# Effect of [PMDETA]/[Cu(I)] Ratio, Monomer, Solvent, Counterion, Ligand, and Alkyl Bromide on the Activation Rate Constants in Atom Transfer Radical Polymerization

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ABSTRACT: A detailed study on the effect of [PMDETA]/[Cu(I)] ratio, monomer, solvent polarity, counterion, ligand, and alkyl bromide on the activation rate constant ($k_{act}$) in ATRP was carried out. The highest values of $k_{act}$ for Cu(I)Br were obtained at [PMDETA]/[Cu(I)Br] ∼ 1/1 in more polar solvents and ascribed to a neutral [Cu(PMDETA)Br] structure of the complex. However, in less polar solvent mixtures a relatively fast reaction was observed already at the 0.5/1 ratio with the smaller rate increase up to [PMDETA]/[Cu(I)Br] ∼ 1/1. The highest values of $k_{act}$ for Cu(I)$PF_6$ were observed at [PMDETA]/[Cu(I)Br] ∼ 1/1 in more polar, less polar solvent mixtures and monomer, which was explained by the formation of an ionic [Cu(PMDETA)]$^+PF_6^-$ complex. In both more polar and less polar media, the values of $k_{act}$ were slightely larger for $PF_6^-$ than $Br^-$ counterion. However, in methyl acrylate, $k_{act}$ was 1.9 times larger for $Br^-$ than $PF_6^-$ counterion. This was attributed to monomer coordination through the open coordination site of an ionic [Cu(PMDETA)]$^+Y^-$ (Y = $PF_6$/$BPh_4$) complex, which reduced complex activity. The values of $k_{act}$ were higher for PMDETA containing three nitrogen atoms as compared to the ligand containing two nitrogen atoms and one oxygen atom (BDMAEE). The relative rates of $k_{act}$ of the alkyl bromides follow the order EBriB (30) ≫ MBrP (3) > t-BBrP (1). In the absence of monomer, the values of the $k_{act}$ for different ligand/counterion follow the order PMDETA/$PF_6^-$ > PMDETA/$Br^-$ > BDMAEE/$Br^-$ > bpy/$PF_6^-$ > bpy/$Br^-$.

## Introduction

Atom transfer radical polymerization (ATRP) is an excellent method to control chain growth and herewith molecular weight distributions and chemical composition distributions in the (co)polymerization of vinyl monomers.[1−7] The success of ATRP relies on the reversible activation of a dormant alkyl halide through halogen abstraction by a transition metal complex in addition to the classical free-radical polymerization scheme (Scheme 1).[8−11] In this equilibrium, an alkyl radical ($P_m^•$) is formed in the activation process, with a rate constant $k_{act}$, by the homolytic cleavage of an alkyl halide bond ($P_m$−X) catalyzed by a transition metal complex in its lower oxidation state (Cu(I)). Concurrently, the alkyl radical ($P_m^•$) adds to the monomer with a rate constant, $k_p$, before it is deactivated, with a rate constant, $k_{deact}$, by the metal complex in its higher oxidation state (Cu(II)). Through these reversible and repetitive cycles, polymers with progressively increasing molecular weights with conversion and low polydispersities are formed. The rate of termination becomes insignificant with time due to the persistent radical effect.[12]

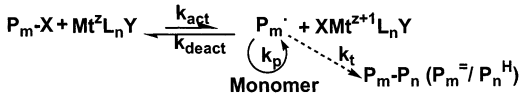
The rate of polymerization and polydispersity in ATRP are shown in eqs 1 and 2, respectively.[6,13,14]

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

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

The rate constants of activation, deactivation, and equilibrium constants ($K_{eq} = k_{act}/k_{deact}$) as well as concentrations of all involved reagents are crucially important for understanding the controlled process and are inherently part of the future developments for the successful ATRP. Our group has a long-standing interest in the structural, kinetic, and mechanistic aspects on ATRP processes.[15−21] Recently, we have reported the influence of [bpy]/[Cu(I)] ratio on $k_{act}$ with respect to polarity of the reaction medium, counterions, and alkyl bromides.[22] The maximal values of $k_{act}$ were observed at the [bpy]/[Cu(I)] ≈ 2/1 and 1/1, respectively, in more polar and less polar solvent mixtures for $Br^-$ counterion. This was attributed to the Cu(bpy)$_2^+Br^-$ and [Cu(bpy)$_2$]$^+$[$CuBr_2$]$^-$ structures of the catalyst complexes. For an ionic [Cu(bpy)]$^+PF_6^-$ catalyst complex in all reaction media, $k_{act}$ was 1.5 times larger in more polar than less polar reaction media. A special solvent effect was noticed for solvents containing oxyethylene groups.[22] More polar solvents were used to homogenize the Cu(I)/bpy catalyst system.[22−26] However, it would be more appropriate to determine activation rate constants in solvents of polarity similar to monomer and even in the presence of monomer to better relate to the real polymerization system in ATRP.

