Effect of [bpy]/[Cu(I)] Ratio, Solvent, Counterion, and Alkyl Bromides on the Activation Rate Constants in Atom Transfer Radical Polymerization

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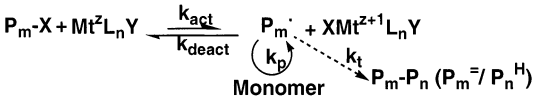
ABSTRACT: The effects of [bpy]/[Cu(I)] ratio, polarity of the medium, counterion, and nature of alkyl bromides on the activation rate constants (k_{act}) in atom transfer radical polymerization were investigated. The highest values of k_{act} for Cu(I)Br were obtained at [bpy]/[Cu(I)Br] ∼ 2/1 and 1/1 in more polar and less polar solvents, respectively. This was ascribed to different structures of the complex, $Cu(bpy)_2^+Br^-$ and $Cu(bpy)_2^+CuBr_2^-$, correspondingly. The highest values of k_{act} for $Cu(I)PF_6$ were observed at [bpy]/[Cu(I)] ∼ 2/1 in both more polar and less polar solvents, which was explained by the formation of the same active $Cu(bpy)_2^+PF_6^-$ complex. Compared to Cu(I)Br, the use of $Cu(I)PF_6$ results in an increased rate of activation by a factor of 1.8. The k_{act} was larger in more polar solvents compared to less polar solvents. An increase in k_{act} was observed in the presence of water, and a decrease in k_{act} was noticed in the presence of solvents containing oxyethylene groups. The relative rates of k_{act} of alkyl bromides in all solvents follow the order: ethyl 2-bromoisobutyrate (EBriB) (∼44) ≫ methyl 2-bromopropionate (MBrP) (∼3) ≅ ethyl 2-bromopropionate (EBrP) (∼3) > *tert*-butyl 2-bromopropionate (*t*-BBrP) (∼1).

Introduction

One of the most successful polymerization techniques in the field of controlled/living radical polymerization[1−3] is atom transfer radical polymerization (ATRP).[4] ATRP allows the preparation of a wide range of polymeric materials with controlled molecular weights and well-defined architectures.[5−7] The success of ATRP relies on the reversible activation of a dormant alkyl halide species through halogen abstraction by a transition metal complex, which is mostly copper based (Scheme 1).[8−11] In the activation step, with the rate constant k_{act}, a metal complex Mt^zL_nY cleaves the carbon−halogen bond of P_mX homolytically and reversibly, generating a carbon-centered radical species $P_m^\bullet$. The latter subsequently adds to the monomer with a rate constant k_p, before it is deactivated, with a rate constant k_{deact}, by the metal complex $Mt^{z+1}L_nY$ to form the dormant species P_mX. Through these reversible and repetitive cycles, well-defined polymers with progressively increasing molecular weights and low polydispersities are formed. Since radical concentration is very low, termination is very slow in the initial stage and decreases with time due to the persistent radical effect.[12]

The kinetic expression and evolution of polydispersities in ATRP are shown in eqs 1 and 2, respectively.[6,13,14] The equilibrium constants ($K_{eq} = k_{act}/k_{deact}$) and individual rate constants of activation and deactivation are crucially important for a controlled ATRP. Several studies on model and macromolecular species have been carried out to determine these rate constants.[14−18] They depend on the structure of the monomers, alkyl halides, and transition metal complexes[15,19] In addition, temperature and reaction medium have pronounced effects on ATRP.[20−23]

Scheme 1. Elementary Reactions in ATRP



$$\ln\left(\frac{[M]_0}{[M]_t}\right) = \frac{k_p k_{act}[P_mX][Cu(I)]}{k_{deact}[Cu(II)]}\,t \qquad (1)$$

$$\frac{M_w}{M_n} = 1 + \left(\frac{k_p[P_mX]}{k_{deact}[XCu(II)]}\right)\left(\frac{2}{p} - 1\right) = 1 + \frac{2}{k_{act}[Cu(I)]t} \qquad (2)$$

In this paper we selected the Cu(I)/bpy catalyst system to systematically study the effect of [bpy]/[Cu(I)] ratio, solvent polarity, counterion, and structure of alkyl bromides on the activation rate constants.

Description of Method for Measuring the Activation Rate Constant

The direct measurement of activation rate constant, k_{act}, was achieved by isolating the activation process (1) from the deactivation process (2) (Scheme 2).[16] The radicals generated by halogen transfer to the copper complex (1) were scavenged with TEMPO. In the presence of a large excess of TEMPO (10 times with respect to the alkyl bromide), nearly all of the alkyl radicals were trapped with TEMPO to form the corresponding alkoxyamine (alkyl-TEMPO adduct) (3).[24] The deactivation step (2) can be neglected under the given conditions due to $k_{deact} < k_{comb}$[16] and $[Cu(II)Br_2] < [TEMPO]$. The

