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Articles

Inverse Temperature Dependence of Chain Transfer Rate Constant for a Chromium Metalloradical in Polymerization of MMA

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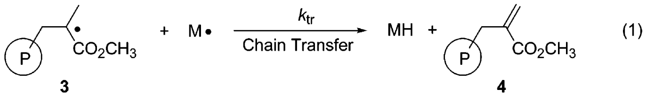
ABSTRACT: Mayo plots have been used to determine the rate constant k_{tr} for chain transfer catalysis by $(C_5Ph_5)Cr(CO)_3^\bullet$ of the AIBN-initiated polymerization of MMA from 60 to 80 °C. The value of k_{tr} *decreases* with temperature, implying that abstraction of $H^\bullet$ from the chain-carrying radical by $(C_5Ph_5)Cr(CO)_3^\bullet$ does not occur in a single step and suggesting the associative formation of a caged radical pair. No CIDNP is observed for the reaction of $(C_5Ph_5)Cr(CO)_3H$ with MMA.

Introduction

Chain transfer catalysis in free radical polymerization has been known for two decades,[1] with the most established catalysts being cobalt(II) complexes.[2−4] This type of polymerization can produce polymers with terminal vinyl groups and much lower molecular weights compared to polymerization in the absence of chain transfer catalysts.

Although there is little direct evidence for the actual mechanism of catalyzed chain transfer (CCT), a two-step process (eqs 1 and 2) has been widely accepted by researchers. The instability of Co hydrides has made it difficult to observe directly the reinitiation step (eq 2), often said to be fast with Co(II) catalysts.[3] We have, however, reported $(C_5Ph_5)Cr(CO)_3^\bullet$ (**1**)[5] as an effective chain transfer catalyst in the polymerization of methyl methacrylate (MMA)[6] and have observed eq 2 directly by treating $(C_5Ph_5)Cr(CO)_3H$ (**2**) with MMA.[7] From H/D exchange between **2** and MMA-d_5 we have measured k_{reinit} as 0.0017 $M^{-1}\ s^{-1}$ at 50 °C.



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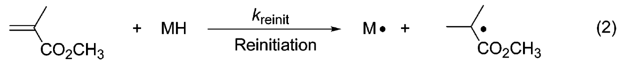

(2)

The Mayo equation[8] (eq 3) is used to determine the chain transfer rate constant k_{tr}. The chain transfer constant, $C_s = k_{tr}/k_p$, is obtained by plotting $1/DP_n$ vs the ratio of the concentration of the chain transfer agent (CTA) to that of the monomer (M). (DP_n is the number-average degree of polymerization, DP_{n0} is the number-average degree of polymerization in the absence of chain transfer agent, k_{tr} is the rate constant for the chain transfer step, and k_p is the rate constant for propagation of the growing polymer chain.)

$$\frac{1}{DP_n} = \frac{1}{DP_{n0}} + \frac{k_{tr}[CTA]}{k_p[M]} \qquad (3)$$

The value of the chain transfer rate constant k_{tr} is affected by many factors, including the viscosity, the concentration of chain-carrying radicals, and the presence of oxygen and other impurities.[2,3,9] It is not clear that eq 1 occurs in a single step, although the observed isotope effects are consistent with that proposal.[10] It is possible that an M−C bond is formed reversibly, which can either decrease the concentration of the chain-carrying radical **3** and the active $M^\bullet$ catalyst species (eq 4) or undergo β-hydrogen elimination to form M−H and $P_n^{=}$ (monomer or the vinyl-terminated polymer 4) (eq 5).[3,11] There is considerable evidence that eq 4 operates during the cobalt(II)-catalyzed chain transfer polymerization of styrene.[4,12]

$$M{-}R_n \rightleftharpoons M^\bullet + R_n^\bullet \rightarrow MH + P_n^{=} \qquad (4)$$

$$M^\bullet + R_n^\bullet \rightleftharpoons M{-}R_n \rightarrow MH + P_n^{=} \qquad (5)$$

