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LETTERS

Understanding Copper-Based Atom-Transfer Radical Polymerization in Aqueous Media

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This study investigates the mechanism of copper(I)-mediated “living” atom-transfer radical polymerization (ATRP) in aqueous media. It is shown that the ATRP apparent rate constant for polymerization of methoxy-capped oligo(ethylene glycol) methacrylate (OEGMA) in water (k_p^{app}) at room temperature correlates with the redox potential ($E_{1/2}$) of the copper complexes. The results are discussed along with previously published results on the kinetics for bulk polymerization of methyl acrylate at 60 °C with the redox potentials measured in MeCN. The faster ATRP kinetics in water can mainly be attributed to a higher equilibrium concentration of propagating radicals [$R^\bullet$] and to solvent effects on the rate of propagation k_p. It is shown that [$R^\bullet$] can be calculated from the redox properties of the alkyl halide and the copper complex. The values of [$R^\bullet$] in MeCN/bulk and in H_2O were determined to be 8.2×10^{-8} and 6.3×10^{-5} M, respectively. The respective k_p values are in good agreement with the literature values (3.6×10^3 M^{-1} s^{-1} for OEGMA in water and 2.5×10^3 M^{-1} s^{-1} for methyl acrylate in bulk).

Introduction

Atom-transfer radical polymerization (ATRP) is a successful method for preparation of macromolecules with narrow polydispersities and predefined molecular weights.[1] The process is initiated by an alkyl halide (R−X) and mediated by a transition-metal complex in a low oxidation state. Copper(I) halides (Cu(I)X) are most frequently used in conjunction with nitrogen-based ligands (L). The metal complex controls the polymerization reaction by mediating a dynamic equilibrium between the propagating radicals and the dormant halide-capped polymer (reaction 1). The rate of propagation is governed by the equilibrium concentration of the propagating radicals ($R_p = k_p[R^\bullet][M]$), which in turn is governed by the ATRP equilibrium. As detailed below, the overall equilibrium constant ($K_{eq} = K_1$) can be expressed as the product of the equilibrium constants of a set of elementary processes ($K_1 = K_2K_3K_4$)

$$R{-}X + Cu(I)X/L \leftrightarrows R^\bullet + X{-}Cu(II)X/L \tag{1}$$

$$Cu(I)X/L \leftrightarrows Cu(II)X/L + e^- \tag{2}$$

$$R{-}X + e^- \leftrightarrows R^\bullet + X^- \tag{3}$$

$$X^- + Cu(II)X/L \leftrightarrows X{-}Cu(II)X/L \tag{4}$$

Matyjaszewski et al. have shown that the redox properties of the metal complex is one of the parameters controlling the ATRP kinetics.[2] In general, more reducing Cu(I) complexes induce a faster polymerization,[3] i.e., give a higher equilibrium concentration of the propagating radicals. The ligands tune the activity of the transition-metal ion, judging from ATRP conducted at high temperature in bulk or in nonaqueous media. Even so, ATRP is effective for the polymerization of hydrophilic

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monomers in aqueous solution.[4] However, polymerization is much faster than in nonpolar media, and a poor "living" character is very often observed. This has been ascribed to polarity effects on the stability of the polymerization intermediates as well as to a competitive complexation of ligand and water molecules to the copper center.[5]

This letter investigates how the redox properties of the copper complex correlate to the ATRP kinetics in aqueous media. The redox potentials ($E_{1/2}$) of Cu(I) complexes with different nitrogen-based ligands were measured by cyclic voltammetry (CV). To our knowledge, this is the first time that the correlation between the kinetics and thermodynamic parameters has been investigated for aqueous ATRP.

Experimental Section

Methoxy-capped oligo(ethylene glycol) methacrylate (OEGMA) was chosen as the model monomer since ATRP is reported to proceed with a "living" character under mild conditions.[6] Our formulation was based on ref 7 (Supporting Information for a detailed protocol). The targeted degree of polymerization was 100 for all experiments controlled by the OEGMA/initiator molar ratio. A water soluble bromo-capped oligo(ethylene glycol)-based alkyl initiator,[7] and Cu(I)Br, with Bpy (1), N-pr-PMA (2), Me_4-Cyclam (3), PMDETA (4), HMTETA (5), and Me_6-TREN (6) as complexing ligands (Figure 1S, Supporting Information) were used. In addition, ammonium oxalate was also included in the study. All the polymerizations were conducted at room temperature (OEGMA/water ratio, 2:1 by weight; [OEGMA] = 4.1 M).

