Macromolecules **2006,** *39,* 8236−8240

Measurement of the Rate Constant for $H^\bullet$ Abstraction from Methylisobutyryl Radical by $(C_5Ph_5)Cr(CO)_3^\bullet$

Lihao Tang and Jack R. Norton*

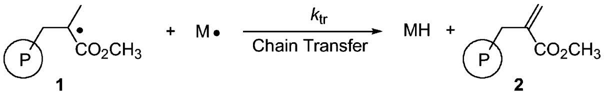
Department of Chemistry, Columbia University, 3000 Broadway, New York, New York 10027

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

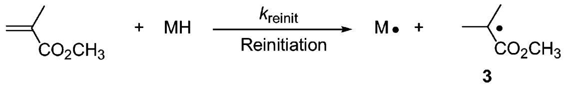
ABSTRACT: In the presence of the metalloradical $(C_5Ph_5)Cr(CO)_3^\bullet$ thermolysis of the radical source AIBMe (dimethyl 2,2′-azobis(isobutyrate)) gave MMA and $(C_5Ph_5)Cr(CO)_3H$. A high concentration of $(C_5Ph_5)Cr(CO)_3^\bullet$ discouraged chain growth when AIBMe was heated in MMA, making the monomeric MMA radical (i.e., methylisobutyryl) the dominant organic radical and enabling us to measure the $H^\bullet$ transfer rate constant, k_{tr}(monomer), from the methylisobutyryl radical to $(C_5Ph_5)Cr(CO)_3^\bullet$. The result, 5.2×10^5 M^{-1} s^{-1} at 70 °C, is smaller than the chain transfer rate constant previously determined for chain-carrying radicals during MMA polymerizations (1.4×10^6 M^{-1} s^{-1} at 70 °C).

Introduction

The past 20 years have seen major achievements, in both academic and industrial labs, in the catalysis of chain transfer during free radical polymerizations. As shown for the polymerization of methyl methacrylate (MMA) in eqs 1 and 2, such catalysis is believed[1] to involve removal of $H^\bullet$ from the propagating radical chain (**1**), giving a vinyl-terminated polymer (**2**) and a metal hydride (eq 1), followed by transfer of that $H^\bullet$ to a monomer to start a new chain (eq 2).



(1)



(2)

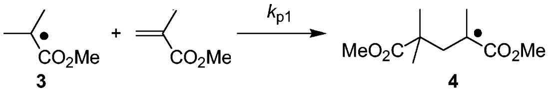
The Mayo equation[2] (eq 3) is generally used to determine the chain transfer rate constant k_{tr}. The chain transfer constant, $C_S = k_{tr}/k_p$, is obtained by plotting $1/DP_n$ vs the ratio of the concentration of the chain transfer agent (CTA) to that of the monomer (M). (DP_n and DP_{n0} are the number-average degree of polymerization with and without the chain transfer agent; k_p is the rate constant for propagation of the growing polymer chain.) However, the derivation of eq 3 involves a long-chain approximation that is not valid when short oligomers are being prepared. Gridnev and co-workers[1,3] have shown that eq 4 is more appropriate for highly active chain transfer catalysts which make DP_n of the resulting polymer small (<10).

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

$$DP_n = 2 + \frac{k_p[M]}{k_{tr}[CTA]} \tag{4}$$

During a free radical polymerization the rate constants for propagation and termination are chain length dependent.[4] It is reasonable to expect that the rate constant for chain transfer (eq 1) will also be affected by the chain length of the chain-carrying radical **1** and the vinyl-terminated polymer **2**.[5] However, there are ambiguous reports in the early literature on the length dependence of the chain transfer constants (C_S) for the widely used cobalt(II) catalysts. Smirnov[6] found that, during MMA polymerization, the C_S of cobalt tetramethoxyhematoporphyrin IX (CoPor) increased as chain length increased when DP_n was ≤6. In contrast, O'Driscoll and co-workers[7] reported that, during a cobaloxime-catalyzed chain transfer polymerization of MMA, C_S decreased as chain length increased when $DP_n \leq 50$. With a different chain transfer catalyst (cobaloxime boron fluoride (COBF)), the same group[8] found that C_S decreased slightly (20−30%) as chain length increased from 3 to 7. In all cases, C_S did not vary with chain length when DP_n was large.

