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Kinetics of Heterogeneous Atom Transfer Radical Polymerization of Methyl Methacrylate

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ABSTRACT: A new kinetic equation for copper-mediated ATRP is introduced based on the experimental observation that the deactivator concentration ([Cu^{II}]) remains constant throughout the polymerization. This constant deactivator concentration can originate from the use of a heterogeneous transition metal/ligand system, resulting in the precipitation of deactivating species when the concentration exceeds a ceiling concentration. Equations are derived in which the decrease of the radical concentration in time is assigned to the decrease of the concentration of the activator and the dormant chains. When the equilibrium constant is low and/or the polymerization rate high, the radical concentration remains constant up to high conversions indicating little termination. In the case where a monomer is used with a high equilibrium constant and a relatively low polymerization rate, the radical concentration is continuously decreasing in time, as the concentration of both the activator and the dormant species is decreasing throughout the polymerization. To validate the kinetic equation, polymerization of methyl methacrylate was performed with an alkyl bromide initiator and a heterogeneous Cu^{I}Br/Cu^{II}Br$_2$/PMDETA system. Electron spin resonance spectroscopy was used to demonstrate that the deactivator concentration remains constant throughout the polymerization. Simulations and experimental results are in very good agreement.

Introduction

Living (or controlled) radical polymerization techniques have caught a lot of attention in the past decade as a new opportunity to prepare a large array of polymer structures without using the more sensitive techniques like ionic or group transfer polymerization. Among the most studied techniques are stable free radical polymerization (SFRP),[1] atom transfer radical polymerization (ATRP),[2,3] and reversible addition fragmentation chain transfer (RAFT)[4] polymerization. These techniques are based on a reversible activation/deactivation cycle of polymer chains resulting in a small fraction of polymer radicals and a main fraction of reversibly deactivated "dormant" chains. Because of the low radical concentration and the fast deactivation of the polymer radicals, the fraction of irreversibly terminated "dead" polymer chains compared to the reversibly terminated "dormant" chains can be low. In copper-mediated ATRP the carbon−halogen bond of an alkyl halide (RX) is reversibly cleaved by a Cu^{I}X/ligand system, resulting in a radical (R*) and Cu^{II}X$_2$/ligand (deactivator). The radical will mainly either reversibly deactivate, add monomer or irreversibly terminate (Scheme 1, eqs 1−7).

Scheme 1

Initiation

$$\mathrm{R_0X + Cu^{I}X/L_{sol}} \underset{k_{d0}}{\overset{k_{a0}}{\rightleftharpoons}} \mathrm{R_0{*} + Cu^{II}X_2/L_{sol}} \quad (1)$$

$$\mathrm{R_0{*} + M} \xrightarrow{k_{po}} \mathrm{P_1{*}} \quad (2)$$

Propagation

$$\mathrm{P_nX + Cu^{I}X/L_{sol}} \underset{k_{d}}{\overset{k_{a}}{\rightleftharpoons}} \mathrm{P_n{*} + Cu^{II}X_2/L_{sol}} \quad (3)$$

$$\mathrm{P_n{*} + M} \xrightarrow{k_{p}} \mathrm{P_{n+1}{*}} \quad (4)$$

Solubilization

$$\mathrm{Cu^{II}X_2/L_{sol}} \underset{k_{sol}}{\overset{k_{insol}}{\rightleftharpoons}} \mathrm{Cu^{II}X_2/L_{insol}} \quad (5)$$

Termination

$$\mathrm{P_m{*} + P_n{*}} \xrightarrow{k_{tD}} \mathrm{D_m + D_n} \quad (6)$$

$$\mathrm{P_m{*} + P_n{*}} \xrightarrow{k_{tC}} \mathrm{D_{m+n}} \quad (7)$$

Next to the overall polymerization kinetics, also the kinetic parameters of initiation can have a profound influence on the overall polymerization kinetics. It was shown[5] that the rate of the activation step of the initiator (k_{a0}) can have a considerable effect on the polymerization kinetics. When the rate is very high compared to the overall activation rate, it can result in a high initial termination rate, diminishing the number of polymer chains and a steep increase of the Cu^{II} concentration. On the other hand, when the activation rate of the initiator is low compared to the overall activation rate, initiation will continue throughout the reaction time, resulting in polymers with a broad polydispersity index. For that reason often initiators are used that resemble the polymer structure, normally resulting in an efficient initiation without having much influence on the overall polymerization kinetics.