Gridnev[3,13] and Heuts[4] have suggested the intermediacy of a caged radical pair in eq 1. There is good evidence for such radical pairs when the reaction occurs in reverse (eq 2), and $H^\bullet$ is transferred from a metal to an olefin. In 1975, Feder and Halpern proposed that the $HCo(CO)_4$-catalyzed hydrogenation of anthracene to 9,10-dihydroanthracene involved $H^\bullet$ transfer inside the solvent cage of a radical pair.[14] In 1977, Sweany and Halpern reported convincing evidence (CIDNP and an inverse isotope effect for $HMn(CO)_5/DMn(CO)_5$) for such a mechanism in the hydrogenation of α-methylstyrene by $HMn(CO)_5$ (Scheme 1).[15] A similar mechanism, leading to isotope exchange that is much faster than the overall reaction, has been established by Jacobsen

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Scheme 1

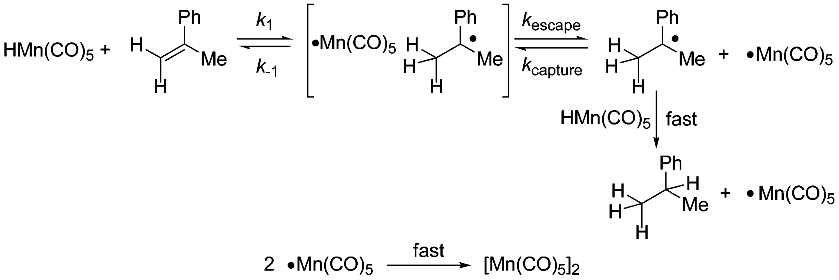


Table 1. Chain Transfer Constants ($C_s = k_{tr}/k_p$) and Chain Transfer Rate Constants (k_{tr}) at Different Temperatures for 1-Catalyzed Polymerization of MMA

temperature (°C)	60.4	65.0	69.8	75.6	80.2
C_s (k_{tr}/k_p) (10^3)	1.9	1.5	1.0	0.82	0.59
k_p (M^{-1} s^{-1})[a] (10^3)	0.831	0.940	1.05	1.18	1.32
k_{tr} (M^{-1} s^{-1}) (10^6)	1.6	1.4	1.1	0.96	0.79

[a] k_p is obtained as a function of temperature: $k_p = 10^{6.427}e^{-22360/RT}$ ($-1 < T < 90$ °C).[22]

and Bergman for the reaction of $[CpCo(CO)]_2(\mu\text{-}C{=}CH_2)$ with $CpMo(CO)_3H$.[16] Other cases have been summarized in a review.[17]

The intermediacy of a caged radical pair can in principle be assessed from the temperature dependence of k_{tr}. With cobalt chain transfer catalysts there have been conflicting reports on the temperature dependence of C_s for MMA polymerization,[9,18−20] although k_{tr} itself has always appeared to increase with temperature. With cobaloxime boron fluoride (COBF) as a catalyst Heuts found no noticeable effect on C_s over the temperature range 40−70 °C,[18] while O'Driscoll,[19] Davis,[20] and later van Herk[9] found that C_s decreased slightly with temperature. With neither the tetraphenyl derivative of COBF[18] nor cobalt(*meso*-tetraphenylporphyrin)[9] has any temperature dependence been found for C_s.

We have therefore examined the temperature dependence of the rate constant k_{tr} for $(C_5Ph_5)Cr(CO)_3^{\bullet}$-catalyzed chain transfer (eq 1) during the free radical polymerization of MMA.

Results and Discussion

Chain Transfer Constants (C_s). Chain transfer constants for **1** in the radical polymerization of bulk MMA were measured at five different temperatures over a range of 20 °C (Table 1). A constant concentration of AIBN (1 mg/mL) was used as initiator, and the degree of polymerization was examined by gel permeation chromatography at low conversion (<10%).

Great care was taken to exclude air, as **1** is very reactive toward O_2. The resulting Mayo plots for MMA with **1** are quite linear. We employed temperatures lower than that (100 °C) used in our previous experiments[6] in order to maintain a constant rate of decomposition of AIBN[21] and to prevent any decomposition of **1**. We also used a constant-temperature bath to maintain precise temperature control (±0.1 °C) during the polymerization reactions and a range of concentrations of **1** sufficient to put at least five evenly distributed points on each Mayo plot.

Figure 1 shows the Mayo plot for the polymerization of MMA with **1** at 70 °C, giving a C_s value of 1000. From 50 to 70 °C, C_s decreases smoothly with temperature.