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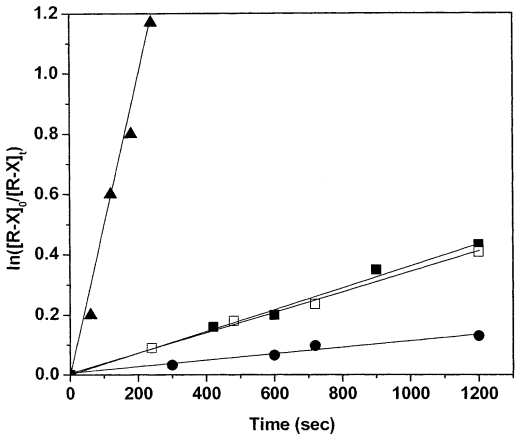
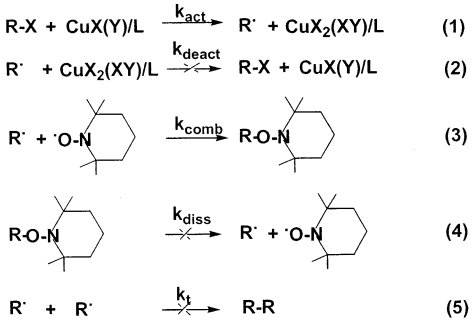


Figure 1. Pseudo-first-order kinetic plot of the activation process with the Cu(I)Br/(bpy)$_2$ catalyst at 35 °C in acetonitrile for (▲) EBriB, (■) MBrP, (□) EBrP, and (●) *t*-BBrP. [EBriB] = [MBrP] = [EBrP] = [*t*-BBrP] = 1 mmol; [Cu(I)Br] = [bpy]/2 = 20 mmol, [TEMPO] = 10 mmol, [biphenyl] = 5 mmol.

Scheme 2. Kinetic Isolation of the Activation Process



contribution of the thermal decomposition of the alkoxyamine (4) should be negligible at low reaction temperatures (T = 35 °C).[25] Reaction 5 can be also neglected due to the low radical concentration in the presence of an excess amount of the radical scavenger.

An excess of Cu(I) (about 20 times with respect to the alkyl bromide) was used to make the kinetic analysis straightforward, i.e., to provide pseudo-first-order kinetic conditions (Figure 1). From the slope of the pseudo-first-order kinetic plot with respect to the concentration of the alkyl halide, the apparent rate constant of activation, k_{app}, was determined, which is the product of the catalyst concentration and the activation rate constant, k_{act} (eq 3).[14] Similar approaches have been reported for the determination of the decomposition rate constants of the alkoxyamine[25,26] and the activation reaction for model compounds and polymeric chain ends in ATRP.[15−18]

$$-\frac{d[R-X]}{dt} = k_{app}[R-X] \approx k_{act}[Cu(I)][R-X] \quad (3)$$

Previously, we reported that the activation rate constant could be measured using HPLC to monitor the consumption of UV-active benzyl and 1-phenylethyl halides in a Cu(I)Br/dNbpy-catalyzed reaction.[16] However, compounds such as ethyl 2-bromoisobutyrate (EBriB), methyl 2-bromopropionate (MBrP), ethyl 2-bromopropionate (EBrP), and *tert*-butyl 2-bromopropionate (*t*-BBrP) (Figure 2) were difficult to analyze by UV detection due to their low extinction coefficients. Therefore, gas chromatography (GC) was found to be an attractive alternative method for these experiments

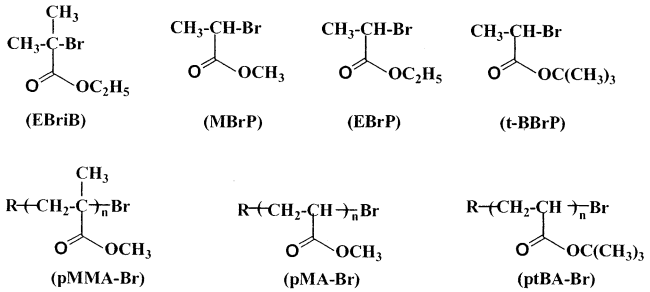


Figure 2. Model compounds for the activation study and their polymeric analogues.

owing to the high sensitivity and universal detection. Furthermore, several alkyl halides could be studied simultaneously in the same activation rate constant measurement due to sufficient separation of the substrates by GC. This approach allowed successful and expedient assaying of several model compounds representing dormant species in ATRP of various monomers.

Results

Three alkyl bromides were used as model compounds for polymeric chain ends in ATRP: ethyl 2-bromoisobutyrate (EBriB) as a model for poly(methyl methacrylate) (pMMA), methyl 2-bromopropionate (MBrP) as a model for poly(methyl acrylate) (pMA), ethyl 2-bromopropionate (EBrP) as a model for poly(ethyl acrylate) (pEA), and *tert*-butyl 2-bromopropionate (*t*-BBrP) as a model for poly(*tert*-butyl acrylate) (ptBA) (Figure 2). These alkyl bromides are among the most widely used initiators in ATRP.[27,28] Therefore, these model systems should provide relevant information about the atom transfer processes during both polymerization and initiation. The activation rate constants were measured at 35 °C using 2,2′-bipyridine (bpy) as the coordinating ligand. Solvents of different polarity, namely, chlorobenzene, acetonitrile, water, and tetra(ethylene glycol) dimethyl ether (TEGDME), were used. Dielectric constants (ϵ) of chlorobenzene, TEGDME, acetonitrile, and water are 5.62, 7.53, 35.94, and 79.39 D, respectively.[29,30] Mixtures of solvents were selected in order to make the bpy/Cu(I) complex and alkyl bromides reaction media homogeneous. The activation rate constants of EBriB, MBrP, and *t*-BBrP at different ratios of [bpy]/[Cu(I)Br] were determined in pure acetonitrile and a mixture of acetonitrile (41.5 wt %) with chlorobenzene (58.5 wt %) (Figures 3 and 4). In acetonitrile, k_{act} increases linearly as the ratio of [bpy]/[Cu(I)Br] increases up to 2/1 (Figure 3). At higher ratio of [bpy]/[Cu(I)Br] (>2/1), k_{act} remained constant or even decreased slightly. In a less polar medium, the activation rate constants increased with [bpy]/[Cu(I)Br] ratio up to 1/1 and then leveled off or slightly decreased (Figure 4).

