

Macromonomer living character in the cobalt(II) porphyrin chain transfer catalysis for radical polymerization of methacrylic acid in water

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Macromonomers formed by cobalt(II) porphyrin catalyzed chain transfer in the aqueous radical polymerization of methacrylic acid acquire living character by continual reinitiation through reaction with an intermediate cobalt hydride.

Cobalt tetra-*p*-sulfonatophenyl porphyrin ((TSPP)Co^{II}) is exceptionally effective in catalytic chain transfer (CCT)¹ for the radical polymerization of methacrylic acid (MAA) in water. The absence of (TSPP)Co^{II} degradation under conditions of catalytic chain transfer (CCT) in water even with acidic substrates like MAA is an important advantage over other reported aqueous chain transfer catalysts.^{2–4} The reaction scheme that is generally used to describe cobalt(II) catalyzed chain transfer [eqn. (1)–(3)] involves cobalt(II) abstracting a hydrogen from a propagating oligomer radical to form (L)Co–H and an oligomer olefin called a macromonomer [eqn. (2)]. Subsequent hydrogen transfer from (L)Co–H to a monomer [eqn. (3)] initiates the propagation of a new oligomer chain.^{1,5–10} A mechanism based exclusively on reactions (1)–(3) requires that the average degree of polymerization (DP) decreases with conversion and this requirement has not been experimentally fulfilled.^{7,10–12} The need to modify this mechanistic scheme is clearly illustrated by the increase in DP with conversion for the (TSPP)Co^{II}/MAA system in water (Fig. 1). This article describes the importance of macromonomer reinitiation by reaction with the cobalt hydride ((TSPP)Co–H) to form an oligomer radical that grows by propagation with the monomer [eqn. (4), (5)]. The continual reinitiation and growth of oligomer olefin chains in the CCT process have profound influences on the distribution of oligomer products and are central aspects of the mechanism that have previously been under appreciated.

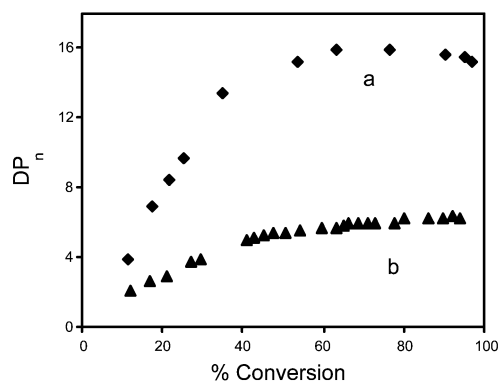
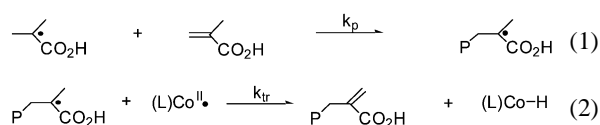
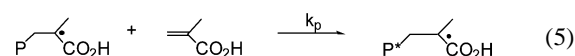
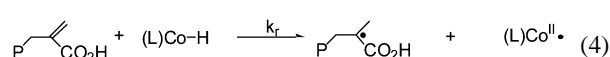
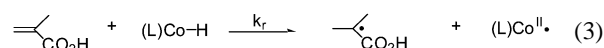


Fig. 1 Average DP as a function of monomer conversion for the polymerization of MAA (2.00 M) in water initiated by V-501 (1.19×10^{-2} M) at a series of (TSPP)Co^{II} concentrations (a) 9.80×10^{-5} M (b) 1.96×10^{-4} M.



Polymerizations of MAA (2.00 M) in water were initiated by 4,4'-azobis(4-cyanopentanoic acid) (V-501) (1.19×10^{-2} M) at 342 K in the presence of various concentrations of (TSPP)Co(II) (10^{-3} to 10^{-5} M). Disappearance of the monomer and appearance of oligomers were monitored continuously by ¹H NMR to determine the time dependence for both the monomer conversion and average DP for the macromonomers that were formed. Integration of the ¹H NMR of the oligomer methyl groups and one vinylic hydrogen was used in evaluating the DP as the conversion proceeded (DP = methyl area/3 (area of one vinylic hydrogen)).¹³ GPC using polystyrene standards was also applied in evaluating trends in the oligomer molecular weight distribution as a function of conversion. The change in degree of polymerization with conversion, first order rate plots, and Mayo type plots for the (TSPP)Co^{II} catalyzed chain transfer of the radical polymerization of methacrylic acid in water are illustrated in Figs. 1–3 respectively.