Since the introduction of ATRP as a tool to prepare polymers in a controlled fashion, two main kinetic descriptions of the conversion vs time have been introduced, namely:

$$\ln\left(\frac{[\mathrm{M}]_0}{[\mathrm{M}]_t}\right) = \frac{k_p k_a [\mathrm{RX}]_0 [\mathrm{Cu^I}]_0}{k_d [\mathrm{Cu^{II}}]_0} t \qquad (8)$$

Equation 8, proposed by Matyjaszewski et al.,[2,6,7] is based on a constant radical concentration due to the equilibrium between polymer radicals, dormant chains and copper species. This seems to hold when the radical concentration is sufficiently low, diminishing the rate of termination and thereby the fraction of irreversibly terminated polymer chains. This can be observed in systems were the ratio k_a/k_d, and/or the Cu^{I} and/or

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initiator concentrations are sufficiently low and the Cu^{II} concentration is sufficiently high.[6,8] To obtain a reasonable polymerization time the used monomers should have a high polymerization rate or a low termination rate.

$$\ln\left(\frac{[M]_0}{[M]_t}\right) = \frac{3}{2}k_p\left(\frac{k_a[RX]_0[Cu^I]_0}{3k_d(2k_t)}\right)^{1/3} t^{2/3} \tag{9}$$

$$[Cu^{II}]_{0,\text{threshhold}} = \left(\frac{3k_a k_t[Cu^1]_0[RX]_0}{k_d k_p}\right)^{1/2} \tag{10}$$

Equation 9, proposed by Fischer et al.,[6,9−11] is based on the persistent radical effect where after a very short time $[Cu^{II}] \gg [R^*]$ and from that point onward all reactant concentrations can be effectively calculated in time. The kinetic equations were derived for a system where no deactivator is added in the beginning of the reaction, and the termination rate is low. Often a small amount of deactivator is added at the start of the polymerization to avoid an uncontrolled reaction in the beginning of the polymerization. Although this is not accounted for, the equation still appears to be applicable in that case.[8] The threshold initial concentration of Cu^{II} ($[Cu^{II}]_{0,\text{ threshold}}$) above which eq 8 is used instead of eq 9 to effectively describe the kinetics of homogeneous ATRP can be calculated using eq 10.[8,12]

A number of metal/ligand complexes have the disadvantage that they do not solubilize the metal species over a wide concentration range. In particular, the produced Cu^{II} species have a limited solubility in nonpolar solvents, leading to a heterogeneous system with a constant low deactivator concentration. In that case, the persistent radical effect is counteracted.[5] This effect is seen in systems with unsubstituted bipyridines[2,13] and multidentate aliphatic amine ligands.[14] As a result these systems tend to be relatively fast, which can result in high termination rates and polymers with a broad polydispersity index. These disadvantages are accompanied by some major advantages, namely the ligands are cheap and easily accessible (especially the multidentate amines), they can be easily modified, and due to the heterogeneity of the metal/ligand complexes, they can be easily separated from the polymer solution.[15]

Kinetic Equation. A new kinetic description is developed which is based on a constant deactivator concentration ($[Cu^{II}]_c$), in which the termination reaction results in a decrease of the concentration of both the "dormant" polymer chains ([PX]) and the activator ($[Cu^I]$). The excess deactivator produced by the irreversible termination reaction will precipitate from the reaction mixture. To simplify the equations, chain length and conversion dependence of variables like termination and propagation rate coefficients are neglected as well as any side reactions like chain transfer. First the initial conditions for the concentrations are fixed, [RX], [R*], [P*], and [D] are respectively the concentration of the initiator, the initiator-derived radical, the polymer-derived radical, and the irreversibly terminated "dead" polymers.

$$[RX]_0 = [Cu^I]_0 \neq 0 \; [Cu^{II}]_c \neq 0 \tag{11}$$
$$[R^*]_0 = [P^*]_0 = [D]_0 = 0$$

Equation 12 is based on stoichiometric considerations given in the case of termination by disproportionation only. For convenience the initiator is considered as a "dormant" polymer chain with $n = 0$.