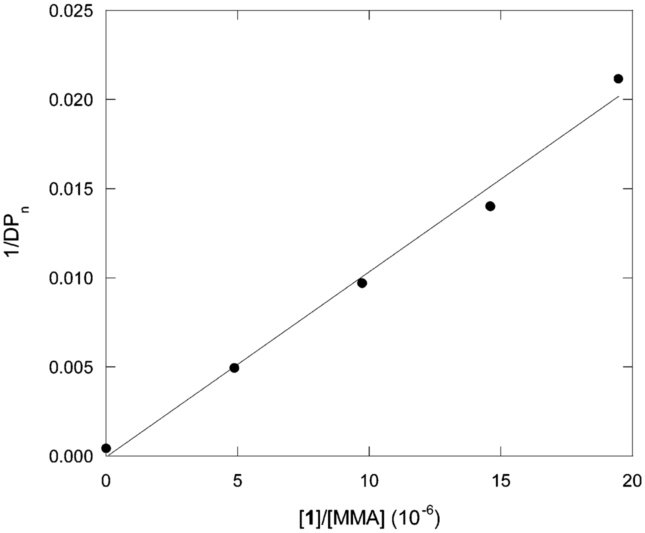


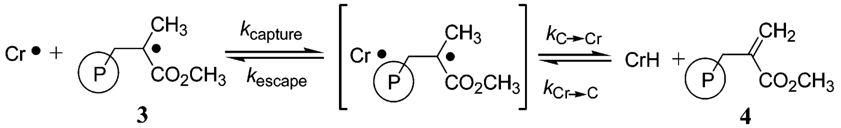
Figure 1. Mayo plot for MMA with **1** at 70 °C. The linear fit equation is $y = (-0.6 \pm 7.3) \times 10^{-4} + (1.04 \pm 0.06) \times 10^{-3}x$, with $R = 0.995$.

Factors Determining Temperature Dependence of Chain Transfer Constants (C_s) and Chain Transfer Rate Constants (k_{tr}). As C_s is the ratio of two rate constants, k_{tr} for chain transfer (eq 1) and k_p for propagation, its temperature dependence reflects the *relative* temperature dependence of these rate constants. If k_{tr} and k_p increase with temperature but have similar activation parameters, C_s will vary little with temperature.[9] If k_{tr} and k_p increase with temperature and $\Delta G^{\ddagger}$ for chain transfer is larger than that for propagation, C_s will increase as the temperature increases; if k_{tr} and k_p increase with temperature and $\Delta G^{\ddagger}$ for chain transfer is smaller than that for propagation, C_s will decrease as the temperature increases.

However, the decrease of C_s with temperature in our experiments is so large that it cannot be explained by a difference between the activation parameters of k_{tr} and those of k_p. Use of established values of k_p as a function of temperature[22] (included in Table 1) shows that k_{tr} *itself decreases with temperature*. Equation 1 must occur in *more than one step*, and it is reasonable to think that it involves an associative preequilibrium.[23,24]

EPR studies of cobalt(II) chain transfer agents during styrene polymerization showed the reversible formation of a bond between Co(II) and the α-methylbenzyl radical, and kinetic measurements also indicated the operation of an equilibrium like eq 4.[11] However, similar experiments during MMA polymerization showed no evidence for the formation of a bond between Co(II) and the methyl isobutyryl radical. The inverse temperature dependence of the MMA k_{tr} data in Table 1 *cannot be explained by an equilibrium like eq 4 alone*, as it would

Scheme 2



cause k_{tr} to increase with increasing temperature. Our data imply that, with the hindered Cr metalloradical **1**, the H$^{\bullet}$ transfer that produces chain transfer (eq 1) must occur *after* the association of **1** with the chain-carrying radical **3**.

