Radical Polymerization

Highly Efficient Cobalt-Mediated Radical Polymerization of Vinyl Acetate**

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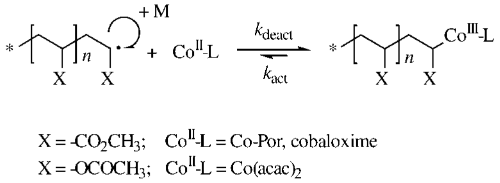
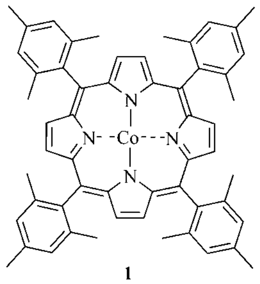
In the last decades, rapidly increasing attention has been paid to so-called macromolecular engineering, that is, the synthesis of novel polymeric materials with well-defined molecular parameters. In this respect, controlled radical polymerization (CRP) proved to be a suitable strategy, because of its mild experimental conditions and tolerance to water. Nowadays, nitroxide-mediated polymerization (NMP),[1] atom-transfer radical polymerization (ATRP),[2] and radical addition–fragmentation chain-transfer (RAFT)[3] are among the more popular CRP techniques. All of them rely on the same concept, which consists of decreasing the radical concentration in the medium and thus the probability of irreversible termination. This is achieved by reversible conversion of the growing macroradicals $P^{\bullet}$ to dormant species PX. The persistent-radical effect (PRE) is the origin of the high propensity of the radicals to undergo reversible deactivation rather than self-coupling reactions.[4]

The lability of the cobalt–carbon bond under thermal and photolytic treatment,[5] and thus the reversibility of its cleavage, make cobalt complexes suitable candidates for PRE[6] and regulation of CRP. The first example of cobalt-mediated radical polymerization (CMRP), reported by Wayland et al., was the radical polymerization of acrylates in the presence of cobalt porphyrin complexes such as (tetramesitylporphyrinato)cobalt complex **1** [Co(TMP)].[7,8] The cobalt complex reversibly end-caps the growing polymeric radicals under heating, which accounts for the equilibrium between dormant ($P-Co^{III}L$) and active species ($P^{\bullet}$) shown in Scheme 1. In this process, the oxidation state of the metal species alternates between two and three. Later, more efficient halogenated cobalt porphyrin complexes were designed, synthesized, and used to improve the polymerization kinetics.[9] Moreover, the process was extended to alkylcobaloximes **2**, which are suitable photoinitiators for CMRP of acrylates.[10] However, in spite of all these improvements, CMRP remains restricted to the polymerization of acrylates. Other monomers, such as methacrylates and styrene, predominantly undergo hydrogen elimination and are accordingly involved in catalytic chain-transfer polymerization (CCTP).[11] More dramatically, vinyl acetate (VAc) polymerization is completely inhibited by the cobalt porphyrin complexes.[12]



$X = \text{-}CO_2CH_3$; Co^{II}-L = Co-Por, cobaloxime
$X = \text{-}OCOCH_3$; Co^{II}-L = $Co(acac)_2$

Scheme 1. Equilibrium between dormant and active species in CMRP of acrylates and vinyl acetate.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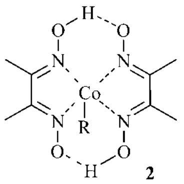
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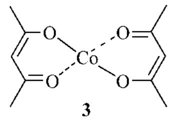
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We tested cobalt(II) acetylacetonate complex **3**, which is commercially available, cheap, and reasonably soluble in acrylic monomers, in the radical polymerization of *n*-butyl acrylate (*n*BuA) and vinyl acetate initiated by 2,2′-azo-bis(4-methoxy-2,4-dimethyl valeronitrile) (V-70) at 30 °C. In contrast to cobalt porphyrin complexes and cobaloximes, **3** is unable to mediate and control the radical polymerization of *n*-butyl acrylate. Indeed, formation of chains with high molar mass and broad molar mass distribution at low conversion is clear indication of an uncontrolled process (Table 1, entry 1).