Since the chain transfer constant C_S is the ratio of chain transfer rate constant to propagation rate constant (k_{tr}/k_p), it is more appropriate to discuss the chain length dependence of k_{tr} than of C_S. For longer chains (hundreds of monomer units) k_p increases slightly as the chain length decreases, while it increases rapidly as the chain becomes very short.[9] Gridnev and Ittel[10] reported that k_{p1} (the rate constant for the addition of a monomeric radical **3** to the monomer, eq 5) for MMA is 14 000 M^{-1} s^{-1} at 60 °C, about 20 times larger than k_p for the addition of a high molecular weight chain-carrying radical (840 M^{-1} s^{-1} at 60 °C).[11] For the addition of the dimeric MMA radical **4** to MMA monomer, k_{p2} proved to be 3600 M^{-1} s^{-1} at 60 °C.[10]



(5)

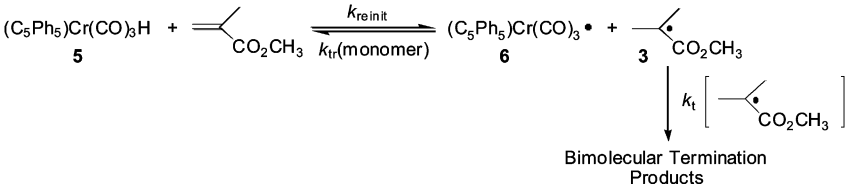
The CoPor experiments by Smirnov[6] gave C_S values of 500 for the dimeric MMA radical **4** and 2100 for the long-chain radicals **1** at 60 °C. Multiplying by the established k_p values (3600 M^{-1} s^{-1} for dimeric MMA radical[10] and 840 M^{-1} s^{-1} for high molecular weight chain-carrying radicals[11]) gives a value of k_{tr} (1.8×10^6 M^{-1} s^{-1}) that appears independent of chain length. This result is consistent with a more recent investigation of the CoPor-catalyzed chain transfer polymerization of MMA by Gridnev and Ittel,[10] who reported a negligible decrease in k_{tr} from the dimeric radical **4** to long-chain radicals **1** (2.8×10^6 and 2.4×10^6 M^{-1} s^{-1}, respectively). However, in the COBF case O'Driscoll[8] reported k_{tr} values ($= k_pC_S$) for $DP_n = 3-7$ that decreased as chain length increased even after the chain length dependence of k_p was taken into account.

---

* To whom correspondence should be addressed. E-mail: jrn11@columbia.edu.

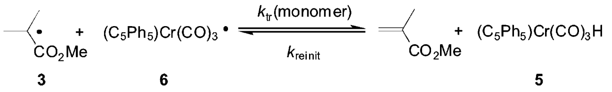
10.1021/ma0615755 CCC: $33.50

Scheme 1



We have found that treating MMA with $(C_5Ph_5)Cr(CO)_3H$ (**5**) slowly establishes the equilibrium in Scheme 1.[12] The concentration of the metalloradical $(C_5Ph_5)Cr(CO)_3^\bullet$ (**6**) increases as termination reactions deplete the methylisobutyryl radical **3**. Measurement of k_{reinit} and simulation of the growth of the metalloradical **6** in Scheme 1 have allowed us to determine the value of k_{tr}(monomer) iteratively as 9.8×10^4 M^{-1} s^{-1} at 50 °C.[12] In contrast, we have determined by the Mayo method[2] the apparent chain transfer rate constant k_{tr} for long-chain radicals to be 1.6×10^6 M^{-1} s^{-1} at 60 °C for an AIBN-initiated chain transfer polymerization of MMA in the presence of the metalloradical **6**.[13,14]

From our previous measurements of k_{reinit},[12] we have the reverse rate constant for eq 6. Now we have found[15] that the reaction between the metalloradical **6** and the methylisobutyryl radical **3** (generated from the radical source AIBMe) enables us to observe eq 6 in the forward direction, resulting in the hydride **5** and MMA. In the present paper we report measurements of the rate constant k_{tr}(monomer), which allows us to assess the dependence of the chain transfer rate constant on chain length.



