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# Catalysis by $C_5Ph_5Cr(CO)_3^{\bullet}$ of Chain Transfer during the Free Radical Polymerization of Methyl Methacrylate

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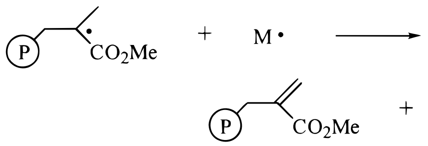
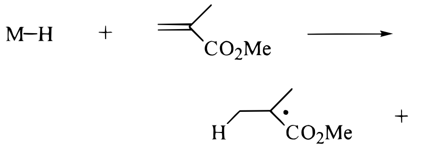
Catalysis of chain transfer during the radical polymerization of methyl methacrylate has been described previously for Co(II) chelate systems.[1] For a general metalloradical $M^{\bullet}$ this process involves reactions 1 and 2, where M−H is the metal hydride (derived from the metalloradical $M^{\bullet}$) that reacts with a monomer unit to start a new chain.



(1)



(2)

The polymer left after chain transfer (eq 1) will have a terminal vinyl group, and its molecular weight will be significantly lower than that produced by radical polymerization under the same conditions in the absence of the chain transfer catalyst. Kinetic studies of radical polymerizations in the presence of chain transfer catalysts have shown a decrease in the "gel effect" due to the decreased molecular weight of the product polymers.[2]

Isotopic labeling experiments where the alkyl methyl substituent of methyl methacrylate monomer was deuterated prior to polymerization support the above mechanism.[1a] Increasing the size of the substituent R on monomers $H_2C{=}C(Me)CO_2R$ decreases the rate of catalytic chain transfer, presumably because of steric interference with reaction 1.[1a,3] Gridnev and co-workers have measured a deuterium kinetic isotope effect of 3.5 on chain length during the polymerizations of MMA-$d_0$ amd MMA-$d_8$ in the presence of a Co(II) porphyrin[4] and have argued that this observation is evidence for a hydrogen atom transfer in the rate-determining step of chain transfer. Although no hydride reported to catalyze chain transfer has been isolated,[5] evidence for reaction 2 has been provided by the observation that methyl methacrylate polymerization is catalyzed by the species formed when a cobalt porphyrin anion is treated with acetic acid;[6] the existence of a related cobalt porphyrin hydride has been established by trapping experiments,[7] and a band in the electronic spectrum (650 nm) observed when cobaloximes are used as chain transfer catalysts has been assigned to LCoH.[8]

We wish to report that the known[9] metalloradical $(\eta^5\text{-}C_5Ph_5)Cr(CO)_3^{\bullet}$, **1**, also produces chain transfer during the radical polymerization of methyl methacrylate. We also report the synthesis of the analogous hydride $(\eta^5\text{-}C_5Ph_5)Cr(CO)_3H$, **2**, and the direct observation of its reaction with methyl methacrylate in the fashion required by eq 2.

**Table 1. Molecular Weight Data from the Polymerization of MMA at 100 °C in the Presence of Varying Concentrations of 1**

| $[\mathbf{1}]_0$ (M) | [AIBN] (M) | $M_n$ (g/mol) | polydispersity |
|---|---|---|---|
| $1.15 \times 10^{-4}$ | $1 \times 10^{-3}$ | 8 400 | 1.9 |
| $5.75 \times 10^{-5}$ | $1 \times 10^{-3}$ | 18 400 | 1.9 |
| $1.15 \times 10^{-5}$ | $1 \times 10^{-3}$ | 212 800 | 1.9 |
| $5.75 \times 10^{-6}$ | $1 \times 10^{-3}$ | 374 400 | 1.9 |
| $1.15 \times 10^{-6}$ | $1 \times 10^{-3}$ | 405 100 | 1.8 |

**Preparation of the Hydride 2.** Treatment of a THF solution of the carbonylmetalate anion related to **1**, $[(\eta^5\text{-}C_5Ph_5)Cr(CO)_3]^-$,[6] with 1 equiv of HCl in ether at 0 °C gives a high yield of the light green **2**.[10] A previous attempt was made to protonate $[(\eta^5\text{-}C_5Ph_5)Cr(CO)_3]^-$ with acetic acid, but no metal hydride was observed.[6] To our knowledge, **2** is the first transition-metal hydride with a pentaphenylcyclopentadienyl ligand to be isolated.