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Table 1: Bulk radical polymerization of vinyl acetate and *n*-butyl acrylate in the presence of [Co(acac)$_2$].

Entry	M	[M]/[Co]	t [h]	$Z^{[c]}$ [%]	$M_{n,SEC}$[d] [10^3 g mol^{-1}]	$M_{n,theor}$[e] [10^3 g mol^{-1}]	M_w/M_n
1	*n*BuA[a]	348	2	<1			
			3	5	35.0	2.4	2.20
			5	8	39.7	3.9	2.00
2	VAc[b]	542	16	29	13.0	13.6	1.13
			18	42	17.9	19.9	1.17
			20	49	20.4	22.8	1.19
			22	56	22.8	26.2	1.22
			24	64	25.4	30.1	1.21
3	VAc[b]	813	13	16	13.0	11.2	1.11
			14	22	19.9	15.4	1.13
			15.5	33	26.5	23.1	1.15
			17	42	33.3	29.4	1.17
			19	55	41.8	38.4	1.20
			22	70	51.4	49.0	1.23
4	VAc[b]	1626	14	56	70.5	78.4	1.22
5	VAc[b]	2168	14	60	99.0	112.0	1.33

[a] Bulk polymerization of *n*BuA at 30 °C, [Co(acac)$_2$]/[V-70] = 1. [b] Bulk polymerization of VAc at 30 °C, [Co(acac)$_2$]/[V-70] = 6.5. [c] The monomer conversion Z is determined gravimetrically after removal of the unconverted monomer in vacuo. [d] Determined by size-exclusion chromatography (SEC) with polystyrene calibration. [e] $M_{n,theor} = ([M]_0/[Co^{II}]_0) \times M_{mono} \times Z$.

When the polymerization of vinyl acetate (VAc) is conducted in the presence of **3** under the same experimental conditions, no polymer is formed for at least 12 h at 30 °C (Table 1, entries 2 and 3). However, the polymerization of vinyl acetate starts after this period of time, and a controlled process is observed, as assessed by the linear increase of the molar mass with monomer conversion (Figure 1). As expected, the molar mass of poly(vinyl acatate), PVAc, is controlled by the [VAc]/[Co(acac)$_2$] ratio; higher molar masses are obtained at higher molar ratios of monomer to Co complex (Figure 1). Therefore, appropriate choice of the [VAc]/[Co(acac)$_2$] ratio allows PVAc to be prepared with molar masses as high as 70 000 and 99 000 g mol^{-1}, with reasonably low polydispersities (Table 1, entries 4 and 5). As a rule the polydispersity is very narrow ($1.1 \leq M_w/M_n \leq 1.2$) throughout the polymerization. The slight but significant increase in polydispersity with monomer conversion is observed in any controlled radical processes as result of irreversible termination reactions and, in this case, possible transfer reactions to monomer and/or polymer. Further evidence for the pronounced efficacy of this cobalt complex in mediating the radical polymerization of vinyl acetate can be found in the good agreement between experimental and theoretical molar masses ($M_{n,theor}/M_{n,SEC} = 1 \pm 0.12$, Table 1). The theoretical values were calculated under the assumption that one polymer chain is growing per [Co(acac)$_2$] unit, according to the mechanism proposed by Wayland and co-workers for the CMRP of acrylates (Scheme 1).[7]

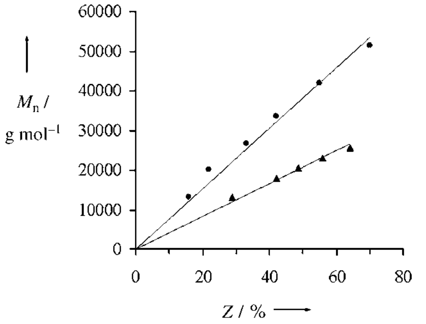

Figure 1. Dependence of PVAc molar mass M_n on monomer conversion Z for bulk polymerization of vinyl acetate at 30 °C. [VAc]/[Co(acac)$_2$] = 542 (▲) and 813 (●) (Table 1, entries 2 and 3).

