Factors Affecting the Apparent Chain Transfer Rate Constants of Chromium Metalloradicals: Mechanistic Implications

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Received July 13, 2006; Revised Manuscript Received September 13, 2006

ABSTRACT: When a high concentration of $(C_5Ph_5)Cr(CO)_3{}^{\bullet}$ (**1**) is present during the initiator-induced oligomerization of MMA, UV−vis spectra show that the concentration of the metalloradical decreases sharply at the beginning of the reaction (an "induction period") and remains constant subsequently (a "stable period"). With dimethyl 2,2′-azobis(isobutyrate) (AIBMe) as the initiator the decrease is due to the transfer of H$^{\bullet}$ from the methyl isobutyryl radical and the chain-carrying radicals to **1**, forming the corresponding hydride **2**. When the catalysis of chain transfer during a polymerization reaction is studied by the Mayo method, it is assumed that all the added **1** remains active. In truth the chain transfer constant (C_S) and chain transfer rate constant (k_{tr}) from the Mayo method are only "apparent" values; the true [**1**] during the polymerization is lower, and the true values of C_S and k_{tr} for this Cr catalyst are larger than those obtained from a Mayo plot. Simulations based on a simplified kinetic model reproduce our observations satisfactorily.

Introduction

Chain transfer catalysis is an effective way of lowering the molecular weight of the polymers produced by a free radical polymerization.[1] Such catalysts are thought to compete with propagation (eq 1) by removing an H$^{\bullet}$ from the chain-carrying radical, giving a vinyl-terminated polymer and a metal hydride (eq 2). The hydride then transfers H$^{\bullet}$ to monomer, initiating a new chain and regenerating the catalyst (eq 3). These processes are known as chain transfer (eq 2) and reinitiation (eq 3), respectively.

$$\frac{1}{DP_n} = \frac{1}{DP_{n0}} + \frac{k_{tr}[CTA]}{k_p[M]} \qquad (4)$$
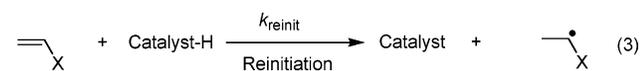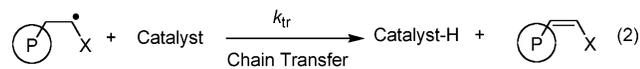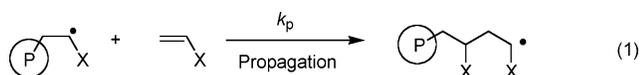
The efficiency of a chain transfer catalyst is expressed as the chain transfer constant (C_S), which is the ratio of the rate constant for the chain transfer reaction (k_{tr}) to that for propagation (k_p). Chain transfer constants are generally determined by the Mayo method,[2] in which the number-average degree of polymerization (DP_n) is determined for a series of reactions with different ratios of the chain transfer agent concentration [CTA] to the monomer concentration [M]. The Mayo equation (eq 4) implies that a plot of $1/DP_n$ vs [CTA]/[M] should give a straight line with a slope equal to the chain transfer constant, $C_S = k_{tr}/k_p$. (DP_{n0} is the number-average degree of polymerization in the absence of chain transfer agent.)

The original chain transfer catalysts were cobalt(II) macrocyclic complexes,[3] and they are still the most effective and the most commonly used. The hydride forms of these Co(II) catalysts were never observed, implying that reinitiation (eq 3) was extremely fast; chain transfer (eq 2) was thus believed to be the rate-determining step in chain transfer catalysis. Evidence for H$^{\bullet}$ transfer was offered by an unpublished experiment of Gridnev and Ittel:[4] AIBN and a Co(II) catalyst induced H/D exchange between MMA and MMA-d_8 before the sample could be put into an NMR spectrometer.

We have reported that chromium metalloradicals $(C_5R_5)Cr(CO)_3{}^{\bullet}$ (R = Ph, Me, H) are effective chain transfer catalysts during the free radical polymerization of MMA,[5,6] and have observed reinitiation (eq 3) directly by treating the corresponding hydrides $(C_5R_5)Cr(CO)_3H$ (R=Ph, Me, H) (which are stable) with MMA.[7] However, the reinitiation rate constants k_{reinit} that we have determined by monitoring H/D exchange between these hydrides and MMA-d_5 are quite small ($10^{-2}-10^{-3}$ M^{-1} s^{-1} at 50 °C).[7]

It has been suggested that, in the polymerization of MMA, the chain transfer in eq 2 occurs through a caged radical pair (eq 5) rather than by β-hydrogen elimination from a coordinated radical (eq 6).[1,8,9,10] However, when cobalt(II) catalyzes chain transfer during the polymerization of styrene[11,12] and acrylates[13,14] there is evidence that a Co−C bond is formed reversibly, decreasing the concentrations of the chain-carrying radical and the active Co(II) catalyst species (eq 7);[8,12b] there is no evidence that such Co−C bonds form when cobalt(II) catalyzes chain transfer during the polymerization of MMA.
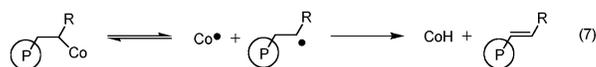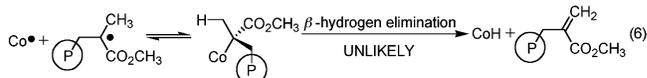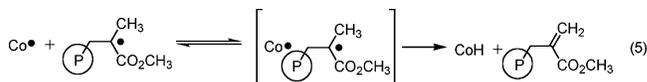
With cobalt(II) catalysts the chain transfer rate constant k_{tr} obtained from a Mayo plot is affected by many factors, including