**Catalysis of Chain Transfer by the Metalloradical 1.** Heating under an inert atmosphere a methyl methacrylate (MMA) solution that contains **1** as well as the initiator AIBN leads to poly(methyl methacrylate) (PMMA) of relatively low molecular weight. The polymerization of 5 mL of MMA containing $5.75 \times 10^{-6}$ mol of **1** and $2.5 \times 10^{-5}$ mol of AIBN at 80 °C for 20 h results in 2.2 g of PMMA with a number-average molecular weight, $M_n$, of 901 g mol$^{-1}$ and a weight-average molecular weight, $M_w$, of 1278 g mol$^{-1}$. Using the weight-average molecular weight to calculate the moles of chains isolated (2.2 g of PMMA/1278 g mol$^{-1}$ PMMA) shows that the number of chains is 2 orders of magnitude higher than the number of initiator molecules and 3 orders of magnitude higher than the number of molecules of the chain transfer agent. IR and UV show a significant concentration of **1** throughout the reaction.

**Reaction of the Hydride 2 with MMA.** Upon heating to 100 °C a degassed $1.15 \times 10^{-4}$ M solution of **2** in 10 mL of MMA turns from light green to blue, the color characteristic of **1**, in approximately 10 min. Removal of excess monomer (conversion ≈ 10%) after 1 h affords PMMA with an $M_n$ of approximately 6500, close to the $M_n$ from an AIBN-initiated polymerization in the presence of a similar concentration of **1** (see Table 1). IR and UV show that the conversion of **2** to **1** is over 90%. Under the conditions employed **2** is thus consumed by reaction 2 more rapidly than it is generated by reaction 1.

**NMR of the Resulting PMMA.** The same resonances appeared in the NMR spectra of PMMA whether it was made from MMA with initiator and **1** or from MMA and **2** alone. $^1$H NMR of the low molecular weight material clearly showed the expected two vinyl resonances (with chemical shifts matching those previously reported from catalytic chain transfer[1a,11]) resolved from the bulk resonances. A spin echo experiment (which takes advantage of the $T_2$ difference between backbone and terminal nuclei in a polymer to suppress the signals from the backbone[12]) confirmed that the vinyl resonances were indeed terminal. Integration of the vinyl

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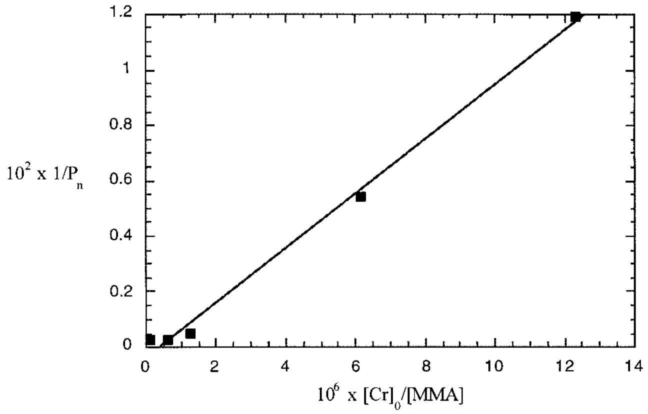
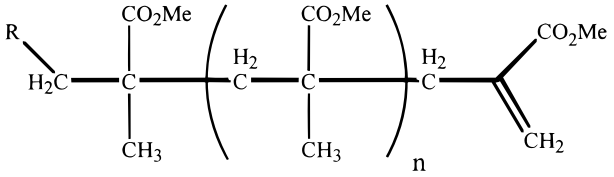


**Figure 1.** Mayo plot for the polymerization of MMA at 100 °C in the presence of **1**.

resonances vs the bulk resonance gave molecular weight data that matched the GPC data.



