Controlled radical polymerisation of methyl acrylate initiated by a well-defined cobalt alkyl complex[†]

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Received (in Cambridge, UK) 21st October 2009, Accepted 8th February 2010 First published as an Advance Article on the web 23rd February 2010 DOI: 10.1039/b922030e

Cobalt-mediated radical polymerisation of methyl acrylate is effected at moderate temperature by both a square planar bis(β -ketoaminato)cobalt(II) complex in the presence of V-70 diazo radical initiator, and by a well-defined cobalt(III) alkyl derivative in the absence of a diazo complex. Polymerisation rates suggest that both reversible termination and degenerative transfer mechanisms are operative.

The controlled radical polymerization (CRP) of functionalized alkenes is a powerful method to craft polymers with wellcontrolled chain lengths and molecular weight distributions via the addition of some mediating species that reduces the concentration of growing radical chains.¹ Among the various methods of CRP, one garnering considerable attention is that of cobalt-mediated radical polymerisation (CMRP),² where the mediating species is a cobalt complex that traps the radicals by forming a Co-C bond. Various CMRP studies have yielded systems capable of forming polymers and block copolymers of acrylates or vinyl acetate (VOAc) in an effectively living fashion.³⁻⁹ Such systems generally rely on the use of diazo compounds as an initial source of radicals, the transportation and low-temperature storage of which can be problematic.¹⁰ Two competing mechanisms have been shown to occur in CMRP reactions. Reversible termination (RT) involves the trap and release of the radical chain via reversible metal-carbon bond homolysis (Scheme 1A), and occurs when the total radical concentration is less than that of the trapping cobalt species. In contrast, a degenerative chain transfer (DT)

A: Reversible Termination

$$L_nCo^{III}R \xrightarrow{k_d} L_nCo^{II} + R \xrightarrow{k_p} X$$

B: Degenerative Chain Transfer

$$X \xrightarrow{k_p} \mathbb{R}^{k_p} \stackrel{K_{exch}}{\longrightarrow} L_n \mathbb{C}o^{|||} \mathbb{R}^{k_p} \xrightarrow{k_p} X$$

Scheme 1 CMRP mechanisms.

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E-mail: s.mcneil@ubc.ca; Fax: +1 250 807 8005; pathway can occur under higher radical concentrations in which a radical species—either a growing polymer chain or a radical injected by the initiator—displaces the trapped radical bound to the metal (Scheme 1B).^{5,7,11}

In either mechanism, the final products of such reactions are cobalt-capped polymer chains, and while such species have themselves been shown to act as effective initiators for CMRP, ^{3,4,8,12} examples of controlled radical polymerisations using a well-defined cobalt(III) alkyl complex as the sole radical source are exceedingly rare.¹³ We wish to report the controlled radical polymerisation of methyl acrylate mediated by the well-known (ketoaminato)cobalt(II) complex LCo (1)¹⁴ (L = bis(benzoylacetone)ethylenediaminate) using V-70 as a radical initiator, and its comparison to the same polymerisation effected by LCoEt (2) in the absence of V-70.

Compound 1‡ exhibits a solution magnetic moment of 1.99 $\mu_{\rm B}$, consistent with the low-spin $S = \frac{1}{2}$ configuration expected for a square-planar Co^{II} species. Our determination of the solid-state structure of 1 conforms to those of previously published¹⁵ structural reports establishing the square planar geometry.

Compound **2** is best prepared by the treatment of **1** with an excess of BEt₃, which releases ethyl radicals upon exposure to air.¹⁶§ The alkyl radicals are trapped by **1** to afford **2** as an air-stable diamagnetic complex. The structure of **2** is shown in Fig. 1.¶ Unfortunately, the crystal exhibits a whole-molecule disorder that limits high precision of the measured metrical parameters (see ESI† for further details). However, the structure unambiguously confirms the expected square pyramidal geometry, comparable to that of similar square pyramidal cobalt alkyl complexes.¹⁷ Upon addition of the alkyl group, the Co–O and Co–N bond lengths increase slightly (on average by ~0.026 and ~0.011 Å, respectively), perhaps contrary to the expectation associated with a formal oxidation



Fig. 1 Molecular structure of **2**, showing one of two disordered orientations. Selected bond lengths [Å] and angles [°]: Co–N1 1.867(9), Co–N2 1.861(9), Co–O1 1.865(8), Co–O2 1.867(8), Co–C23 1.991(6); O1–Co–O2 76.6(6), O1–Co–N1 98.6(14), N1–Co–N2 86.9(16), N2–Co–O2 97.1(12), O1–Co–C23 89.7(11), O2–Co–C23 99.3(7), N1–Co–C23 88.4(17), N2–Co–C23 96.5(8).