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the viscosity, the concentration of chain-carrying radicals, and the presence of oxygen and other impurities.[8] We found similar results for our chromium metalloradical $(C_5Ph_5)Cr(CO)_3^{\bullet}$ (**1**): C_S decreased as (a) the concentration of the initiator increased, (b) the concentration of the monomer decreased by the addition of toluene, or (c) the temperature increased.[15] It seemed possible that a solvent cage like the one in eq 5 explained these observations.[15]

When a chain transfer constant C_S is obtained from the Mayo equation (eq 4),[2] it is tacitly assumed that all of the "catalyst" added remains active. This is, however, not always true. For example, formation of a Co–C bond like that in eq 7 decreases the concentration of the Co(II) active catalyst during the polymerization of styrene or acrylates.[1,8,11–14] It seems appropriate to call a chain transfer rate constant derived from the Mayo method an *apparent* value (k_{tr}(app)) if a significant fraction of the added catalyst is not in the active form. In the present manuscript we have added a large concentration of our Cr chain transfer catalyst ($Cr^{\bullet}$) to a solution of MMA and a radical initiator, and monitored the time dependence of [$Cr^{\bullet}$] and [CrH]. We have then studied *by kinetic simulation* the behavior of such systems with the *lower concentrations of chain transfer catalyst* that are *actually employed during polymerization*s.

Results and Discussion

Reaction between $(C_5Ph_5)Cr(CO)_3^{\bullet}$ and AIBN upon Heating. We began by examining the stability of the metalloradical $(C_5Ph_5)Cr(CO)_3^{\bullet}$ (**1**). At 70 °C in benzene under N_2 **1** showed no sign of decomposition after 1 day; the UV–vis and ^{1}H NMR spectra were unchanged. When **1** (0.1 M in benzene) was heated with MMA at 50 °C, no significant decomposition was observed by IR within 1.5 h (each of the polymerizations used to determine C_S takes about 30 min[15]). However, the concentration of **1** decreased slowly when an 0.005 M solution of it in C_6D_6 was heated with AIBN (0.03M) at 60 °C. Small amounts of methacrylonitrile and the chromium hydride $(C_5Ph_5)Cr(CO)_3H$ (**2**) were observed by ^{1}H NMR during the first 2 h, while the total concentration (estimated from the C_5Ph_5 signals of **1** and **2**) of the two Cr species decreased continuously. Heating for a longer time (24 h) resulted in the complete decomposition of these Cr species.

These results suggested a reaction like that in eq 2 $-H^{\bullet}$ transfer from the cyanoisopropyl radical (generated from the homolytic cleavage of AIBN, eq 8) to **1** (eq 9).

$$\text{AIBN} \xrightarrow{\text{heat}} 2 \text{ (cyanoisopropyl radical)} + N_2 \quad (8)$$

$$\text{(cyanoisopropyl radical)} + (C_5Ph_5)Cr(CO)_3^{\bullet} \longrightarrow \text{(methacrylonitrile)} + (C_5Ph_5)Cr(CO)_3H \quad (9)$$
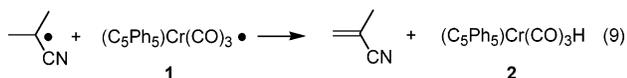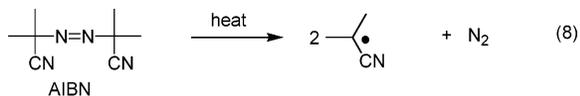
When **2** was treated with excess methacrylonitrile at 50 °C in C_6D_6, ^{1}H NMR showed that **2** disappeared within 2 h and that no **1** was generated. The decomposition of **2** was confirmed by the changing color of the solution (from pale green to black). New peaks observed at δ 5.21, 4.96, and 1.33, near those of free methacrylonitrile (δ 5.10, 4.77, and 1.25), suggested that methacrylonitrile had become coordinated to the metal center. The displacement of carbonyls by nitriles is well-known, e.g., in the reaction of $Cr(CO)_6$ with MeCN to yield $Cr(CO)_3$-$(MeCN)_3$,[16] and metalloradicals are known to be labile; e.g., $(C_5Me_5)Cr(CO)_3^{\bullet}$ reacts with *tert*-butyl isocyanide to yield $(C_5Me_5)Cr(CO)_2(t\text{-BuNC})^{\bullet}$.[17]
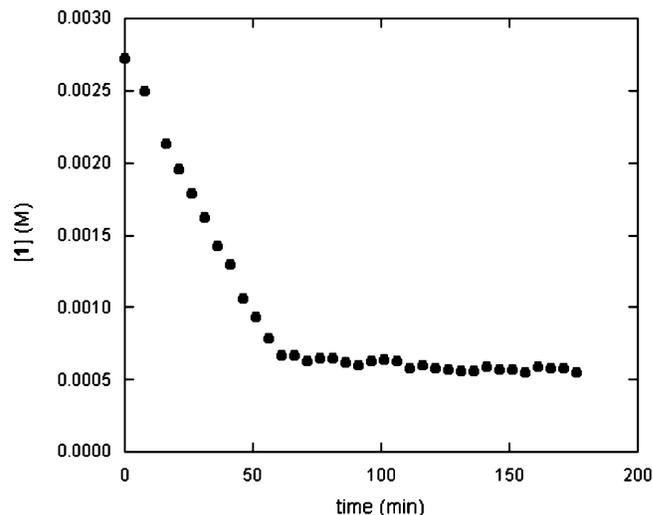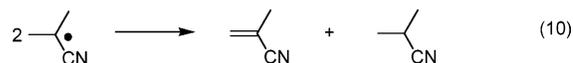

Figure 1. Concentration of $(C_5Ph_5)Cr(CO)_3^{\bullet}$ (**1**) in the presence of AIBN and MMA at 70 °C. [**1**]$_0$ = 0.0027 M, [AIBN]$_0$ = 0.0061 M, [MMA]$_0$ = 3.0 M in benzene, and **1** was monitored by UV–vis at 611 nm.