The maximal values of k_{act} were observed at [bpy]/[Cu(I)Br] ratio ∼ 2/1 and 1/1 in acetonitrile and less polar solvent, respectively, irrespective of the nature of the alkyl bromides. The k_{act} was 2.5 times larger in acetonitrile than in less polar solvents for all alkyl bromides. The maximal values of k_{act} of EBriB, MBrP, EBrP, and t-BBrP in acetonitrile and less polar solvents are summarized in Table 1. The relative rate constants of activation in acetonitrile and less polar solvents follow the order EBriB (∼44) ≫ MBrP (∼3) ≅ EBrP (∼3) > *t*-BBrP (∼1) (Table 1). EBriB activates very fast with an activation rate constant approximately 44 times

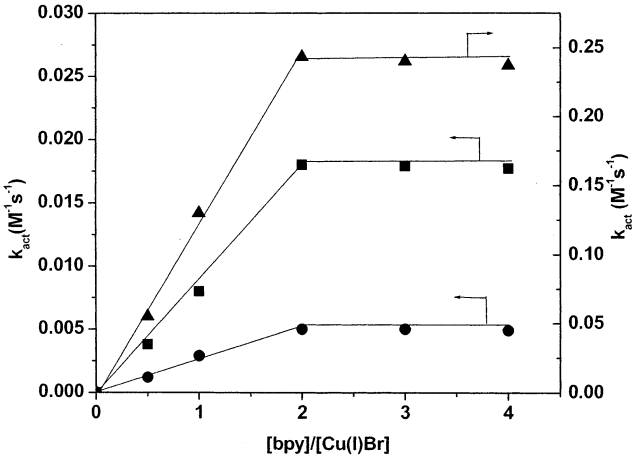


Figure 3. Plot of k_{act} as a function of increasing bpy concentration at constant Cu(I)Br concentration for (▲) EBriB, (■) MBrP, and (●) *t*-BBrP in acetonitrile at 35 °C. [EBriB] = [MBrP] = [*t*-BBrP] = 1 mmol; [Cu(I)Br] = 20 mmol, [TEMPO] = 10 mmol; [biphenyl] = 5 mmol.

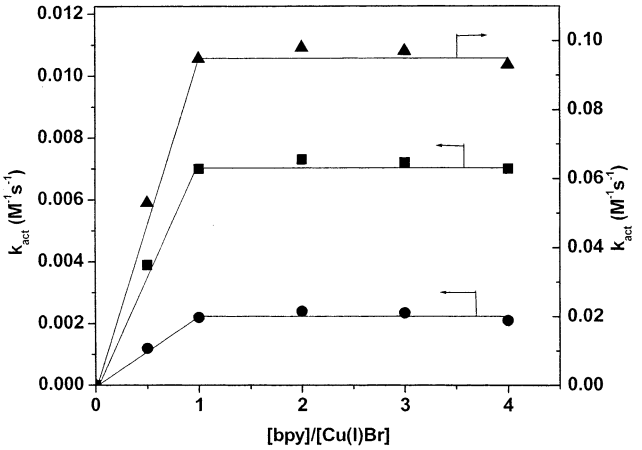


Figure 4. Plot of k_{act} as a function of increasing bpy concentration at constant Cu(I)Br concentration for (▲) EBriB, (■) MBrP, and (●) *t*-BBrP in less polar solvents, acetonitrile (41.5 wt %) with chlorobenzene (58.5 wt %) at 35 °C. [EBriB] = [MBrP] = [*t*-BBrP] = 1 mmol; [Cu(I)Br] = 20 mmol; [TEMPO] = 10 mmol; [biphenyl] = 5 mmol.

Table 1. Activation Rate Constants and Their Relative Ratios for Alkyl Halides in Polar and Less Polar Solvents at [Bpy]/[Cu(I)Br] ~ 2/1[a]

	acetonitrile		acetonitrile/chlorobenzene (41.5/58.5 wt %)	
alkyl halide	k_{act} (M^{-1} s^{-1})	relative ratio	k_{act} (M^{-1} s^{-1})	relative ratio
EBriB	0.243	45	0.098	43
MBrP	0.018	3.3	0.0071	3.1
EBrP	0.017	3.1		
t-BBrP	0.0054	1	0.0023	1

[a] Temperature = 35 °C, Cu(I)Br = [bpy]/2 = 20 mmol, [TEMPO] = 10 mmol.

larger than *t*-BBrP. Activation rate constants for MBrP and EBrP are similar, and their values are 3 times larger than that for *t*-BBrP.

