Macromolecules **2001,** *34,* 6169−6173

Articles

Effect of Cu(II) on the Kinetics of the Homogeneous Atom Transfer Radical Polymerization of Methyl Methacrylate

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Received March 19, 2001; Revised Manuscript Received June 15, 2001

ABSTRACT: The kinetics of CuBr-mediated homogeneous atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) using 2-hydroxyethyl-2-bromoisobutyrate (HEBIB) as initiator and *N*-(*n*-hexyl)pyridylmethanimine (NHPMI) as ligand was investigated. The experimental results showed that initially added Cu(II) can have strong effects on the kinetics of the ATRP depending on the $[\mathrm{Cu(II)}]_0/[\mathrm{Cu(I)}]_0$ ratio. When ≤10% Cu(II) relative to Cu(I) was added at the beginning of the polymerization, the kinetics can be well described by Fischer's equation ($\ln([\mathrm{M}]_0/[\mathrm{M}]) \propto t^{2/3}$).[9] The obtained reaction orders for initiator, Cu(I) and Cu(II), are quite close to or the same as those in Fischer's equation, verifying the applicability of Fischer's equation in ATRP systems. On the other hand, when $[\mathrm{Cu(II)}]_0/[\mathrm{Cu(I)}]_0 \geq 0.1$, the kinetics can be well interpreted by Matyjaszewski's equation ($\ln([\mathrm{M}]_0/[\mathrm{M}]) \propto t$).[8] The polymerization rate shows almost first order with respect to the concentrations of initiator and Cu(I) and inverse first order with respect to the concentration of Cu(II), suggesting that the "self-regulation" and radical termination becomes unimportant for the ATRP process when enough Cu(II) is added at the beginning of the reaction. This result is of great potential importance for better control of ATRP systems. Besides, the equilibrium constant K_{eq} and termination constant k_{t} of the ATRP system at 90 °C were determined to be 7.2×10^{-8} and $8.9 \times 10^{7}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, respectively.

Introduction

Recently, some controlled/"living" radical polymerization systems have been reported, such as stable free radical polymerization (SFRP) with 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO),[1] atom transfer radical polymerization (ATRP),[2,3] and reversible addition−fragmentation chain transfer (RAFT) polymerization.[4] In particular, ATRP has attracted great attention in the past few years due to its applicability to both styrenic and (meth)acrylate monomers and its remarkable tolerance of functional groups.[5−7] So far, a variety of monomers have been successfully polymerized by ATRP, such as styrene, (meth)acrylates, acrylonitrile, and so on, and polymers with narrow molecular weight distribution and specific functional end groups have been obtained.[5]

To understand the mechanistic aspects of the ATRP and to better control the polymerization process, both experimental and theoretical kinetic studies on ATRP have been conducted.[8−15] Up to now, two equations have been proposed to describe the kinetics of ATRP by Matyjaszewski (eq 1)[8] and by Fischer (eq 2),[9] respectively.

$$\ln\left(\frac{[\mathrm{M}]_0}{[\mathrm{M}]}\right) = k_{\mathrm{p}}K_{\mathrm{eq}}\frac{[\mathrm{RX}][\mathrm{Cu(I)}]}{[\mathrm{Cu(II)}]}t = K_{\mathrm{app}}t \qquad (1,\ \text{M-Eq})^{16}$$

$$\ln\left(\frac{[\mathrm{M}]_0}{[\mathrm{M}]}\right) = \frac{3}{2}k_{\mathrm{p}}([\mathrm{RX}]_0[\mathrm{Cu(I)}]_0)^{1/3}\left(\frac{K_{\mathrm{eq}}}{3k_{\mathrm{t}}}\right)^{1/3}t^{2/3} = K_{\mathrm{Fischer}}t^{2/3} \qquad (2,\ \text{F-Eq})^{16}$$