$$[RX]_0 - [RX]_t - [PX]_t = [PX]_0 - [PX]_t = [D]_t \tag{12}$$

Under the conditions that both k_{sol} and k_{insol} are high, the concentration of dissolved Cu^{II} species is constant from the start of the polymerization.[5] It is acknowledged that in the initial stage of the polymerization a constant deactivator concentration has not been accomplished when no deactivator is introduced prior to the polymerization, but simulations using the Fischer equations show that the constant deactivator concentration is reached at a low degree of conversion as also shown in the literature.[16,17] On the basis of eq 12, it can be derived that a differential equation can be setup for the formation of "dead" polymer chains.

$$\frac{d[D]}{dt} = 2k_{tD}[P^*]^2 = 2k_{tD}\left(\frac{K_{eq}}{[Cu^{II}]_c}\right)^2 [PX]_t{}^2[Cu^I]_t{}^2 =$$
$$\xi([RX]_0 - [D]_t)^2([Cu^I]_0 - [D]_t)^2 \Rightarrow$$
$$\frac{d[D]}{([RX]_0 - [D]_t)^2\,([Cu^I]_0 - [D]_t)^2} = \xi\, dt$$
$$\text{with } \xi = 2k_{tD}\left(\frac{K_{eq}}{[Cu^{II}]_c}\right)^2 \tag{13}$$

This equation can easily be solved in the case $[RX]_0 = [Cu^I]_0$, resulting in eqs 14−16

$$[D]_t = [PX]_0 - [3\xi t + [RX]_0{}^{-3}]^{-1/3} \tag{14}$$

$$[P^*]_t = \frac{K_{eq}}{[Cu^{II}]_c}[3\xi t + [RX]_0{}^{-3}]^{-2/3} \tag{15}$$

$$\ln\frac{[M]_0}{[M]} = \frac{k_p[Cu^{II}]_c}{2k_{tD}K_{eq}}[3\xi t + [RX]_0{}^{-3}]^{1/3} - \frac{k_p[Cu^{II}]_c}{2k_{tD}K_{eq}[RX]_0} \tag{16}$$

As can be seen from eqs 14−16, the concentration of all active species can be calculated easily when the initial activator and alkyl halide concentration are equal, assuming a constant deactivator concentrations. When this is not the case, only the number of "dead" polymer chains can be calculated analytically, eq 17, and the concentration of the remaining active species can be determined numerically.

If $[RX]_0 \neq [Cu^I]_0$

$$\left(\frac{2}{\delta^3}\right)\ln\left(\frac{[RX]_0 - [D]_t}{[Cu^I]_0 - [D]_d}\right) +$$
$$\frac{[Cu^I]_0 + [RX]_0 - 2[D]_t}{\delta^2\,([RX]_0 - [D]_t)([Cu^I]_0 - [D]_t)} =$$
$$\xi t + \left(\frac{2}{\delta^3}\right)\ln\left(\frac{[RX]_0}{[Cu^I]_0}\right) + \frac{[Cu^I]_0 + [RX]_0}{\delta^2[RX]_0\,[Cu^I]_0} \tag{17}$$
$$\text{with } \delta = [Cu^I]_0 - [RX]_0$$

To validate the new kinetic equation, a ligand was chosen that generally results in a heterogeneous system, namely N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA).[14] It is favorable to use a monomer that has a fast buildup of Cu^{II} with respect to the polymerization rate. Acrylates have a high polymerization rate and a low equilibrium constant ($K_{eq} = k_a/k_d$) and the conversion at which the Cu^{II} solubility limit will be reached will be very high. Styrenes have a lower polymerization rate but also a low equilibrium constant and will still polymerize to a large extent before the equilibrium deactivator concentration is reached, only at high activator concentrations the criteria can be met. Methyl methacrylate (MMA) appears to be a good choice because in a wide range of concentrations a fast buildup of deactivator species is expected due to the relatively high equilibrium constant and the relatively low polymerization rate.

Experimental Section

Materials. Methyl methacrylate (Aldrich, 99%) and toluene (Biosolve Ltd, AR) were vacuum distilled from CaH_2 and stored at −18 °C. N,N,N',N'',N''-Pentamethyldiethylenetriamine (99%), ethyl 2-bromoisobutyrate (EBiB, 98%), and $Cu^{II}Br_2$(99%) were obtained from Aldrich and used without further purification. $Cu^{I}Br$ (98%, Aldrich) was stirred with glacial acetic acid for 24 h, washed with glacial acetic acid, ethanol, and diethyl ether, and dried at 75 °C for 3 days. The purified $Cu^{I}Br$ was stored in an argon atmosphere.

