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New Life for Living Radical Polymerization Mediated by Cobalt(II) Metalloradicals

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Atom transfer radical polymerization (ATRP)[1−5] and stable free radical polymerization (SFRP)[6−10] are two complementary approaches to achieve living radical polymerization (LRP) of olefins. Any strategy to obtain living radical polymerization must control the radical concentration by an equilibrium with a dormant species such that bimolecular radical termination becomes suppressed relative to polymer growth. The dormant species for ATRP is typically a halide-terminated polymer formed reversibly by reaction of a polymer radical with a metal halide (M−X) while in SFRP a stable persistent organic[8−10] or metal-centered radical ($A^\bullet$)[6,7] reversibly binds the growing polymer radical ($P^\bullet$) to form a complex (A−P). These two approaches are complementary because they have different kinetic and thermodynamic criteria for the dormant species that control the concentration of the propagating radical. ATRP is currently more highly developed and employed in part because of the relative convenience and simplicity in applying the method. We have previously reported that organometallic complexes of cobalt tetramesitylporphyrin ((TMP)Co−R) function as a source of nonpersistent organic radicals ($R^\bullet$) that initiates radical polymerization and a persistent cobalt(II) metalloradical ($(TMP)Co^{II\bullet}$) that mediates a living polymerization process for acrylate monomers (eqs 1−3).[6,7] This metalloradical SFRP gives excellent control[6,7] but has not yet found broad applications because of the difficulty and impracticality of preparing the organo-cobalt catalyst reagents. This Communication reports on a more convenient and practical procedure that uses an organic radical source in combination with $(TMP)Co^{II\bullet}$ to obtain a living radical polymerization that occurs with enhanced rates and produces low-polydispersity acrylate homopolymers and acrylate block copolymers.

$$(TMP)Co{-}R \rightleftharpoons (TMP)Co^{II\bullet} + {}^\bullet R \tag{1}$$

$$n\mathrm{CH_2{=}CH(CO_2R')} + {}^\bullet R \rightarrow {}^\bullet P \tag{2}$$

$$(TMP)Co^{II\bullet} + {}^\bullet P \rightleftharpoons (TMP)Co{-}P \tag{3}$$

Solutions of methyl acrylate (2.5 M), V-70 ($[((CH_3)_2(CH_3O)CCH_2)(CN)(CH_3)C]_2N_2$) ($(0.7-2.0) \times 10^{-3}$ M), and $(TMP)Co^{II}$ (1.2×10^{-3} M) in benzene were heated to 333 K, and the conversion to polymer was followed by ^{1}H NMR (Figure 1). The induction time periods prior to observing polymerization, which decrease with increasing concentration of V-70, correspond to the time required to inject sufficient radicals to convert effectively all of the $(TMP)Co^{II}$ into an organometallic (TMP)Co−R. Production of a modest excess of total organic radicals[11,12] compared to the concentration of $(TMP)Co^{II}$ results in large increases in the rate of polymerization without substantial increase in the polydispersity or change in molecular mass (M_n)[13] (Figure 2). The polymers formed when using this convenient procedure showed a linear increase in number-average molecular weight (M_n) with conversion, unusually low polydispersity (~1.05), and molecular weights close to the theoretical values corresponding to one polymer chain per cobalt porphyrin (Figure 2).