So far, almost all experimental results were analyzed according to Matyjaszewski's equation (eq 1, M-Eq). Some results were in agreement with M-Eq in terms of reaction orders for initiator and Cu(I),[8,11,15] while some others deviated to various extents.[12−14] The deviations were generally ascribed to the existence of "self-regulation" caused by the so-called "persistent radical effect" in ATRP.[17] On the basis of the existence of the persistent radical effect, Fischer derived his kinetic equation for the ATRP system (eq 2, F-Eq). Fischer's equation has already proven to be applicable in nitroxide-mediated living radical polymerization.[18,19] But up to now, to the best of our knowledge, no experimental results have been reported to support this equation in ATRP systems. Besides, in the derivation of F-Eq, it is assumed that $[\mathrm{Cu(II)}]_0 = 0$. In actual experiments, however, it is difficult to achieve this as can be seen by direct measurement of [Cu(II)].[20]

In this paper, both F-Eq and M-Eq are experimentally verified in CuBr-mediated homogeneous ATRP of MMA

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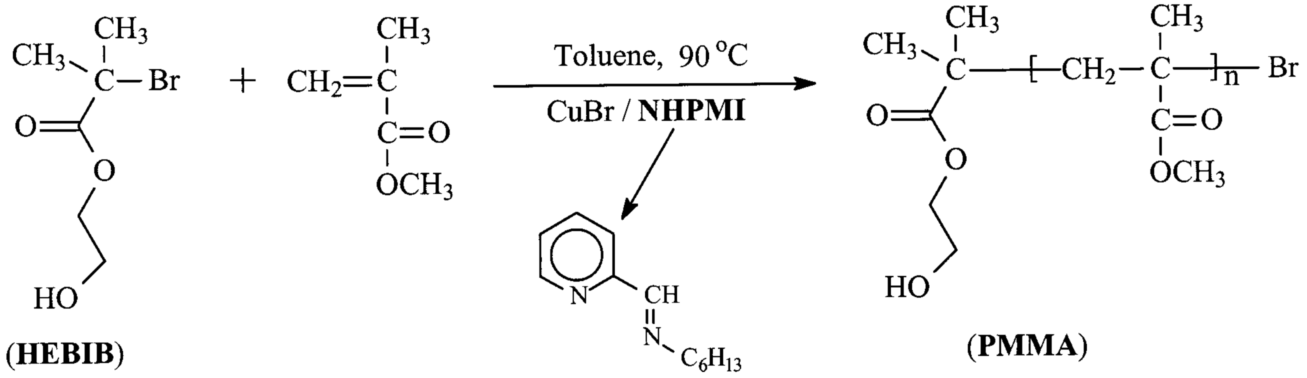
10.1021/ma0104736 CCC: $20.00

Scheme 1



using 2-hydroxyethyl-2-bromoisobutyrate (HEBIB) as initiator and *N*-(*n*-hexyl)pyridylmethanimine (NHPMI) as ligand. The effects of initially added Cu(II) on the kinetics of the ATRP will be discussed in detail.

Experimental Section

Materials. MMA (Aldrich, 99%) was washed twice with aqueous solution of sodium hydroxide (5%) and twice with water, dried with anhydrous magnesium sulfate, and then distilled over calcium hydride under vacuum. The distillate was stored at −18 °C before use. Toluene (Biosolve Ltd., AR) was distilled over calcium hydride. CuBr (Aldrich, 98%) was stirred with acetic acid for 12 h, washed with ethanol and diethyl ether, and then dried under vacuum at 75 °C for 3 days. The purified CuBr was stored in an argon atmosphere. HEBIB was provided by DSM Resins and distilled under reduced pressure before use. NHPMI was synthesized by condensation of pyridine-2-carboxaldehyde and *n*-hexylamine.[15] $CuBr_2$ (Aldrich, 99%), aluminum oxide (activated, basic, for column chromatography, 50−200 μm), tetrahydrofuran (THF) (Biosolve Ltd., AR), and all the other chemicals were used as received.

Polymerization Procedure. A typical ATRP was carried out as follows: To a 250 mL three-neck round-bottom flask, CuBr (4.677 mmol) and $CuBr_2$ (if necessary) were added to a solution of toluene (30 mL) and MMA (141.181 mmol, 15 mL). NHPMI (14.031 mmol) was then added. After the reaction mixture was bubbled by argon for 30 min in an ice bath, the flask was immersed in a thermostated oil bath at 90 °C and stirred for 10 min. A dark brown homogeneous system was then obtained. The initiator HEBIB (4.651 mmol) was added slowly via a degassed syringe. The polymerization was sampled at suitable time periods throughout the reaction. The sample was diluted with THF, and part of it was used for gas chromatography (GC) measurements to determine the monomer conversion. The rest was passed through a column of basic aluminum oxide prior to size exclusion chromatography (SEC) and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements.