Simulations. A program was written in Microsoft Excel to be used for the calculations of the concentration of all active and inactive species using eqs 8, 9, 14, 15, and 16. Simulations using the kinetic description mentioned in this paper were performed to determine the concentration of all active species in case eq 17 applied. To validate the numerical simulation of eq 17, the results were compared to results using eqs 14−16 in the case where $[Cu^{I}]_0$ approaches $[RX]_0$, and no differences were noticed.

Solution Polymerization. A dry three-necked flask was charged with PMDETA, toluene, MMA, $Cu^{II}Br_2$, and $Cu^{I}Br$ and sealed with a rubber septum. Oxygen was removed by three freeze−pump−thaw cycles, and the solution was heated to the polymerization temperature of 90 °C in an argon atmosphere. The polymerization was started by slowly adding EBiB. During the reaction, samples were drawn using degassed syringes and added to THF. A fraction of the diluted samples was used to determine the conversion by GC analysis using toluene as an internal standard. The remaining part of the sample was put over a small silica column to remove copper and dried for molecular weight determination.

ESR Measurements. ESR spectra were recorded on a Bruker ER300 ESP spectrometer, operating with an X-band standard cavity and interfaced to a Bruker Aspect 300 data system. The temperature was kept constant at 130 K using a Bruker ER4111 variable temperature unit. During the polymerization experiments, samples of ca. 1 mL were drawn, filtered through a 0.1 μm Whatman Puradisc syringe filter, and injected into a degassed NMR tube. The sample was immediately frozen in liquid nitrogen. The concentration of Cu^{II} species was estimated using a calibration curve based on copper(II) trifluoroacetylacetonate.[16,17] The samples for calibration were measured between the other samples under the same conditions and in the same media as the polymerization mixtures. A relative error of ca. 10% is expected.

Characterization. GC measurements were carried out on a Hewlett-Packard 5890 SII. An HP 3393a integrator was used to analyze the spectra. For GC characterization, dilute samples in THF were made in 1.5 mL crimp neck vials and measured using an autosampler.

GPC was carried out using a WATERS model 510 pump, model 486 UV detector (at 254 nm), and model 410 refractive index detector (at 313 K). The columns used were, a PLgel guard (5 μm particles) 50 × 7.5 mm guard column, followed by two PLgel mixed-C (5 μm particles) 300 × 7.5 mm columns (313 K) in series. THF was used as an eluent at a flow rate of 1 mL/min. Low polydispersity index polystyrene standards (Polymer Labs) with molar masses ranging from 580 to 7.1 × 10^6 g·mol^{-1} were used for calibration of the columns. Molecular weights were recalculated using the Mark−Houwink parameters of styrene ($K = 1.14 \times 10^{-4}$ dL/g, $a = 0.716$) and PMMA ($K = 0.944 \times 10^{-4}$ dL/g, $a = 0.719$).[18] The samples (10 mg/mL THF) were filtered through a 0.2 μm syringe filter prior to injection. Data acquisition and processing were performed using Waters Millenium32 (v3.00) software.

Table 1. Kinetic Parameters of Styrene and MMA for Simulations[a]

parameter	styrene	MMA
k_p (L·mol^{-1}·s^{-1})[19]	1580	1620
k_t (L·mol^{-1}·s^{-1})[20,21]	1×10^8	1×10^8
K_{eq} (−)[5,a]	4×10^{-8}	1.6×10^{-7}
$[RX]_0$ (mol·L^{-1})	3×10^{-2}	3×10^{-2}
$[Cu^{I}]_0$ (mol·L^{-1})	3×10^{-2}	3×10^{-2}
$[Cu^{II}]_c$ (mol·L^{-1})[a]	1.0×10^{-3}	0.8×10^{-3}
$[M]_0$ (mol·L^{-1})	3	3
temp (°C)	110	90

[a] Derived from measurements.

