Living Radical Polymerization of Acrylates by Organocobalt Porphyrin Complexes

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A polymerization process is said to be fully living when each polymer unit contains an active site where chain growth occurs indefinitely without termination or chain transfer reactions.[1,2] Living polymerizations based on anionic,[3] cationic,[4] and several types of covalent initiations[5-9] have been identified, but achieving near ideal properties for a living radical polymerization has proven to be a more elusive objective.[1,10-14] Radical polymerizations with living character can be obtained by using a combination of one radical that only initiates polymerization and a second that only reversibly binds with the growing polymer radical.[10] Carbon-, sulfur-, and oxygen-centered radicals that function as reversible radical capping agents have been utilized in illustrating the potential of this strategy,[10-14] and polymer products with relatively small polydispersities have recently been obtained by using stable nitroxide radicals as the radical capping group.[14] Detailed knowledge of organometallic reactivity patterns and mechanisms has resulted in the design of well-characterized living organometallic systems that initiate and propagate polymerization of alkenes,[6] alternating copolymerization of alkenes with CO[7] and ring-opening metathesis polymerization of unsaturated rings.[8]

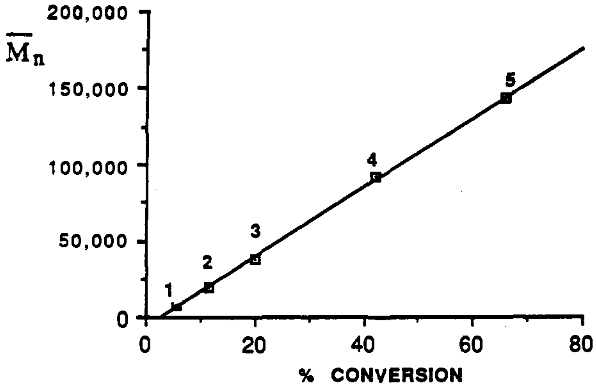

Figure 1. Number average molecular weight of PMA versus percent of monomer conversion that results from reaction of (TMP)Co–neopentyl and methyl acrylate (60 °C, benzene; $[(TMP)Co\text{–}neopentyl]_i = 1.0 \times 10^{-3}$ M; $[MA]_i = 2.5$ M). Molecular weights of PMA were determined relative to polystyrene standards. (1) $\bar{M}_w/\bar{M}_n = 1.10$; (2) $\bar{M}_w/\bar{M}_n = 1.16$; (3) $\bar{M}_w/\bar{M}_n = 1.21$; (4) $\bar{M}_w/\bar{M}_n = 1.17$; (5) $\bar{M}_w/\bar{M}_n = 1.21$.

This article reports that organometallic derivatives of cobalt tetramesitylporphyrin initiate and control the polymerization of acrylates to form homopolymers and block copolymers where the linear increase in number average molecular weight with monomer conversion and relatively small polydispersities (1.1–1.3) are indicative of an effective living radical polymerization process.

Solutions of methyl acrylate, $CH_2{=}CH(CO_2CH_3)$ (MA), and (tetramesitylporphyrinato)cobalt neopentyl,[15] $(TMP)Co\text{–}CH_2C(CH_3)_3$ (**1**), in benzene under an argon atmosphere when heated at 60 °C react to form atactic poly(methyl acrylate), PMA. Addition of $(TMP)Co^{II\bullet}$ reduces the rate of polymerization, and the polymerization process can be effectively stopped and restarted repetitively by cycling the reaction temperature between 5 °C and 60 °C. A plot of the number average molecular weight ($\bar{M}_n$) for PMA versus monomer conversion (5–70%) from a reaction where the mole ratio of MA to **1** is 2500 is shown in Figure 1. A linear increase in $\bar{M}_n$ with MA conversion along with relatively small PMA polydispersities ($\bar{M}_w/\bar{M}_n = 1.1\text{–}1.2$) indicates that a preponderance of the polymer chains are growing in a manner characteristic of a living polymerization process.