Measurements. Monomer conversion was determined from the concentration of residual monomer using a Hewlett-Packard (HP 5890) GC, equipped with AT-Wax capillary column (30 m × 0.53 mm × 10 μm), and toluene was used as internal reference. Molecular weights and molecular weight distributions were measured by SEC at ambient temperature using a Waters GPC equipped with a Waters model 510 pump and a model 410 differential refractometer (40 °C). THF was used as eluent at a flow rate of 1.0 mL/min. A set of two linear columns (Mixed-C, Polymer Laboratories, 30 cm, 40 °C) was used. Calibration was carried out using low-polydispersity polystyrene (PS) standards ranging from 600 to 7×10^6, and molecular weights were calculated using the universal calibration principle and Mark−Houwink parameters (PS: $K = 1.14 \times 10^{-4}$ dL g^{-1}, $a = 0.716$; PMMA: $K = 0.944 \times 10^{-4}$ dL g^{-1}, $a = 0.719$). Data acquisition and processing were performed using Waters Millennium 32 software. MALDI-TOF MS measurements were performed on a Voyager-DE STR (Applied Biosystems, Framingham, MA) instrument equipped with a 337 nm nitrogen laser. Positive-ion spectra were acquired in reflectron mode. *trans*-3-Indoleacrylic acid (IAA) was chosen as the matrix. Polymer samples were dissolved in THF at 1 mg/mL and the matrix at 19 mg/mL. 1.5 μL of sodium trifluoroacetate (5 mg/mL) was added to 1 mL of IAA solution. 0.7 μL of matrix solution (with sodium salt) was added on a stainless steel plate to form a layer, on which 0.7 μL of polymer solution was added.

Results and Discussion

MMA was polymerized in toluene with HEBIB as initiator, CuBr as catalyst, and NHPMI as ligand at 90 °C via ATRP (Scheme 1). The ligand was added in excess (3 times the molar amount of CuBr) to ensure the total solubility of Cu(I) and Cu(II). The number-average molecular weights (M_n) of PMMAs determined by SEC increase linearly with monomer conversion, and their polydispersity indices (PDI) are less than 1.2, indicating that the polymerization is living and controlled. However, the obtained M_n values by SEC ($M_{n,SEC}$) are higher than the theoretical values ($M_{n,th}$). For instance, a $M_{n,SEC}$ of 6884 (PDI = 1.17) was obtained for a PMMA sample against a $M_{n,th}$ of 5393, which may be due to inaccuracies from recalculation of the PS calibration curve to a PMMA calibration curve via the universal calibration principle. MALDI-TOF MS has proven to be a powerful technique in determining accurate molecular weights of polymers with low PDI (<1.2), virtually independent of hydrodynamic volume and other physical properties.[21,22] The M_n determined by MALDI-TOF MS, $M_{n,MALDI}$, for the above PMMA sample is 5406 (PDI = 1.13), which is very close to the theoretical value, suggesting that the studied ATRP systems are almost exempt of side reactions. Detailed MALDI-TOF MS results will be included in a forthcoming paper.

Effect of Cu(II) Concentration. $CuBr_2$ was added at the beginning of ATRP to study its effect on the kinetics. The kinetic plots of $\ln([M]_0/[M])$ vs reaction time (t and $t^{2/3}$) for the ATRP are shown in Figure 1. When initially added Cu(II) concentrations relative to Cu(I) are lower than 10% (i.e., $[Cu(II)]_0/[Cu(I)]_0 < 0.1$), the kinetics deviates from M-Eq, as demonstrated by two curves (Figure 1a). When $\ln([M]_0/[M])$ is plotted against $t^{2/3}$, however, straight lines with linearity regression coefficients (R^2) greater than 0.99 are obtained (Figure 1b), suggesting that the studied ATRP systems can be better fitted by F-Eq.