**Scheme 1. Elementary Reactions in ATRP**




Apart from bipyridines, linear triamines were successfully used as ligands for ATRP catalysts.[27−36] Particularly, a commercially available tridentate ligand, *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA), showed a high potential for the controlled polymerization of variety of monomers due to its low cost, high

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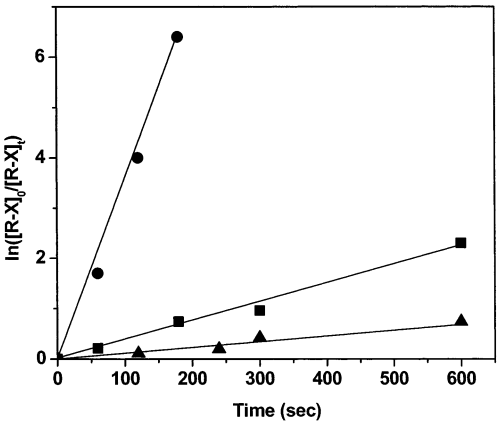
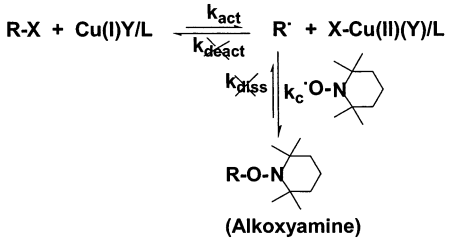



**Figure 1.** First-order kinetic plot of the activation process with the Cu(I)Br(PMDETA) catalyst at 35 °C in acetonitrile for (●) EBriB, (■) MBrP, and (▲) t-BBrP. $[EBriB]_0 = [MBrP]_0 = [t\text{-}BBrP]_0 = 1$ mmol/L, $[Cu(I)Br(PMDETA)]_0 = 20$ mmol/L, $[TEMPO]_0 = 10$ mmol/L, [trichlorobenzene]$_0 = 5$ mmol/L.

**Scheme 2. Kinetic Isolation of the Activation Process**




activity and miscibility in less polar media and monomer, and less color.[27−37] In this article, the Cu(I)/PMDETA catalytic system was used to analyze systematically the effect of [PMDETA]/[Cu(I)] ratio, structure of the catalyst complexes, counterions, ligands, polarity of the reaction medium, monomer, and alkyl bromides on the activation rate constants in ATRP. The monomer coordination to the ionic copper complexes and its effect on $k_{act}$ for $PF_6^-$ and $BPh_4^-$ counterions were also studied.

## Method

The activation rate constants were determined using the trapping experiments that are also the basis for determining the dissociation rate parameters of alkoxyamines.[38,39] The radicals originating from alkyl bromides are irreversibly trapped by a stable nitroxide radical, 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO), to yield corresponding alkoxyamines (Scheme 2).[19] To obtain pseudo-first-order kinetics, the radicals originating from an alkyl bromide should be irreversibly trapped by TEMPO with no transformation back to the dormant species. This was facilitated by using a large excess of TEMPO (∼10 times) with respect to alkyl bromides and the higher rate constants of coupling than deactivation ($k_c \gg k_{deact}$).[19] The dissociation of alkoxyamine was suppressed due to low reaction temperature (35 °C).[40]

An excess of Cu(I) (about 20 times with respect to 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 bromide, the apparent rate constant of activation, $k_{app}$, was determined, which was the product of the catalyst concentration and the activation rate constant, $k_{act}$ (eq 3).[14] Similar approaches have been

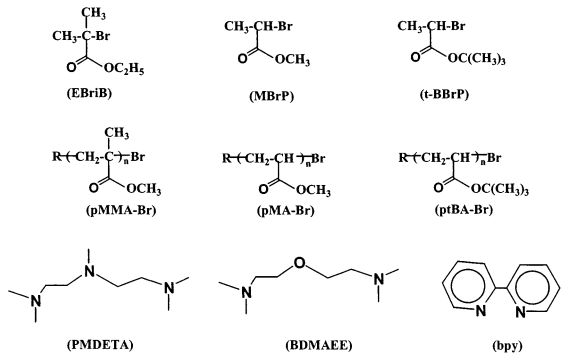



**Figure 2.** Model compounds, their polymeric analogues, and ligands for the activation study.

reported for the determination of the decomposition rate constants of the alkoxyamine[40,41] and the activation reaction for model compounds and polymeric chain ends in ATRP.[17−19,38]