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[†] Electronic supplementary information (ESI) available: CIF file for **2**; experimental data for X-ray structure determination of **2**, synthetic procedures and characterisation data for **1** and **2**, experimental procedures for polymerisation experiments (11 pages). CCDC [CCDC NUMBER(S)]. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b922030e



Fig. 2 Variation of pMA mass (M_n) and polydispersity (M_w/M_n) with monomer conversion in toluene at 50 °C. $[1]_i : [V-70]_i : [MA]_i = 1 : 0.6 : 500, [1]_i = 0.010 \text{ M}.$

from Co^{II} to Co^{III}. However, the cobalt ion is low-spin in both compounds, minimizing the effect on bond lengths of such a change, and the small increase can be attributed primarily to the raising of the cobalt atom in $2 \sim 0.11$ Å above the mean plane of the ketoaminate ligand donor atoms.

Treatment of red-orange 1 with 0.6 equiv. V-70 and 500 equiv. methyl acrylate (MA) in toluene at 50 °C yields poly(methyl acrylate) (pMA), a reaction accompanied by a colour change to brown. As shown in Fig. 2, the polymer mass is consistently somewhat above the theoretical value assuming one growing polymer chain per cobalt centre, indicating that not every molecule of **1** is involved in mediating the reaction. Indeed, this must be the case: assuming an initiator efficiency of 0.6,⁵ the total amount of radicals derived from V-70 never equals that of 1. As well, the gradual decomposition of V-70 should result in initially low f values $(f = M_n(\text{theo})/M_n(\text{obs}))$ that slowly increase as the reaction proceeds, as observed. The plot of ln([MA]₀/[MA]) vs. time (Fig. 3) illustrates a linear first-order consumption of monomer for more than six V-70 half lives,¹⁸ indicating the maintenance of a constant radical concentration during and beyond the decomposition of the initiator.¹⁹ This suggests that the reaction occurs solely via reversible release and trapping of the growing polymer chain by 1 to form an organocobalt(III) intermediate (i.e. RT, Scheme 1A). Increasing the concentration of V-70 to 0.9 equivalents yields the kinetic plot in Fig. 4. The calculated induction period (until $[R^{\bullet}]_{tot} = [1]_{init}$) is 2.3 h, as observed. As well, the induction period rate compares reasonably well to that observed in Fig. 3 ($0.060 \pm 0.010 \text{ h}^{-1} \text{ vs.} 0.046 \pm 0.003 \text{ h}^{-1}$),



Fig. 4 Kinetic plot for polymerization of MA with 1 and V-70 in toluene at 50 °C. $[1]_i : [V-70]_i : [MA]_i = 1 : 0.9 : 500, [1]_i = 0.010 M.$

again suggesting a common RT mechanism independent of the initial amount of V-70. After induction, the rate accelerates as the concentration of radicals increases, and a DT mechanism is presumed to apply.

In both cases, the observed polydispersity gradually increases over the course of the reaction, and the observed polymer weights begin to drop relative to the theoretical value (Fig. 2 and Fig. S1, see ESI†). These results suggest a gradual loss of control of the polymerization. A likely cause is the increasing role of non-reversible terminations, due in part to a catalytic chain transfer mechanism,²⁰ a commonly observed effect at longer reaction times in CMRP, particularly at somewhat elevated temperatures.²

Reaction of brown 2 with 500 equiv. MA in toluene at 50 °C initially affords pMA at much faster rates that follow nonlinear kinetics (Fig. 5). However, the reaction soon exhibits a first-order loss of monomer comparable to that observed in previous experiments during the RT induction period $(0.058 \pm 0.004 \text{ h}^{-1})$. This variation indicates that the generation of alkyl radicals from ethyl complex 2 is slower than from a polymer chain bound to 1, affording a lower initial concentration of trapping agent 1.²¹ With less Co^{II} initially available to act as a trapping agent, fewer terminations result in faster polymer growth $(k_{obs} = k_p[MA](k_d[Co^{III}R]/k_t[Co^{II}])$. After 2 is consumed and the concentration of Co^{II} is higher, new radicals can only be generated by the RT equilibrium, and the original rate is observed. Further evidence for this conclusion is offered by MA polymerization in the presence of a 1 : 1 mixture of 1 and 2. In this case, monomer loss exhibits linear kinetics immediately at a rate identical to reactions



Fig. 3 Kinetic plot for polymerization of MA with 1 and V-70 in toluene at 50 °C. $[1]_i : [V-70]_i : [MA]_i = 1 : 0.6 : 500, [1]_i = 0.010 M.$