Our kinetic results *seem consistent* with a mechanism like the one in eq 5, with the β-elimination of a hydrogen occurring *after* the reversible formation of the Cr−C bond. However, such a Cr alkyl complex would have no vacant coordination site and should thus be unable to undergo β-hydrogen elimination.[25]

The bond between the sterically encumbered Cr in **1** and the tertiary radical **3** will be relatively weak.[26,27] The strength of the Mo−C bond in $CpMo(CO)_3CH_2Ph$ has been given as 32 kcal/mol,[28] while the Mo−H bond in $CpMo(CO)_3H$ is 8 kcal/mol stronger than the Cr−H bond in $CpCr(CO)_3H$,[29] allowing us to estimate the Cr−C bond in $CpCr(CO)_3CH_2Ph$ as 24 kcal/mol; the Cr−C "bond" in the hypothetical $(C_5Ph_5)Cr(CO)_3C(Me)_2CO_2Me$ must be 10 kcal/mol or less.[30] A weak interaction between the Cr metalloradical **1** and the radical **3** could, however, contribute to the formation of a solvent cage like that in Scheme 1.

Does Chain Transfer Involve a Solvent Cage? The H$^{\bullet}$ transfer in eq 1 may occur only after the formation of the sort of solvent cage depicted in Scheme 1, giving us the sequence of events in Scheme 2. The first step, rate constant $k_{capture}$, is merely the microscopic reverse of escape from the sort of cage generated in Scheme 1; the last step will be H$^{\bullet}$ transfer inside the solvent cage ($k_{C\rightarrow Cr}$).

The observed rate constant k_{tr} will then be given by eq 6. The cage-forming equilibrium $k_{capture}/k_{escape}$ will lie further to the left (i.e., there will be more dissociation of the solvent cage in Scheme 2) with increasing temperature, so k_{tr} will decrease with increasing temperature.

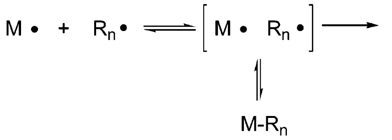
$$k_{tr} = \frac{k_{capture}k_{C\rightarrow Cr}}{k_{escape} + k_{C\rightarrow Cr}} \approx \frac{k_{capture}k_{C\rightarrow Cr}}{k_{escape}} \qquad (6)$$

The "$\Delta H^{\ddagger}$" implied by the temperature dependence of our k_{tr}, −9 kcal/mol, is more negative than that reported for most other radical combination reactions with inverse temperature dependence.[23,24] Our $\Delta H^{\ddagger}$ is comparable only to that (−8 kcal/mol) reported for the combination of 3,5,5-trimethyl-2-oxomorpholin-3-yl radicals in benzene (our $\Delta H^{\ddagger}$ is more negative than the values reported for the same reaction in other solvents).[23a] The origin of such preequilibria is generally entropic, not enthalpic (there is normally no enthalpy change when a caged pair is formed from two free radicals),[23b,c] but in our case the enthalpic contribution may be significant. The cage in Scheme 2 has the advantage of a weak interaction (≈10 kcal/mol, see above) between two centers (the Cr metalloradical **1** and the chain-carrying radical **3**) that cannot form a stable bond and thus disproportionate by H$^{\bullet}$ transfer.

Of course, k_{reinit}[7] from the H/D exchange reaction between the Cr hydride **2** and MMA-d_5 may not be exactly the same as $k_{Cr\rightarrow C}$ for H$^{\bullet}$ transfer from **2** to the vinyl-terminated polymer **4**. However, if we assume they are equal, we can determine ΔG for Scheme 2 from k_{tr}/k_{reinit}, and we can calculate the bond dissociation energy (BDE) of the C−H bond in the radical **3** as 46.1 kcal/mol at 50 °C[7]—to our knowledge the first determination of the strength of a C−H bond in the chain-carrying radical of a polymerization.

Catalytical Chain Transfer of Styrene with Cr Metalloradical 1. Cobalt complexes are much more active as chain transfer catalysts during the polymerization of monomers with an α-methyl group (i.e., MMA) than during the polymerization of monomers without such a group (i.e., styrene, acrylate). There are two possible reasons for this decrease in efficiency: (a) the absence of an accessible α-methyl group makes H$^{\bullet}$ abstraction more difficult and causes a decrease in k_{tr}, and (b) the formation of a Co−C bond is easier when the chain-carrying radical is secondary. Co−C bonds are known to form according to eq 4 during styrene polymerization (see above[4,12]), and their formation has also been reported when the monomer is methyl acrylate.[31] Our metalloradical $(C_5Ph_5)Cr(CO)_3^{\bullet}$ has also proven to be much less effective as a chain transfer catalyst during the polymerization of styrene, with a chain transfer constant of 15 at 70 °C—presumably because **1** can form a bond with the secondary chain-carrying radical.