On the contrary, when $[Cu(II)]_0/[Cu(I)]_0 > 0.1$, the kinetics of the studied ATRP systems fits M-Eq better than F-Eq (Figure 1, parts a and b). This may be

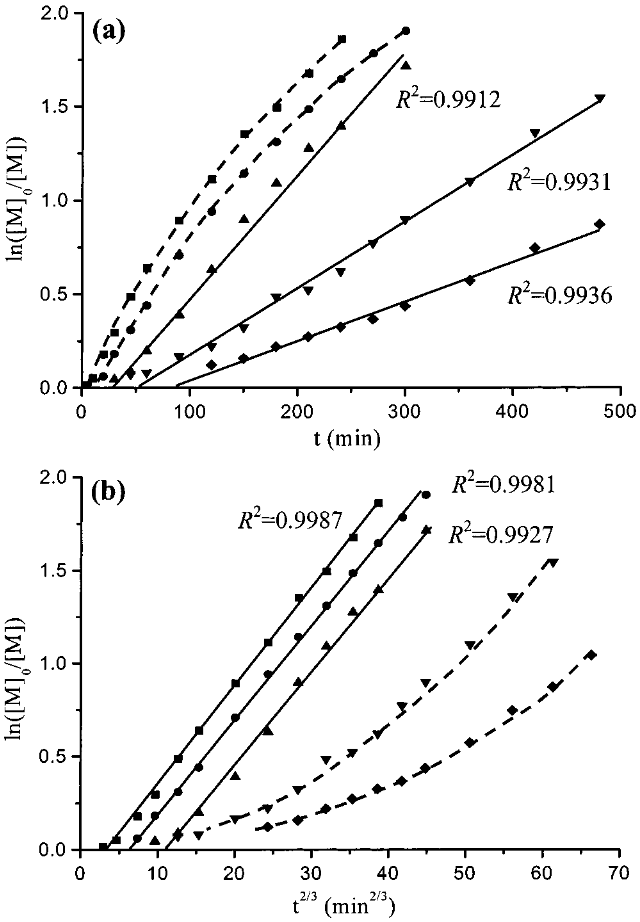


Figure 1. Plots of ln([M]$_0$/[M]) vs reaction time (t and $t^{2/3}$) for the ATRP of MMA in toluene at 90 °C using different amounts of initially added CuBr$_2$. [MMA]$_0$ = 2.8879 M, [HEBIB]$_0$ = 0.0959 M, [CuBr]$_0$ = [NHPMI]$_0$/3 = 0.0969 M. [CuBr$_2$]$_0$/[CuBr]$_0$: 0 (■), 0.05 (●), 0.1 (▲), 0.2 (▼), 0.3 (◆).

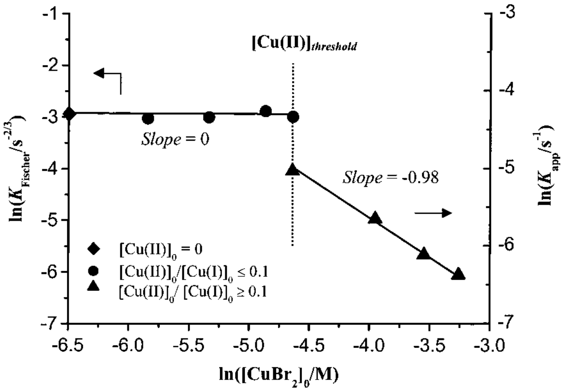


Figure 2. Dependence of K_{Fischer} and K_{app} on the concentration of initially added CuBr$_2$ for the ATRP of MMA in toluene at 90 °C. [MMA]$_0$ = 2.8879 M, [HEBIB]$_0$ = 0.0959 M, [CuBr]$_0$ = [NHPMI]$_0$/3 = 0.0969 M. When [CuBr$_2$]$_0$/[CuBr]$_0$ ≤ 0.1, K_{Fischer} is used, and K_{app} is used when [CuBr$_2$]$_0$/[CuBr]$_0$ ≥ 0.1.

