period of time is shorter (4−5 h instead of 5−7 h), the polymerization rate is higher (2−3 times, Figure 3), and the control over the molar mass seems to be better (Figure 2). Compared to polymerization carried out without ascorbic acid (Figure 1A,B), the SEC chromatograms are now monomodal and symmetric, and they are shifted toward higher molar mass upon increasing monomer conversion (Figure 4). Low amounts of dead chains of a low molar mass, however, appear at higher monomer conversion as supported by a tail on the low molar mass side. It must be noted that the polymers were not precipitated before SEC analysis. When the polymers are precipitated in heptane prior to SEC analysis, the polydispersity is ∼1.2 at the end of the polymerization. The tailing on the low molar mass side is slightly more important when BPO is the peroxide.

When ascorbic acid is replaced by citric acid (CA) in the LPO system, the polymerization is very fast after an induction period of 2.5 h, even for a $[LPO]_0/[CA]_0/[Co(acac)_2]_0$ ratio of 1/1/2 (Table 3). Indeed, the molar mass of PVAc increases rapidly with the monomer conversion (Table 3, Figure 5), which is close to 80% after only 3 h with molar mass of 79 000 g/mol and a polydispersity of 1.40. The SEC chromatograms are monomodal and shifted toward higher molar mass with monomer conversion, whereas the polydispersity is relatively narrow (Figure 5). Upon increasing the VAc/LPO molar ratio and keeping the LPO/CA/$Co(acac)_2$ ratio constant, molar mass increases as expected for a controlled process (Table 3, entries 1−3). When the molar ratio $[LPO]_0/[CA]_0/[Co(acac)_2]_0$ is increased to 1/1/3 by increasing the amount of $Co(acac)_2$, the induction period is slightly increased to about 3 h, and the polymerization rate is slightly decreased although it remains much higher than for the LPO/AA/$Co(acac)_2$ system. The polymerization rate is thus much faster when CA is the reducing agent rather than AA, but the initiator efficiency (calculated on the amount of $Co(acac)_2$) still remains low ($f \approx 0.10$). Substitution of citric acid instead of ascorbic acid increases the initiation rate, such that the initiating radicals are formed more rapidly and the length of the induction period is shorter. The effect that the reducing agent (citric acid) has on the polymerization rate might indicate that this compound (and/or the oxidation products) interacts with $Co(acac)_2$ with impact on the position of the active/dormant species equilibrium.

Finally, poly(vinyl acetate) end-capped by the cobalt complex was prepared with the LPO/AA/$Co(acac)_2$ system ($M_{n,SEC}$ = 8200 g/mol, M_w/M_n = 1.10) and used as a macroinitiator for the polymerization of an additional feed of vinyl acetate at 30 °C. The VAc polymerization was resumed, as assessed by the SEC chromatogram of the macroinitiator that shifts toward higher molar mass (Figure 6). This resumption experiment supported that the major part of the macroinitiator remains active after synthesis and initiates the vinyl acetate polymerization. A small tailing on the low molar mass side was observed, which is the signature for some dead chains formed during the synthesis of the PVAc macroinitiator.

Addition of a degassed solution of TEMPO to the VAc polymerization medium results in chain termination and transfer of the cobalt complex from the chain ends to solution.[19] Filtration of this solution through a silica column is thus a very simple and direct way for the polymer to be rid of the metal. For instance, VAc was polymerized by the LPO/AA/$Co(acac)_2$ system (1/1/1.3 molar ratio), and the polymer collected at 21% monomer conversion (M_n = 32 800 g/mol; M_w/M_n = 1.05) contained 17500 ppm of Co, as determined by inductively coupled plasma (ICP). However, after addition of an excess of TEMPO compared to $Co(acac)_2$ (30 °C for 24 h), 95.5% of the cobalt was eliminated after filtration and PVAc precipitation in heptane. This strategy is thus effective in removing most of the cobalt that contaminates PVAc prepared by CMRP with a redox initiator.

Conclusions

Until now, the cobalt-mediated radical polymerization (CMRP) of vinyl acetate[15−17] was effective when the initiator was V-70, whose transportation and thus supplying are an issue because of poor thermal stability. To overcome this limitation, we reported for the first time on the synthesis of well-defined PVAc by CMRP initiated by redox systems in the presence of $Co(acac)_2$. These redox systems consist of (i) lauroyl peroxide (LPO) or benzoyl peroxide (BPO) as oxidant and $Co(acac)_2$with the dual role of reducing agent and control agent and (ii) LPO or BPO as oxidant and ascorbic acid (AA) or citric acid (CA) as reducing agent in the presence of $Co(acac)_2$. Although some control is obtained for the first system (peroxide + $Co(acac)_2$), the SEC chromatograms of PVAc are bimodal, more likely because of coupling reactions during the polymer recovery. When a reducing agent (ascorbic acid) is added to the peroxide/$Co(acac)_2$ system, the control of the VAc polymerization is improved, and the SEC chromatograms remain monomodal. The initiator efficiency ($f = M_{n,th}/M_{n,exp}$) is however low ($0.1 \leq f \leq 0.25$), which suggests that $Co(acac)_2$ also participates in the redox initiation. When ascorbic acid is replaced by citric acid, polymerization is much faster, although the polymerization control is maintained. Clearly, the oxidant/reducing agent pair is crucial for the success of CMRP. The underlying mechanism seems to be very complex and is under current investigation. The potential of these redox initiating systems is now investigated for the synthesis of block copolymers on a large scale of 10−100 g.

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