(6)

Results and Discussion

Estimating the Termination Rate Constant between Methylisobutyryl Radicals. Obtaining k_{tr} from eq 6 requires a reliable value for the bimolecular termination rate constant (k_t) between two methylisobutyryl radicals. Unfortunately, this rate constant has never been directly measured. In principle, it could be deduced from the chain length dependence of the termination rate constant for the chain-carrying radicals formed during MMA polymerization. Equation 7 has been the standard way of treating this chain length dependence: i denotes the chain length of chain-carrying radical, $k_t^{i,i}$ is the termination rate constant between two radicals of chain length i, $k_t^{1,1}$ is the termination rate constant between two monomeric radicals, and a is an adjustable exponent. In our previous work,[12] we estimated $k_t^{1,1}$ for MMA to be 1.65×10^8 M^{-1} s^{-1} by using eq 7.

$$k_t^{i,i} = k_t^{1,1} i^{-a} \tag{7}$$

Russell and Heuts[16] have recently proposed a composite model for the termination rate constants over a large range of chain length for MMA and styrene polymerization in dilute solution. This model includes different power-law behavior below (eq 8) and above (eq 9) a critical chain length i_c, where e_S is the scaling exponent for short-chain radicals and e_L is that for long-chain radicals.

$$k_t^{i,i} = k_t^{1,1} i^{-e_S} \qquad \text{for } i \le i_c \tag{8}$$

$$k_t^{i,i} = k_t^{1,1} i_c^{-e_S} + e_L i^{-e_L} \qquad \text{for } i > i_c \tag{9}$$

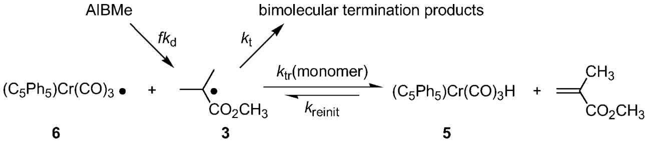
The composite model of Russell and Heuts enables one to estimate a more accurate $k_t^{1,1}$ than eq 7 does. Using eqs 8 and 9, we have estimated (for details see the Supporting Information) the values of $k_t^{1,1}$ in Table 1 for MMA at different temperatures.

Table 1. Estimated Values of $k_t^{1,1}$ between Two Methylisobutyryl Radicals[a]

t (°C)	$k_t^{1,1}$ (M^{-1} s^{-1})
50	1.25×10^9
60	1.29×10^9
70	1.33×10^9
80	1.37×10^9

[a] More details see Table S1 in the Supporting Information.

Scheme 2



The calculations in Table 1 estimate that k_t increases by a factor of 38 when i decreases from 10^4 to 1, in good agreement with a suggestion by Stickler[17] that k_t should increase by 50 from long chain-carrying radicals to the monomeric radical. More importantly, these results are very close to $k_t^{1,1}$ between two cyanoisopropyl radicals, which can be calculated from the well-established equation[18] ($2k_t^{1,1} = 10^{11.8}e^{-15700/RT}$) as 0.91×10^9, 1.09×10^9, 1.29×10^9, and 1.50×10^9 M^{-1} s^{-1} at 50, 60, 70, and 80 °C, respectively. Gridnev and Ittel have argued that the bimolecular termination rate constant $k_t^{1,1}$ between two methylisobutyryl radicals should not differ significantly from that between two cyanoisopropyl radicals.[10]

In our early work we estimated $k_t^{1,1}$ to be 1.65×10^8 M^{-1} s^{-1} at 50 °C by using eq 7, and our subsequent kinetic modeling (see Scheme 1) gave a value of 9.8×10^4 M^{-1} s^{-1} for k_{tr}(monomer).[12] With the more accurate estimate of $k_t^{1,1}$ just given (1.25×10^9 M^{-1} s^{-1} at 50 °C, Table 1), the value of k_{tr}(monomer) should be revised to 2.5×10^5 M^{-1} s^{-1} at 50 °C.

Obtaining k_{tr}(Monomer) between $(C_5Ph_5)Cr(CO)_3^\bullet$ and the Methylisobutyryl Radical (3). A sufficiently high concentration of chain transfer catalyst will (as eq 4 indicates) leave all the organic radicals in a radical polymerization monomeric or dimeric and will make the vinyl-terminated dimer the only oligomer produced. The addition of more catalyst will decrease the concentration of the dimeric radical, leaving the radicals generated during such a reaction almost entirely monomeric.[10] Thus, when a high concentration of **6** is present[19] during the AIBMe-initiated polymerization of MMA, the monomeric radical **3** will be dominant, and the only significant reactions will be those in Scheme 2.