Such carbonyl displacement probably explains the slow disappearance of the Cr metalloradical **1** when heated with AIBN. Methacrylonitrile would have been produced by the operation of eq 9, whereas the disproportionation of cyanoisopropyl radicals (eq 10) would have produced methacrylonitrile and isobutyronitrile (also observed by ^{1}H NMR).

$$2 \text{ (cyanoisopropyl radical)} \longrightarrow \text{(methacrylonitrile)} + \text{(isobutyronitrile)} \quad (10)$$

Disappearance of $(C_5Ph_5)Cr(CO)_3^{\bullet}$ (1) during AIBN-Initiated Polymerization. The disappearance of the Cr metalloradical **1** in the presence of AIBN suggested that we examine the concentration of **1** as it catalyzed chain transfer during an AIBN-initiated polymerization—and indeed [**1**] appeared to decrease during experiments like the ones involved in determining C_S. The solutions, originally pale blue (with an intensity varying with the concentration of **1**), became colorless after 20–35 min of heating and polymerization.[15] However, [**1**] was so small (typically from 10^{-5} to 2×10^{-4} M)[15] in the experiments to determine C_S that it was difficult to quantify it by UV–vis.

Use of a much higher initial concentration of **1** ([**1**]$_0$ = 0.0027 M) confirmed that [**1**] decreased during an AIBN-initiated polymerization of MMA. Figure 1 shows a sharp decrease in [**1**] during the first 50 min of the reaction (an "induction period"), although [**1**] remains stable subsequently (a "stable period").

Both the operation of eq 9 and the substitution of **1** (by nitriles) should be effective in decreasing [**1**] under the conditions in Figure 1,[18] although the situation becomes more complicated as chain length increases: the chain-carrying radicals can also convert **1** into **2** through chain transfer reactions (eq 2). The presence of these longer-chain radicals will not affect the rate at which nitriles are formed by the homolytic cleavage of AIBN. The observation of a "stable period" after the "induction period" in Figure 1 suggests that the induction period arises from chain transfer (eqs 2 and 9) rather than from nitrile substitution.

In Figure 1 the concentration of **1** during the "stable period" ([**1**]$_{st}$) is about 20% of that originally added ([**1**]$_0$). Thus, the values of C_S reported in our previous work,[15] obtained by the Mayo method,[2] should be considered apparent chain transfer constants (C_S(app)); the true chain transfer constant, C_S(true),

will be 5 times larger (as derived from eq 11).

$$\frac{C_S(app)}{C_S(true)} = \frac{[\mathbf{1}]_{st}}{[\mathbf{1}]_0} \qquad (11)$$

Any factors that change $[\mathbf{1}]_{st}$ will affect the determination of C_S by the Mayo method.[2] For example, at a higher temperature or with a larger [initiator], the total concentration of free radical species will be larger, and the operation of eqs 2 and 9 will consume more active catalyst **1**. In principle, a higher temperature or larger [AIBN] will also generate nitriles more quickly, which will consume **1** (by decomposition) more quickly. As a result, the decrease of [**1**] at a higher temperature or with a larger [AIBN] will cause the decrease in C_S values that we have reported previously.[15]

AIBMe-Initiated Polymerization of MMA in the Presence of (C₅Ph₅)Cr(CO)₃•. As discussed above, three factors (eq 2, eq 9 and substitution of $(C_5Ph_5)Cr(CO)_3^{\bullet}$ (**1**) by nitriles) contribute to the decrease of the active catalyst **1** during an AIBN-initiated polymerization. Of course the reaction in eq 2 (chain transfer) is necessary during a catalytic chain transfer polymerization, but it will be much easier to obtain accurate rate constants for chain transfer if the other two reactions can be eliminated.

Equation 9 can be eliminated by using an initiator that produces a radical with no β-hydrogen. The widely used benzoyl peroxide (BPO) appeared to be a good candidate, but it induced slow decomposition of **1** (^{1}H NMR) when they were heated at 60 °C in C_6D_6; after 24 h all the **1** was gone. Furthermore, **1** proved *inactive* at catalyzing chain transfer ($C_S = 17$) when BPO was used to initiate the polymerization of MMA at 70 °C, perhaps because **1** had been oxidized by BPO.

Equation 9 can be made identical to eq 2 by using AIBMe (dimethyl 2,2′-azobis(isobutyrate)) as the initiator. AIBMe generates (eq 12) the same methyl isobutyryl radical **3** that is generated by H• transfer to MMA, so the reaction between **3** and the metalloradical **1** (eq 13) is a "chain transfer" like eq 2. Furthermore, using AIBMe as an initiator avoids generating polymer chains ended by initiator fragments.