$(TMP)Co\text{–}CH(CO_2CH_3)CH_3$ (**2**)[15] was substituted for **1** in the polymerization of MA in order to initiate the process with a species that more nearly emulates the oligomer–Co(TMP) complex that produces growing polymer chains. Reaction of **2** with MA (MA/**2** = 2500, $[\mathbf{2}]_i = 1.0 \times 10^{-3}$ M) at 60 °C in benzene results in formation of PMA with relatively small polydispersity (1.1–1.3) and linear increase in $\bar{M}_n$ (1×10^4 to 1.7×10^5) with MA conversion (5–80%, DP = 125–2000). A parallel reaction in a sealed NMR tube with a MA/**2** mole ratio of only 50 results in the sequential transformation of $(TMP)Co\text{–}CH(CO_2CH_3)CH_3$ (**2**) to $(TMP)Co\text{–}CH(CO_2CH_3)CH_2CH(CO_2CH_3)CH_3$ (**3**) and then to an oligomer complex, $(TMP)Co\text{—}CH(CO_2CH_3)CH_2CH(CO_2CH_3)CH_2\text{—}PMA$ (**4**), that is directly observed by ^1H NMR (Figure 2). Assignment of the structures for **3** and **4** by ^1H NMR is based on comparisons with **2**, observation of diastereomers of **3** and related isomers of **4**, and

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[15] $(TMP)Co\text{–}CH_2C(CH_3)_3$ (**1**) and $(TMP)Co\text{–}C^{*}H(CO_2CH_3)CH_3$ (**2**) were prepared by literature methods and characterized by ^1H NMR and FAB MS. Ogoshi, H.; Watanabe, E.; Koketsu, N.; Yoshida, Z. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2529. $(TMP)Co\text{–}CH_2C(CH_3)_3$ (**1**): pyrrole region and high-field ^1H NMR (C_6D_6) δ 8.86 (s, 8H, pyrrole), −1.88 (s, 9H, $C(CH_3)_3$), −3.24 (br s, 2H, CH_2); FAB MS *m/e* 910. $(TMP)Co\text{–}C^{*}H(CO_2CH_3)CH_3$ (**2**): pyrrole region and high-field ^1H NMR (C_6D_6) δ 8.77 (d, 4H, pyrrole, $^3J_{H\text{-}H} = 4.8$ Hz), 8.72 (d, 4H, pyrrole, $^3J_{H\text{-}H} = 4.8$ Hz), −2.74 (q, 1H, $-CH(CO_2CH_3)CH_3$, $^3J_{H\text{-}H} = 7.2$ Hz), −4.61 (d, 3H, $-CH(CO_2CH_3)CH_3$, $^3J_{H\text{-}H} = 7.2$ Hz); FAB MS *m/e* 926. (The presence of a chiral carbon center in the axial ligand is manifested in the ^1H NMR by inequivalence of the adjacent hydrogens on the porphyrin pyrrole units.)

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doublet methyl end groups in **2** and **3**.[16] At higher monomer concentration ([MA]/[**2**] = 2500), only **4** is observed, and as the polymerization continues the resonances of **4** broaden slightly. Even though (TMP)Co$^{II\bullet}$ was not detected in the ^{1}H NMR, small quantities must be produced from inherent radical termination reactions.

The living nature of the MA polymerization induced by (TMP)-Co organo complexes is also illustrated by formation of acrylate block copolymers. Reaction of **2** with MA in benzene (MA/**2** = 2500) (60 °C) is used in forming a block of PMA attached to (TMP)Co (DP ~ 500, $\bar{M}_n$ = 40 600, $\bar{M}_w/\bar{M}_n$ = 1.22). Removal of unreacted MA followed by addition of butyl acrylate (BA) and benzene to the preformed PMA—Co(TMP) complex and heating at 60 °C results in BA polymerization to form an $(MA)_n(BA)_m$ block copolymer ($\bar{M}_n$ = 131 400, $\bar{M}_w/\bar{M}_n$ = 1.29).