explained in terms of the radical concentration change following the addition of Cu(II) at the beginning of the reaction. When [Cu(II)]$_0$/[Cu(I)]$_0$ < 0.1, the radical termination rapidly leads to a concentration of Cu(II) which is higher than [Cu(II)]$_0$. In this case, the prerequisite of F-Eq (formation of excess Cu(II) only by radical termination) is approximately met, and thus the kinetics should be well interpreted by F-Eq. On the other hand, when [Cu(II)]$_0$/[Cu(I)]$_0$ > 0.1, the radical termination is effectively diminished. This leads to retarded buildup of additional Cu(II) and is therefore consistent with the assumption of M-Eq (i.e., radical concentration remains constant), and the kinetics would fit M-Eq. In addition, at a Cu(II) concentration relative to Cu(I) of 10%, the kinetics of the system can be equally well fitted by both M-Eq and F-Eq (both fitted lines show linearity regression coefficients of greater than 0.99). This implies that a concentration of 10% Cu(II) relative to Cu(I) is a threshold level for the switch between two kinetic regimes. The reasonable agreement of the conversion–time data at [Cu(II)]$_0$/[Cu(I)]$_0$ = 0.1 with F-Eq as well as with M-Eq supports the existence of a smooth rather than a sudden transition. Besides, as shown in Figure 1, an induction period appears to be dependent on the added Cu(II) concentration. The cause of this induction period is yet unknown, and further investigation is under way.

Some kinetic data such as equilibrium and termination constants (K_{eq} and k_{t}) for the studied ATRP system can be obtained from Figure 1. When [Cu(II)]$_0$/[Cu(I)]$_0$ ≥ 0.1, the kinetics of the ATRP system fits M-Eq, and the steady-state concentrations of initiator and Cu(I) ([RX] and [Cu(I)]) will be close to their initial concentrations ([RX]$_0$ and [Cu(I)]$_0$). Therefore, M-Eq can be rewritten to eq 3 in this case.

$$\ln\left(\frac{[\mathrm{M}]_0}{[\mathrm{M}]}\right) = k_{\mathrm{p}}K_{\mathrm{eq}}\frac{[\mathrm{RX}]_0[\mathrm{Cu(I)}]_0}{[\mathrm{Cu(II)}]_0}t = K_{\mathrm{app}}t \qquad (3)$$

On the basis of eq 3 and the propagation rate constant of MMA (k_{p} = 1625 M^{-1} s^{-1} at 90 °C),[23] a K_{eq} of 7.2 × 10^{-8} is obtained from the slopes of the three straight lines in Figure 1a. Using F-Eq, k_{p}, and the obtained K_{eq}, we can also obtain a k_{t} of 8.9 × 10^7 M^{-1} s^{-1} from the average slope of the straight lines in Figure 1b. These results look reasonable compared with the kinetic data reported elsewhere.[11,24]

In the following study, F-Eq will be used to analyze the kinetics when [Cu(II)]$_0$/[Cu(I)]$_0$ ≤ 0.1 and M-Eq will be used when [Cu(II)]$_0$/[Cu(I)]$_0$ ≥ 0.1.

Shown in Figure 2 is a plot of lnK_{Fischer} and lnK_{app} vs ln[Cu(II)]$_0$ for the ATRP systems with different amounts of initially added Cu(II).[16] When [Cu(II)]$_0$/[Cu(I)]$_0$ ≤ 0.1, lnK_{Fischer} remains almost constant with respect to the increase of [Cu(II)]$_0$, indicating that the same amount of Cu(II), i.e., 10% relative to Cu(I), is present in the ATRP systems because of the persistent radical effect. As a consequence, the polymerization shows zero order with respect to [Cu(II)]$_0$. This result reveals that F-Eq is also applicable as long as [Cu(II)]$_0$ ≤ [Cu(II)]$_{\mathrm{threshold}}$ although it is assumed that [Cu(II)]$_0$ = 0 in the derivation of F-Eq. When [Cu(II)]$_0$/[Cu(I)]$_0$ ≥ 0.1, lnK_{app} decreases linearly with the increasing ln[Cu(II)]$_0$. An inverse first-order relationship between the polymerization rate and [Cu(II)]$_0$ was obtained, in accordance with Matyjaszewski's equation. Therefore, when enough Cu(II) is added at the beginning of ATRP, the "self-regulation" is unimportant, and the real Cu(II) concentrations in ATRP systems will be close to the added Cu(II) concentrations.