The reactions in Scheme 2 can be written in more compact form as eqs 10−13, where R$^\bullet$ denotes the monomeric MMA radical (the methylisobutyryl radical **3**) and TP denotes the bimolecular termination products of **3** (MMA, methyl isobutyrate, and dimethyl tetramethylsuccinate).[20]

$$\mathrm{AIBMe} \xrightarrow{f k_\mathrm{d}} 2\mathrm{R}^{\bullet} \tag{10}$$

$$\mathrm{R}^{\bullet} + \mathbf{6} \xrightarrow{k_\mathrm{tr}(\mathrm{monomer})} \mathbf{5} + \mathrm{MMA} \tag{11}$$

$$\mathbf{5} + \mathrm{MMA} \xrightarrow{k_\mathrm{reinit}} \mathrm{R}^{\bullet} + \mathbf{6} \tag{12}$$

$$2\mathrm{R}^{\bullet} \xrightarrow{k_\mathrm{t}^{1,1}} \mathrm{TP} \tag{13}$$

The methylisobutyryl radical $R^{\bullet}$ was generated from AIBMe in the presence of **6** and excess MMA, and $(C_5Ph_5)Cr(CO)_3^{\bullet}$ (**6**) and $(C_5Ph_5)Cr(CO)_3H$ (**5**) were monitored as a function of time (Figure 1). The concentration of **6** was determined by UV−vis at a λ of 611 nm (**5** has no absorbance at this wavelength), while the concentration of **5** was determined by ^{1}H NMR. As shown in Figure 1a,b, an "induction period" for the disappearance of **6** and the appearance of **5** was followed by a "stable period" for both **6** and **5**; no other chromium species was observed by IR, UV−vis, or ^{1}H NMR. (The difference between the induction period in Figure 1a and that in Figure 1b is probably the result of inaccurate temperature control in the UV−vis spectrometer.[21])

During the "stable period" the concentrations of **5** and **6** ($[\mathbf{5}]_{st}$ and $[\mathbf{6}]_{st}$, respectively) remained sufficiently constant that the steady-state approximation can be applied to them, resulting in eq 14. The monomeric radical should, as shown by calculations in the literature,[22] reach a steady state in the presence of a high concentration of chain transfer catalyst, resulting in eq 15. Similar approaches have been used to estimate the concentration of monomeric radicals during measurements of k_{p1}[10] and BDE(Co−C),[23] with high concentrations of cobalt(II) catalyst present.

$$-\frac{\mathrm{d}[\mathbf{6}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathbf{5}]}{\mathrm{d}t} = k_\mathrm{tr}(\mathrm{monomer})[\mathbf{6}]_\mathrm{st}[\mathrm{R}^{\bullet}] - k_\mathrm{reinit}[\mathbf{5}]_\mathrm{st}[\mathrm{MMA}] \cong 0 \tag{14}$$

$$\frac{\mathrm{d}[\mathrm{R}^{\bullet}]}{\mathrm{d}t} = 2f k_\mathrm{d}[\mathrm{AIBMe}] - 2k_\mathrm{t}^{1,1}[\mathrm{R}^{\bullet}]^2 \cong 0 \tag{15}$$

Combining eqs 14 and 15 gives eq 16, which can be used to determine k_{tr}(monomer) from the ratio of $[\mathbf{5}]_{st}$ to $[\mathbf{6}]_{st}$ when **6** is heated with AIBMe and MMA. Equation 16 should be valid because eq 6 reaches an equilibrium during the "stable period".

$$k_\mathrm{tr}(\mathrm{monomer}) = \frac{k_\mathrm{reinit}[\mathrm{MMA}][\mathbf{5}]_\mathrm{st}}{[\mathrm{R}^{\bullet}][\mathbf{6}]_\mathrm{st}} = \frac{k_\mathrm{reinit}[\mathrm{MMA}][\mathbf{5}]_\mathrm{st}}{\sqrt{\frac{fk_\mathrm{d}[\mathrm{AIBMe}]}{k_\mathrm{t}^{1,1}}}[\mathbf{6}]_\mathrm{st}} \tag{16}$$

As shown in Figure 1, $[\mathbf{6}]_{st}$ and $[\mathbf{5}]_{st}$ can be determined by UV−vis and ^{1}H NMR, respectively. However, the experimental error is minimized[24] by obtaining the value of $[\mathbf{5}]_{st}/[\mathbf{6}]_{st}$ from the absorbance (at 611 nm) of **6** at the beginning of the reaction (A_0) and during the "stable period" (A_{st}),[25] turning eq 16 into eq 17.

$$k_\mathrm{tr}(\mathrm{monomer}) \cong \frac{k_\mathrm{reinit}[\mathrm{MMA}]}{\sqrt{\frac{f k_\mathrm{d}[\mathrm{AIBMe}]}{k_\mathrm{t}^{1,1}}}} \times \frac{A_0 - A_\mathrm{st}}{A_\mathrm{st}} \tag{17}$$