(eq 12)

(eq 13)
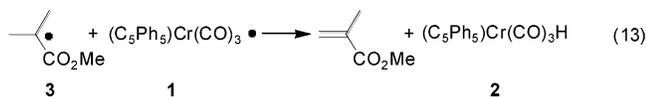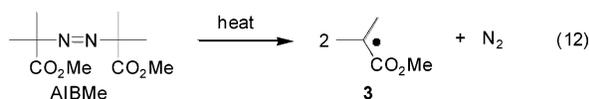
As expected, an increase in [**2**] and [MMA] was observed by ^{1}H NMR when **1** (0.005 M) was heated with AIBMe (0.025 M) at 70 °C in C_6D_6; there was no significant loss of total Cr (**1** + **2**) in 28 h. Small amounts of **3**/**3** termination products (methyl isobutyrate and dimethyl tetramethylsuccinate) and MMA dimer were also generated.[19]

Behavior like that in Figure 1 was observed (Figure 2) when a high concentration of **1** was heated with AIBMe and MMA in C_6D_6 at 70 °C. As discussed above, with AIBMe the sharp decrease of [**1**] during the "induction period" can *only* be due to H• transfer from the monomeric MMA radical (eq 13) or chain-carrying radicals[18] (eq 2). The similarity of Figures 1 and 2 argues that the sharp decrease of [**1**] at short times in Figure 1 (with AIBN as initiator) was largely due to H• transfer from chain-carrying radicals (eq 2) and monomeric MMA radical **3** (eq 13) rather than to the slow decomposition of **1**.
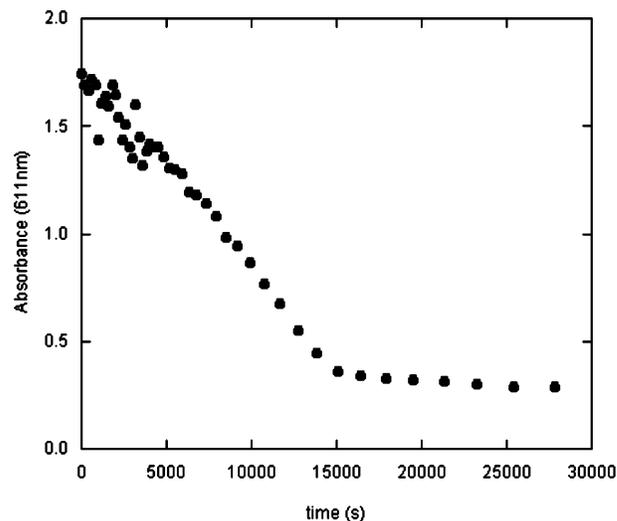

Figure 2. Absorbance of $(C_5Ph_5)Cr(CO)_3^{\bullet}$ (**1**) in the presence of AIBMe and MMA. $[\mathbf{1}]_0 = 0.00909$ M, [AIBMe] = 0.0148 M, [MMA] = 0.0935 M in C_6D_6 at 70 °C, and **1** was monitored by UV−vis at 611 nm in a cell with $l = 0.5$ cm.

Table 1. C_S(app) and k_{tr}(app) at Different Temperatures during the AIBMe-Initiated Polymerization of MMA in the Presence of $(C_5Ph_5)Cr(CO)_3^{\bullet}$ (1)^a

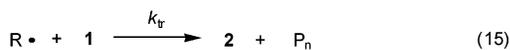| temperature (°C)	60.2	70.0	80.0
C_S(app)	1900	1300	990
k_p (M^{-1} s^{-1}) ^{b}	840	1050	1320
k_{tr}(app) (M^{-1} s^{-1})	1.6×10^6	1.4×10^6	1.3×10^6

^{a} Initial [AIBMe]$_0$ = 0.0434 M. ^{b} k_p is obtained as a function of temperature: $k_p = 10^{6.427} \times e^{-22360/RT}(-1 < T < 90 $ °C).[20]

The Cr radical **1** proved active at catalyzing chain transfer even if the polymerization of neat MMA was initiated by AIBMe instead of AIBN. The apparent chain transfer constants, from Mayo plots at various temperatures with 0.00434 M of AIBMe, are given in Table 1. The apparent chain transfer rate constant k_{tr} for the AIBMe-initiated polymerization still (as we reported earlier for AIBN-initiated MMA polymerization[15]) decreased with temperature (Table 1); the apparent C_S value decreased to 730 as the initial [AIBMe] increased to 0.00869 M at 70 °C.

Effect of the Conversion of 1 to 2 on C_S Measurement. Rate Constants for Modeling the AIBMe System. At the high [**1**] in the experiments in Figures 1 and 2, only oligomers are produced because chain transfer is extensive. However, when **1** is used as a chain transfer catalyst during a normal polymerization, its concentration is so low (usually between 10^{-5} and 2×10^{-4} M) that it cannot be determined accurately by UV−vis or ^{1}H NMR. With AIBMe as the initiator the only reactions that consume **1** are chain transfers from monomeric MMA radical **3** (eq 13) or from chain-carrying radicals (eq 2). The situation is straightforward enough that, even at low [**1**], kinetic simulation can clarify the difference between the apparent chain transfer constant C_S(app) obtained by the Mayo method (eq 4)[2] and the true chain transfer constant C_S(true).

During most radical polymerizations there is extensive propagation before termination. High molecular weight polymer is generated soon after the reaction begins, and the fraction of all radicals that are monomeric is very small. This statement remains true in the presence of moderate concentrations of a chain transfer catalyst, as long as polymer of high molecular weight is produced.[21] We can therefore treat all radicals as chain-carrying, with a single rate constant for chain transfer[22] and termination, and ignore propagation reactions, which do not change the total radical concentration.