Substituting the pure dimer of MAA for the monomer in the above polymerization procedure did not result in any measurable extent of MAA dimer polymerization. This is consistent with prior reports that methacrylate dimers and higher oligomers do not form homopolymers by radical polymerization.¹⁴ This is an important mechanistic feature because the observed growth in the macromonomers is not from reinitiation by direct reaction with the monomer or oligomer radicals (R_1^{\cdot} ; R_n^{\cdot}). Reinitiation of the macromonomers occurs only by reaction with the cobalt hydride to form the radical (R_n^{\cdot}) that propagates exclusively with the monomer (MAA). This central mechanistic feature of the catalysis is reflected by reactions (4) and (5) in the mechanistic scheme. This aspect of the mechanism is also

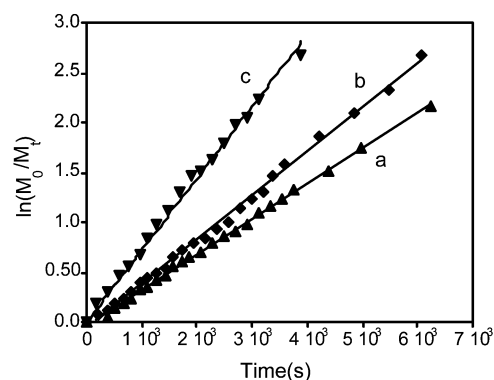


Fig. 2 1st order rate plots for polymerization of MAA (2.00 M) initiated by V-501 (1.19×10^{-2} M) in water at a series of (TSPP)Co^{II} concentrations: (a) 1.96×10^{-4} M; (b) 9.80×10^{-5} M; (c) 1.96×10^{-5} M.

supported by the absence of observed branching in the polymer products that would occur from productive reactions of radicals with the oligomer olefins.

Linearity of the first order rate plots ($\ln[M_0]/[M_t] = k_p[R^\cdot]t$) shows that radical polymerization of methacrylic acid in water in the presence of (TSPP)Co^{II} is kinetically well behaved and proceeds to high conversion (Fig. 2). One of the inherent reactions of monomer and oligomer radicals (R_1^\cdot , R_n^\cdot) with (TSPP)Co^{II} is formation of organometallic complexes [eqn. (6)]. Formation of organometallic complexes traps the radicals produced and results in an induction period for polymerization until the equilibrium for reaction (6) is established. The observed induction periods for MAA polymerization are short and correspond to only a few percent of the (TSPP)Co^{II} being combined with radicals before polymerization of MAA occurs (Fig. 2). The organometallic derivatives of (TSPP)Co with methacrylate radicals approach complete dissociation and thus most of the (TSPP)Co is in the form of the active cobalt(II) chain transfer catalyst. When the water soluble styrene derivative ($\text{CH}_2=\text{CHC}_6\text{H}_5\text{SO}_3\text{Na}$) is substituted in the polymerization process the (TSPP)Co^{II} catalyst is essentially removed from solution by organometallic complex formation and chain transfer is effectively quenched.