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

## Results

Recently, activation rate constants were determined for model alkyl halides.[18,19,22] These alkyl halides are commonly used initiators and mimic the chain ends in ATRP. Ethyl 2-bromoisobutyrate (EBriB), methyl 2-bromopropionate (MBrP), and *tert*-butyl 2-bromopropionate (t-BBrP) were used respectively to mimic the chain ends of poly(methyl methacrylate) (pMMA-Br), poly(methyl acrylate) (pMA-Br), and poly(*tert*-butyl acrylate) (ptBA-Br) (Figure 2). These alkyl bromides are among the most widely used initiators in ATRP. 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 PMDETA and bis(2-dimethylaminoethyl) ether (BDMAEE) as the coordinating ligands. Three Cu(I) species, namely, Cu(I)Br, Cu(I)$PF_6$, and Cu(I)$BPh_4$, were used. Solvents of different polarity, namely, acetonitrile, ethyl acetate, toluene, and monomers, such as methyl acrylate (MA) and *tert*-butyl acrylate (t-BA), were used. The dielectric constants of acetonitrile, ethyl acetate, and toluene are 35.94, 6.02, and 2.38 D, respectively.[42] Mixtures of solvents were chosen to homogenize the PMDETA/Cu(I) and BDMAEE/Cu(I) catalyst complexes in the reaction media.

The activation rate constants of EBriB, MBrP, and t-BBrP at different ratios of [PMDTA]/[Cu(I)] were determined in pure acetonitrile and a mixture of acetonitrile (47.7 wt %) with toluene (52.3 wt %) (Figures 3 and 4). In acetonitrile, $k_{act}$ increases linearly as the ratio of [PMDETA]/[Cu(I)Br] increases up to 1/1 (Figure 3). At higher ratio of [PMDETA]/[Cu(I)Br] (>1/1), $k_{act}$ remained constant or even decreased slightly. In a less polar solvent mixture, a strong increase of $k_{act}$ with increase in [PMDETA]/[Cu(I)Br] up to 0.5/1 was observed, and thereafter a slow increase was noticed up to the [PMDETA]/[Cu(I) ratio ∼ 1/1 and then leveled off or decreased slightly at higher ratio (>1/1) (Figure 4). The maximal values of $k_{act}$ were observed at [PMDETA]/[Cu(I)Br] ratio ∼ 1/1 in more polar and less polar solvent mixtures irrespective of the nature of alkyl bromides. The values of $k_{act}$ was 1.66 times larger in acetonitrile compared to less polar solvent mixtures.

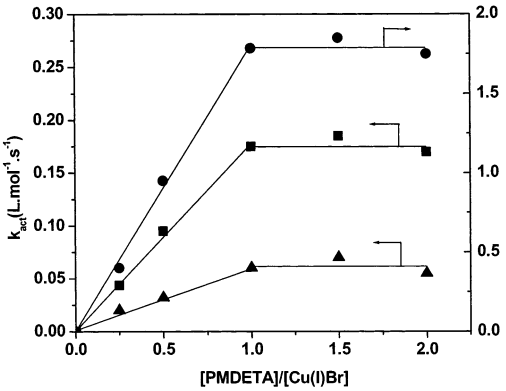



**Figure 3.** Plot of $k_{act}$ as a function of increasing PMDETA concentration at constant Cu(I)Br concentration for (●) EBriB, (■) MBrP, and (▲) t-BBrP in acetonitrile at 35 °C. $[EBriB]_0 = [MBrP]_0 = [t\text{-}BBrP]_0 = 1$ mmol/L; $[Cu(I)Br]_0 = 20$ mmol/L, $[TEMPO]_0 = 10$ mmol/L; $[trichlorobenzene]_0 = 5$ mmol/L.

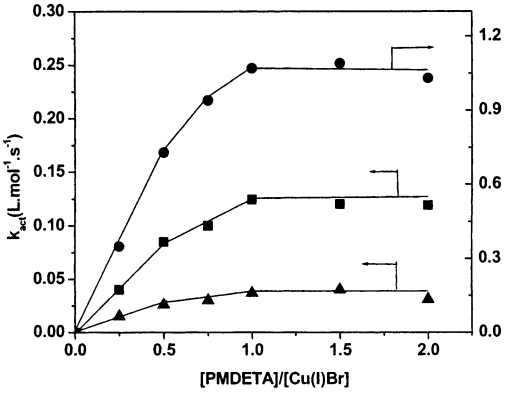



**Figure 4.** Plot of $k_{act}$ as a function of increasing PMDETA concentration at constant Cu(I)Br concentration for (●) EBriB, (■) MBrP, and (▲) t-BBrP in less polar solvent mixture, acetonitrile (47.7 wt %) and toluene (52.3 wt %) at 35 °C. $[EBriB]_0 = [MBrP]_0 = [t\text{-}BBrP]_0 = 1$ mmol/L; $[Cu(I)Br]_0 = 20$ mmol/L, $[TEMPO]_0 = 10$ mmol/L; $[trichlorobenzene]_0 = 5$ mmol/L.

To study the effect of counterions, the activation rate constants were determined using $Cu(I)PF_6$ at different ratios of [PMDETA]/[$Cu(I)PF_6$] in acetonitrile and less polar solvent mixtures (Figures 5 and 6). A linear increase of $k_{act}$ with increase in [PMDETA]/[$Cu(I)PF_6$] ratio up to 1/1 was observed. Furthermore, $k_{act}$ was 1.7 times larger in acetonitrile compared to those in less polar solvent mixtures.