Polymerization of acrylates induced by (TMP)Co—R complexes is envisioned as occurring by the reaction sequence given by eqs 1–5 (X = CO_2R', R' = CH_3, $(CH_2)_3CH_3$). Bond homolysis

$$\text{(TMP)Co—R} \rightleftharpoons \text{(TMP)Co}^{II\bullet} + \text{R}^\bullet \qquad (1)$$

$$\text{R}^\bullet + \text{CH}_2\text{=CHX} \rightarrow \text{RCH}_2\text{CHX}^\bullet \qquad (2)$$

$$\text{RCH}_2\text{CHX}^\bullet + \text{(TMP)Co}^{II\bullet} \rightleftharpoons \text{RCH}_2\text{CHX—Co(TMP)} \qquad (3)$$

$$\text{RCH}_2\text{CHX}^\bullet + (n+1)\text{CH}_2\text{=CHX} \rightarrow \text{RCH}_2\text{CHX(CH}_2\text{CHX)}_n\mathit{CH}_2\text{CHX}^\bullet \qquad (4)$$

$$\text{RCH}_2\text{CHX(CH}_2\text{CHX)}_n\text{CH}_2\text{CHX}^\bullet + \text{(TMP)Co}^{II\bullet} \rightleftharpoons \text{RCH}_2\text{CHX(CH}_2\text{CHX)}_n\text{CH}_2\text{CHX—Co(TMP)} \qquad (5)$$

of (TMP)Co–R produces a carbon-centered radical (R$^\bullet$) (eq 1) that initiates polymerization by reacting with an acrylate monomer to form $RCH_2CHX^\bullet$ (eq 2), which either combines reversibly with (TMP)Co$^{II\bullet}$ (eq 3) or reacts with additional acrylate monomers to form an oligomer radical (eq 4) that subsequently combines reversibly with (TMP)Co$^{II\bullet}$ (eq 5). Repetition of these events without radical termination or chain transfer would result in a fully living radical polymerization process. The real polymerization process cannot be fully living because of inherent bimolecular radical termination processes (eqs 6 and 7) and H$^\bullet$ transfer reactions with monomer, polymer, solvent (eq 8) and (TMP)Co$^{II\bullet}$ (eq 9) which result in nonliving polymer chains.

$$2{\sim}\text{CH}_2\text{CHX}^\bullet \rightarrow {\sim}\text{CH}_2\text{CHX—CHXCH}_2{\sim} \qquad (6)$$

$$2{\sim}\text{CH}_2\text{CHX}^\bullet \rightarrow {\sim}\text{CH}_2\text{CH}_2\text{X} + {\sim}\text{CH=CHX} \qquad (7)$$

$${\sim}\text{CH}_2\text{CHX}^\bullet + \text{HT} \rightarrow {\sim}\text{CH}_2\text{CH}_2\text{X} + \text{T}^\bullet \qquad (8)$$

$${\sim}\text{CH}_2\text{CHX}^\bullet + \text{(TMP)Co}^{II\bullet} \rightarrow {\sim}\text{CH=CHX} + \text{(TMP)Co—H} \qquad (9)$$

In spite of the processes that can limit polymer growth (eqs 6–9), observation of linear increases in $\bar{M}_n$ with conversion, formation of block copolymers, and relatively small polydispersities clearly demonstrate that **1** and **2** initiate an effective living radical polymerization of acrylates. ^{1}H NMR observations of the polymerization process and GPC data show that at least 95% of the polymer chains are living even at relatively high conversions. The small fraction of organoradicals that irreversibly terminate produce an increase in the (TMP)Co$^{II\bullet}$ concentration which suppresses the R$^\bullet$ concentration through the equilibrium with (TMP)Co—R (eqs 1, 3, and 5) until further irreversible inter-radical termination events (eqs 6 and 7) become improbable relative to polymer propagation (eq 4). This self-regulating suppression of radical termination by the presence of the stable (TMP)Co$^{II\bullet}$ metalloradical is an example of the persistent radical effect.[17] The capping agent in a living radical polymerization must additionally not initiate polymerization or produce irreversible reactions with the polymer radical such as β-H abstraction which terminate polymer chain growth. These criteria are fulfilled by (TMP)Co$^{II\bullet}$ because cobalt–carbon bonds are too weak to initiate alkene polymerization and the steric requirements of the TMP ligand effectively prohibit β-H abstraction. Recognition that organo–Co(TMP) complexes promote an effective living radical polymerization of acrylates along with an outline understanding of the phenomena is guiding our current effort in defining the range of metal complexes and alkene monomers that can participate in living radical polymerization processes.