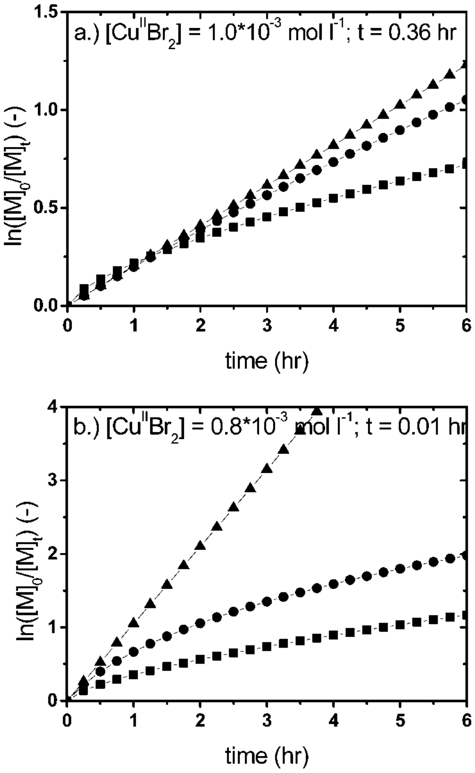

Figure 1. Simulations of ATRP using eq 8 (▲), eq 9 (■), and eq 16 (●) using parameters from Table 1: (a) styrene; (b) MMA.

Results and Discussion

Simulations. Simulations were performed using eqs 8 and 9 and the one postulated in this paper, eq 16. Table 1 shows the kinetic parameters used, taken from the literature[5,19−21] and determined in our research. As can be seen from Figure 1a, using the parameters of styrene, the new equation resembles the Matyjaszewski equation to a large extent, as the termination rate is very low and as a result the concentration of active chain remains constant. Only at higher conversions a deviation is observed. The Fischer equation shows a larger deviation. The initial polymerization rate is much higher as in the simulations $[Cu^{II}]_0$ was set to 0 mol·L^{-1}, but after a short period the Cu^{II} concentration exceeds

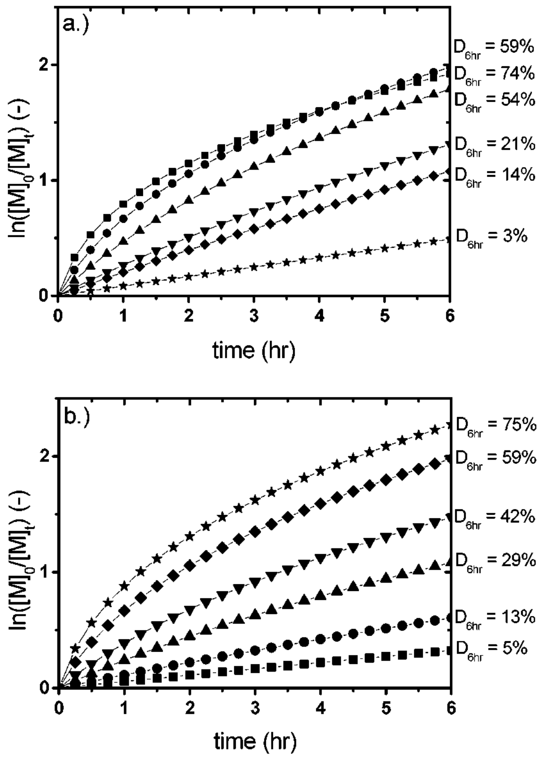

Figure 2. (a) Simulations with increasing deactivator concentrations. $[Cu^{II}]_c = 4 \times 10^{-4}$ (■), 8×10^{-4}(●), 1.5×10^{-3}(▲), 3×10^{-3}(▼), 5×10^{-3}(♦), and 1×10^{-2} (★) mol·L^{-1}. (b) Simulations with increasing activator and initiator concentrations. $[RX]_0 = [Cu^I]_0 = 7 \times 10^{-3}$(■), 1×10^{-2}(●), 1.5×10^{-2}(▲), 2×10^{-2}(▼), 3×10^{-2}(♦), 5×10^{-2} (★) mol·L^{-1}, with remaining parameters according to Table 1.

$[Cu^{II}]_c$ used in both other equations and, consequently, the polymerization rate becomes lower.

