Controlled Radical Polymerization

Effective Cobalt Mediation of the Radical Polymerization of Vinyl Acetate in Suspension**

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Controlled radical polymerization (CRP)[1] is a common technique for the synthesis of (co)polymers with well-defined molecular parameters (M_n, M_w/M_n), reactive end groups, composition, and architecture. Radical polymerization of a variety of monomers can be controlled by three mechanisms: nitroxide-mediated polymerization (NMP),[2] atom-transfer radical polymerization (ATRP),[3] and radical addition/fragmentation chain-transfer (RAFT).[4] However, control of the radical polymerization of vinyl acetate remains a concern, even though substantial progress by degenerative chain transfer,[5] ATRP,[6,7] and RAFT based on xanthates[8,9] and dithiocarbamates[10] has been reported. Additional effort needs to be devoted to this issue, because vinyl acetate can be polymerized only by a radical process and poly(vinyl acetate) (PVAc) is widely used, for example, as precursor of the water-soluble and otherwise inaccessible poly(vinyl alcohol).[11] Therefore, molecular engineering of PVAc and development of suitable techniques are of utmost importance for the production of novel polymeric materials.

Controlled radical polymerization is most often carried out in bulk or in solution in organic solvents. However, the use of water as dispersion medium may have a number of advantages, including better control of heat transfer, absence of volatile organic solvents, fast polymerization, and possibly high monomer conversion and production of high molar mass polymers. For all these reasons, ever-increasing attention is being paid to the extension of CRP to heterogeneous polymerization techniques, that is, suspension, emulsion, and miniemulsion polymerization.[12–14]

Recently, we reported a system based on cobalt acetylacetonate [Co(acac)$_2$] that imparts control to the radical polymerization of vinyl acetate initiated by 2,2′-azobis(4-methoxy-2,4-dimethyl valeronitrile), V-70, in the bulk at 30 °C.[15] The molar mass of poly(vinyl acetate) indeed changes linearly with monomer conversion, in good agreement with the predicted values (Table 1, entry 1). Moreover, the polydispersity is as low as 1.2. These observations are consistent with a mechanism based on reversible addition of the growing radicals to the cobalt complex and establishment of an equilibrium between alkylcobalt(III) and cobalt(II) complexes, that is, the dormant and the active species, respectively (Scheme 1). A similar mechanism was previously proposed for acrylate polymerization mediated by cobalt porphyrin[16–18] and cobaloxime complexes.[19]

Because of the advantages of using water as a continuous phase, cobalt-mediated radical polymerization of vinyl acetate was tentatively conducted in suspension in water. Therefore, in addition to [Co(acac)$_2$] and V-70, water and a poly(vinyl alcohol-*co*-vinyl acetate) dispersant (0.16 wt % in water) were added to vinyl acetate to give a dispersion in water of the azo initiator (V-70) and the monomer (Scheme 2). Under these conditions, the cobalt-mediated radical polymerization of vinyl acetate remains controlled, as assessed by the clear increase of the molar mass with monomer conversion (Table 1, entry 2). In parallel, the polydispersity increases rapidly with monomer conversion (from 1.3 to 2.35), and the experimental molar masses exceed the theoretical values calculated from the [VAc]/[Co(acac)$_2$] molar ratio, which indicates a loss of control as the polymerization progresses. The poor solubility of the [Co(acac)$_2$] complex in the organic phase (vinyl acetate) is thought to be the reason for the low polymerization efficiency ($M_{n,\text{theor}}$/

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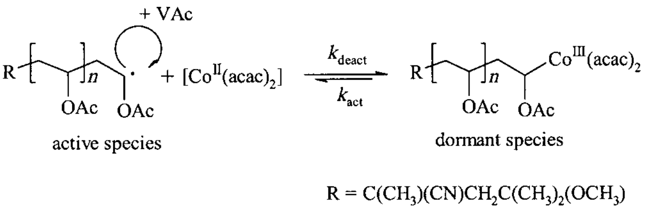
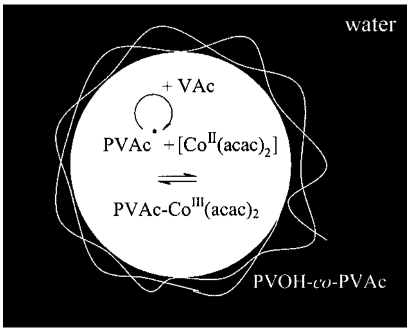
Table 1: Radical polymerization of vinyl acetate initiated by V-70 in the presence of [Co(acac)$_2$] at 30 °C in bulk and in suspension in water.