To study the effect of monomer, activation rate constants were determined in the presence of methyl acrylate (MA) (Figure 7). The maximum values of $k_{act}$ were observed at the [PMDETA]/[$Cu(I)PF_6$] ≈ 1/1 for all the alkyl bromides (Figure 7). The activation rate constants in acetonitrile, less polar solvent mixture, and monomer for $Cu(I)PF_6$/PMDETA catalyst systems are displayed in Figure 8. The relative values of $k_{act}$ follow the order: acetonitrile (3.9) > less polar solvent mixture (2.3) > MA (1). However, for the Cu(I)Br/PMDETA catalyst system, $k_{act}$ increases linearly as the [PMDETA]/[Cu(I)Br] increases up to 0.5/1, and thereafter a slow increase in $k_{act}$ was noticed up to [PMDETA]/[Cu(I)] ratio ~ 1/1 (Figure 9). The relative values of $k_{act}$ in different solvents and monomer for PMDETA/Cu(I)Br system follow the order: acetonitrile (1.9) > less polar solvent mixture (1.1) > MA (1) (Figure 10).

The activation rate constants for Cu(I)Br, $Cu(I)PF_6$, and $Cu(I)BPh_4$ in more and less polar solvents along

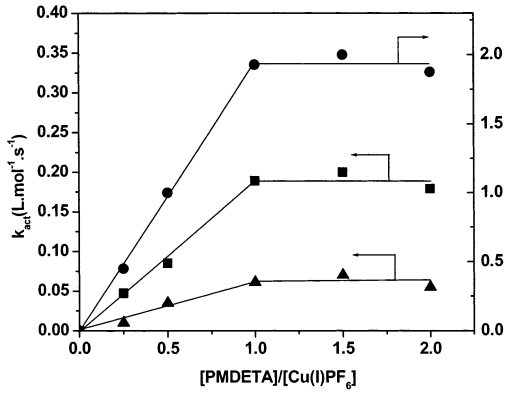



**Figure 5.** Plot of $k_{act}$ as a function of increasing PMDETA concentration at constant $Cu(I)PF_6$ concentration for (●) EBriB, (■) MBrP, and (▲) t-BBrP in acetonitrile at 35 °C. $[EBriB]_0 = [MBrP]_0 = [t\text{-}BBrP]_0 = 1$ mmol/L; $[Cu(I)PF_6]_0 = 20$ mmol/L, $[TEMPO]_0 = 10$ mmol/L; $[trichlorobenzene]_0 = 5$ mmol/L.

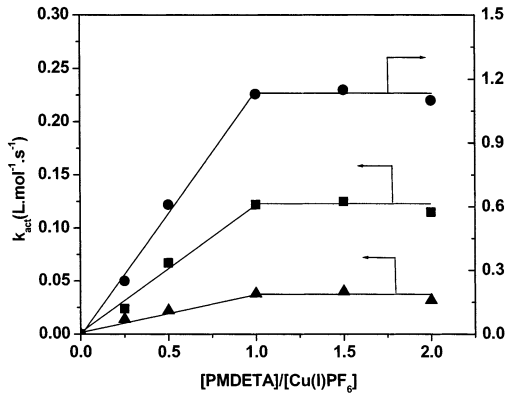



**Figure 6.** Plot of $k_{act}$ as a function of increasing PMDETA concentration at constant $Cu(I)PF_6$ concentration for (●) EBriB, (■) MBrP, and (▲) t-BBrP in less polar solvent mixture, acetonitrile (47.7 wt %) and toluene (52.3 wt %) at 35 °C. $[EBriB]_0 = [MBrP]_0 = [t\text{-}BBrP]_0 = 1$ mmol/L; $[Cu(I)PF_6]_0 = 20$ mmol/L, $[TEMPO]_0 = 10$ mmol/L; $[trichlorobenzene]_0 = 5$ mmol/L.

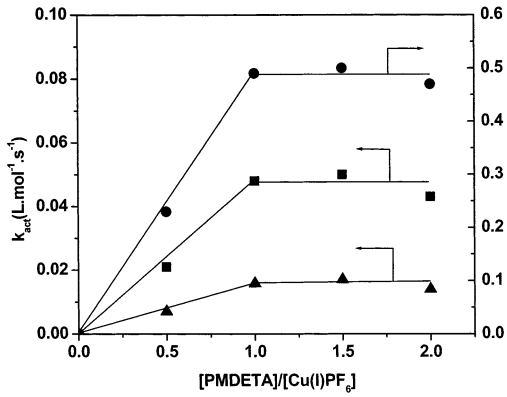



**Figure 7.** Plot of $k_{act}$ as a function of increasing PMDETA concentration at constant $Cu(I)PF_6$ concentration for (●) EBriB, (■) MBrP, and (▲) t-BBrP in methyl acrylate at 35 °C. $[EBriB]_0 = [MBrP]_0 = [t\text{-}BBrP]_0 = 1$ mmol/L; $[Cu(I)PF_6]_0 = 20$ mmol/L, $[TEMPO]_0 = 10$ mmol/L; $[trichlorobenzene]_0 = 5$ mmol/L.