The threshold concentration of Cu(II) is also clearly shown in Figure 2, where both kinetic equations may be applied. This concentration corresponds to the Cu(II) level that is produced by the self-regulation process when no Cu(II) is present at the beginning of the polymerization. Using the electron spin resonance (ESR) method, Matyjaszewski et al. have measured the con-

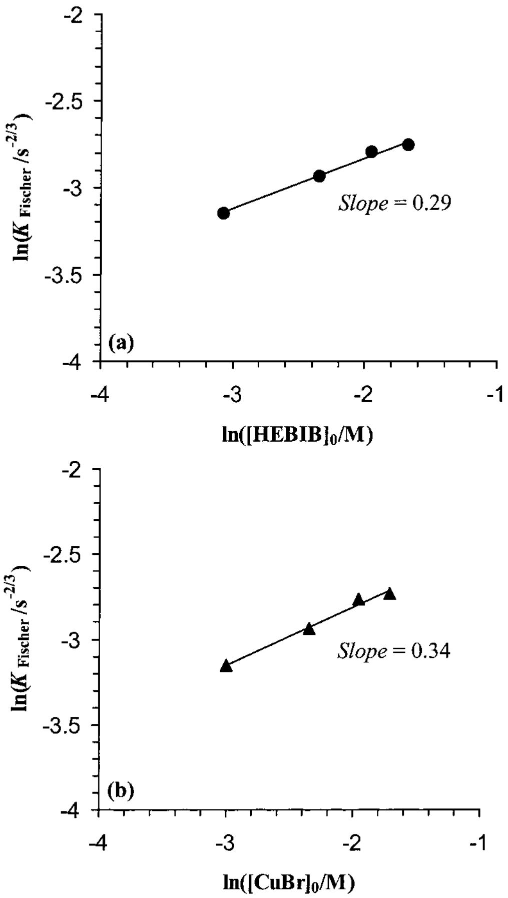


Figure 3. Dependence of K_{Fischer} on $[\mathrm{HEBIB}]_0$ and $[\mathrm{CuBr}]_0$ for the ATRP of MMA in toluene at 90 °C ($[\mathrm{CuBr_2}]_0 = 0$). (a) $[\mathrm{MMA}]_0 = 2.8856$ M, $[\mathrm{CuBr}]_0 = [\mathrm{NHPMI}]_0/3 = 0.0958$ M. (b) $[\mathrm{MMA}]_0 = 2.8581$ M, $[\mathrm{HEBIB}]_0 = 0.0946$ M, $[\mathrm{CuBr}]_0 = [\mathrm{NHPMI}]_0/3$.

centration of Cu(II) produced by the self-regulation process for the ATRP of MMA in diphenyl ether ($\mathrm{Ph_2O}$) at 90 °C with $[\mathrm{Cu(II)}]_0 = 0$, where ethyl 2-bromoisobutyrate (EBIB) was used as initiator, CuBr as catalyst, and 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbipy) as ligand.[25] The results showed that the steady-state concentration of Cu(II) is approximately 6% relative to $[\mathrm{Cu(I)}]_0$, which is lower than that of our ATRP system. The higher steady-state concentration of Cu(II) in the MMA/HEBIB/CuBr/NHPMI/toluene system than in the MMA/EBIB/CuBr/dNbipy/$\mathrm{Ph_2O}$ system may be attributed to higher equilibrium constant and higher radical concentrations in the former system. Since $[\mathrm{Cu(II)}]_{\mathrm{threshold}}$ can be experimentally determined by ESR,[20,25] the "self-regulation" in the ATRP system could be easily minimized by adding $[\mathrm{Cu(II)}]_0 \geq [\mathrm{Cu(II)}]_{\mathrm{threshold}}$. This should lead to better controlled ATRP systems, i.e., less bimolecular termination.