Equations 14−17 model an AIBMe-initiated polymerization of MMA with chain transfer catalysis by $(C_5Ph_5)Cr(CO)_3{}^\bullet$ (**1**). $R^\bullet$ represents all free radical species—monomeric, oligomeric, and polymeric MMA-derived radicals. P_n denotes the vinyl-terminated polymers, and TP denotes all termination products.

$$\text{AIBMe} \xrightarrow{fk_d} 2\ R\bullet \tag{14}$$

$$R\bullet + \mathbf{1} \xrightarrow{k_{tr}} \mathbf{2} + P_n \tag{15}$$

$$\mathbf{2} + \text{MMA} \xrightarrow{k_{reinit}} R\bullet + \mathbf{1} \tag{16}$$

$$2\ R\bullet \xrightarrow{k_t} \text{TP} \tag{17}$$

The effects of temperature on the decomposition rate constant k_d and the efficiency of initiation f are known: $\ln k_d = 33.1 - 14800/T$ and $\ln f = 0.58 - 330/T$ for the homolytic decomposition of AIBMe in MMA,[23] equations comparable to those known for AIBMe[24,25] and AIBN[26] in other solvents. We have extrapolated the reinitiation rate constants k_{reinit} between $(C_5Ph_5)Cr(CO)_3H$ (**2**) and MMA at different temperatures from our previous work.[7] We have extrapolated the termination rate constants at different temperatures from the temperature dependence[27] of k_t ($9.8 \times 10^7 e^{-2930/RT}$) during an MMA polymerization with $DP_n = 10^4$; we have extended these termination rate constants to shorter chains by taking DP_n as 150,[28] the length typical for chain transfer catalysis with $[\mathbf{1}] = 5 \times 10^{-5}$ M.[21] Table 2 shows the rate constants for eqs 14, 16, and 17 at different temperatures.

From $k_{tr}(\text{app}) = 1.4 \times 10^6$ M^{-1} s^{-1} at 70 °C in Table 1, and the observed ratio of $[\mathbf{1}]_{st}$ to **1** in Figures 1 and 2 (about 1/5− 1/4), we have estimated $k_{tr}(\text{true})$ in eq 15 to be 6×10^6 M^{-1} s^{-1} at the same temperature.

Simulations. The first h of reaction time for the AIBMe system (eqs 14−17) in neat (9.35 M) MMA was simulated with Kintecus (version 3.7)[29] and the above rate constants. Taking $[\text{AIBMe}]_0 = 0.00434$ M and $[\mathbf{1}]_0 = 5 \times 10^{-5}$ M gave the results in Figure 3. [AIBMe] decreased slowly as its homolysis proceeded, while [TP] (concentration of termination products) and $[P_n]$ (concentration of vinyl-terminated polymers) increased (Figure 3a). However, the increase of $[P_n]$ was much faster than that of [TP], as expected in the presence of a chain transfer catalyst.

Figure 3b shows the "induction period" followed by a "stable period" obtained for [**1**], in good agreement with the behavior observed (Figure 2) when a large amount of **1** was heated with AIBMe and MMA under the same conditions; the same Figure shows that [**2**] increased rapidly during the "induction period" and remained constant during the "stable period". Figure 3c shows that [Rdot] ($[R^\bullet]$) increased rapidly during the "induction period" and remained in a steady state during the "stable period".

The model in eqs 14−17 implies the rate laws in eqs 18 and 19.

$$-\frac{d[\mathbf{1}]}{dt} = \frac{d[\mathbf{2}]}{dt} = k_{tr}(\text{true})[\mathbf{1}][R^\bullet] - k_{reinit}[\mathbf{2}][\text{MMA}] \tag{18}$$

$$\frac{d[R^\bullet]}{dt} = 2fk_d[\text{AIBMe}] + k_{reinit}[\mathbf{2}][\text{MMA}] - k_{tr}(\text{true})[\mathbf{1}][R^\bullet] - 2k_t[R^\bullet]^2 \tag{19}$$

The fast decrease of [**1**] and the fast increase of [**2**] during the "induction period" were due to the fact that chain transfer (eq 15) was then faster than reinitiation (eq 16). The constant
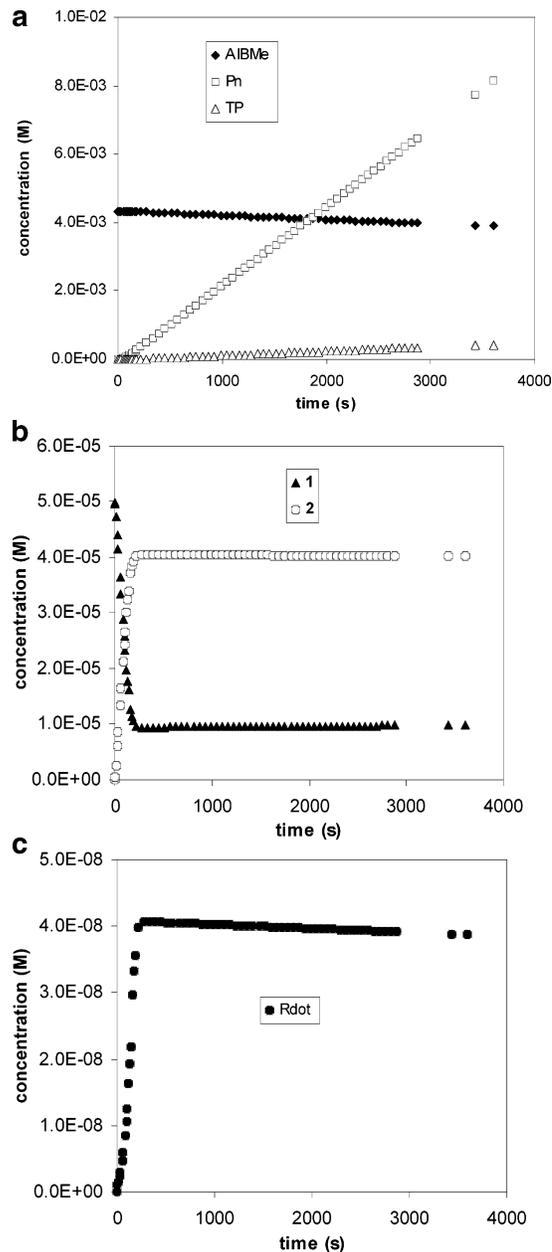
Figure 3. Simulation of concentration changes during the AIBMe-initiated polymerization of MMA at 70 °C with $(C_5Ph_5)Cr(CO)_3{}^\bullet$ as a chain transfer catalyst. Key: (a) simulated concentration changes of AIBMe, P_n and TP; (b) simulated concentration changes of $(C_5Ph_5)Cr(CO)_3{}^\bullet$ (**1**) and $(C_5Ph_5)Cr(CO)_3H$ (**2**); (c) simulated concentration changes of $R^\bullet$. $[\text{MMA}]_0 = 9.35$ M, $[\text{AIBMe}]_0 = 0.00434$ M, $[\mathbf{1}]_0 = 5 \times 10^{-5}$ M, and $k_{tr}(\text{true}) = 6 \times 10^6$ M^{-1} s^{-1}.

