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# Communications to the Editor

## Effect of Steric Congestion on the Activity of Chromium and Molybdenum Metalloradicals as Chain Transfer Catalysts during MMA Polymerization

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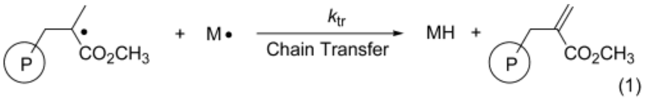
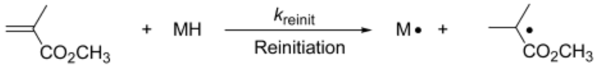
Catalysis of chain transfer is an efficient way of preparing low molecular weight polymers. In the generally accepted mechanism the catalyst $M^{\bullet}$ abstracts a hydrogen atom from a growing radical chain, yielding a vinyl-terminated polymer and an intermediate hydride complex M−H (eq 1); M−H then transfers $H^{\bullet}$ to monomer, initiating a new chain and regenerating the catalyst (eq 2).[1,2]



(1)



(2)

The original chain transfer catalysts were cobalt(II) macrocyclic complexes,[3] and they are still the most effective and the most commonly used. There has, however, been some investigation of other organometallic complexes. Recently Poli and co-workers[4] reported modest activity for an Mo(III) complex during the polymerization of styrene. In 1988, Dupont described in a patent the use of dimeric cyclopentadienyl metal carbonyl complexes as chain transfer catalysts (although they were generally not very effective) during the polymerization of MMA, methyl acrylate, and styrene.[5] In 2000, we reported that the hindered chromium metalloradical $(\eta^5\text{-}C_5Ph_5)Cr(CO)_3^{\bullet}$ (**1a**)[6] can catalyze ($C_S = 1000$) chain transfer during the AIBN-initiated polymerization of MMA.[7,8] We, and others,[1] explained the activity of **1a** relative to that of its unsubstituted analogue $(\eta^5\text{-}C_5H_5)Cr(CO)_3^{\bullet}$ (**1c**) (a modest $C_S$ of 100 had been reported for **1c** in the Dupont patent[5]) by the fact that its steric congestion keeps **1a** monomeric,[6] whereas **1c** dimerizes to a significant extent in solution.[9,10]

Many Co(II) macrocycles have been tested as chain transfer catalysts, and empirical generalizations have been offered, e.g., “a core of four nitrogen atoms ... is crucial”, “substituents on the equatorial ligand have only a moderate effect”, “planarity of the macrocycle is important”, “catalytic activity gradually decreases with increasing steric interference”, and “[other $N_4$ macrocyclic complexes of Co] are much less active than cobaloximes”.[1,11] There is, however, little understanding of *why* these generalizations are valid for the Co(II) systems. For our Cr systems we have already studied the effect of steric bulk on the reinitiation rate constant ($k_{reinit}$ in eq 2) for $(\eta^5\text{-}C_5R_5)Cr(CO)_3H$ (R = Ph, **2a**; R = Me, **2b**; R = H, **2c**) with MMA-$d_5$ and styrene-$d_8$: with MMA, $k_{reinit}$ decreases substantially as the steric bulk of the hydride complex increases; with styrene, the steric bulk of the hydride complex has little effect.[12] We have now studied the effects of steric bulk on the efficiency of the entire Cr catalytic cycle and suggest explanations for our results that should guide the choice of organometallic compounds to be tested for catalytic activity in the future.

We began by examining the substituted derivatives of the monomeric $C_5Ph_5$ metalloradical **1a**, e.g., $(C_5Ph_5)Cr(CO)_2(PMe_3)^{\bullet}$ and $(C_5Ph_5)Cr(CO)_2P(OMe)_3^{\bullet}$.[13] As Table 1 shows, they are much less active than **1a**—arguably because they are *too* hindered to permit facile $H^{\bullet}$ transfer. It appears that the phenyl substituents on **1a** serve no useful purpose beyond preventing dimerization.