The monomer conversion was monitored by ^{1}H NMR. High conversions were obtained within 5−20 min. The initial slopes of the ln(conversion) vs time plots were used to determine the apparent ATRP rate constant, $k_p^{app} = k_p[R^\bullet]$. k_p^{app} was used to evaluate the activity of the copper complexes for aqueous ATRP instead of the apparent equilibrium constant predefined from kinetic studies by Matyjaszewski et al. ($K_{eq}^{app} = K_{eq}/[Br-Cu(II)X/L]$).[3]

CV measurements were conducted in a solvent mixture (OEGMA/water, 2:1 by weight) identical to the one used in the polymerization. Since the present study mainly concerns the relationship between ATRP kinetics and the redox properties of the copper complexes, it is important that the conditions used for the electrochemical studies are the same as in the polymerization. All potentials were measured against a saturated calomel reference electrode (SCE). The voltammograms were reproducible on several scans for all the complexes (Supporting Information). However, an excess of ligand was required to detect the oxidation wave for Cu(I)X/Me_6−TREN.

Results and Discussion

The potentials, $E_{1/2}$, and the apparent ATRP rate constants, k_p^{app}, are given in Table 1.

Most of the redox processes were quasireversible as seen by the peak-to-peak separation ΔE values ($E_{red} - E_{ox}$) being larger than the ideal 60 mV for a one-electron-transfer process.[8] As reported earlier in ref 3, the ligand affects the redox properties of the copper complexes. A general trend in increasing reducing properties N-pr-PMA < Me_6-TREN < Bpy < Me_4-Cyclam < HMTETA < PMDETA is observed both for bromo- and chlorocomplexes. It should be noted that this trend does not correlate with the trend obtained in MeCN. The rationale for this discrepancy is probably that protonation of the amino groups alters the trend.

TABLE 1: Redox Potentials[a] and k_p^{app} Values for Copper Complexes Cu(I)X/L in OEGMA/water (2:1 by weight) at Room Temperature

salt	ligand	[CuX]:[L]	$E_{1/2}$/V	ΔE/mV	$k_p^{app} 10^3/s^{-1}$
CuBr	2	1:2	0.060	108	25.5
CuCl	2	1:2	0.068	80	4.3
CuBr	6	1:13	0.012	256	100
CuCl	6	1:13	0.070	328	3.6
CuBr	oxalate	1:2	−0.015	126	57
CuBr	1	1:2	−0.064	88	219
CuCl	1	1:2	−0.044	64	74
CuBr	3	1:1	−0.143	94	639
CuBr	5	1:1	−0.186	104	367
CuCl	5	1:1	−0.174	84	455
CuBr	4	1:1	−0.268	96	463
CuCl	4	1:1	−0.261	114	378

[a] $E_{1/2} = {}^1/_2(E_{ox} + E_{red})$ (V vs SCE).

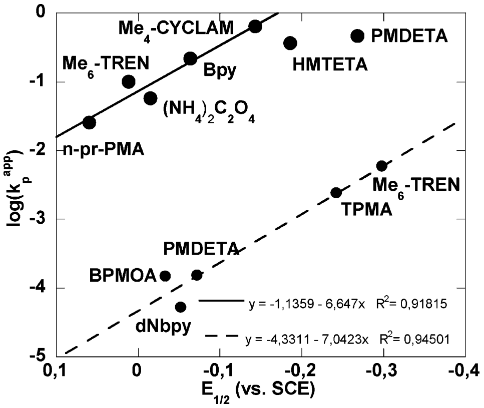

Figure 1. log(k_p^{app}) vs $E_{1/2}$ for CuBr complexes in OEGMA/H_2O (solid line) (system 1) and in bulk/MeCN (dashed line)[3] (system 2).

To examine the relationship between k_p^{app} and $E_{1/2}$ of the complexes, log(k_p^{app}) ($k_p^{app} = K_{eq}^{app} k_p [Cu(I)]_0 [I]_0$)[3] was plotted against $E_{1/2}$ in Figure 1 (system 1). A linear dependence is observed for log(k_p^{app}) lower than −0.4. This is consistent with the redox mechanism underlined in reaction 1 and with the previous electrochemical studies of copper complexes with similar nitrogen-based ligands in MeCN.[3] The maximum limit depends on the experimental time resolution, i.e., it is not possible to study the kinetics for faster reactions using the present technique. It should be noted that the potentials of the copper complexes in pure water do not correlate to the ATRP kinetics in OEGMA/H_2O. This suggests a solvent effect on the redox properties of the complex. Interestingly, the complex formed with ammonium oxalate also follows the trend.

The log(k_p^{app}) plot of the bulk polymerization of methyl acrylate against $E_{1/2}$ in MeCN[3] is also included in Figure 1 (system 2). As can be seen, the trends parallel each other. However, at a given potential, k_p^{app} is approximately 3 orders of magnitude higher in system 1 than in the system 2. Part of this difference can be accounted for by the difference in k_p (different monomers[9] and solvent effects[10]), and the remaining difference in kinetics at a fixed redox potential value can be explained by a difference in propagating radical concentration [R$^\bullet$] ($k_p^{app} = k_p[R^\bullet]$). Usually the Cu(II) concentration is much higher than the propagating radical concentration, [R$^\bullet$], due to the persistent radical effect (i.e., termination reactions).[11] However, the simplest assumption (based solely on the contributing reactions described above) would be that [R$^\bullet$] is equal to the total [Cu(II)] concentration ([R$^\bullet$] = [X−Cu(II)X/L] + [Cu(II)X/L]) and can be derived from the equilibrium constants.