Using the parameters of MMA, the outcome of the new equation does not resemble the other equations. The main difference originates from the high value of the equilibrium constant resulting in a high termination rate. In the equation of Matyjaszewski, termination does not play a role, and therefore, the rate of polymerization is high throughout the polymerization. Initially the rate of polymerization is the highest using the Fischer equation, but that is not noticeable since the Cu^{II} concentration exceeds the $[Cu^{II}]_c$ of the other equations within 1 min. After this time, it results in a high Cu^{II} concentration, thus decreasing the polymerization rate. In our scheme, the Cu^{II} concentration is constant and irreversible bimolecular termination will be the main result. To have an indication what the predicted effects of changing the reaction conditions would have on the number of irreversible terminated "dead" polymer chains, this value was calculated after 6 h. The Matyjaszewski equation does not account for termination so $[D]_{6h} = 0$, in the Fischer equation $[D]_{6h} = [Cu^{II}]_{6h} = 22\%$ of $[RX]_0$ and in our equation $[D]_{6h} = 60\%$. It should be emphasized that both the Matyjaszewski and the Fischer equation do not apply under these conditions as they both originate from the assumption that the "dormant" chain and Cu^I concentrations remain constant throughout the polymerization.

Figure 2a shows the influence of the ceiling Cu^{II} concentration on the polymerization kinetics in eq 16; this is evaluated by solely altering this parameter. As expected, the initial polymerization rate decreases with increasing deactivator concentration. During the polymerization the concentrations of both RX and Cu^I are continiously decreasing, resulting in a decrease of the polymerization rate. When the radical concentration, and thereby the polymerization rate, is determined after for example 6 h of polymerization, a different trend is seen compared to the initial rate. The polymerization rate increases, as expected, when $[Cu^{II}]_c$ decreases, but the maximal polymerization rate after 6 h is reached at $[Cu^{II}]_c = 2.2 \times 10^{-3}$ mol L^{-1}, below this concentration the rate decreases again (calculated using eq 15). The concentration of "dead" polymer chains after 6 h of polymerization increases as expected with decreasing deactivator concentration. In Figure 2, parts a and b, the theoretical percentage of "dead" polymer chains is shown after 6 h of polymerization.

Figure 2b shows the effects in case the initiator and activator concentration ($[RX]_0 = [Cu^I]_0$) are varied, the remaining parameters are according to Table 1. The rate of polymerization is increasing when the initiator concentration is increased, but as the rate of termination is also higher, the concentration of the activator and the reversibly terminated polymer chains are constantly decreasing and the difference in rate decreases at increasing times. The number of dead polymer chains is increasing with increasing initiator concentration.

Electron Spin Resonance. To determine whether the Cu^{II} concentration can be treated as constant, electron spin resonance (ESR) experiments were performed. Because of the heterogeneous character of the polymerization mixture, online measurements during polymerization could not be performed as both dissolved and precipitated Cu^{II} would be measured. Initially samples were taken from a polymer solution where the particles were allowed to settle. The samples were immediately frozen and measured after the experiment. The ESR showed a complex signal indicating the presence of solid particles, which was substantiated by a strongly fluctuating Cu^{II} concentration. Therefore, it was decided to filter the solution in an argon atmosphere immediately after the sample was taken, after which the samples were frozen in liquid nitrogen and measured with ESR. These spectra were less complex, which suggest the efficient removal of solid Cu^{II} particles. The concentration of Cu^{II} species in solution was determined by double integration of the spectra and comparing these to a calibration curve of copper(II) trifluoroacetylacetonate.[16,17] The samples for the calibration curve were measured throughout the entire ESR experiment, so changes in the signal intensity could be determined. The results of the measurements are shown in Figure 3, where not all samples were measured, but as the monomer-to-toluene ratio is kept constant, no large deviations are expected. There are several aspects that catch our attention, first of all the initial Cu^{II} concentration before the addition of initiator is lower than the equilibrium value. This indicates that the initially added solid $Cu^{II}Br_2$ does not dissolve well[22] and as a result will not contribute to the control of the polymerization. Second, shortly after initiation, the different polymer solutions have a large scatter in the concentration of Cu^{II} species. This could be caused by the presence of very small Cu^{II} particles that are not removed by filtration. The concentration of Cu^{II} species seems to level off to $\approx 8 \times 10^{-4}$ mol·L^{-1} (overall standard deviation 1×10^{-4} mol·L^{-1}). The Cu^{II} concentration measured with ESR is comparable to the concentrations