Our MMA and styrene results with the Cr metalloradical **1** show that neither eq 4 nor eq 5 *alone* is correct for the Cr system; a caged radical pair (proposed by Gridnev[3,13] and Heuts[4] for Co catalysts) must be added, resulting in the mechanism of eq 7. This mechanism is also consistent with the fact that Co−C bonds are formed during the polymerization of styrene in the presence of cobalt(II) chain transfer catalysts.[12]



(7)

When MMA is polymerized in the presence of the Cr catalyst **1**, steric hindrance precludes the formation of a bond between **1** and the tertiary chain-carrying radicals **3**; deletion of M−R$_n$ from eq 7 gives us Scheme 2. When styrene is polymerized in the presence of the Cr catalyst **1**, a Cr−C bond is formed, decreasing the efficiency of **1** as a chain transfer catalyst.

Effect of Other Factors on C_s. We found C_s decreased to 450 at 70 °C as the initial [AIBN] increased to 4 mg/mL. van Herk[9] also observed a reduction in C_s at higher initiator concentrations and explained it by the formation of inactive species between radical and cobalt catalyst. Although the $Cr-CMe_2CN$ bond should be as weak as the $Cr-CMe_2CO_2Me$ one, we may have an inactive species similar to van Herk's—a solvent cage formed by metalloradical **1** and the cyanoisopropyl radical.

Although Haddleton[32] reported a decrease of C_s between neat MMA and toluene solution, Heuts[33] found that chain transfer remained essentially unchanged when toluene was added. Later work showed that the decrease of C_s in the presence of toluene could be avoided if the toluene was carefully purified.[34] We found that C_s of $(C_5Ph_5)Cr(CO)_3^•$ decreased from 1000 in neat MMA to 400 in an MMA/toluene (1:1) mixture at 70 °C even when the toluene was "thoroughly purified" by the method of previous workers.[34b,35] A trace impurity may have remained, or the change in viscosity resulting from the addition of toluene may have affected the cage formation preequilibrium in Scheme 2.

CIDNP in the Reaction of 2 with MMA? The fact that CIDNP had been observed with $HMn(CO)_5$/α-methylstyrene by Sweany and Halpern (demonstrating competition between $H^•$ return and cage escape after $H^•$ transfer)[15] suggested that we look for it in the reaction of $(C_5Ph_5)Cr(CO)_3H$ (**2**) with MMA. However, with **2**/MMA we saw no polarization (at 70 °C in C_6D_6) at 300 MHz.

To determine whether our negative **2**/MMA result arose from the magnetic field employed or from a difference in mechanism between **2**/MMA and $HMn(CO)_5$/α-methylstyrene, we repeated the Sweany/Halpern experiment at a field (58.3 MHz) approximately equal to that originally employed (60 MHz) and reproduced the reported[15] results. At higher field (300 MHz), however, we saw no polarization with $HMn(CO)_5$/α-methylstyrene—presumably because of "the generally observed tendency that the CIDNP originated from a radical pair with a large Δg or a small a_A decreases towards relatively high fields".[36]

Even at 58.3 MHz we observed no CIDNP with either $(C_5Ph_5)Cr(CO)_3H$(**2**)/MMA or $(C_5H_5)Cr(CO)_3H$/MMA. The absence of CIDNP in these Cr systems is not particularly surprising, as two factors will make CIDNP harder to observe with Cr than with Mn: (1) the g value of the Cr metalloradical **1**[5] exceeds that of $^•Mn(CO)_5$,[15] making Δg larger in the Cr system and causing CIDNP to decrease at lower magnetic fields (see end of previous paragraph); (2) the persistence of paramagnetic Cr species (**1** is entirely monomeric and $CpCr(CO)_3^•$ significantly so in dilute solution,[37] while $^•Mn(CO)_5$ dimerizes completely) will cause loss of spin memory and nuclear polarization.[38]

Experimental Section

General. All manipulations were carried out using Schlenk, high-vacuum, or inert-atmosphere-box techniques.