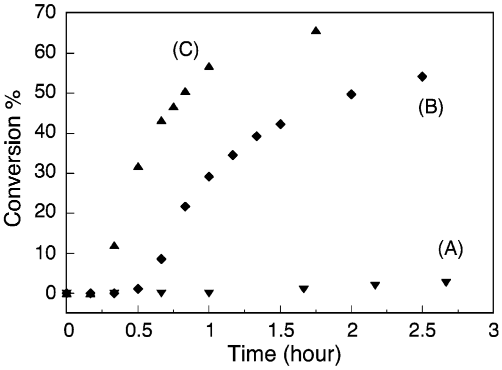

Figure 1. Monomer conversion as a function of time in the radical polymerization of methyl acrylate in benzene at 333 K with $[MA]_i = 2.5$ M and $[(TMP)Co^{II\bullet}]_i = 1.2 \times 10^{-3}$ M. A series of quantities of V-70 radical initiator were added to produce different ratios of the total $^\bullet C(CN)(CH_3)(CH_2C(CH_3)_2(OCH_3))$ radicals injected into solution to that of total cobalt porphyrin ($R^\bullet_T/Co^{II\bullet}_T$).[11] **(A)** ($R^\bullet_T/Co^{II\bullet}_T$) = 0.70; conversion = 47%, reaction time = 62 h, $M_n = 9.9 \times 10^4$, $M_w/M_n = 1.11$, theoretical $M_n = 1.2 \times 10^5$. **(B)** ($R^\bullet_T/Co^{II\bullet}_T$) = 1.2; conversion = 54%, reaction time = 150 min, $M_n = 9.5 \times 10^4$, $M_w/M_n = 1.04$, theoretical $M_n = 9.7 \times 10^4$. **(C)** ($R^\bullet_T/Co^{II\bullet}_T$) = 2.0; conversion = 69%, reaction time = 105 min, $M_n = 1.2 \times 10^5$, $M_w/M_n = 1.06$, theoretical $M_n = 1.2 \times 10^5$.

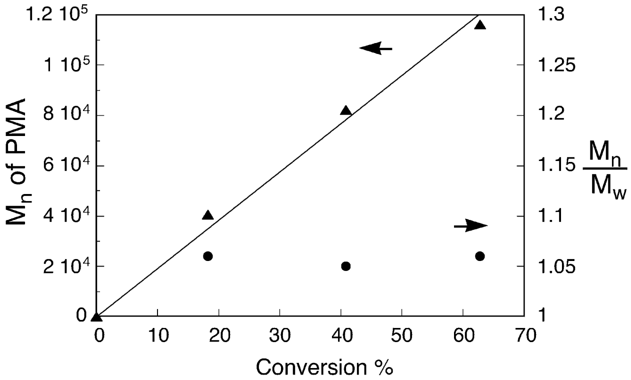

Figure 2. Change in the number-average molecular weight and polydispersity with methyl acrylate conversion to PMA initiated by V-70 when $[MA]_i = 2.5$ M, $[(TMP)Co^{II\bullet}]_i = 1.2 \times 10^{-3}$ M, and ($R^\bullet_T/Co^{II\bullet}_T$) = 1.2 at 333 K in benzene.[11]

Low-polydispersity poly(methyl acrylate)−poly(butyl acrylate) (PMA−PBA) block copolymers are formed by initially building one block of PMA, replacing MA with BA under vacuum, and heating to 333 K to reinitiate polymerization. Linear increase in the number-average molecular mass (M_n) with conversion and low polydispersity ($M_w/M_n \sim 1.07$) demonstrate the formation of a PMA−PBA block copolymer (Figure 3).

The first step in this polymerization process is injection of radicals into solution from an organic radical

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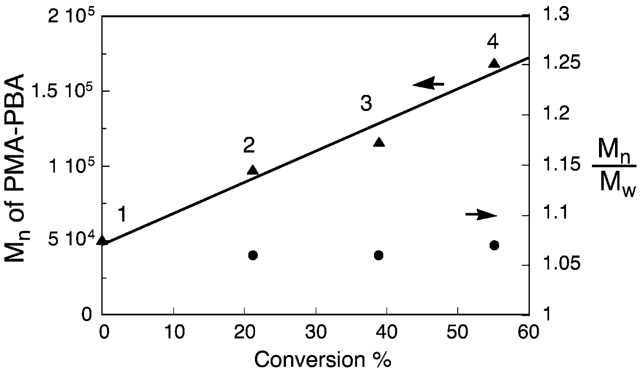

Figure 3. Change in number-average molecular weight and polydispersity with conversion in forming a block copolymer of PMA with PBA initiated by V-70 and mediated by $(\text{TMP})\text{Co}^{\text{II}\bullet}$ with $[(\text{TMP})\text{Co}^{\text{II}\bullet}]_i = 1.2 \times 10^{-3}$ M and $(\text{R}^\bullet{}_\text{T}/\text{Co}^{\text{II}\bullet}{}_\text{T}) = 1.2$ at 333 K in benzene.[11] **(1)** (TMP)Co−PMA block: $[\text{MA}]_i = 2.5$ M, conversion = 20%, reaction time = 45 min, $M_n = 5.1 \times 10^4$, $M_w/M_n = 1.09$. **(2−4)** (TMP)Co−PMA−PBA block initiated by (TMP)Co−PMA: **(2)** $[\text{BA}]_i = 2.5$ M, conversion = 20%, reaction time = 20 min, $M_n = 9.8 \times 10^4$, $M_w/M_n = 1.06$; **(3)** $[\text{BA}]_i = 2.5$ M, conversion = 39%, reaction time = 50 min, $M_n = 1.2 \times 10^5$, $M_w/M_n = 1.06$; **(4)** $[\text{BA}]_i = 2.5$ M, conversion = 55%, reaction time = 110 min, $M_n = 1.7 \times 10^5$, $M_w/M_n = 1.07$.