Solvents containing O-coordinating centers such as water and polyethers reportedly accelerate ATRP.[21,23] To expand the study of the effect of solvent polarity on k_{act}, we used mixtures of acetonitrile with water (56 wt %). EBriB was chosen for this study because it is hydrolytically stable. The activation rate constants increase strongly in the presence of water (Figure 5).

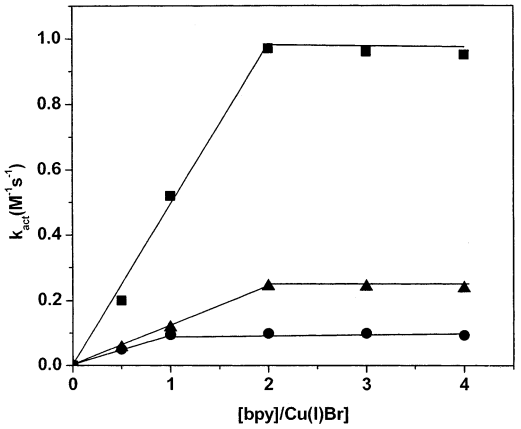


Figure 5. Plot of k_{act} as a function of increasing bpy concentration at constant Cu(I)Br concentration of EBriB in (■) acetonitrile (44 wt %) with water (56 wt %); (▲) pure acetonitrile and (●) acetonitrile (41.5 wt %) with chlorobenzene (58.5 wt %) at 35 °C. [EBriB] = 1 mmol; [Cu(I)Br] = 20 mmol, [TEMPO] = 10 mmol; [biphenyl] = 5 mmol.

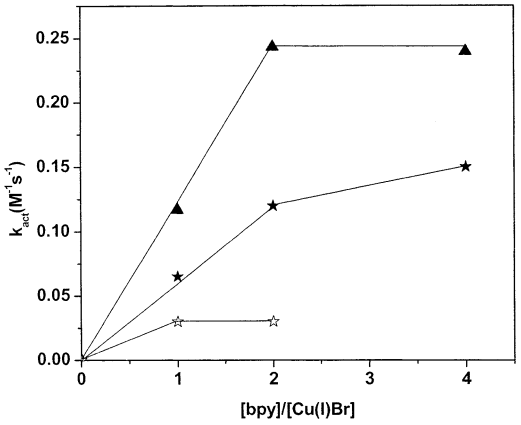


Figure 6. Plot of k_{act} as a function of increasing bpy concentration at constant Cu(I)Br concentration of EBriB in (▲) acetonitrile and (★) acetonitrile with TEGDME (13.7, wt %) and (☆) TEGDME (61.1, wt %) at 35 °C. [EBriB] = 1 mmol; [Cu(I)Br] = 20 mmol, [TEMPO] = 10 mmol; [biphenyl] = 5 mmol.

The maximal value of k_{act} was observed at a ratio of [bpy]/[Cu(I)Br] ~ 2/1 as in acetonitrile, although it was 4 times larger.

A solvent containing oxyethylene groups, namely, tetra(ethylene glycol) dimethyl ether (TEGDME), was also used (Figure 6). The maximal value of k_{act} was observed at [bpy]/[Cu(I)Br] ~ 2/1 in the presence of 13.7 wt % TEGDME. However, in the presence of 61.1 wt % TEGDME the maximal value of k_{act} was observed at [bpy]/[Cu(I)Br] ~ 1/1. The activation rate constants were smaller by factors of 2 and 8 respectively in 13.7 and 61.1 wt % TEGDME compared to pure acetonitrile. This indicates that TEGDME reduces the rate of activation, perhaps by displacing one molecule of bpy and making the copper complex less reactive.

To study the effect of counterions, we determined the activation rate constants using Cu(I)PF_6 at different ratios of [bpy]/[Cu(I)PF_6] in acetonitrile and less polar solvent mixtures (Figure 7). The maximal values of activation rate constants were observed at a ratio of [bpy]/[Cu(I)PF_6] ~ 2/1 in both the solvents. Furthermore, the value of k_{act} was 1.5 times larger in acetonitrile than in the less polar solvent mixtures. A comparative study of Cu(I)Br and Cu(I)PF_6 on the rates of

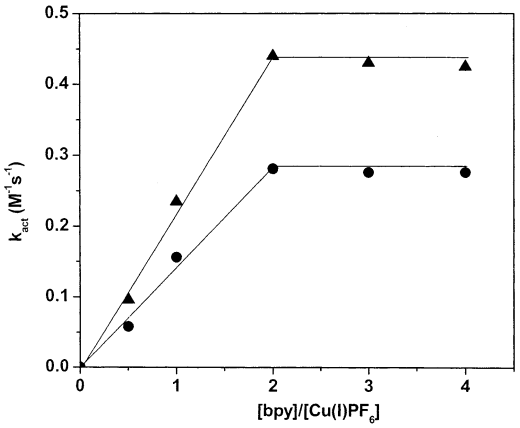


Figure 7. Plot of k_{act} as a function of increasing bpy concentration at constant Cu(I)PF_6 concentration for EBriB in (▲) acetonitrile and (●) less polar solvent, acetonitrile (41.5 wt %) with chlorobenzene (58.5 wt %) at 35 °C. [EBriB] = 1 mmol; [Cu(I)PF_6] = 20 mmol; [TEMPO] = 10 mmol; [biphenyl] = 5 mmol.