Entry	Conditions[a]	t [h]	Conv. [%][b]	$M_{n,SEC}$[c] [g mol^{-1}]	$M_{n,theor}$[d] [g mol^{-1}]	$M_{n,theor}/M_{n,SEC}$	M_w/M_n
1	bulk	20	11	7500	5100	0.68	1.25
		22	21	12000	9800	0.82	1.20
		25	36	19500	16800	0.86	1.20
		28	51	24000	23800	0.99	1.20
		44	70	30000	32700	1.09	1.40
2	suspension	4	5	21500	2300	0.11	1.30
		5.5	16	40000	7500	0.19	1.45
		7.5	32	54500	14900	0.27	1.55
		24	>99	95500	46200	0.48	2.35

[a] Bulk: [Co(acac)$_2$]/[V-70]/[VAc] 1:3.25:542; Suspension: VAc/H$_2$O 2.5:3 (v/v), PVOH-*co*-PVAc in water (0.16 wt%). [b] Monomer conversion was determined gravimetrically after removal of the unconverted monomer in vacuo. [c] Determined by size exclusion chromatography (SEC) with polystyrene calibration. [d] $M_{n,theor} = ([M]_0/[Co]_0) \times M_{mono} \times conv.$



Scheme 1. Equilibrium between dormant and active species in the cobalt-mediated radical polymerization of vinyl acetate.



Scheme 2. Equilibrium between dormant and active species within vinyl acetate droplets in suspension polymerization.

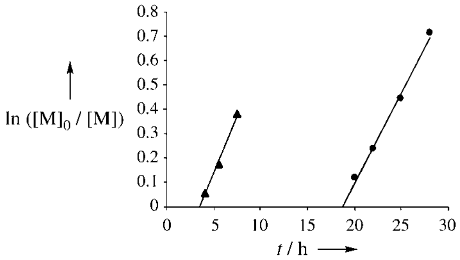


Figure 1. Plot of ln([M]$_0$/[M]) versus time for the vinyl acetate polymerization initiated by V-70 in the presence of [Co(acac)$_2$] at 30 °C in bulk (●) and in suspension in water (▲) (Table 1).

$M_{n,SEC}$). The partition coefficient of the cobalt complex between vinyl acetate and water was determined by weighing the solid residue left by each liquid phase after decantation. The concentration of [Co(acac)$_2$] in water was ten times higher than in the monomer, consistent with the color of the aqueous phase, which had the typical purple color of [Co(acac)$_2$]. That only a small part of the cobalt complex is available in the monomer droplets is confirmed by the polymerization kinetics. Plots of ln([M]$_0$/[M]) versus time are shown in Figure 1 for bulk and suspension CRP of vinyl acetate. The induction period is much shorter for suspension polymerization (3 h) than for bulk polymerization (19 h). Because this period is the time required for the growing radicals to add to the cobalt complex with formation of dormant species (Scheme 1), the shorter induction time qualitatively agrees with the smaller amount of cobalt in the monomer phase in suspension polymerization.