The high concentration of $(C_5Ph_5)Cr(CO)_3^{\bullet}$ (**6**) that is required to ensure that the monomeric radical is dominant (and eq 17 is valid) causes practical difficulties. If $A \geq 1$, it is difficult for [**6**] to be determined from Beer's law; the extinction coefficient (720 ± 80 M^{-1} cm^{-1}) of **6** indicates a maximum $[\mathbf{6}]_0$ of 0.014 M when a cell of 0.1 cm path length is used. The formation of oligomeric radicals (mainly k_{p1}, see eq 5) could also be suppressed by holding down the concentration of AIBMe or MMA to decrease chain growth, but a high concentration of MMA is required to minimize the error of A_{st} measurements,[26] while a large ratio of $[\mathrm{AIBMe}]_0$ to $[\mathbf{6}]_0$ is necessary to keep the induction period short.[15]

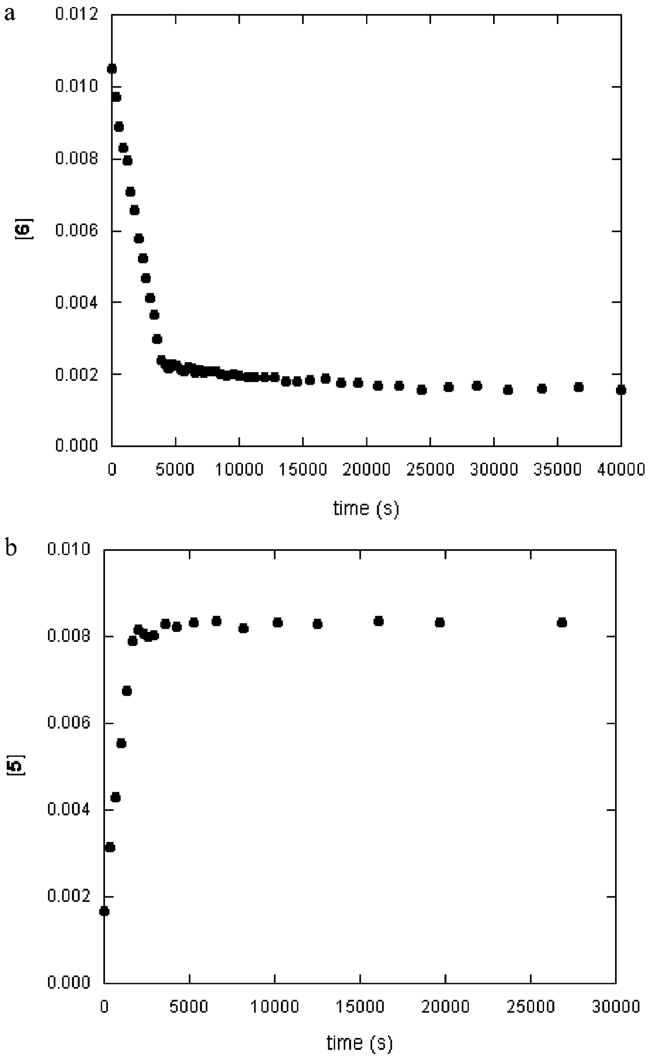


Figure 1. Appearance of (a) $(C_5Ph_5)Cr(CO)_3^{\bullet}$ and (b) $(C_5Ph_5)Cr(CO)_3H$ when $(C_5Ph_5)Cr(CO)_3^{\bullet}$ was treated with MMA and AIBMe: (a) disappearance of $(C_5Ph_5)Cr(CO)_3^{\bullet}$ (**6**) monitored by UV−vis; (b) appearance of $(C_5Ph_5)Cr(CO)_3H$ (**5**) monitored by ^{1}H NMR. 70 °C, $[\mathbf{6}]_0 = 0.01$ M, [AIBMe] = 0.1 M, $[\mathrm{MMA}]_0 = 0.08$ M.

In a typical experiment, 20−30% of MMA turned into MMA dimer within 2 h at 70 °C (higher oligomers were not observed). If we assume that the dimeric radical **4** has the same reactivity toward termination[27] and chain transfer as the methylisobutyryl radical **3**, while the MMA dimer has the same reactivity toward reinitiation as MMA,[5] this 20−30% conversion of MMA to the MMA dimer results in only a 10−15% loss of "total monomer"; in practice, we have assumed that $[\mathrm{MMA}] \cong [\mathrm{MMA}]_0$.