with monomer are displayed in Table 1. In acetonitrile, $k_{act}$ follows the order $BPh_4^- > PF_6^- > Br^-$. The values of $k_{act}$ decreased by 1.2, 2.2, and 2.3 times respectively for $Br^-$, $PF_6^-$, and $BPh_4^-$ in mixtures with MA (11.9 wt %) compared to that for pure acetonitrile. Notably, in 11.9 wt % MA the rate of decrease on $k_{act}$ follows the

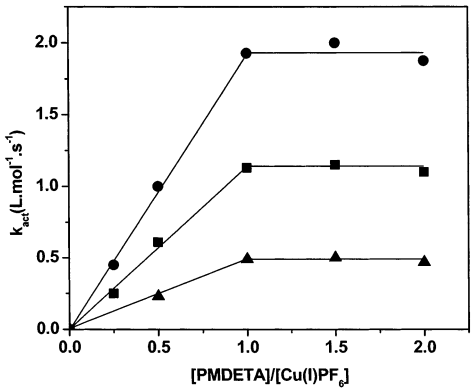



**Figure 8.** Plot of $k_{act}$ as a function of increasing PMDETA concentration at constant Cu(I)$PF_6$ concentration of EBriB in (●) acetonitrile, (■) acetonitrile (47.3 wt %) with toluene (52.3 wt %), and (▲) methyl acrylate at 35 °C. $[EBriB]_0 = 1$ mmol/L; $[Cu(I)PF_6]_0 = 20$ mmol/L, $[TEMPO]_0 = 10$ mmol/L; [trichlorobenzene]$_0 = 5$ mmol/L.

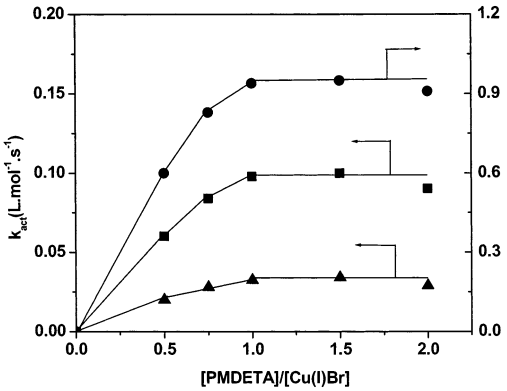



**Figure 9.** Plot of $k_{act}$ as a function of increasing PMDETA concentration at constant Cu(I)Br concentration for (●) EBriB, (■) MBrP, and (▲) t-BBrP in methyl acrylate at 35 °C. $[EBriB]_0 = [MBrP]_0 = [t\text{-}BBrP]_0 = 1$ mmol/L; $[Cu(I)Br]_0 = 20$ mmol/L, $[TEMPO]_0 = 10$ mmol/L; [trichlorobenzene]$_0 = 5$ mmol/L.

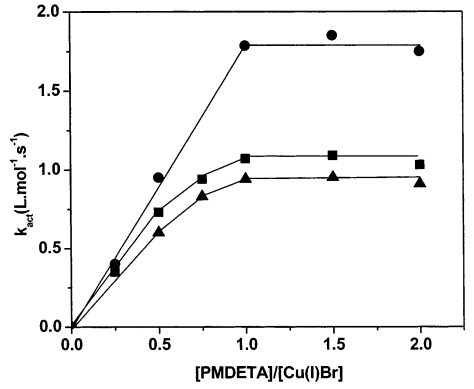



**Figure 10.** Plot of $k_{act}$ as a function of increasing PMDETA concentration at constant Cu(I)Br concentration of EBriB in (●) acetonitrile, (■) acetonitrile (47.7 wt %) with toluene (52.3 wt %), and (▲) methyl acrylate at 35 °C. $[EBriB]_0 = 1$ mmol/L; $[Cu(I)Br]_0 = 20$ mmol/L, $[TEMPO]_0 = 10$ mmol/L; [trichlorobenzene]$_0 = 5$ mmol/L.

order $Br^- > PF_6^- > BPh_4^-$. In acetonitrile and less polar solvent mixtures, $k_{act}$ of $PF_6^-$ was 1.1 times larger than $Br^-$; however, in MA, $k_{act}$ of $Br^-$ was 1.9 times larger than that of $PF_6^-$.

The activation rate constants of alkyl bromides with different ligand/counterions are displayed in Table 2. EBriB is 35 ± 5 more reactive than t-BBrP, and MBrP is 3 times more reactive than t-BBrP irrespective of the nature of ligands/counterions. In acetonitrile, the values of $k_{act}$ of alkyl bromide in the ligand/counterion follow the order PMDETA/$PF_6^-$ > PMDETA/$Br^-$ > BDMAEE/$Br^-$ > bpy/$PF_6^-$ > bpy/$Br^-$.