To increase the polymerization efficiency and to restrict the extent of irreversible termination, the concentration of the cobalt complex in the organic phase must be increased to increase the amount of dormant species (Scheme 2). For this purpose, suspension polymerization of vinyl acetate was initiated by a poly(vinyl acetate) macroinitiator, end-capped by [Co^{III}(acac)$_2$] and preformed in the bulk, in the presence of the cobalt complex and V-70, at low monomer conversion. This prereacted mixture, which consists of poly(vinyl acetate) chains in unconverted monomer, was merely poured into an aqueous solution of poly(vinyl alcohol-*co*-vinyl acetate) under vigorous stirring at 30 °C. According to this strategy, the [Co(acac)$_2$] complex, covalently bonded as an end group to the dormant chains, is located in the vinyl acetate droplets, that is, where it must be present to efficiently mediate the polymerization. This technique was tested at two [VAc]/[Co(acac)$_2$] molar ratios (Table 2). Under these conditions, the molar mass increases with reaction time, and the molar mass distribution is rather narrow ($M_w/M_n = 1.2$–1.4), even at high monomer conversion (90%; Table 2, Figure 2). As expected, compared to suspension polymerization in the presence of [Co(acac)$_2$], the use of a PVAc-Co(acac)$_2$ macroinitiator results in a much higher efficiency ($M_{n,theor}/M_{n,SEC} \approx 0.7$; see entry 2 in Table 1 and data in Table 2). Dependence of the molar mass on monomer conversion is linear, and the molecular weight of PVAc is dictated by the [VAc]/[PVAc-Co(acac)$_2$] molar ratio, as is the case for a controlled process. Figure 3 illustrates the shift of the size exclusion chromatogram with polymerization time. Importantly, very high molecular weight PVAc with a rather low polydispersity ($M_{n,SEC} = 100000$ g mol^{-1}, $M_w/M_n = 1.40$, Table 2, entry 2) can be prepared. Moreover, the cobalt-mediated polymerization of vinyl acetate in suspension is very fast at low temperature (30 °C) and is quasicomplete 2 h after addition of the prereaction mixture to the aqueous solution of dispersant. Indeed, the slope of monomer conversion versus time

Table 2: Radical polymerization of vinyl acetate initiated at 30 °C by a low molar mass poly(vinyl acetate) macroinitiator in suspension in water.[a]

Entry	[VAc]/[Co]	t [min][b]	Conv. [%][c]	$M_{n,SEC}$[d] [g mol^{-1}]	$M_{n,theor}$[e] [g mol^{-1}]	$M_{n,theor}/M_{n,SEC}$	M_w/M_n
1	542	0	1	–	–	–	–
		30	37	26 000	17 300	0.67	1.20
		60	46	33 500	21 500	0.64	1.20
		120	65	44 000	30 300	0.69	1.20
		240	95	60 500	44 300	0.73	1.35
2	1084	0	9	14 000	8400	0.60	1.20
		25	36	49 000	33 600	0.69	1.35
		40	48	66 000	44 800	0.68	1.30
		70	75	100 000	70 000	0.70	1.40
		240	99	99 000	92 400	0.93	1.80

[a] Prereaction in bulk: [Co(acac)$_2$]/[V-70] 1:3.25. PVOH-*co*-PVAc in water (0.16 wt%). 1) 22 h of prepolymerization in bulk, [VAc]/[Co] 542:1. 2) 14 h of prepolymerization in bulk, [VAc]/[Co] 1084:1. [b] t_0: time of addition of the prepolymerized VAc to a PVOH-*co*-PVAc aqueous solution, VAc/H$_2$O 2.5:3 (v/v). [c] Monomer conversion was determined gravimetrically after removal of the unconverted monomer in vacuo. [d] Determined by SEC with PS calibration. [e] $M_{n,theor} = ([M]_0/[Co]_0) \times M_{mono} \times$ conv.

increases drastically when the prepolymerized medium is poured into water (Figure 4). This spectacular increase in polymerization rate may be attributed to the diffusion of [Co(acac)$_2$] from the monomer droplets to the aqueous phase, which induces a shift of the equilibrium towards the active species (Scheme 2). Finally, poly(vinyl acetate) beads, with a diameter in the millimeter range, are obtained at high monomer conversion, as observed by optical microscopy (Figure 5).