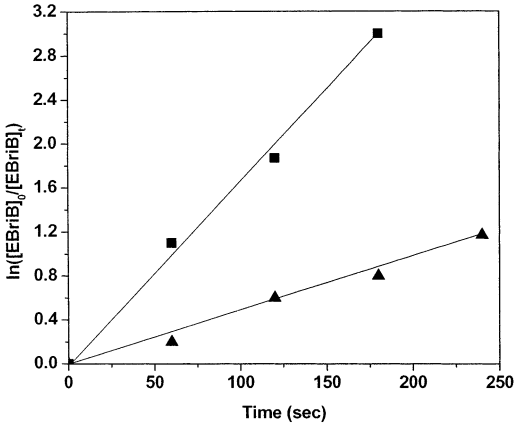


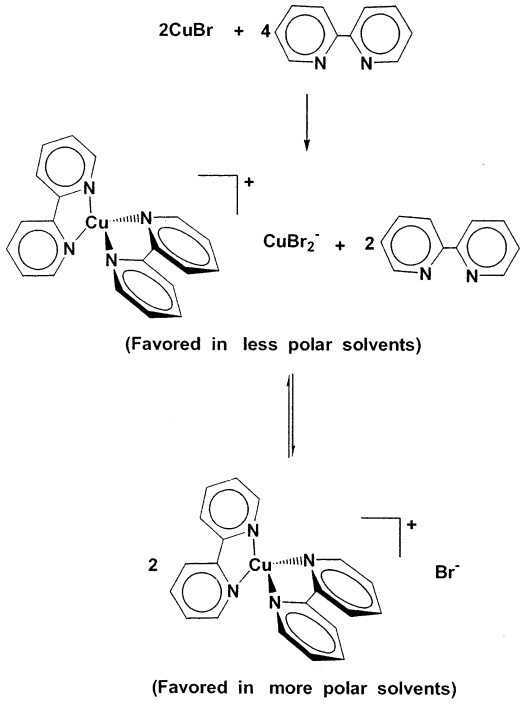
Figure 8. First-order kinetic plot of the activation rate constant measurement of EBriB with the (■) Cu(I)PF_6/$(bpy)_2$ and (▲) Cu(I)Br/$(bpy)_2$ catalysts at 35 °C in acetonitrile. [EBriB] = 1 mmol; [Cu(I)PF_6] = [Cu(I)Br] = 20 mmol, [bpy] = 40 mmol, [TEMPO] = 10 mmol, [biphenyl] = 5 mmol.

activation were carried out in acetonitrile (Figure 8). Both systems follow pseudo-first-order kinetics. The k_{act} for $Cu^I(bpy)_2{}^+PF_6{}^-$ was 1.8 times larger than for $Cu^I(bpy)_2{}^+Br^-$.

Discussion

Effect of [bpy]/[Cu(I)] Ratio. Irrespective of the nature of alkyl bromides, the maximal values of activation rate constants for Cu(I)Br in polar acetonitrile and mixtures with water were obtained at [bpy]/[Cu(I)Br] ratio ~ 2/1 (Figures 3 and 5). However, in mixtures with less polar chlorobenzene, the [bpy]/[Cu(I)Br] ratio was ~1/1 (Figures 4 and 5). In more polar media like acetonitrile and mixtures with water, the bromide anion is sufficiently stable and well solvated, resulting in $Cu(bpy)_2{}^+Br^-$ species (Scheme 3). However, in less polar media, Br^- is destabilized and concurrently binds much stronger to Cu(I)Br than bpy does, resulting in $Cu(bpy)_2{}^+CuBr_2{}^-$ species (Scheme 3). The excess bpy (more than 1:1 or 2:2) cannot displace Br^- from the $CuBr_2{}^-$ anion. The dibromocuprate anion ($CuBr_2{}^-$) is inactive and does not participate in the ATRP activation process.[19,31] Therefore, only half of the copper species is involved in the activating Cu(I) cation. The effect of

Scheme 3. Complex Formation Equilibrium in Polar and Nonpolar Solvents



[bpy]/[Cu(I)Br] in TEGDME is more complex and will be discussed later.

In agreement with this explanation, for Cu(I)PF_6 species the maximum rates were always observed at [bpy]/[CuPF_6] ~ 2/1 in both polar and less polar solvents. The noncoordinating $PF_6{}^-$ ion cannot bind to copper and forms $Cu(bpy)_2{}^+PF_6{}^-$ species in all reaction media. This observation is supported by earlier kinetic and structural studies of copper complexes.[27,31−33]

Solvents Effects. Solvent changes the structure of the bpy/Cu(I)Br complexes. In less polar media, $Cu(bpy)_2{}^+CuBr_2{}^-$ complexes are formed; however, in more polar acetonitrile and mixtures with water, $Cu(bpy)_2{}^+Br^-$ is preferred. This should correspond to doubling the apparent rate constants based on added Cu(I) species because only half of Cu(I)Br is in the active $Cu(bpy)_2{}^+$ form in less polar media.