**Table 1. Activation Rate Constants (in L mol$^{-1}$ s$^{-1}$) for Various Counterions in Solvents of Different Polarity and Monomer at $[PMDETA]_0/[Cu(I)]_0$ Ratio ~ 1/1[a]**

| reaction medium | $Br^-$ | $PF_6^-$ | $BPh_4^-$ |
|---|---|---|---|
| acetonitrile | 1.78 | 1.93 | 2.32 |
| acetonitrile (88.1 wt %) with MA (11.9 wt %) | 1.47 | 0.86 | 0.98 |
| acetonitrile (47.7 wt %) with toluene (52.3 wt %) | 1.07 | 1.13 | |
| MA | 0.94 | 0.49 | |

[a] Temperature = 35 °C, $[EBriB]_0 = 1$ mmol/L; $[Cu(I)]_0 = [PMDETA]_0 = 20$ mmol/L, $[TEMPO]_0 = 10$ mmol.

## Discussion

**Effect of [PMDETA]/[Cu(I)] Ratio.** The maximal values of $k_{act}$ for Cu(I)Br in acetonitrile were observed at [PMDETA]/[Cu(I)Br] ratio ≈ 1/1 (Figure 3). In less polar solvent mixtures, although the maximal values were still obtained at the ratio ≈ 1/1, a rather slow increase in $k_{act}$ was noticed between the [PMDETA]/[Cu(I)Br] ratio ≈ 0.5/1−1/1 (Figure 4). The structure of the Cu(I)/PMDETA complex in acetonitrile could be either a neutral [$Cu^I$(PMDETA)Br] or ionic [$Cu^I$(PMDETA)]$^+Br^-$ complex (Scheme 3). However, in less polar medium the structure of the complex could be ionic [Cu(PMDETA)]$^+$-[$CuBr_2$]$^-$ as described earlier for the Cu(I)/bpy catalyst system.[22] In such a case, the maximal values of $k_{act}$ should be obtained at the [PMDETA]/Cu(I)Br ≈ 0.5/1, if the [Cu(PMDETA)]$^+$[$CuBr_2$]$^-$ complex is exclusively formed in the reaction, because the $CuBr_2^-$ anion is an inactive complex and does not participate in the activation process.[43,44] Therefore, only half of the copper would be active and would participate in the activation process. The relatively smaller increase in $k_{act}$ at [PMDETA]/Cu(I)Br > 0.5/1 indicates some contribution of [Cu(I)-[PMDETA]$^+CuBr_2^-$ species, which transform at higher [PMDETA]/[CuBr] ratio to the neutral [Cu(PMDETA)-Br] or [Cu(PMDETA)]$^+Br^-$ complex. Tridentate aliphatic PMDETA is a stronger complexing ligand compared to the bidentate aromatic bpy ligand. Most probably, it also coordinates and partially activates the $CuBr_2^-$ anion easier than the bpy ligand due to its rigid structure. Additional studies on the structural aspects of the Cu(I) complexes are necessary to provide more insight into the activation process. In the presence of pure monomer, MA, similar behavior on $k_{act}$ with respect to [PMDETA]/Cu(I) ratio was noticed (Figure 9), confirming the existence of similar structural behavior of the complex as seen for less polar solvent mixtures.

For the Cu(I)$PF_6$ species, the maximum rates were always observed at $[PMDETA]/[Cu(I)PF_6] \sim 1/1$ in more polar, less polar solvent mixtures and monomer (Figures 5, 6, and 7). The structure of the complex was presumably ionic [Cu(PMDETA)]$^+PF_6^-$ in all reaction media (Scheme 3). This observation is supported by recent structural studies of copper complexes.[20,41,45−47]

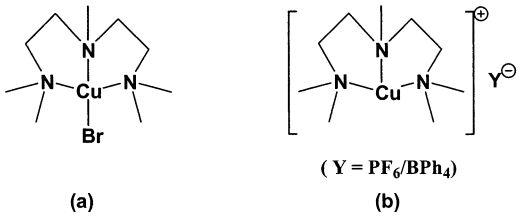
**Effect of Monomer and Counterions.** In MA, for $Br^-$ counterion, the values of $k_{act}$ were 1.9 times smaller than that for acetonitrile but nearly similar to the values in less polar solvent mixtures (Figure 10 and Table 1). However, for $PF_6^-$ counterion, the activation rate constants in MA were smaller by 3.9 and 2.3 times respectively compared to those in pure acetonitrile and

**Table 2. Activation Rate Constants (in L mol$^{-1}$ s$^{-1}$) and Their Relative Ratios for Various Alkyl Bromides, Ligands, and Counterions in Acetonitrile[a]**