For the first time, the radical polymerization of vinyl acetate can be easily controlled in suspension in water to give poly(vinyl acetate) with predictable molecular weight and low polydispersity up to very high molecular weight and high monomer conversion. Because the reactivity of vinyl acetate is comparable to that

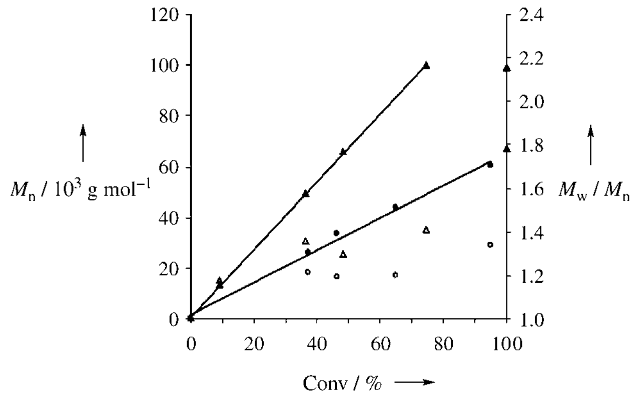


Figure 2. Dependence of M_n (filled symbols) and M_w/M_n (open symbols) on monomer conversion for VAc polymerization initiated at 30 °C by a low molar mass poly(vinyl acetate) macroinitiator in suspension in water (Table 2). VAc/H$_2$O = 5:6 (v/v), PVOH-*co*-PVAc in water (0.16 wt%). ●: $M_{n,SEC}$ for [Co(acac)$_2$]/[V-70]/[VAc] 1:3.25:542; ▲: $M_{n,SEC}$ for [Co(acac)$_2$]/[V-70]/[VAc] 1:3.25:1084; ○: M_w/M_n for [Co(acac)$_2$]/[V-70]/[VAc] 1:3.25:542; △: M_w/M_n for [Co(acac)$_2$]/[V-70]/[VAc] 1:3.25:1084.

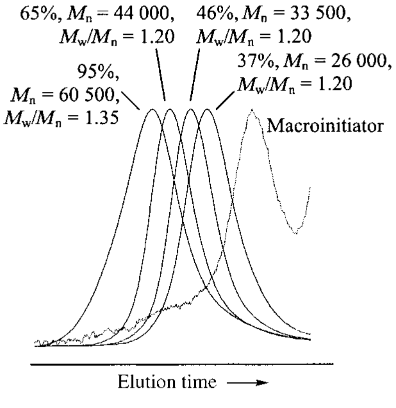


Figure 3. Size exclusion chromatograms for poly(vinyl acetate) initiated by PVAc oligomers end-capped by [Co(acac)$_2$] at 30 °C in the presence of water and PVOH-*co*-PVAc (0.16 wt%) as stabilizer. [Co(acac)$_2$]/[V-70]/[VAc] 1:3.25:542 (Table 2, entry 1).

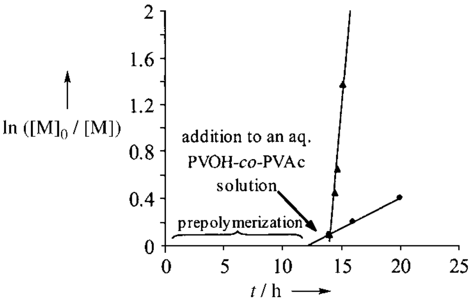


Figure 4. Conversion versus time for VAc bulk polymerization initiated by V-70 in the presence of [Co(acac)$_2$] at 30 °C (●) on addition of the polymerization medium at 10% conversion to an aqueous solution of PVOH-*co*-PVAc (▲; Table 2, entry 2). [Co(acac)$_2$]/[V-70]/[VAc] 1:3.25:1084.

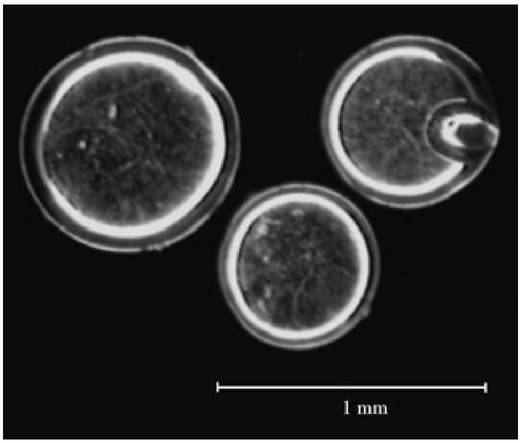


Figure 5. Poly(vinyl acetate) beads prepared by cobalt-mediated polymerization of VAc initiated by a low molar mass PVAc macroinitiator in the presence of water and a PVOH-*co*-PVAc dispersant at 30 °C (Table 2, entry 1, 95%).

of vinyl chloride, this new process will be extended to the radical polymerization of vinyl chloride in the near future.