The CMRP of vinyl acetate was also initiated at higher temperature (60 °C) by AIBN instead of V-70 in the presence of [Co(acac)$_2$]. Under these conditions, the molar mass again increases with monomer conversion, the polymerization rate is higher, but the experimental molar masses are higher than predicted ($M_{n,theor}/M_{n,SEC} \approx 0.5$), which is evidence for higher probability of irreversible chain termination. Consistently, the molar mass distribution is much broader ($M_w/M_n = 2.0$–3.5).

The kinetics of this CMRP of vinyl acetate are first-order in monomer, as assessed by the linear dependence of $\ln([M]_0/[M])$ versus time (Figure 2). This observation confirms that the macroradical concentration remains essentially constant and that irreversible termination reactions do not play a major role. In contrast to acrylates, an induction period of several hours is systematically observed in the radical polymerization of VAc, which would be the time for the radicals generated in situ to convert Co^{II} into Co^{III}–P. During this nonproductive period, a drastic change in the color of the medium, from purple to dark brown-green, is observed, consistent with the suggested change in oxidation state of the cobalt complex.

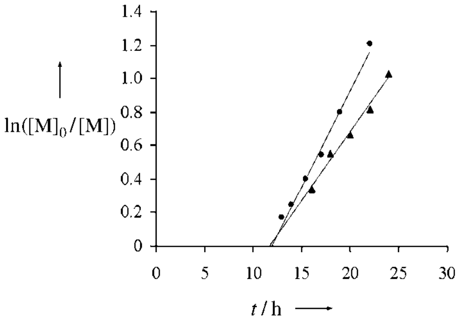

Figure 2. Time dependence of $\ln([M]_0/[M])$ for the bulk polymerization of vinyl acetate at 30 °C. [VAc]/[Co(acac)$_2$] = 542 (▲) and 813 (●) (Table 1, entries 2 and 3). $[M]_0$ and [M] are the vinyl acetate concentration at times 0 and t, respectively.

Vinyl acetate oligomers ($M_n = 1300$ g mol^{-1}, $M_w/M_n = 1.13$), preformed in bulk at 30 °C with V-70 in the presence of [Co(acac)$_2$], were collected and purified by repeated precipitation in heptane, and finally used as macroinitiators for vinyl acetate polymerization. Resumption of the VAc polymerization was successful, as assessed by the shift of the SEC chromatograms with time towards lower elution volumes, a polydispersity that remains narrow, and a very small amount of unconverted macroinitiator (Figure 3). This observation paves the way for the synthesis of block copolymers by sequential polymerization of VAc and any comonomer whose polymerization is controlled by the same initiator/Co complex system. This may be a restriction, because the Co complex that controls VAc polymerization is not necessarily effective in the polymerization of other monomers, such as acrylates. In that case, exchange of Co complexes is required between the consecutive polymerization steps.

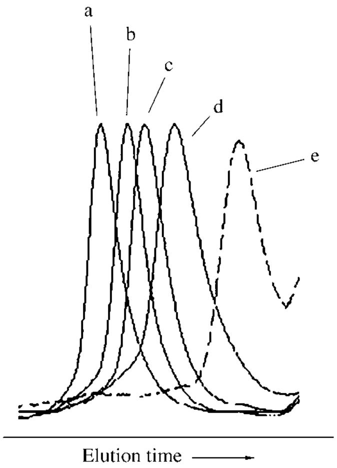

Figure 3. Size-exclusion chromatograms for PVAc initiated at 30 °C by a preformed PVAc macroinitiator end-capped by [Co(acac)$_2$]. ([VAc]/[PVAc–Co] = 319). a) $M_n = 24\,300$, $M_w/M_n = 1.11$, 57% conversion; b) $M_n = 13\,300$, $M_w/M_n = 1.24$, 30% conversion; c) $M_n = 9900$, $M_w/M_n = 1.16$, 20% conversion; d) $M_n = 5800$, $M_w/M_n = 1.13$, 10% conversion; e) PVAc macroinitiator, $M_n = 1300$, $M_w/M_n = 1.13$.