However, there are some additional solvent effects. For example, the rate constant of activation of $Cu(bpy)_2PF_6$ is 1.5 times larger in acetonitrile than in mixtures with chlorobenzene (Figure 7). Rate constants in mixtures with water are even higher. Figure 9 presents the evolution of the apparent rate constant in various solvent mixtures as a function of weight-average dielectric constant.

Three solvent effects can be considered. The first one is associated with the aforementioned transformation of the $Cu(bpy)_2{}^+Br^-$ to $Cu(bpy)_2{}^+CuBr_2{}^-$ species. The second effect may be related to solvent polarity (dielectric constant) and can be explained by a higher reactivity of the free ions than ion pairs of copper species. The third effect may affect the transition state of the atom transfer process. The values of k_{act} increase in more polar solvents, in which the proportion of more active free ions is higher. Nevertheless, differences between Cu(I)PF_6 and Cu(I)Br remain even in the most polar media, indicating some contributions of ion pairs (Figure 9). This agrees with earlier studies on Cu(II) species.[34] The strong effect of the solvent polarity on the rate

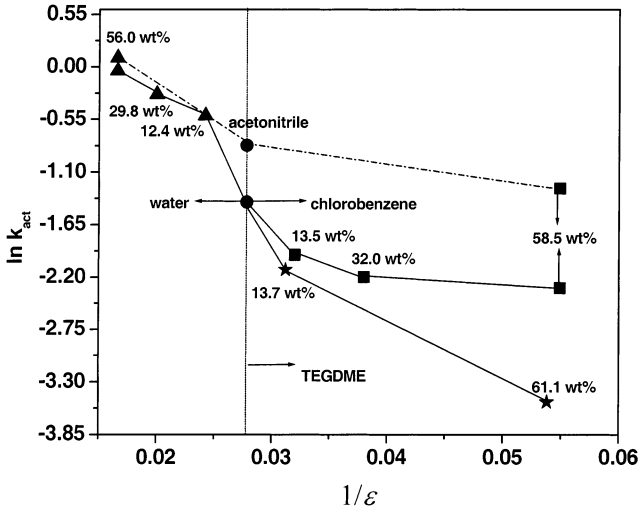


Figure 9. Plot of ln k_{act} as a function of $1/\epsilon$ at constant Cu(I)Br/$(bpy)_2$ (—) and Cu(I)PF_6/$(bpy)_2$ (· - ·) concentrations of EBriB in (●) acetonitrile and mixtures with (▲) water; (■) chlorobenzene, and (★) TEGDME at 35 °C. [EBriB] = 1 mmol; [Cu(I)Br] = 20 mmol, [bpy] = 40 mmol, [TEMPO] = 10 mmol; [biphenyl] = 5 mmol.

constants of activation could be due to some contribution of the outer-sphere electron-transfer mechanism for the atom transfer process (eq 4; cf. also latter discussion on the structure of alkyl halides). However, there might be a more specific solvent effect as exemplified by differences between mixtures of acetonitrile with either chlorobenzene or TEGDME of similar polarity. Copper species may be specifically solvated, and bpy ligands may even be partially displaced by either H_2O or TEGDME, which can strongly affect the rate constants of activation. Surprisingly, in the presence of TEGDME, the rate constant of activation is smaller than in mixtures of chlorobenzene with similar polarity. Therefore, faster polymerization rates of ATRP in these ethers cannot be ascribed to faster activation but rather to slower deactivation or X−Cu(II) bond dissociation, lowering the true deactivator concentration.[21,23]

$$R{-}X + Mt^nL_n \rightleftharpoons RX^{\bullet -} + M_t^{n+1}L_n \rightleftharpoons R^{\bullet} + X{-}Mt^{n+1}L_n \quad (4)$$

Effect of Counterion. If the activation rate constant depends only on $Cu(bpy)_2^+$, then the rate constants should be the same for $Cu(bpy)_2^+Br^-$, $Cu(bpy)_2^+CuBr_2^-$, and $Cu(bpy)_2^+PF_6^-$. However, there are some effects of counterions. In acetonitrile, k_{act} with $Cu(bpy)_2^+PF_6^-$ is 1.8 times larger than with $Cu(bpy)_2^+Br^-$ (Figure 8). In the mixed solvent with chlorobenzene, the ratio between k_{act} with $Cu(bpy)_2^+PF_6^-$ and $Cu(bpy)_2^+CuBr_2^-$ is 1.4. Thus, in addition to solvent effects, the effect of counterion on the rate constants of activation may be summarized as PF_6^- (1.8):$CuBr_2^-$ (1.3):Br^- (1) assuming similar dissociation constants. The smaller differences in water may be assigned to the increased proportions of free ions with reactivities independent of the counterion.