Table 2. Rate Constants for Equations 14, 16, and 17

temp (°C)	fk_d (s^{-1})	k_{reinit} (M^{-1} s^{-1})	k_t (M^{-1} s^{-1})
60	8.0×10^{-6}	0.0030	7.6×10^7
70	3.0×10^{-5}	0.0061	7.8×10^7
80	1.0×10^{-4}	0.011	8.0×10^7

[**1**] and [**2**] during the "stable period" implied that the rates of chain transfer and reinitiation were balanced during this period $(k_{tr}(\text{true})[\mathbf{1}][R^\bullet] = k_{reinit}[\mathbf{2}][\text{MMA}])$.[30] As a result, during the "stable period" eq 19 turned into eq 20.

$$\frac{d[R^\bullet]}{dt} = 2fk_d[\text{AIBMe}] - 2k_t[R^\bullet]^2 \tag{20}$$

Table 3. Values of $[1]_{st}/[1]_0$ and Induction Period Seen in Simulations with Different $[AIBMe]_0$ and $[1]_0$ at 70 °C[a]

trial no.	$[AIBMe]_0$ (M)	$[1]_0$ (M)	$[1]_{st}/[1]_0$ (%)	induction period (s)
1[b]	0.00434	5×10^{-5}	19	277
2	0.00434	5×10^{-4}	20	2060
3	0.00434	1.5×10^{-4}	19	676
4	0.00434	5×10^{-6}	19	46
5	0.00109	5×10^{-5}	32	815
6	0.00109	1.25×10^{-5}	32	287
7	0.0434	5×10^{-4}	7	221

[a] $k_{tr}(true) = 6 \times 10^6$ M^{-1} s^{-1}. [b] Values from Figure 3.

Table 4. Values of $[1]_{st}/[1]_0$ and Induction Period from Simulations with Different k_{reinit} at 70 °C[a]

trial no.	k_{reinit} (M^{-1} s^{-1})	$[1]_{st}/[1]_0$ (%)	induction period (s)
1[b]	0.0061	19	277
8	0.01	29	269
9	0.1	79	153
10	1	97	19

[a] $[1]_0 = 5 \times 10^{-5}$ M, $[AIBMe]_0 = 0.00434$ M, $k_{tr}(true) = 6 \times 10^6$ M^{-1} s^{-1}. [b] Values from Figure 3.

Figure 3c showed R$^•$ reaching a steady state $(d[R^•]/dt = 0)$ during the "stable period". During this period, from eq 20

$$[R^•] = \sqrt{fk_d[AIBMe]/k_t}$$

which is the same as the equation for a free radical polymerization in the absence of chain transfer catalyst.[31] This result is reasonable since chain transfer catalysis should not change the total concentration of radical species.

During the "stable period", when the time derivatives in eq 18 and eq 20 are both zero, **1** and **2** are the only chromium species present, so $[1]_0 = [1]_{st} + [2]_{st}$, leading to eq 21. This result implies that the value of $[1]_{st}/[1]_0$ should be affected by the rate constants and by the concentrations of monomer and of initiator. ($[1]_{st}$ is the concentration of **1** during the stable period.)

$$\frac{1}{[1]_{st}/[1]_0} = 1 + \frac{k_{tr}(true)\sqrt{fk_d}}{k_{reinit}\sqrt{k_t}[MMA]}\sqrt{[AIBMe]} \quad (21)$$

Plots similar to those in Figure 3 have been obtained from kinetic simulations with different $[AIBMe]_0$ and $[1]_0$ at 70 °C (with $[AIBMe]_0$ always well in excess of $[1]_0$). The induction period that each simulation displays, and the ratio $[1]_{st}/[1]_0$ that it produces during the stable period, are listed in Table 3.