From reactions 1−4, we obtain the following expression for the radical concentration ($x = [\mathrm{R}^\bullet]$)

$$x^2 - a\sqrt{x} - b = 0 \tag{5}$$

where $a = (K_2K_3[\mathrm{R{-}X}][\mathrm{Cu(I)X/L}])^{1/2}$ and $b = K_2K_3K_4[\mathrm{R{-}X}][\mathrm{Cu(I)X/L}]$, respectively (Supporting Information). The analytical solution to eq 5 is too complex to be used in this context. Roughly, we can identify two extremes for which the solution becomes reasonably simple. In case 1, we assume equilibrium 4 to be insignificant ($[\mathrm{X{-}Cu(II)X/L}] \ll [\mathrm{Cu(II)X/L}]$). The radical concentration is then given by $[\mathrm{R}^\bullet] = (K_2K_3[\mathrm{R{-}X}][\mathrm{Cu(I)X/L}])^{1/3}$. In case 2, we assume that K_4 is very high. The radical concentration is then given by $[\mathrm{R}^\bullet] = (K_2K_3K_4[\mathrm{R{-}X}][\mathrm{Cu(I)X/L}])^{1/2}$. We can also identify a critical value for $K_{4,\,\mathrm{crit}}$, given by eq 6 (given by $[\mathrm{R}^\bullet]_{\mathrm{case1}} = [\mathrm{R}^\bullet]_{\mathrm{case2}}$)

$$K_{4,\mathrm{crit}} = \left(\frac{1}{K_2K_3[\mathrm{R{-}X}][\mathrm{Cu(I)X/L}]}\right)^{1/3} \tag{6}$$

If $K_4 \ll K_{4,\mathrm{crit}}$, case 1 applies, and if $K_4 \gg K_{4,\mathrm{crit}}$, case 2 applies. To analyze the two systems given in Figure 1, we calculate the radical concentration at a fixed $E_2(\mathrm{Cu(I)/Cu(II)}) = -0.05$ V vs SCE. The product K_2K_3 is calculated from the potential difference $E_3 - E_2$. $E_3°(\mathrm{R{-}X/R^\bullet,X^-})$ can be approximated using values for reduction of alkyl halide in water[12] ($E_3° \approx -0.63$ V) (Supporting Information) and in DMF[13] ($E_3° \approx -1.15$ V; assuming that the equilibrium constant K_3 in MeCN is similar to DMF[14]). The reported values for K_4 in water (12 $\mathrm{M^{-1}}$) and in DMF (1.4×10^5 $\mathrm{M^{-1}}$) are much lower than the calculated $K_{4,\mathrm{crit}}$ values (2×10^4 and 1.7×10^7 $\mathrm{M^{-1}}$, respectively).[14] Hence, case 1 should apply for both systems. The resulting radical concentrations are 6.3×10^{-5} M in water and 8.2×10^{-8} M in MeCN. The exact (numerical) solution to eq 5 gives $[\mathrm{R}^\bullet] = 6.3 \times 10^{-5}$ M in H_2O and 8.2×10^{-8} M in MeCN. From this, we can estimate k_p to be 3.6×10^3 $\mathrm{M^{-1}\,s^{-1}}$ for OEGMA in water and 2.5×10^3 $\mathrm{M^{-1}\,s^{-1}}$ for methyl acrylate in the organic solvent. This is in good agreement with literature data (1.5×10^3 $\mathrm{M^{-1}\,s^{-1}}$ for methacrylic acid in water (25 °C) and 2.1×10^3 $\mathrm{M^{-1}\,s^{-1}}$ for acrylate in bulk polymerization (60 °C)).[9,10] It should be noted that k_p for 2-hydroxyethyl methacrylate (HEMA) in water has been reported to be 415 $\mathrm{M^{-1}\,s^{-1}}$ at room temperature[15] and k_p for bulk polymerization of butyl acrylate has been reported to be 2.7×10^4 $\mathrm{M^{-1}\,s^{-1}}$ at 50 °C.[16]

Employing $[\mathrm{R}^\bullet] = (K_2K_3[\mathrm{R{-}X}][\mathrm{Cu(I)X/L}])^{1/3}$, it can be shown that the theoretical slope, s, for the plot given in Figure 1 is

$$s = -\frac{1}{3}\frac{F}{RT}\frac{1}{2.30} = -5.64 \tag{7}$$

The experimental slope is in good agreement with this value ($s(H_2O) = -6.65 \pm 1.15$), confirming the validity of the proposed approach to determine $[\mathrm{R}^\bullet]$. Studies of the solvent effects on K_2 and the ATRP kinetics are currently underway.

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Supporting Information Available: Detailed experimental procedures, determination of $[\mathrm{R}^\bullet]$, estimation of alkyl halide reduction potentials, kinetic plots, and voltammograms. This material is available free of charge via Internet at http://pubs.acs.org.

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