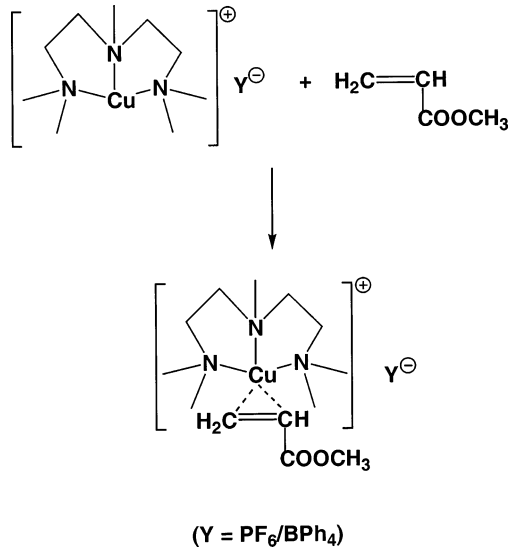
| Cu(I) complex | EBriB | $Rel_{RX}$ | $Rel_{L/A^-}$ | MBrP | $Rel_{RX}$ | $Rel_{L/A^-}$ | tBBrP | $Rel_{RX}$ | $Rel_{L/A^-}$ |
|---|---|---|---|---|---|---|---|---|---|
| PMDETA/$PF_6^-$ | 1.93 | 32 | 7.9 | 0.19 | 3.1 | 10.5 | 0.061 | 1 | 11.3 |
| PMDETA/$Br^-$ | 1.78 | 30 | 7.3 | 0.17 | 3.0 | 9.7 | 0.060 | 1 | 11.1 |
| BDMAEE/$Br^-$ | 0.55 | 32 | 2.2 | 0.058 | 3.4 | 3.2 | 0.017 | 1 | 3.1 |
| bpy/$PF_6^-$ [b] | 0.44 | 35 | 1.8 | 0.041 | 3.4 | 2.2 | 0.012 | 1 | 2.3 |
| bpy/$Br^-$ [b] | 0.24 | 45 | 1 | 0.018 | 3.3 | 1 | 0.0054 | 1 | 1 |

[a] Temperature = 35 °C, $[Cu(I)]_0 = [PMDETA]_0 = [BDMAEE]_0 = 20$ mmol/L, $[TEMPO]_0 = 10$ mmol; $[RX]_0 = [EBriB]_0 = [MBrP]_0 = [t\text{-}BBrP]_0 = 1$ mmol/L. $Rel_{RX}$ = relative rates of $k_{act}$ of alkyl bromides for same ligand/counterion system. $Rel_{L/A^-}$ = relative rates of $k_{act}$ of different ligands/counterions for same alkyl bromide. [b] Data from ref 22.

**Scheme 3. Structure of the (a) [Cu(PMDETA)Br] and (b) [Cu(PMDETA)]$^+$PF$_6$− Complexes**




**Scheme 4. Monomer Complexation through Open Coordination Site in [Cu(PMDETA)]$^+$PF$_6$− Complexes**




less polar solvent mixtures (Figure 8 and Table 1). Furthermore, in less polar solvent mixtures and acetonitrile, the values of $k_{act}$ were 1.1 times larger for $PF_6^-$ compared to $Br^-$ counterion. However, in MA, the activation rate constants for $Br^-$ was 1.9 times larger than that for $PF_6^-$ counterion (Table 1). A strong decrease in $k_{act}$ for $PF_6^-$ counterion in MA could be assigned to the monomer coordination to [Cu(PMDETA)]$^+PF_6^-$ (Scheme 4). The monomer coordination occurs via $\pi$-bond formation through an empty coordination site of an ionic [Cu(PMDETA)]$^+PF_6^-$ complex.[48]

To reach a deeper understanding of the coordinating ability of the monomer to the copper complexes, activation rate constants were determined using various solvent mixtures with MA (Table 1). In pure acetonitrile, $k_{act}$ was decreased in the following order: $BPh_4^- > PF_6^- > Br^-$. With the addition of MA (11.9 wt %), activation rate constants were decreased by 2.3, 2.2, and 1.2 times respectively for $BPh_4^-$, $PF_6^-$, and $Br^-$ counterions and followed the order $Br^- > BPh_4^- > PF_6^-$. The monomer coordination through an open coordination site of [Cu(PMDETA)]$^+Y^-$ complex (Y = $PF_6$/$BPh_4$) generates

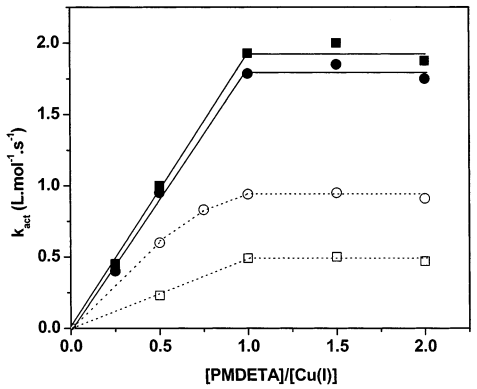



**Figure 11.** Plot of $k_{act}$ as a function of increasing PMDETA concentration at constant Cu(I) concentration of EBriB in acetonitrile (—) for $PF_6^-$ (■) and $Br^-$ (●) and in MA (· · ·) for $PF_6$ (□) and Br (○) counterions at 35 °C. $[EBriB]_0 = 1$ mmol/L; $[Cu(I)]_0 = 20$ mmol/L, $[TEMPO]_0 = 10$ mmol/L; [trichlorobenzene]$_0 = 5$ mmol/L.