Recently, Fischer et al. studied the effects of the initially added persistent species on the polymerization rate in nitroxide-mediated living radical polymerization and found that the time (t) dependence of the polymerization index ($\ln([\mathrm{M}]_0/[\mathrm{M}])$) also changes from the nonlinear behavior ($\ln([\mathrm{M}]_0/[\mathrm{M}]) \propto t^{2/3}$) to the linear behavior ($\ln([\mathrm{M}]_0/[\mathrm{M}]) \propto t$) at a threshold initial concentration of the persistent species, i.e., $[\mathrm{Y}]_{0,t} = (3K_{\mathrm{eq}}[\mathrm{I}]_0 k_t/k_p)^{1/2}$, where Y is the persistent species and I the alkoxyamine initiator.[26] This result can be extended to ATRP systems, and accordingly the transition from the nonlinear behavior to the linear behavior for the kinetic plot of ATRP systems (i.e., the plot of $\ln([\mathrm{M}]_0/[\mathrm{M}])$ vs reaction time t) should occur at a threshold initial concentration $[\mathrm{Cu(II)}]_{0,t} = (3K_{\mathrm{eq}}[\mathrm{RX}]_0[\mathrm{Cu(I)}]_0 k_t/k_p)^{1/2}$, which corresponds to a $[\mathrm{Cu(II)}]_{0,t}$ of 0.0105 M in our ATRP system. This value is in good agreement with the experimental result ($[\mathrm{Cu(II)}]_{\mathrm{threshold}} = 0.0097$ M).

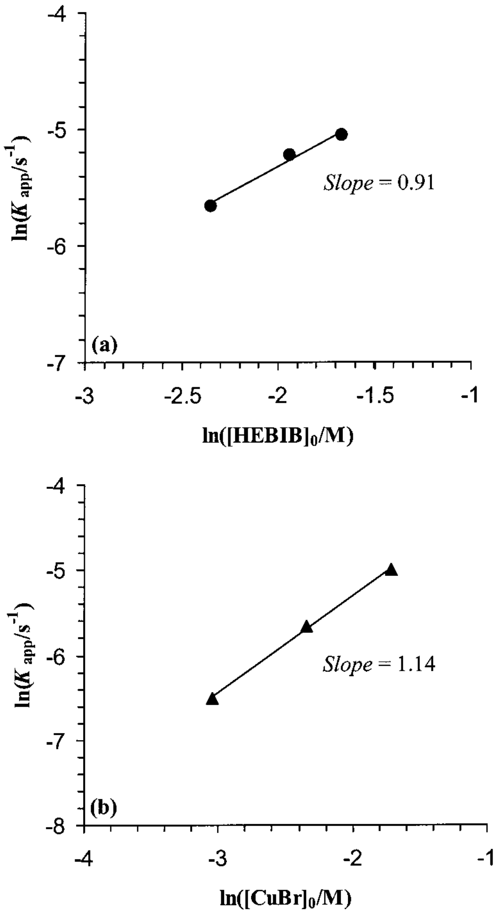


Figure 4. Dependence of K_{app} on $[\mathrm{HEBIB}]_0$ and $[\mathrm{CuBr}]_0$ for the ATRP of MMA in toluene at 90 °C ($[\mathrm{CuBr_2}]_0/[\mathrm{CuBr}]_0 \geq 0.1$). (a) $[\mathrm{MMA}]_0 = 2.8589$ M, $[\mathrm{CuBr}]_0 = [\mathrm{NHPMI}]_0/3 = 0.0950$ M, $[\mathrm{CuBr_2}]_0 = 0.0191$ M. (b) $[\mathrm{MMA}]_0 = 2.9169$ M, $[\mathrm{HEBIB}]_0 = 0.0936$ M, $[\mathrm{CuBr_2}]_0 = 0.0192$ M, $[\mathrm{CuBr}]_0 = [\mathrm{NHPMI}]_0/3$.

Reaction Orders of Initiator and Catalyst. According to F-Eq, the reaction orders for both initiator and Cu(I) should be $^1/_3$. The concentrations of HEBIB and CuBr were changed to determine their reaction orders in the studied ATRP systems without initially added Cu(II). It is known that F-Eq has been derived for an ideal living radical polymerization which involves all the well-known reaction steps, i.e., initiation, propagation, (de)activation, and bimolecular termination (chain transfer is not taken into account), and where the rate constants are considered to be independent of chain length.[19] The molecular weights determined by MALDI-TOF MS have indicated the absence of significant side reactions in our ATRP systems. To meet the second prerequisite, i.e., the rate constants are independent of chain length, the targeted molecular weights in ATRP systems should be as low as possible. In this case, the monomer conversions in our ATRP systems were maintained low enough to ensure the expected $M_n \leq 3000$. The plots of $\ln([\mathrm{M}]_0/[\mathrm{M}])$ vs $t^{2/3}$ give good straight lines for each of them, indicating that all kinetics fit F-Eq. The polymerization rate was determined to be 0.29 and 0.34 order with respect to the concentrations of HEBIB and CuBr, respectively (Figure 3, parts a and b), which are quite close to those in F-Eq and further verify the applicability of F-Eq in ATRP systems.