Representative Mayo type plots of $1/(\text{DP} - 1)$ versus $[(\text{L})\text{Co}^{\text{II}}]/[\text{MAA}]_0$ are given in Fig. 3. The slope of the Mayo plot at limiting small conversion gives the lower limit for the ratio of the chain transfer rate constant (k_{tr}) [eqn. (2)] to the monomer propagation constant (k_p). Only the lower limit for k_{tr} can be determined by this experiment because monomer propagation is effectively irreversible but hydrogen abstraction from the growing oligomer radical is reversible such that multiple hydrogen transfer events may occur for each oligomer chain. The slope of the Mayo type plot at 10% conversion is 3900 (Fig. 3) and using the k_p value of $7800 \text{ M}^{-1} \text{ s}^{-1}$ for MAA in water at 342 K¹⁵ gives $3.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ as the lower limit for the chain transfer rate constant at 342 K. The slope of Mayo type plots (Fig. 3) decreases with conversion primarily because of the increasing DP. The apparent chain transfer constant for (TSPP)Co^{II} in the radical polymerization of MAA in water ($k_{tr(342 \text{ K})} \geq 3.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) is exceptionally large. The comparable k_{tr} value for (TPP)Co^{II} with MMA in benzene is $\sim 1 \times 10^6$.^{1,16} It is clear that water as a solvent does not inhibit the cobalt(II) catalyzed chain transfer process.

In order for (TSPP)Co^{II} to function as an effective chain transfer catalyst there must be facile access of oligomer radicals (R_n^\cdot) to the metal center where hydrogen atom transfer occurs. It is surprising that (TSPP)Co^{II} is such an effective chain

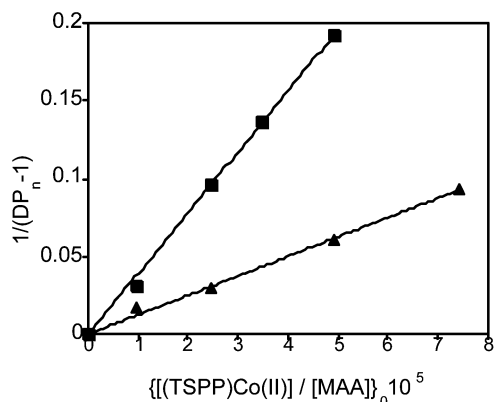


Fig. 3 Mayo type plots for (TSPP)Co^{II} and MAA ($[\text{MAA}]_0 = 2.00 \text{ M}$) in water (342K) and V-501 ($1.19 \times 10^{-2} \text{ M}$). ■ 10% conversion; $k_{tr} \geq 3.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$; ▲ 60% conversion; $k_{tr} \geq 9.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (slope $\leq k_{tr}k_p$; $k_p(342 \text{ K}) = 7800 \text{ M}^{-1} \text{ s}^{-1}$).

transfer catalyst in water where solvation of the cobalt(II) center might be expected to inhibit access of the organic radicals to the active metal site. The half filled d_{z^2} orbital makes cobalt(II) a relatively weak Lewis acid metal center which resists addition of two water molecules that would block access to the metal center.

The unexpected feature for the radical polymerization of MAA in the presence of (TSPP)Co^{II} is that the average degree of polymerization (DP) increases substantially as the fraction of monomer conversion increases (Fig. 1). In a radical polymerization where only chain transfer to monomer occurs [eqn. (1)–(3)] the DP regularly decreases as the monomer is consumed ($\text{DP} = k_p[R^\cdot][M]/k_{tr}[R^\cdot][\text{Co}^{\text{II}}]$) which is opposite to the experimental observations. Prior reports of changes in the DP with conversion that were inconsistent with exclusive chain transfer to monomer in a CCT process were ascribed to catalyst degradation⁷ and organometallic complex formation.¹⁰ In the case of the (TSPP)Co^{II}/MAA system studied here where the catalyst is indefinitely stable and the organometallic is highly dissociated, the observed increase in DP with conversion is clearly associated with the reinitiation and growth of the macromonomers produced in prior cycles [eqn. (1)–(5)]. Even when the DP remains approximately constant with conversion there is more monomer consumed in chain growth of the existing macromonomers than from initiation and propagation of new chains through chain transfer to monomer. Reinitiation of oligomer olefins and chain growth are significant inherent reactivity features of the (TSPP)Co^{II} catalyzed chain transfer process. Incorporation of reversible termination of oligomer radicals in the mechanistic model for chain transfer catalysis by (L)Co^{II} complexes resolves many of the inconsistencies of experimental observations with the over simplified mechanism that considers only chain transfer to monomer.

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