source. The dialkyl diazo compound V-70 is used because it is a relatively short-lived radical source ($t_{1/2}$(333 K) = 11 min) and effectively decays fully within 90 min. Fast methyl β-H abstraction from organic radicals by $(\text{TMP})\text{Co}^{\text{II}\bullet}$ forms a cobalt hydride ((TMP)Co−H) that subsequently adds reversibly to the olefin monomers to form an organo-cobalt complex (eqs 4−6). The organo-cobalt complex functions as a source of a monomer radical that propagates to form a polymer radical (eqs 7 and 8). Dimer and larger olefin radicals ($\text{P}^\bullet$) react with $(\text{TMP})\text{Co}^{\text{II}\bullet}$ exclusively to form a polymer organo-cobalt complex that controls the polymer radical concentration and mediates the living radical polymerization (eq 9). Hydrogen abstraction from the propagating radical by $(\text{TMP})\text{Co}^{\text{II}\bullet}$ which would terminate polymer growth and destroy the living character is virtually precluded by the combined steric requirements of the polymer radical and the cobalt tetramesityl porphyrin units (eq 10).

$$(\text{CN})(\text{R})(\text{CH}_3)\text{C}_2\text{N}_2 \xrightarrow{\Delta} 2(\text{CN})(\text{R})(\text{CH}_3)\text{C}^\bullet \tag{4}$$

$$(\text{CN})(\text{R})(\text{CH}_3)\text{C}^\bullet + (\text{TMP})\text{Co}^{\text{II}\bullet} \rightarrow (\text{TMP})\text{Co{-}H} + (\text{CN})(\text{R})\text{C{=}CH}_2 \tag{5}$$

$$(\text{TMP})\text{Co{-}H} + \text{CH}_2\text{{=}CH(X)} \rightleftharpoons (\text{TMP})\text{Co{-}CH(X)CH}_3 \tag{6}$$

$$(\text{TMP})\text{Co{-}CH(X)CH}_3 \rightleftharpoons (\text{TMP})\text{Co}^{\text{II}\bullet} + {}^\bullet\text{CH(X)CH}_3 \tag{7}$$

$$\text{CH}_3(\text{X})\text{HC}^\bullet + n\text{CH}_2\text{{=}CH(X)} \xrightarrow{k_p} {}^\bullet\text{CH(X)CH}_2\sim\sim \tag{8}$$

$$(\text{TMP})\text{Co}^{\text{II}\bullet} + {}^\bullet\text{CH(X)CH}_2\sim\sim \rightleftharpoons (\text{TMP})\text{Co{-}CH(X)CH}_2\sim\sim \tag{9}$$

$$(\text{TMP})\text{Co{-}CH(X)CH}_2\sim\sim \not\rightleftharpoons (\text{TMP})\text{Co{-}H} + \text{CH(X){=}CH}\sim\sim \tag{10}$$

Low-polydispersity homopolymers and block copolymer of acrylates are produced at relatively fast rates when $(\text{TMP})\text{Co}^{\text{II}\bullet}$ is used in conjunction with an organic radical source (V-70). The simplicity of this procedure is expected to expand the applications of the metallo-radical SFRP approach as a methodology for living radical polymerization of vinyl monomers.

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(11) The fraction of radicals that enter solution is 0.60 ± 0.02 of the total number produced in the thermal dissociation of V-70 at 333 K in C_6D_6. The rate of injection of freely diffusing radicals into solution was measured by a chemical trapping method.[12] The rate of radicals entering solution ($\text{d}[\text{R}^\bullet]/\text{d}t$ equals 1.2 times the rate of decomposition of V-70 ($-\text{d}[\text{V-70}]/\text{d}t$) which means that 60% of the potential radicals formed actually escape into solution.
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(13) Molecular weight of the polymer product was determined in THF by size exclusion chromatography employing both multiangle light scattering and DRI detectors calibrated with polystyrene standards.

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