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**Table 1. Chain Transfer Constants ($C_S$) of Metalloradicals in Radical Polymerization of MMA at 70 °C[a]**

| metalloradical | $C_S$ |
|---|---|
| $(C_5Ph_5)Cr(CO)_3^•$ | 1040[8] |
| $(C_5Ph_5)Cr(CO)_2(PMe_3)^•$ | 3.7 |
| $(C_5Ph_5)Cr(CO)_2P(OMe)_3^•$ | 35.7 |
| $(C_5Me_5)Cr(CO)_3^•$ | 6300[b] |
| $(C_5Me_5)Cr(CO)_2(PMe_3)^•$ | 4200[b] |
| $(C_5H_5)Cr(CO)_3^•$ | 25 000[b,c] |
| $(C_5H_5)Cr(CO)_2(PPh_3)^•$ | 1210 |
| $TpMo(CO)_3^•$ | 52 |
| $Tp^*Mo(CO)_3^•$ | 22 |

[a] The $C_S$ values were obtained from Mayo plots in the polymerization of neat MMA with 0.1% w/v AIBN as initiator. [b] The Mayo plot showed noticeable curvature; the $C_S$ values were obtained from the best linear fit. [c] The $C_S$ value was calculated on the assumption that **1c** is monomeric.

We have therefore examined *less* hindered Cr metalloradicals. Because our H/D exchange measurements showed that $(\eta^5\text{-}C_5Me_5)Cr(CO)_3H$ (**2b**) transferred $H^•$ to MMA more rapidly than $(\eta^5\text{-}C_5Ph_5)Cr(CO)_3H$ (**2a**),[12] we tried $(\eta^5\text{-}C_5Me_5)Cr(CO)_3^•$ (**1b**) as a chain transfer catalyst. The known strength of the Cr−Cr bond in $[(C_5Me_5)Cr(CO)_3]_2$, 14.7 kcal/mol,[10,14] implies that it will be 99.96% dissociated under typical MMA polymerization conditions (70 °C) when $[Cr]_{total}$ is $5 \times 10^{-5}$ M. At this temperature a Mayo plot, with $[Cr]_{total}$ ranging from 0 to $1 \times 10^{-5}$ M, showed some curvature (see discussion below) but considerable activity, with a chain transfer constant $C_S$ of about 6300—6 times that of **1a**.

In view of the **1b** result it seemed worthwhile to measure the activity of **1c** ourselves. Published data[9,10] imply that **1c** will be 98% dissociated under MMA polymerization conditions (70 °C) when $[Cr]_{total}$ is $5 \times 10^{-5}$ M. In our hands (Table 1) **1c** has proven to be a very active chain transfer catalyst, with a Mayo plot that is again curved (see below) but implies a $C_S$ of about 25 000—almost as high as the $C_S$ values of the most effective cobalt catalysts.[1,11] The discrepancy between our results and those in the Dupont patent[5] may reflect the air sensitivity of **1c** or its thermal decomposition during the longer polymerization time (6 h, compared to 30 min in our experiments) they employed.

The phosphine-substituted derivatives of **1b**, $(C_5Me_5)Cr(CO)_2(PMe_3)^•$,[15] and **1c**, $(C_5H_5)Cr(CO)_2(PPh_3)^•$,[16] have also proven active as a chain transfer catalysts (Table 1), although such substitution again decreases activity. We have also examined metalloradicals that contain hydridotris(pyrazolyl)borate (Tp) ligands in place of cyclopentadienyl ligands.[17] Both $TpCr(CO)_3^•$ [18] and its more stable (Tp* = hydridotris(3,5-dimethylpyrazolyl)borate) analogue $Tp^*Cr(CO)_3^•$ [18] decompose too rapidly at 70 °C to be practical as chain transfer catalysts during the radical polymerization of MMA. The more stable molybdenum metalloradicals $TpMo(CO)_3^•$ [19] and $Tp^*Mo(CO)_3^•$ [20] do indeed catalyze chain transfer, but with low $C_S$ values (52 and 22, respectively).

**Nonlinearity of Mayo Plots.** Although we obtained straight lines in the Mayo plots from most of the metalloradicals above, we found curved Mayo plots with the three most active catalysts, $(C_5H_5)Cr(CO)_3^•$ (**1c**), $(C_5Me_5)Cr(CO)_3^•$ (**1b**), and $(C_5Me_5)Cr(CO)_2(PMe_3)^•$. (The curvature was reproduced in several experiments and with MMA from either Aldrich or Rohm & Haas.) The Mayo plot of MMA with **1b** is shown in Figure 1.