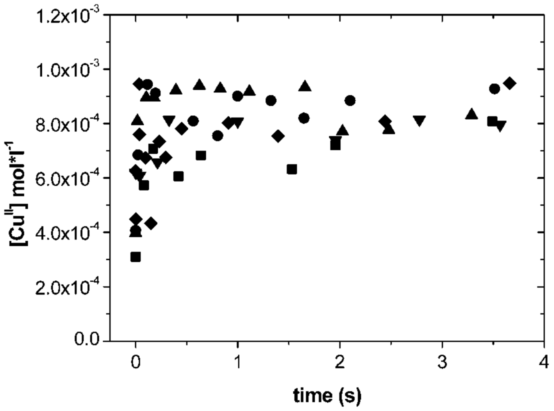

Figure 3. ESR experiments with $[RX]_0 = 3.1 \times 10^{-2}$ mol·L^{-1}, $[MMA]_0 = 3.1$ mol·L^{-1}, and $[Cu^I] + [Cu^{II}] = [PMDETA] = 1.6 \times 10^{-2}$ mol·L^{-1}; solvent toluene; $[Cu^{II}Br_2]_0/[Cu^IBr]_0 = 0$ (■), 0.25 (●), 4 (▲), and 19 (▼, ♦).

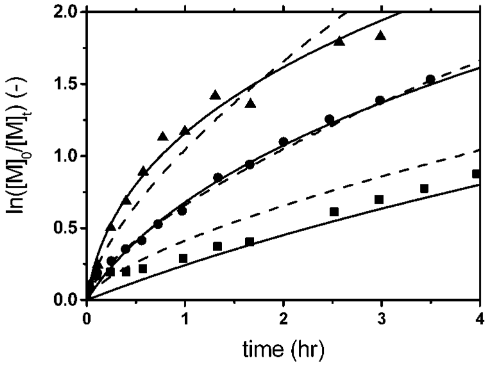

Figure 4. Polymerization using equal amounts of initiator and deactivator. $[RX]_0 = [Cu^I]_0 = 1.5 \times 10^{-2}$ mol·L^{-1} (■), 3.0×10^{-2} mol·L^{-1} (●), and 6.0×10^{-2} mol·L^{-1} (▲). The solid lines are simulations using eq 16 with parameters as in Table 1; the dotted lines are simulations using eq 9 with $k_a/(k_dk_t) = 1 \times 10^{-14}$, obtained by fitting the data of $[RX]_0 = [Cu^I]_0 = 3.0 \times 10^{-2}$ mol·L^{-1}.

measured in the ATRP of MMA[16] in Ph_2O with dinonylbipyridine ligand, but is substantially lower than the concentration measured in styrene polymerization using almost the same conditions.[17] In conclusion, the assumption that the Cu^{II} concentration is constant during the polymerization seems to be substantiated.

Experiments with Equal Initiator and Activator Concentrations. To validate the new kinetic equation, experiments were performed using equal concentrations of initiator and activator. Figure 4 shows both the results from these experiments and simulations using the parameters for MMA from Table 1. The Cu^{II} concentration was determined on systems discussed in the next paragraph, but as the solvent composition of the polymerizations was equal in all experiments, this concentration was used for the simulations. As can be seen, the measured and theoretical values correspond well. There is a monotonic decrease in reaction rate originating from the constant decrease of the concentration of both the activator and the "dormant" polymer. Although an adequate amount of Cu^{II} species was added prior to polymerization, the dissolved deactivator will be insufficient to control the polymerization. It can be clearly seen that eq 8 does not apply in this system as this equation would give a straight line in a $\ln([M]_0/[M])$ vs time plot. Equation 9 on the other hand also gives curved lines; therefore, the data of one of the experiments ($[RX]_0 = [Cu^I]_0 = 3.0 \times 10^{-2}$ M) were fitted using eq 9. The result is shown as a dotted line in Figure 4, and is fairly consistent with the measured data. The estimated equilibrium constant would be 1×10^{-6} (all remaining constants as in Table 1). When this equilibrium constant is used in the other experiments of Figure 4, a large deviation is seen indicating that also this equation does not apply. Furthermore, when this equilibrium constant would be used the fraction of "dead" polymer chains would be very high (over 50% in 2 h), and eq 9 is not applicable anymore.