When a C_6D_6 solution with appropriate concentrations of $(C_5Ph_5)Cr(CO)_3^{\bullet}$ (**6**), AIBMe, and MMA was heated to 70 °C, the concentration of $(C_5Ph_5)Cr(CO)_3H$ (**5**) (monitored by ^{1}H NMR) reached a steady state in less than 1 h (see Table 2). Therefore, A_{st} was measured by UV−vis 1.5 h after the solution was heated, and $[\mathrm{AIBMe}]_{st}$ at that time was taken from eq 18.

$$[\mathrm{AIBMe}]_\mathrm{st} = [\mathrm{AIBMe}]_0 \exp(-fk_\mathrm{d}t) \tag{18}$$

Table 2. Data for the Measurements of k_{tr}(Monomer)

temp (°C)	$[AIBMe]_0$ (M)	$[MMA]_0$ (M)	$[\mathbf{6}]_0$ (M)	induction time (s)	$[AIBMe]_{st}$ (M)^a	$(A_0 - A_{st})/A_{st}$	k_{tr}(monomer) ($M^{-1}\ s^{-1}$)^b
60	0.0966	0.856	0.006 84	4800	0.0899	3.50	3.8×10^5
70	0.0842	0.772	0.006 07	1800	0.0678	3.72	4.5×10^5
70	0.0480	0.804	0.006 26	2300	0.0387	2.90	4.8×10^5
70	0.0471	0.903	0.005 71	1800	0.0380	3.39	6.4×10^5
80	0.0328	0.978	0.003 76	360	0.0229	3.64	9.6×10^5

^{a} Calculated using eq 18. ^{b} Calculated using eq 17.

The induction period increased significantly as the temperature decreased (see Table 2). A_{st} was measured 2.5 h after the solution was heated to 60 °C, while it was measured 1 h after the solution was heated to 80 °C; again, $[AIBMe]_{st}$ was taken from eq 18.

The values of $(A_0 - A_{st})/A_{st}$ and $[AIBMe]_{st}$ calculated from our observations under different experimental conditions are listed in Table 2. Values of k_{tr}(monomer) calculated from eq 17, and of the rate constants $f\,k_d$,[28] k_{reinit},[29] and $k_t^{1,1}$ (from Table 1), are also shown in Table 2. The average value of k_{tr}(monomer) (three experiments) is $(5.2 \pm 1.0) \times 10^5\ M^{-1}\ s^{-1}$ at 70 °C.

The k_{tr}(monomer) values in Table 2 are consistent with those we obtained from kinetic modeling of reactions between **5** and MMA (see revised value above, $2.5 \times 10^5\ M^{-1}\ s^{-1}$ at 50 °C). The 70 °C value of k_{tr}(monomer) for the methylisobutyryl radical **3** in Table 2 is smaller than that at the same temperature for the chain-carrying radical in an MMA polymerization ($k_{tr} = 1.4 \times 10^6\ M^{-1}\ s^{-1}$ with AIBMe as an initiator[15]); i.e., k_{tr} decreases significantly as we go from a monomeric to a polymer-chain-carrying radical.

Experimental Section

General. All manipulations were carried out using Schlenk, high-vacuum, or inert-atmosphere-box techniques. ^{1}H NMR spectra were recorded on a Bruker 300 or 400 MHz instrument. UV−vis spectra were recorded on a Hewlett-Packard 8543 diode array UV−vis spectrometer equipped with a Peltier temperature controller.

Materials. Hexamethylcyclotrisiloxane was purified by vacuum transfer. C_6D_6 was distilled under N_2 from Na/benzophenone. MMA was purified as in our previous work.[13] AIBMe was prepared by a literature procedure[30] and stored at −30 °C. $(C_5Ph_5)Cr(CO)_3H$ (**5**)[31] and $(C_5Ph_5)Cr(CO)_3^\bullet$ (**6**)[32] were prepared by the procedures cited.

Measurements of k_{tr}(Monomer). In a typical experiment, 22.1 mg of AIBMe, 10 mg of **6**, and 161.0 mg of MMA were weighed into a 2 mL volumetric flask in an inert atmosphere box. A C_6D_6 solution (100 μL) of hexamethylcyclotrisiloxane (as an internal standard, 0.005 57 M) was then added, followed by enough C_6D_6 added to bring the total volume to 2.0 mL.