Structure of Alkyl Groups and Mechanism of Activation. All alkyl bromides behave similarly in solvents irrespective of the polarity. The strong solvent effects, especially in polar media, could suggest contribution of an outer-sphere electron-transfer (OSET) process (eq 4). The OSET should depend primarily on the electron affinity of the alkyl bromide and less on steric effects. Thus, MBrP might be more reactive than EBriB, and the steric effect of the alkyl substituents should be relatively small. However, comparison of the values of the activation rate constants supports the inner-sphere electron transfer (ISET) being the dominant process (eq 5) rather than OSET, because EBriB is 13 times more reactive than EBrP and *t*-BBrP is 3 times less active than EBrP/MBrP in all reaction media (Table 1). This suggests that the rate-determining step should involve the bimolecular process of the Br atom transfer from alkyl bromide to copper via ISET (eq 5).

$$R{-}X + Mt^nL_n \rightleftharpoons R\text{- - -}X\text{- - -}Mt^nL_n \rightleftharpoons R^{\bullet} + X{-}Mt^{n+1}L_n \quad (5)$$

The rates of activation of alkyl bromides primarily depend on two factors: (1) the formed radicals and (2) steric effects. The first effect is more important since activation is faster with EBriB, which generates more stable tertiary radical, despite the higher steric congestion. The steric effects are easier to analyze at the remote substituent, when secondary radicals with the same stabilities are generated. In this case, *tert*-butyl group slows down the activation 3 times in comparison with the methyl or ethyl groups.

Conclusions

Detail studies on the effect of [bpy]/[Cu(I)] ratio, polarity of the reaction medium, counterion, and alkyl bromides on the activation rate constants (k_{act}) revealed that it is necessary to adjust the reaction parameters for the successful ATRP. The maximal values of k_{act} were obtained at the [bpy]/[Cu(I)] ratio ∼ 2/1 and 1/1 respectively in more and less polar media for Br^- counterions. However, for the PF_6^- counterion, the maximal values were always obtained at the [bpy]/[Cu(I)] ∼ 2/1 irrespective of the polarity of solvents. The k_{act} was 1.8 times larger for PF_6^- than Br^- counterions. The activation rate constants increased with increase in polarity of the medium; however, an unexpected decrease in k_{act} was observed for solvents containing oxyethylene groups. The relative values of k_{act} of alkyl bromides decreased in the following order: EBriB (44) ≫ MBrP (3) ∼ EBrP (3) > *t*-BBrP (1). These results suggest that the activation process is dominated by an inner-sphere electron-transfer process. Further studies on the effect of different ligands, counterions, monomer, alkyl halides, and temperature on the activation rate constants will provide more insight into ATRP.

Experimental Section

Materials. Cu(I)Br (99.999%, Aldrich) was purified according to the published procedure.[35] Cu(I)Br (5 g) was stirred in glacial acetic acid (100 mL) overnight. The content was filtered though a Buchner funnel and washed three times with ethanol and diethyl ether, dried in a vacuum overnight, and stored under nitrogen. $[Cu(CH_3CN)_4]^+PF_6^-$ was synthesized using the procedure reported earlier.[36] Ethyl 2-bromoisobutyrate (EBriB) (99%, Aldrich), methyl 2-bromopropionate (MBrP) (99%, Aldrich), ethyl 2-bromopropionate (EBrP) (99%, Aldrich), and *tert*-butyl 2-bromopropionate (*t*-BBrP) (99%, Aldrich) were purified by passing through activated basic alumina. 2,2,6,6-Tetramethylpiperidinyl-1-oxy (TEMPO) (99%, Aldrich), 2,2′-bipyridine (bpy) (99%, Aldrich), and tetra(ethylene glycol) dimethyl ether (TEGDME) (99.5%, Acros) were used as received. Chlorobenzene (Aldrich, 99+%), acetonitrile (Aldrich, 99+%, HPLC grade), and deionized water were distilled before use.

Activation Rate Constant Measurements. Stock solutions of EBriB, MBrP, EBrP, and *t*-BBrP were prepared by adding 1 mmol of the corresponding reactant along with biphenyl (5 mmol) and 10 mmol of TEMPO in acetonitrile in a 10 mL volumetric flask. Similarly, 20 mmol stock solution of bpy was prepared in acetonitrile. In a Schlenk flask, 20 mmol of Cu(I)Br was placed, and the flask was degassed and back-filled with N_2 three times. A 20 mmol stock solution of bpy along with 3 mL of acetontrile was freeze−pump−thawed three times and transferred to the Schlenk flask through a degassed syringe. Then, 1 mL of the stock solution of the mixture of alkyl bromides, namely, MBrP, EBriB, and tBBrP, biphenyl, and TEMPO was freeze−pump−thawed and transferred to the Schlenk flask through a degassed syringe. The flask was stirred, and a sample was taken immediately for GC analysis for time zero. The reaction was carried out at 35 °C under constant stirring. A sample was taken at timed intervals, and the consumption of alkyl halide with time was analyzed by GC. The experiments for EBrP were conducted separately. Experiments were conducted by varying bpy/Cu(I) ratio using chlorobenzene, water, and TEGDME. In the case of water, the sample was taken from the Schlenk flask and diluted with an equal volume of toluene. The mixture was shaken for 2 min, and the organic layer was taken for GC analysis. Similar experiments were conducted for $[Cu(CH_3CN)_4]^+PF_6^-$ systems and in the presence of solvents of different polarity. GC was performed using a Schimadzu GC-17A, AOC-20i autosampler, and J & W Scientific DB 608 column (30 m × 0.53 mm) with a FID detector. The injector and detector temperature were kept constant at 250 °C. The temperature program for GC column was as follows: initial temperature, 45 °C, 0 min; ramp, 5 °C/min; final temperature, 200 °C. For the fast kinetic reactions, electron capture detector (ECD) was used, which is very sensitive to alkyl halides and governed by radiation (β-ray) from the ^{63}Ni source sealed in the ECD cell ionized by an inert gas (N_2).