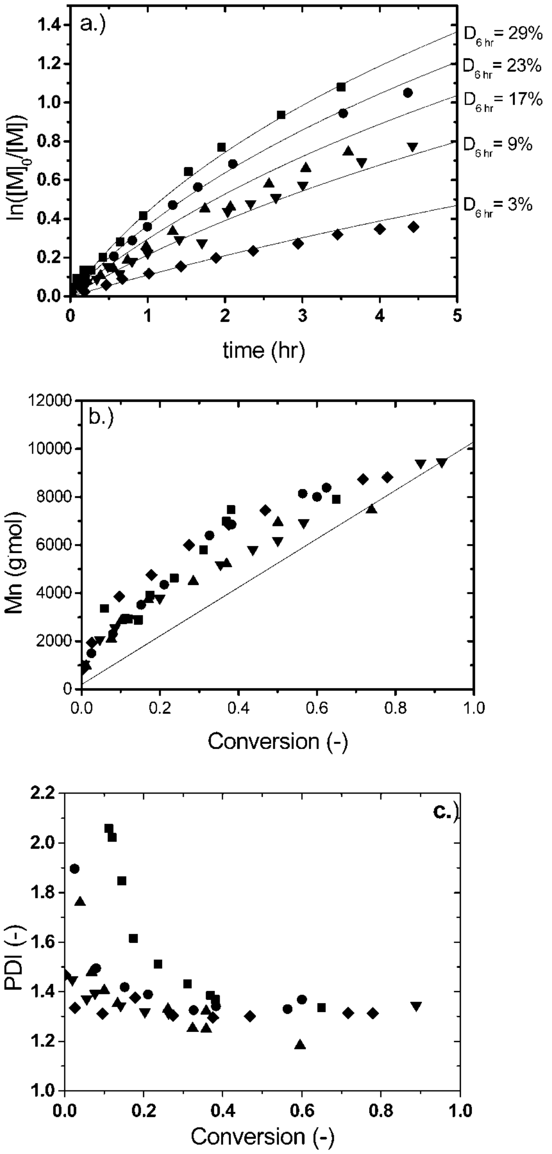

Figure 5. Polymerization experiments with $[RX]_0 = 3.1 \times 10^{-2}$ mol·L^{-1}, $[MMA]_0 = 3.1$ mol·L^{-1}, and $[Cu^IBr]_0 + [Cu^{II}Br_2]_0 = [PMDETA] = 1.6 \times 10^{-2}$ mol·L^{-1}, solvent toluene, and $[Cu^{II}Br_2]_0/[Cu^IBr]_0 = 0$ (■), 0.25 (●), 0.67 (▲), 1.5 (▼), and 4(♦). Key: (a) polymerization kinetics; (b) number-average molecular weight vs conversion; (c) polydispersity index vs conversion.

Experiments with a Decreasing Initial Cu^I Concentration. Figure 5a shows the results of some experiments performed with an increasing deactivator concentration, while the total molar concentration of Cu species is kept constant. The measured data correspond well with theoretical values up to high conversion, indicating a good description of these polymerizations using the newly postulated model. Small deviations are observed at low initial Cu^I concentrations. This could originate from several reasons including a larger effect of conversion-dependent parameters or the presence of a secondary initiation source like oxidized Cu species;[23] this would be more prone to occur when the initial Cu^I concentration is low. The molecular weight and the polydispersity index were determined using GPC. The molecular weights of the polymers, Figure 5b, have a higher offset than expected but seem to approach the theoretical values. The initial deviation could originate from the termination reaction especially in the initial stage of the polymerization, when the termination rate is highest. Some deviations could also originate from the exclusion of small oligomers by the molecular weight determination by GPC. In Figure 5c, the polydispersity of the polymers is shown. The polydispersity of the polymers is highest in the polymerizations with the highest Cu^I concentration and at the beginning of the reaction. The polymerizations with the higher Cu^I concentration have a high radical flux especially in the beginning of the reaction, and the termination rate will be the highest (Figure 5a); consequently, the polydispersity index will be high. After the initial period, the reaction rate decreases and so does the termination rate, and at higher conversions the polydispersity indices converge to a value of 1.3 for all samples.

Conclusions

The newly proposed kinetic scheme for a heterogeneous ATRP system with a constant concentration of active Cu^{II} species provides a new insight in the ATRP kinetics when irreversible termination cannot be neglected. It was shown that when the equilibrium constant is appropriately low and/or the polymerization rate is high, polymers can be prepared with only a small fraction of irreversibly terminated chains. Simulations using methyl methacrylate with a relatively high equilibrium constant and a low polymerization rate show, depending on the concentration of the activator and initiator, an appreciable fraction of “dead” polymer chains resulting in a constant decrease of the polymerization rate. Experimental data of conversion vs time show good agreement with simulations.

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