Materials. $HMn(CO)_5$,[39] $(C_5Ph_5)Cr(CO)_3^•$ (**1**),[5] $(C_5Ph_5)Cr(CO)_3H$ (**2**),[6] and $(C_5H_5)Cr(CO)_3H$[40] were prepared by literature procedures. Methyl methacrylate was predried over $MgSO_4$ and then passed through an Aldrich inhibitor removal column (for removal of 4-methoxyphenol). After three freeze−pump−thaw cycles the monomer was transferred in vacuo from CaH_2, stored at −30 °C, and transferred in vacuo again prior to use. Styrene was treated by a similar procedure above, with another type of Aldrich inhibitor removal column (for removal of 4-*tert*-butylcatechol). α-Methylstyrene was distilled under N_2 from CaH_2. AIBN was recrystallized twice from methanol and stored at −35 °C. Toluene was degassed and passed through columns of activated alumina and supported copper.[35] C_6D_6 was distilled under N_2 from Na/benzophenone.

Chain Transfer Constants C_s from Mayo Plots. An initiator stock solution of AIBN (1 mg/mL) in MMA was prepared in a glovebox. A stock solution of chain transfer agent (CTA) was prepared by dissolving 20 mg of **1** in 10 mL of AIBN stock solution and diluting 1 mL with additional (19 mL) AIBN stock solution. An appropriate volume (0, 1, 2, 3, or 4 mL) of the CTA stock solution was put into each of five vacuum bulbs, and enough AIBN stock solution was added to bring the total volume in each bulb to 4.0 mL. The bulbs were closed, brought out of the glovebox, and put into a constant-temperature bath regulated ±0.1 °C. After 20−35 min (adjusted empirically to keep the conversion ≤10%) the reactions were stopped by adding 4-methoxylphenol and cooling them to −30 °C. The conversion was determined gravimetrically. Gel permeation chromatography (GPC) was carried out, with THF as eluant at a flow rate of 1 mL/min, on a PLGel 5 μm guard column (50 × 7.5 mm) followed by two Polymer Labs 5 μm mixed C columns (300 × 7.5 mm), equipped with a Varian 9050 pump and a Varian Star 9040 RI detector. Polymer Labs PMMA standards were used to create the calibration curve. The process was repeated at each of the temperatures in Table 1.

When the initiator stock solution contained 4 mg/mL of AIBN, C_s at 70 °C was 450. When the effect of solvent on C_s was examined, a 4 mg/mL AIBN stock solution was prepared with toluene instead of MMA. The stock solution of CTA was prepared by dissolving 20 mg of **1** in 10 mL of toluene and diluting it 5 times with toluene. An appropriate volume (0.0, 0.25, 0.50, 0.75, or 1.0 mL) of this CTA stock solution was put into each of five vacuum bulbs. AIBN stock solution (1.0 mL) and MMA (2.0 mL) were added, followed by enough toluene to bring the solution within each bulb to a volume of 4.0 mL; the final concentration of AIBN was 1 mg/mL. After polymerization at 70 °C the C_s value (400) was determined by the procedure above.

Styrene was polymerized by a similar procedure.

CIDNP Experiments. A C_6D_6 solution of α-methylstyrene (0.2 M) and $HMn(CO)_5$ (1.0 M) was sealed in a J. Young tube. No CIDNP was observed at 70 °C on a Bruker 300 MHz instrument.

Other ^1H NMR spectra were obtained on a FoxboroNMR D NMR system operating at 58.3 MHz, equipped with a FoxboroNMR variable temperature probe. Single pulse acquisitions were obtained at a sweep width of 4 kHz, a relaxation delay of 15 s, and a 60° tip angle.

A C_6D_6 solution of α-methylstyrene (0.2 M) and $HMn(CO)_5$ (1.2 M) was sealed in a 5 mm NMR tube, and single-pulse ^1H NMR spectra (58.3 MHz) were obtained at 70 °C. CIDNP spectra like those reported by Sweany and Halpern[15] were obtained.

A similar experiment was carried out at the same temperature (70 °C) with a C_6D_6 solution containing **2** (0.01 M) and MMA (0.04 M). For 1 h there was almost no change in the NMR spectrum. Similar results (i.e., no CIDNP) were observed in 1 h at 70 °C with a C_6D_6 solution containing **2** (0.015 M) and MMA (0.006 M) or a C_6D_6 solution containing $(C_5H_5)Cr(CO)_3H$ (0.074 M) and MMA (0.1 M).

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