Fig. 5 Kinetic plot for polymerization of MA with 2 in toluene at 50 °C. $[2]_i$: $[MA]_i = 1 : 500, [2]_i = 0.010 \text{ M}.$



Fig. 6 Kinetic plot for polymerization of MA with 1 and 2 in toluene at 50 °C. $[1]_i : [2]_i : [MA]_i = 1 : 500, [1]_i = 0.010$ M.

using low concentrations of V-70 as initiator rather than 2 (Fig. 6, $0.046 \pm 0.003 \text{ h}^{-1}$). As with V-70, using 2 as the initiator yields polydispersities from 1.4 to 1.6 at longer reactions times, the similar behaviour again indicative of a common underlying mechanism once the initiator is consumed. In other words, 1 is an effective agent for CMRP of methyl acrylate, which can be initiated by the thermal decomposition of either a diazo complex or the air-stable cobalt alkyl complex 2, to afford pMA by a common RT mechanism.

The square-planar Co^{II} complex 1 is an effective agent for the CMRP of methyl acrylate,²² although polydispersities at longer reaction times are large, suggesting a competitive catalytic chain transfer process. Polymerization may occur by either a reversible termination or a degenerative transfer mechanism, depending on the concentration of available radicals. The polymerisation may be initiated by the thermal decomposition of either a diazo complex or 2, the Co^{III} derivative of 1, and in either case the reaction initially proceeds at the same rate, suggesting a common reversible termination mechanism. Ethyl complex 2 is therefore a rare example of a well-characterized air-stable five-coordinate cobalt alkyl complex capable of both initiating and controlling the radical polymerization process. Studies are underway to probe the potential effects of temperature, added donor ligands, and variation in the alkyl and β-ketoaminate substituents on CMRP efficiency.

We thank both NSERC of Canada and UBC Okanagan for funding.

Notes and references

‡ Compound 1: ¹H NMR (CDCl₃ 25 °C) δ 24.7 (2H), 14.2 (2H), 7.7 (4H), 1.7 (4H), -20.7 (6H), -78.5 (2H); magnetic moment (CDCl₃): 1.99 $\mu_{\rm B}$; anal. calcd for C₂₂H₂₂N₂O₂Co (found): C 65.19 (64.88), H 5.47 (5.58), N 6.91 (6.65)%.

§ Compound **2**: ¹H NMR (CDCl₃ 25 °C) δ 7.93 (m 4H), 7.35 (m 6H), 5.80 (s 2H), 3.56 (m 4H), 3.39 (q 2H), 2.13 (s 12H), -0.16 (t 3H); anal. calcd for C₂₄H₂₇N₂O₂Co (found): C 66.36 (66.04), H 6.26 (6.33), N 6.26 (6.08)%.

¶ Crystal data for **2**: $C_{24}H_{27}N_2O_2Co$, M = 434.41, monoclinic, a = 7.5525(2), b = 17.4630(6), c = 15.6446(5), $\beta = 96.808(2)^\circ$, $U = 2048.8(1) Å^3$, T = 173 K, space group $P2_1/n$, Z = 4, 31367 reflections measured, 6288 unique ($R_{int} = 0.061$) and used in all calculations, final w $R(F^2) = 0.139$.

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- 18 V-70 $t_{\frac{1}{2}}(50 \text{ °C})$ calculated as 37 min, given $t_{\frac{1}{2}}(30 \text{ °C}) = 10$ h and $t_{\frac{1}{2}}(60 \text{ °C}) = 10.2 \text{ min}^6$.
- 19 In this and other experiments under RT conditions, longer (>8 h) reaction times exhibit rates that begin to slow dramatically after approximately 40% MA conversion, in part due to reduced MA concentration. Compound 1 is not sufficiently soluble in MA for controlled polymerization in the absence of solvent.
- 20 A. A. Gridnev and S. D. Ittel, *Chem. Rev.*, 2001, **101**, 3611–3659.
- 21 This result stands in contrast to polymerisations initiated by porphyrin cobalt alkyl complexes¹³ or polymer chains capped with Co(acac)₂,^{8,12} which exhibit linear kinetic behaviour at their outset. This illustrates the important role of relative strengths of the Co–C bonds in the dormant polymer chain *vs*. the initial alkyl initiator.
- 22 That square planar **1** is an effective CMRP agent for methyl acrylate is consistent with previous results that show square planar Co porphyrin compounds control polymerisation of acrylates but effectively inhibit that of vinyl acetate (VOAc) under RT conditions.^{3,5} Similarly, treatment of **1** with V-70 and VOAc at 60 °C in toluene ([**1**]_i : [V-70]_i : [VOAc]_i = 1 : 0.6 : 500) affords only 18% conversion and $M_n = 3000$ after 8 d.