As mentioned previously, vinyl acetate polymerization is inhibited by cobalt porphyrin,[12] which reacts irreversibly with the very reactive radicals of the VAc type. In this particular case, the equilibrium is completely shifted towards the dormant form. However, quite an appropriate balance is established between dormant and active species by [Co(acac)$_2$], with an instantaneous concentration of active chains low enough to impart control on the polymerization. In case of acrylates, the deactivation rate of the propagating radicals into dormant species is very low compared to the rate of propagation, and this leads rapidly to a large number of active chains. This drastic change in the position of the dormant/active species equilibrium when VAc is substituted for *n*BuA can be explained by the more pronounced leaving character and the lower reactivity of the polyacrylate radicals, as result of a stabilizing substituent.

Finally, ^{13}C NMR analysis of PVAc confirmed that the Co complex has no influence on the stereoregularity of the polymer formed by the radical process.[13]

Up to now only few systems were able to mediate the polymerization of vinyl acetate with more or less success, such as degenerative chain transfer with alkyl iodides,[14] ATRP,[15] and RAFT with xanthates[16] and dithiocarbamates,[17] whereas cobalt-mediated radical polymerization was inactive.

In the light of the results reported herein, the role of the ligand in CMRP is essential. This technique, restricted to acrylates, until now, can be tuned by the appropriate choice of ligand (e.g., substitution of acetylacetonate for porphyrin) and extended even to reluctant monomers such as VAc. This is expected to renew interest in CMRP and its extension to other vinylic monomers. Moreover, this very efficient control of vinyl acetate polymerization paves the way to macromolecular engineering of poly(vinyl acetate) and directly derivatized poly(vinyl alcohol), including tailored telechelic polymers and block and graft copolymers of different architectures.

Experimental Section

Vinyl acetate and *n*-butyl acrylate were dried over calcium hydride, degassed by several freeze/thaw cycles, distilled under reduced pressure, and stored under argon. Cobalt(II) acetylacetonate (> 98%, Merck), 2,2′-azobisisobutyronitrile (AIBN, Fluka) and 2,2′-azobis(4-methoxy-2,4-dimethyl valeronitrile) (V-70, Wakko) were used as received.

General procedure: V-70 (200 mg, 0.65 mmol) and [Co(acac)$_2$] (25.7 mg, 0.1 mmol) were placed in a 30 mL flask and degassed by three vacuum/argon cycles. Dry, degassed vinyl acetate (5 mL, 54.2 mmol) was then added by syringe under argon. The purple mixture was stirred and heated at 30 °C. After a few hours, the color changed from purple to dark brown-green. No polymerization occurred for at least 12 h, after which the viscosity of the solution increased substantially. Samples were withdrawn at different reaction times, and monomer conversion was determined by weighing the collected polymer after removal of the unconverted monomer in vacuo. The same procedure was used for *n*-butyl acrylate (5 mL, 34.8 mmol) polymerization initiated by V-70 (31 mg, 0.1 mmol).

PVAc oligomers (110 mg, 0.085 mmol, $M_{n,SEC} = 1300\ \mathrm{g\,mol^{-1}}$, $M_w/M_n = 1.13$) were prepared according to the general procedure and collected at low monomer conversion by repeated precipitation in heptane. They were dissolved in degassed vinyl acetate (2.5 mL, 27.1 mmol) and heated at 30 °C to resume the controlled radical polymerization.

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