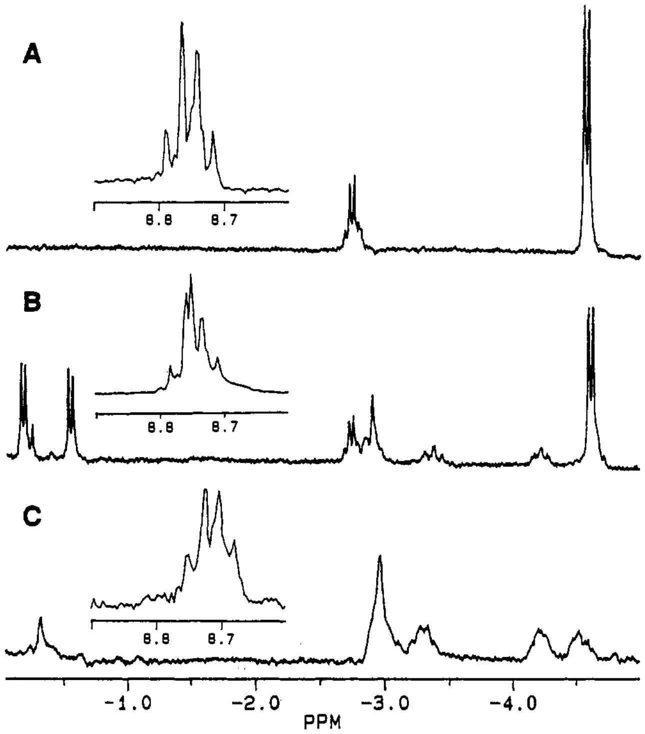

Figure 2. ^{1}H NMR (200 MHz) spectra for the high-field axial ligand and the porphyrin pyrrole regions that are observed during the reaction of (TMP)Co–CH(CO_2CH_3)CH_3 (1.0 × 10^{-3} M) and methyl acrylate (5.0 × 10^{-2} M) (60 °C, C_6D_6). (A) (t = 0) (TMP)Co–CH(CO_2CH_3)-CH_3 (**2**). (B) (t = 10 min) Mixture of **2** and (TMP)Co–CH(CO_2-CH_3)CH_2CH(CO_2CH_3)CH_3 (**3**). (C) (t = 6 h) (TMP)Co–CH(CO_2-CH_3)CH_2CH(CO_2CH_3)CH_2–PMA (**4**).

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[16] (TMP)Co–C*H(CO_2CH_3)CH_2C*H(CO_2CH_3)CH_3 (**3**): pyrrole region and high-field ^{1}H NMR (C_6D_6) δ 8.79–8.72 (4d, 4 × 4H, pyrrole), –0.17 (d, 3H, –CH(X)CH_3, $^3J_{H-H}$ = 7.2 Hz), –0.55 (d, 3H, –CH(X)CH_3, $^3J_{H-H}$ = 7.2 Hz), –2.85 to –2.92 (3H), –3.38 (1H), –4.22 (1H), –4.65 (1H) (CoCH(CO_2CH_3)CH_2–) (two sets of resonances are associated with the two diastereomers of **3**). (TMP)Co–C*H(CO_2CH_3)CH_2C*H(CO_2CH_3)CH_2–PMA (**4**): pyrrole region and high-field ^{1}H NMR (COCH(CO_2CH_3)CH_2–, C_6D_6) δ 8.76 (d, 4H, pyrrole, $^3J_{H-H}$ = 4.8 Hz), 8.72 (d, 4H, pyrrole, $^3J_{H-H}$ = 4.8 Hz), –2.9 (3H), –3.3 (1H), –4.3 (1H), –4.6 (1H) (As the oligomer organometallic complex increases in size, the high-field resonances slightly broaden but the positions remain essentially unchanged).

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