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References and Notes

(1) Matyjaszewski, K., Ed. *Controlled Radical Polymerization;* American Chemical Society: Washington, DC, 1998.
(2) Matyjaszewski, K., Ed. *Controlled/Living Radical Polymerization. Progress in ATRP, NMP, and RAFT*; American Chemical Society: Washington, DC, 2000.
(3) Matyjaszewski, K., Davis, T. P., Eds. *Handbook of Radical Polymerization*; Wiley-Interscience: Hoboken, 2002.
(4) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614−5615.
(5) Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901−915.
(6) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921−2990.
(7) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689−3745.
(8) Matyjaszewski, K. *Chem.—Eur. J.* **1999**, *5*, 3095−3102.
(9) Patten, T. E.; Matyjaszewski, K. *Acc. Chem. Res.* **1999**, *32*, 895−903.
(10) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866−868.
(11) Wang, J.-S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901−7910.
(12) Fischer, H. *J. Am. Chem. Soc.* **1986**, *108*, 3925−3927.
(13) Matyjaszewski, K. *J. Macromol. Sci., Pure Appl. Chem.* **1997**, *A34*, 1785−1801.
(14) Goto, A.; Fukuda, T. *Macromol. Rapid Commun.* **1999**, *20*, 633−636.
(15) Matyjaszewski, K.; Goebelt, B.; Paik, H.-j.; Horwitz, C. P. *Macromolecules* **2001**, *34*, 430−440.
(16) Matyjaszewski, K.; Paik, H.-j.; Zhou, P.; Diamanti, S. J. *Macromolecules* **2001**, *34*, 5125−5131.
(17) Chambard, G.; Klumperman, B.; German, A. L. *Macromolecules* **2000**, *33*, 4417−4421.
(18) Pintauer, T.; Zhou, P.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2002**, *124*, 8196−8197.
(19) Matyjaszewski, K.; Patten, T. E.; Xia, J. *J. Am. Chem. Soc.* **1997**, *119*, 674−680.
(20) Matyjaszewski, K.; Nakagawa, Y.; Jasieczek, C. B. *Macromolecules* **1998**, *31*, 1535−1541.
(21) Haddleton, D. M.; Perrier, S.; Bon, S. A. F. *Macromolecules* **2000**, *33*, 8246−8251.
(22) Pascual, S.; Coutin, B.; Tardi, M.; Polton, A.; Vairon, J. P. *Macromolecules* **1999**, *32*, 1432−1437.
(23) Wang, X. S.; Armes, S. P. *Macromolecules* **2000**, *33*, 6640−6647.
(24) Matyjaszewski, K.; Woodworth, B. E.; Zhang, X.; Gaynor, S. G.; Metzner, Z. *Macromolecules* **1998**, *31*, 5955−5957.
(25) Skene, W. G.; Belt, S. T.; Connolly, T. J.; Hahn, P.; Scaiano, J. C. *Macromolecules* **1998**, *31*, 9103−9105.
(26) Kothe, T.; Marque, S.; Martschke, R.; Popov, M.; Fischer, H. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1553−1559.
(27) Wang, J.-L.; Grimaud, T.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 6507−6512.
(28) Davis, K. A.; Paik, H.-j.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 1767−1776.
(29) Yorimitsu, H.; Shinokubo, H.; Matsubara, S.; Oshima, K.; Omoto, K.; Fujimoto, H. *J. Org. Chem.* **2001**, *66*, 7776−7785.
(30) Pereira, S. M.; Iglesias, T. P.; Legido, J. L.; Rivas, M. A.; Real, J. N. *J. Chem. Thermodyn.* **2001**, *33*, 433−440.
(31) Levy, A. T.; Olmstead, M. M.; Patten, T. E. *Inorg. Chem.* **2000**, *39*, 1628−1634.
(32) Kickelbick, G.; Reinohl, U.; Ertel, T. S.; Weber, A.; Bertagnolli, H.; Matyjaszewski, K. *Inorg. Chem.* **2001**, *40*, 6−8.
(33) Pintauer, T.; Reinohl, U.; Feth, M.; Bertagnolli, H.; Matyjaszewski, K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2002**, *43* (2), 219−220.
(34) Pintauer, T.; Qiu, J.; Kickelbick, G.; Matyjaszewski, K. *Inorg. Chem.* **2001**, *40*, 2818−2824.
(35) Keller, R. N. *Inorg. Synth.* **1946**, *2*, 247−250.
(36) Hathaway, B. J.; Holah, D. G.; Postlethwaite, J. D. *J. Chem. Soc.* **1961**, 3215−3218.

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