R = initiator or H

$^{13}C$ NMR spectra, an HMQC experiment, and $^{13}C$ DEPT spectra obtained on low-molecular-weight oligomers matched previous NMR results[11b] and confirmed the structure above. The integrations from an inverse gated decoupled $^{13}C$ spectrum fit these assignments and also agreed with the GPC data.

**Molecular Weight Distribution of the Resulting PMMA.** The Mayo equation[13] (eq 3) relates the reciprocal of the number-average degree of polymerization to the ratio of the concentration of the chain transfer agent to that of the monomer; $P_N$ is the number-average degree of polymerization, $P_{N0}$ is the number-average degree of polymerization in the absence of chain transfer agent, $k_{tr}$ is the rate constant for chain transfer by a growing polymer chain, and $k_p$ is the rate constant for addition of an additional monomer unit to a growing polymer chain. This equation has previously been used with catalytic chain transfer agents.[1a,b,14]

$$\frac{1}{P_N} = \frac{1}{P_{N0}} + \frac{k_{tr}}{k_p}\frac{[CTA]}{[MMA]} \qquad (3)$$

Low conversion (<10%) polymerizations were run in neat methyl methacrylate, with the concentration of **1** varied and the concentration AIBN held constant. The data, in Table 1, fit eq 3 and demonstrate that **1** can serve as a catalyst for chain transfer. The slope of the plot (Figure 1) yields a chain transfer constant, $k_{tr}/k_p$, at 100 °C of 984—a value of the same magnitude as those for other transition-metal catalysts for chain transfer.[1a,b] The most recent published Arrhenius parameters for the radical polymerization of methyl methacrylate[15] give 1800 $M^{-1}$ $s^{-1}$ for $k_p$ at 100 °C, implying a value of $1.77 \times 10^6$ $M^{-1}$ $s^{-1}$ for $k_{tr}$ at that temperature.

The metalloradical **1** is not an effective initiator of the polymerization of MMA. Neat MMA kept for 1 h at 100 °C (a temperature at which the autoinitiation of the polymerization of MMA is known to be very slow[16]) left only a minute residue of polymer after vacuum removal of the excess monomer. The same reaction with **1** also present ([**1**] = $4.3 \times 10^{-4}$ M) only reached 0.05% conversion after 1 h at the same temperature.

**Summary.** The agreement of the data in Figure 1 and Table 1 with eq 3 confirms that **1** catalyzes chain transfer during the radical polymerization of methyl methacrylate and thus that **1** can serve as $M^•$ in eq 1. The Cr-containing **1** is thus the first effective non-cobalt-containing CT catalyst.[17] The observation that **2** can (while being converted to **1**) initiate the polymerization of MMA marks the first time that an intermediate in eqs 1 and 2 has been isolated and its competence established.

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**Supporting Information Available:** Experimental details. The material is free of charge via the Internet at http://pubs.acs.org.

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(10) $^1H$ NMR (300 MHz, $C_6D_6$): $\delta$ 7.22–7.16 (m, 10H), 6.84–6.82 (m, 15H), −3.94 (s, 1H). IR ($CH_2Cl_2$): $\nu_{CO}$ 2004.2, 1921.3 $cm^{-1}$. Anal. Calcd for $C_{38}H_{26}CrO_3$: C, 78.35; H, 4.50. Found: C, 78.24; H, 4.49. A parent ion, $P^+$ *m/e* 582 ($^{52}Cr$), with the appropriate isotopic distribution was observed in the mass spectrum (a small amount of $P-1^+$ was also observed).

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(17) A patent on CT catalysis by dinuclear Cp carbonyl complexes (Janowicz, A. H. U.S. Patent 4,746,713, May 24, 1988) has been brought to our attention; they are far less active than the *monomeric* **1** that we have employed.

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