An appropriate volume (0.5 mL) of this stock solution was placed in a J. Young tube. The NMR probe was equilibrated to 70.0 ± 0.2 °C (calibrated by ethylene glycol[33]) and tuned with another J. Young tube before the sample was inserted. The induction period was determined by monitoring the increase in the height (relative to that of the internal standard) of the hydride resonance (δ −3.98).

The rest of the stock solution was put into a Schlenk cell (quartz, path length = 0.1 cm)[34] in an inert atmosphere box, and its A_0 at 611 nm was measured in the UV spectrometer at room temperature. The solution was then transferred to another Schlenk cell (quartz, path length = 0.5 cm) in the inert atmosphere box. The new cell was placed in a constant-temperature bath regulated to 70.0 ± 0.1 °C. After 1.5 h, the absorbance of **6** at 611 nm was measured and divided by 5 to give A_{st}. The value of k_{tr}(monomer) was calculated from eq 17.

Similar procedures were repeated three times at 70 °C. At 60 °C the stock solution was heated for 2.5 h before measuring A_{st}, while at 80 °C it was heated for 1 h before measuring A_{st}.

Acknowledgment. This work was supported by the Department of Energy, Grant DE-FG02-97ER14807.

Supporting Information Available: Details of the estimate of the bimolecular termination rate constant ($k_t^{1,1}$) between two methylisobutyryl radicals. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Gridnev, A. A.; Ittel, S. D. *Chem. Rev.* **2001**, *101*, 3611−3659.

(2) Mayo, F. R. *J. Am. Chem. Soc.* **1943**, *65*, 2324−2329.

(3) Gridnev, A. A.; Bel'govskii, I. M.; Enykolopyan, N. S. *Vysokomol. Soedin., Ser. B* (*Polym. Sci.*) **1986**, *B28*, 85 (Russian); *Chem. Abstr.* **1986**, *105*, 6846.

(4) Smith, G. B.; Heuts, J. P. A.; Russell, G. T. *Macromol. Symp.* **2005**, *226*, 133−146.

(5) There is evidence that the H$^\bullet$ transfer rate constant between (C_5Ph_5)-$Cr(CO)_3H$ and a vinyl-terminated macromonomer decreases as the chain length increases. See: Tang, L. Scope and Mechanism of Chain Transfer Catalysis with Metalloradicals and Metal Hydrides. Ph.D. Thesis, Columbia University, New York, 2005.

(6) Smirnov, B. R.; Marchenko, A. P.; Plotnikov, V. D.; Kuzayev, A. I.; Yenikolopyan, N. S. *Polym. Sci. U.S.S.R.* **1981**, *23*, 1169−1178.

(7) Burczyk, A. F.; O'Driscoll, K. F.; Rempel, G. L. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3255−3262.

(8) Sanayei, R. A.; O'Driscoll, K. F. *J. Macromol. Sci., Chem.* **1989**, *A26*, 1137−1149.

(9) Olaj, O. F.; Zoder, M.; Vana, P.; Kornherr, A.; Schnöll-Bitai, I.; Zifferer, G. *Macromolecules* **2005**, *38*, 1944−1948 and references therein.

(10) Gridnev, A. A.; Ittel, S. D. *Macromolecules* **1996**, *29*, 5864−5874.

(11) Beuermann, S.; Buback, M.; Davis, T. P.; Gilbert, R. G.; Hutchinson, R. A.; Olaj, O. F.; Russell, G. T.; Schweer, J.; van Herk, A. M. *Macromol. Chem. Phys.* **1997**, *198*, 1545−1560.

(12) Tang, L.; Papish, E. T.; Abramo, G. P.; Norton, J. R.; Baik, M.-H.; Friesner, R. A.; Rappé, A. *J. Am. Chem. Soc.* **2003**, *125*, 10093−10102; **2006**, *128*, 11314.

(13) Tang, L.; Norton, J. R.; Edwards, J. C. *Macromolecules* **2003**, *36*, 9716−9720.

(14) Tang, L.; Norton, J. R. *Macromolecules* **2004**, *37*, 241−243.

(15) Tang, L.; Norton, J. R., submitted to *Macromolecules*.

(16) Smith, G. B.; Russell, G. T.; Heuts, J. P. A. *Macromol. Theory Simul.* **2003**, *12*, 299−314.

(17) Stickler, M. *Makromol. Chem.* **1986**, *187*, 1765−1775.

(18) Korth, H. G.; Lommes, P.; Sicking, W.; Sustmann, R. *Int. J. Chem. Kinet.* **1983**, *15*, 267−279.