In all cases in Table 3 $[1]_{st}/[1]_0$ decreases as $[AIBMe]_0$ increases. $[1]_{st}/[1]_0$ remains constant as $[1]_0$ varies (comparison of trial nos. 1−4 and of trial no. 5 with no. 6) when $[AIBMe]_0$ is fixed (recall that $[MMA] \approx [MMA]_0$). These simulations confirm the predictions of eq 21—the value of $[1]_{st}/[1]_0$ decreases with $[AIBMe]_0$, but does not vary with $[1]_0$. Simulations with different k_{reinit} (Table 4) and $k_{tr}(true)$ (trial nos. 1, 12, and 14 in Table 5) show that an increase in k_{reinit} or a decrease in $k_{tr}(true)$ leads to an increase in $[1]_{st}/[1]_0$, also as predicted by eq 21.

The induction period is the time needed for the rates of chain transfer and reinitiation to become balanced (i.e., the time for eq 18 to become equal to zero). Simulations with different k_{reinit} (Table 4) reveal that an increase in k_{reinit} leads to a significant decrease in the induction period, while simulations with different $k_{tr}(true)$ (Table 5) show that the induction period does not change significantly with k_{tr} as long as $[AIBMe]_0/[1]_0$ is fixed. This

Table 5. Values of $[1]_{st}/[1]_0$ and Induction Period from Simulations with Different $[AIBMe]_0$ and $k_{tr}(true)$ at 70 °C[a]

trial no.	$[AIBMe]_0$ (M)	$k_{tr}(true)$ (M^{-1} s^{-1})	$[1]_{st}/[1]_0$ (%)	induction period (s)
1[b]	0.00434	6×10^6	19	277
11	0.00869	6×10^6	14	147
12	0.00434	1×10^6	58	246
13	0.00869	1×10^6	50	154
14	0.00434	6×10^7	2	213

[a] $[1]_0 = 5 \times 10^{-5}$ M. [b] Values from Figure 3.

Table 6. Time Dependence of Conversion, M_n, and Polydispersity during the $(C_5Ph_5)Cr(CO)_3^•$-Catalyzed Chain Transfer of MMA[a]

reaction time (min)	conversion (%)	M_n (10^4)	polydispersity
20	1.2	1.3	2.08
40	1.3	1.1	2.07
60	2.3	1.2	2.07
89	5.7	1.5	2.00
114	7.3	1.5	1.97
144	8.4	1.4	1.95
174	9.8	1.4	1.96
214	11.1	1.4	2.00

[a] At 70 °C, with $[(C_5Ph_5)Cr(CO)_3^•]_0 = 9 \times 10^{-5}$ M, $[AIBN]_0 = 0.0061$ M, and $[MMA]_0 = 4.7$ M, in benzene as solvent.

result is not surprising, as the time required to reach a balance will be determined by the slower reaction, reinitiation.

Simulations in Table 3 (trial nos. 1, 6, and 7) show that the induction period decreases as the ratio of $[AIBMe]_0$ to $[1]_0$ increases, but remain constant when $[AIBMe]_0$ is varied (by a factor of over 40) with $[AIBMe]_0/[1]_0$ constant. These predictions agree very well with the results observed: small $[initiator]_0/[1]_0$ ratios (2.3 in Figures 1 and 1.6 in Figure 2) gave long induction periods (1 and 4 h, respectively).

Molecular Weight Distribution. The fact that $[1]$ decreases during the "induction period" and remains constant during the "stable period" suggests that the molecular weight of the resulting polymer will increase during the "induction period" (due to the loss of the active chain transfer catalyst) and remain constant during the "stable period". As a result, one would expect that the molecular weight distribution for the resulting polymers would differ from those obtained from free radical polymerizations either (a) in the absence of chain transfer catalysts, or (b) in the presence of cobalt(II) catalysts (which remain almost entirely in the M$^•$ form). The simulations in Table 3 (trial nos. 2, 3 and 5) predict induction periods over 10 min, long enough to take up a substantial fraction of the total time of polymerization (which is 20−35 min during the $C_S(app)$ measurements[15]). Such behavior should lead to a broad molecular weight distribution, but such a distribution has not been observed during our previous $C_S(app)$ measurements[15] or in the present work. No such broad distribution was observed even when the polymerization experiment was carried out under exactly the same conditions as simulation no. 3 in Table 3 (a simulation that shows an induction period of 11 min during 30 min of reaction time).

As Table 6 shows, use of **1** to catalyze chain transfer during MMA polymerization gave time dependences for conversion, M_n, and polydispersity (M_w/M_n) that are typical of radical polymerizations. No significant increase of M_n was observed at the beginning of the polymerization.[32] Furthermore, the polydispersity was found always to be close to 2, the polydispersity typical of a free radical polymerization either in the absence of a chain transfer catalyst or in the presence of a Co(II) catalyst.

The reason no broad molecular weight distribution was observed during **1**-catalyzed chain transfer is still not clear. Perhaps the simulations neglect some important process. The accuracy of the estimate of k_{tr}(true) (6×10^6 M^{-1} s^{-1}) should not be a factor, as the induction period seen in the simulations does not change significantly with k_{tr} when [AIBMe]$_0$/[**1**]$_0$ is fixed (as discussed above).