As stated above, when enough Cu(II) is added into the ATRP system at the beginning of the polymerization (i.e., $[\mathrm{Cu(II)}]_0/[\mathrm{Cu(I)}]_0 \geq 0.1$), the kinetics will fit M-Eq. The polymerization rate should, therefore, show first order with respect to the concentrations of HEBIB and CuBr. This is clearly demonstrated in Figure 4a,b.

Conclusions

A full kinetic analysis of CuBr-mediated homogeneous ATRP of MMA has demonstrated that initially added Cu(II) has strong effects on the kinetics of ATRP systems. When $[\mathrm{Cu(II)}]_0/[\mathrm{Cu(I)}]_0 \leq 0.1$, the reaction kinetics fits Fischer's equation ($\ln([\mathrm{M}]_0/[\mathrm{M}]) \propto t^{2/3}$) quite well, and the polymerization rate shows 0.29, 0.34, and 0 order with respect to the initial concentrations of initiator, Cu(I), and Cu(II), confirming that Fischer's equation is applicable in ATRP systems. Besides, our results also reveal that F-Eq can be applied as long as $[\mathrm{Cu(II)}]_0 \leq [\mathrm{Cu(II)}]_{\mathrm{threshold}}$. When $[\mathrm{Cu(II)}]_0/[\mathrm{Cu(I)}]_0 \geq 0.1$, the kinetics can be well described by Matyjaszewski's equation ($\ln([\mathrm{M}]_0/[\mathrm{M}]) \propto t$). The polymerization rate shows almost first order with respect to the concentrations of initiator and Cu(I) and inverse first order with respect to the concentration of Cu(II), revealing that the "self-regulation" and radical termination during the ATRP process become unimportant when enough Cu(II) is added at the beginning of the reaction. This result is of great potential importance for the better control of ATRP systems, especially for the synthesis of well-defined macroinitiators that can be further used for preparing block polymers or for carrying out functionalization reactions. In addition, the equilibrium and termination constants (K_{eq} and k_{t}) of the ATRP system at 90 °C were determined to be 7.2×10^{-8} and $8.9 \times 10^{7}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, respectively. Furthermore, the experimental evidence for Fischer's theoretically derived value of the threshold initial Cu(II) concentration, $[\mathrm{Cu(II)}]_{0,t} = (3K_{\mathrm{eq}}[\mathrm{RX}]_0[\mathrm{Cu(I)}]_0 k_{\mathrm{t}}/k_{\mathrm{p}})^{1/2}$, is provided.

Acknowledgment. This work is financially supported by DSM Resins and Senter. The authors thank Dr. Ir. Martijn M. G. Antonisse (DSM Resins), Mr. John Rietberg (DSM Resins), and Ir. Auke Snijder for inspiring discussions and Mr. Wieb Kingma and Dr. Rainer Vollmerhaus for carrying out SEC and MALDI-TOF MS analyses, respectively.

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(16) In Fischer's equation, k_{t} is defined by $\mathrm{d}[\mathrm{R}]/\mathrm{d}t = -k_{\mathrm{t}}[\mathrm{R}]^2$, and a parameter K_{Fischer} is introduced by us to express the coefficient of $t^{2/3}$. The reaction order for each reactant in F-Eq can be obtained by plotting $\ln K_{\mathrm{Fischer}}$ against $\ln[\mathrm{RX}]_0$, $\ln[\mathrm{Cu(I)}]_0$, and $\ln[\mathrm{Cu(II)}]_0$. If we plot $\ln K_{\mathrm{app}}$ against $\ln[\mathrm{RX}]$, $\ln[\mathrm{Cu(I)}]$, and $\ln[\mathrm{Cu(II)}]$, the reaction orders for each reactant in M-Eq can also be determined.
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MA0104736