Experimental Section

Materials: Vinyl acetate ($>99\%$, Acros) was dried over calcium hydride, degassed by several freeze/thaw cycles, distilled under reduced pressure, and stored under argon. Doubly distilled water was degassed by several freeze/thaw cycles. Cobalt(II) acetylacetonate ([Co(acac)$_2$], $>98\%$, Merck), poly(vinyl alcohol-*co*-vinyl acetate) (72.5% hydrolyzed, Alcotex), and 2,2′-azobis(4-methoxy-2,4-dimethyl valeronitrile) (V-70, Wakko) were used as received. Size exclusion chromatography (SEC) was carried out in 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 columns (four columns HP PL gel 5 μL 10^5 Å, 10^4 Å, 10^3 Å, 10^2 Å). Polystyrene (PS) standards were used for calibration. The molar mass of PVAc determined by SEC with PS calibration was in good agreement with that determined by ^{1}H NMR whenever the α end group of the initiator ($-$OCH$_3$ at $\delta = 3.13$ ppm) could be observed and compared to the $-\mathrm{C}H\mathrm{OCOCH_3}$ proton at $\delta = 4.8$ ppm of the monomer unit. An optical microscope (Zeiss) was used to observe the PVAc beads.

Cobalt-mediated radical polymerization of vinyl acetate in the bulk: [Co(acac)$_2$] (25.7 mg, 10^{-4} mol) and V-70 (100 mg, 3.25×10^{-4} mol) were added to a glass tube capped by a three-way stopcock. The reactor was purged by three vacuum/argon cycles before addition of vinyl acetate (5 mL, 542×10^{-4} mol). The reaction mixture was heated in an oil bath thermostatically controlled at 30°C. No polymerization occurred for a few hours, after which the viscosity increased. Samples were withdrawn at different reaction times, and the vinyl acetate conversion was determined by weighing the polymer collected on removal of the unconverted monomer in vacuo at 50°C.

Cobalt-mediated radical polymerization of vinyl acetate in suspension in water: [Co(acac)$_2$] (78 mg, 3×10^{-4} mol) and V-70 (300 mg, 9.75×10^{-4} mol) were added to a glass tube capped by a three-way stopcock. The reactor was purged by three vacuum/argon cycles before vinyl acetate (15 mL, 1626×10^{-4} mol) was added. Then known volumes (2.5 mL) of the purple reaction mixture were added to a degassed aqueous solution of PVOH-*co*-PVAc (3 mL, 0.16 wt%) in several round-bottom flasks, previously purged by argon and containing a magnetic stirrer. All these flasks were heated in an oil bath thermostatically controlled at 30°C with vigorous stirring (1000 rpm). Samples were taken from the flasks at different reaction times, the monomer conversion was determined gravimetrically as descibed above, taking into account the amount of water and stabilizer.

Cobalt-mediated radical polymerization of vinyl acetate initiated by a PVAc macroinitiator in suspension in water: [Co(acac)$_2$] (78 mg, 3×10^{-4} mol) and V-70 (300 mg, 9.75×10^{-4} mol) were added to a glass tube capped by a three-way stopcock. The reactor was purged by three vacuum/argon cycles before vinyl acetate (15 mL, 1626×10^{-4} mol) was added. The flask was heated to 30°C for a few hours, during which the color turned green-brown. Samples (2.5 mL) of this reaction mixture were added to a degassed aqueous solution of PVOH-*co*-PVAc (3 mL, 0.16 wt%) in several round-bottom flasks, previously purged with argon. All these flasks were heated in an oil bath thermostatically controlled at 30°C with vigorous stirring (1000 rpm). At high monomer conversion, PVAc beads were collected by filtration, washed with water, and dried in vacuo.

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