Apparent and True Chain Transfer Constants. Substituting eq 11 and C_S(true) $= k_{tr}$(true)/k_p into eq 21 gives eq 22, the relation between C_S(app) and C_S(true) (or k_{tr}(true) and k_{tr}(true)) after chain transfer catalysis has reached a steady state.

$$\frac{C_S(\text{true})}{C_S(\text{app})} = \frac{k_{tr}(\text{true})}{k_{tr}(\text{app})} = 1 + \frac{k_{tr}(\text{true})\sqrt{fk_d}}{k_{reinit}\sqrt{k_t}[\text{MMA}]}\sqrt{[\text{AIBMe}]}$$
(22)

The difference between the apparent and the true values is determined by the relative rates of chain transfer and reinitiation, and affected by the concentrations of monomer and radical species. For the chromium catalysts, reinitiation is slow and the hydride **2** builds up, and the concentration of the active metalloradical **1** decreases. As a result C_S(app) is significantly smaller than C_S(true), which agrees with calculations from eq 22 that employ the small values of k_{reinit} that have been measured[7] for the Cr systems. For the Co(II) systems the hydride concentration is below detection limits,[1] so C_S(app) is close to C_S(true). This is possible because k_{reinit} for these systems is large enough to make the second term on the right of eq 22 much less than unity. (The simulations in Table 4 demonstrate the effect of k_{reinit} on [**1**]$_{st}$/[**1**]$_0$.)

Equation 22 predicts that, at any given temperature, the value of C_S(app) will decrease as (a) the concentration of the initiator increases or (b) the concentration of MMA decreases. These predictions agree well with the observations (values of C_S(app) obtained with different concentrations of MMA, AIBN, and AIBMe) in our previous work[15] and in this work. It is difficult to estimate the temperature dependence of C_S(app) from eq 22, as knowledge of the temperature dependences of k_{tr}(true), k_{reinit}, fk_d, k_t, and k_p would be required.

Estimating k_{tr}(true). Rewriting eq 22 gives eq 23, which calculates k_{tr}(true) from C_S(app). However, the error in this k_{tr}(true) calculation will be large since the two terms on right of eq 23 are approximately equal. Furthermore, the derivation of eq 23 has involved several approximations: (1) propagation has been ignored, and all chain-carrying radicals were assumed to be equally reactive at chain transfer and termination; (2) reinitiation between metal hydrides and vinyl-terminated polymers has been ignored; (3) all of the Cr has been assumed to be metalloradical **1** or the hydride **2**, i.e., [**1**] + [**2**] has been assumed constant; (4) steady-state approximations have been applied to the total concentration of radicals R$^\bullet$, and to the concentrations of **1** and **2**. Finally, the termination rate constant k_t is not perfectly known, varying as it does with temperature, pressure, conversion, choice and amount of solvent, molecular weight distribution, choice and amount of initiator, choice and amount of chain transfer agent, etc.[33]

$$\frac{1}{k_{tr}(\text{true})} = \frac{1}{C_S(\text{app})k_p} - \frac{\sqrt{fk_d}}{k_{reinit}\sqrt{k_t}[\text{MMA}]}\sqrt{[\text{AIBMe}]} \quad (23)$$

In theory it should also be possible to estimate k_{tr}(true) from eq 11. However, as discussed above, during a polymerization the concentration of the chromium catalyst is so low that it is not practical to determine the concentration of **1** or **2** accurately

by UV–vis or ^{1}H NMR. The *best estimate*, from the results in Figures 1 and 2 at higher concentrations of **1**, is 6×10^6 M^{-1} s^{-1} at 70°C (the value used in the simulations).

Experimental Section

General Data. All manipulations were carried out with Schlenk, high-vacuum, or inert-atmosphere-box techniques. IR spectra were recorded on a Perkin-Elmer Spectrum 2000 FT-IR, using solution cells with Teflon caps. ^{1}H NMR spectra were recorded on a Bruker 300 or 400 MHz spectrometer. When reactions at elevated temperatures were followed by ^{1}H NMR, the sample was sealed in a J. Young tube and placed in a constant-temperature bath; at appropriate intervals the tube was withdrawn, cooled, and placed in the spectrometer at room temperature while a spectrum was obtained. UV–visible spectra were recorded on a Hewlett-Packard 8543 diode array UV–visible spectrometer equipped with a Peltier temperature controller.

Materials. Benzene/C$_6$D$_6$ was distilled under N$_2$ from Na/benzophenone. Methacrylonitrile was transferred by vacuum from CaH$_2$. BPO was recrystallized twice from methanol and stored at −30 °C. MMA was purified as described in our previous work.[15] (C$_5$Ph$_5$)Cr(CO)$_3$$^\bullet$ (**1**),[34] (C$_5$Ph$_5$)Cr(CO)$_3$H (**2**),[5] and AIBMe[35] were prepared by the procedures cited.

Chain Transfer Constants C_S from Mayo Plots. C_S values with BPO or AIBMe as initiator were obtained by procedures analogous to that previously described[15] with AIBN.

Characterization of Polymers Obtained at Different Reaction Times. A benzene solution (5 mL) of (C$_5$Ph$_5$)Cr(CO)$_3$$^\bullet$ (9×10^{-5} M), AIBN (0.0061 M) and MMA (4.7 M) was put into each of eight Schlenk tubes in an inert atmosphere box; the tubes were sealed and placed in a constant-temperature bath at 70.0 ± 0.1 °C. At appropriate intervals one of the tubes was removed, and the resulting polymer characterized by the procedure previously described[15] to give the data in Table 6.

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(22) Chain transfer between the methyl isobutyryl radical **3** and **1** can be ignored not only because the fraction of **3** is very small, but because the rate constant of chain transfer from **3** (eq 13) is smaller than that from chain-carrying radicals (eq 2) (see ref 7).

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(31) Calculations in ref 9 also confirmed that the total concentration of free radical species was equal to $(fk_d[\text{initiator}]/k_t)^{1/2}$ during chain transfer polymerization with cobalt(II) catalysts.

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