(19) In a typical experiment, $[\mathbf{6}]_0 = 0.007$ M and $[MMA]_0 = 0.8$ M. With a C_S value of 1000 for **6**, eq 4 gives a DP_n very close to 2 for the resulting oligomers.

(20) Equations 10−13 are related to eqs 14−17 in the companion paper.[15] In eqs 10−13 all free radical species are monomeric, whereas in the companion paper eqs 14−17 deal with long chain-carrying radicals during a polymerization.

(21) The temperature was monitored by an external thermocouple on the Peltier temperature controller of the UV−vis spectrometer. However, this thermocouple is not calibrated, and the cell holder is designed for a cell of 1 cm path length, while these experiments required cells of 0.1 or 0.5 cm path length.

(22) Gridnev, A. A.; Ittel, S. D.; Fryd, M.; Wayland, B. B. *Organometallics* **1996**, *15*, 222−235.

(23) (a) Wayland, B. B.; Gridnev, A. A.; Ittel, S. D.; Fryd, M. *Inorg. Chem.* **1994**, *33*, 3830−3833. (b) Woska, D. C.; Xie, Z. D.; Gridnev, A. A.; Ittel, S. D.; Fryd, M.; Wayland, B. B. *J. Am. Chem. Soc.* **1996**, *118*, 9102−9109.

(24) Within experimental error, it was found that $[\mathbf{6}]_0 = [\mathbf{6}]_{st} + [\mathbf{5}]_{st}$. For example, in trial 2 of Table 2, $[\mathbf{6}]_0 = 0.006\ 07$ M, while $[\mathbf{6}]_{st} + [\mathbf{5}]_{st} = 0.006\ 73$ M. The difference (about 10%) came from the combined uncertainties in the ^{1}H NMR and UV−vis measurements. The uncertainty in the UV−vis measurement itself was larger than 10%, given that the extinction coefficient of **6** at 611 nm is 720 ± 80 $M^{-1}\ cm^{-1}$.

(25) Since no other chromium species were observed by IR, UV−vis, or ^{1}H NMR, $[\mathbf{5}]_{st}/[\mathbf{6}]_{st} = (A_0 - A_{st})/A_{st}$.

(26) As seen from eq 17, $K_{eq} = [\mathrm{MMA}](A_0 - A_{st})/[\mathrm{R}^\bullet]A_{st}$. A small [MMA] will result in a small A_{st}, which may not be accurately measured by UV−vis.

(27) Equation 8 suggests that the termination rate constant between dimeric MMA radicals **4** is about 1/3 of that between methylisobutyryl radicals **3**.

(28) Values of fk_d in MMA at different temperatures were extrapolated by $\ln k_d = 33.1 - 14800/T$ and $\ln f = 0.58 - 330/T$: Kouloumbris, M. Dissertation, University of Mainz, 1984, as quoted in ref 17. These fk_d values (in MMA) are used directly in our work (in C_6D_6) since the decomposition rate constant for AIBN does not change much with solvent. It has been reported to be 3.1×10^{-5} s^{-1} in pure MMA but 3.27×10^{-5} s^{-1} in benzene (at 70 °C). See: Bamford, C. H.; Denyer, R.; Hobbs, J. *Polymer* **1967**, *8*, 493−496. Also see: Tobolsky, A. V.; Baysal, B. *J. Polym. Sci.* **1953**, *11*, 471−486 and references therein.

(29) The reinitiation rate constants k_{reinit} between **5** and MMA at various temperatures were extrapolated from data in Tables 1 and 2 in ref 12.

(30) Bizilj, S.; Kelly, D. P.; Serelis, A. K.; Solomon, D. H.; White, K. E. *Aust. J. Chem.* **1985**, *38*, 1657−1673.

(31) Abramo, G. P.; Norton, J. R. *Macromolecules* **2000**, *33*, 2790−2792.

(32) Hoobler, R. J.; Hutton, M. A.; Dillard, M. M.; Castellani, M. P.; Rheingold, A. L.; Rieger, A. L.; Rieger, P. H.; Richards, T. C.; Geiger, W. E. *Organometallics* **1993**, *12*, 116−123.

(33) Cavanagh, J.; Fairbrother, W. J.; Palmer III, A. G.; Skelton, N. J. *Protein NMR Spectroscopy Principles and Practice*; Academic Press: New York, 1996.

(34) There would be a significant error ($A > 1$) if a Schlenk cell with an 0.5 cm path length were used to determine A_0.

MA0615755