The origin of these departures from linearity is not clear. One possibility is that some chain transfer catalyst is deactivated, by decomposition or by reaction with trace impurities. Such deactivation will produce observable results only with the most active catalysts, which are employed at the lowest concentrations. (A simulated Mayo plot showing the effect of such deactivation is given in the Supporting Information.) Deactivation has been noted earlier with cobalt catalysts at low concentrations, although it has generally been confined to the early stages of the reaction.[21]

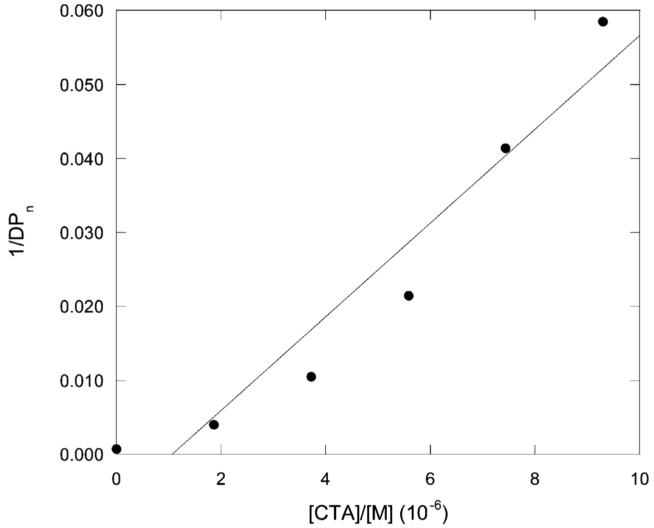

**Figure 1.** Mayo plot for MMA with $(C_5Me_5)Cr(CO)_3^•$ at 70 °C. Linear fit equation: $y = (-7 \pm 5) \times 10^{-3} + (6.3 \pm 0.9) \times 10^{-3}x$, $R = 0.963$, and $C_S = 6300$.

The nonlinearity of the Mayo plots for our three most active catalysts makes it difficult to be sure of their exact $C_S$ values. From the maximum and minimum slopes of the Mayo plot (over a range of catalyst concentrations as wide as possible), the $C_S$ value of $(C_5Me_5)Cr(CO)_3^•$ (**1b**) can be calculated to be between 2600 and 10 000; similarly, the $C_S$ value of $(C_5Me_5)Cr(CO)_2(PMe_3)^•$ is between 2300 and 6200, and the $C_S$ value of $(C_5H_5)Cr(CO)_3^•$ (**1c**) is between 8600 and 35 000. However, to make it easy to compare the $C_S$ values of all the metalloradicals, we have determined the $C_S$ values in Table 1 for the three most active catalysts from the best linear fits to *all* the points in their Mayo plots (Figure 1, Figure S4, and Figure S5). The true $C_S$ values for these catalysts may be higher or lower.

**Effect of Steric Hindrance on Catalysis of Chain Transfer.** The results in Table 1 show that steric hindrance on a metalloradical decreases its effectiveness as a chain transfer catalyst. However, our previous work suggests that steric hindrance can also *discourage* two side reactions that can *interfere* with chain transfer.

(i) The metalloradical can form an M−C bond with the chain-carrying radical. While rarely observed with the tertiary chain-carrying radical involved in MMA polymerization, M−C bond formation is often an issue when the chain-carrying radical is secondary, as it is during the polymerization of styrene.[1,2,8]

(ii) The hydride M−H can transfer $H^•$ to the chain-carrying radical, giving net hydrogenation of the monomer. Hydrogenation is not an issue when MMA is treated with any hydride **2** (because the radical formed by the initial $H^•$ transfer to MMA is tertiary), but there is significant hydrogenation when styrene is treated with **2c** and some when it is treated with **2b**.[12]

These results and the present ones have established what *features a metalloradical must possess in order to* *be an effective catalyst for chain transfer during free radical polymerizations*:

(a) It must be stable at the temperature of the polymerization.

(b) It should be *just crowded enough to discourage* (i) its own dimerization, (ii) the formation of an M−C bond with the chain-carrying radical, or (iii) transfer of $H^•$ from M−H to the chain-carrying radical. Additional steric hindrance on the metalloradical will slow its abstraction of $H^•$ from the chain-carrying radical and reduce its effectiveness.

(c) It should form an M−H bond as close as possible in strength to the $\beta$ C−H bond in the chain-carrying radical, making $H^•$ transfer facile in both eq 1 and eq 2.

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**Supporting Information Available:** Experimental details, Mayo plots, and a simulation of a nonlinear Mayo plot. The material is free of charge via the Internet at http://pubs.acs.org.

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