the [Cu($\pi$-MA)(PMDETA)]$^+PF_6^-$ complex.[48] As a result of this, the bromine atom transfer process from alkyl bromide was hindered, resulting in the decrease of $k_{act}$. On the contrary, the neutral [Cu(PMDETA)Br] complex reacts efficiently with alkyl bromide due to weaker MA coordination, resulting in higher values of $k_{act}$ compared to that for $PF_6^-/BPh_4^-$. This observation also points out the neutral complex, [Cu(PMDETA)Br], as the dominating structure at [PMDETA]/[CuBr] > 1/1.

In acetonitrile the values of $k_{act}$ were 1.1 times larger for $PF_6^-$ compared to $Br^-$ counterion, and they remained constant at higher [PMDETA]/[Cu(I)] ratio (>1/1). In MA, the values of $k_{act}$ also remained constant for [PMDETA]/[Cu(I) > 1/1. The decrease in $k_{act}$ for both the counterions in MA compared to acetonitrile was assigned to the decrease in polarity of the reaction medium. Furthermore, the additional decrease in $k_{act}$ (1.9 times) for $PF_6^-$ counterion compared to $Br^-$ was attributed to the MA coordination (Figure 11).

**Effect of Solvent Polarity.** There was some effect of polarity of solvents/monomer as exemplified by the decrease in activation rate constants for $Br^-$ counterion with the decrease in polarity of the solvents/monomer. To better understand polarity effects, $k_{act}$ for $PF_6^-$ counterion was determined in the presence of ethyl acetate, a solvent of nearly the same polarity as MA (Table 3). In presence of mixtures with 11.3 and 53.4 wt % ethyl acetate, activation rate constants decreased by 1.3 and 1.7 times, respectively, compared to that for pure acetonitrile. However, in the presence of the same quantity of MA, they were lowered by 2.2 and 3.5 times, respectively. In pure MA, the $k_{act}$ decreased even more (3.9 times). The $k_{act}$ was not determined in pure ethyl acetate due to heterogeneity of the reaction mixture leading to nonlinear kinetic plots. The larger decrease of $k_{act}$ in MA compared to ethyl acetate can be explained

**Table 3. Activation Rate Constants in Various Solvents and MA at [PMDETA]/[Cu(I)$PF_6$] Ratio ~ 1/1[a]**

| reaction medium | $k_{act}$ (L $mol^{-1}$ $s^{-1}$) |
|---|---|
| acetonitrile | 1.93 |
| acetonitrile (88.7 wt %) with ethyl acetate (11.3 wt %) | 1.51 |
| acetonitrile (46.6 wt %) with ethyl acetate (53.4 wt %) | 1.21 |
| acetonitrile (47.7 wt %) with toluene (52.3 wt %) | 1.13 |
| acetonitrile (88.1 wt %) with MA (11.9 wt %) | 0.86 |
| acetonitrile (45.1 wt %) with MA (54.9 wt %) | 0.55 |
| MA | 0.49 |
| ethyl acetate (48.5 wt %) with MA (51.5 wt %) | 0.42 |
| toluene (47.5 wt %) with MA (52.5 wt %) | 0.40 |
| acetonitrile (89.0 wt %) with t-BA (11.0 wt %) | 0.80 |

[a] Temperature = 35 °C, $[EBriB]_0$ = 1 mmol/L; $[Cu(I)PF_6]_0$ = $[PMDETA]_0$ = 20 mmol/L, $[TEMPO]_0$ = 10 mmol.

by the formation of the $[Cu(\pi\text{-MA})(PMDETA)]^+PF_6^-$ complex through monomer coordination. In ethyl acetate and toluene, the activation rate constants decreased respectively by 1.3 and 1.4 times in the presence of MA as compared to acetonitrile (Table 3). In more polar media some contribution of the outer-sphere electron-transfer process (eq 4) in addition to the inner-sphere electron-transfer process (eq 5) could be postulated. In addition, free ions may be more reactive than ion pairs in more polar solvents. *tert*-Butyl acrylate (t-BA) (Table 3) has similar effect on $k_{act}$ as MA.

$$R{-}X + Mt^zL_n \rightleftharpoons RX^{\bullet -} + Mt^{z+1}L_n \rightleftharpoons R^\bullet + X{-}Mt^{z+1}L_n \quad (4)$$

$$R{-}X + Mt^zL_n \rightleftharpoons [R{---}X{---}Mt^zL_n] \rightleftharpoons R^\bullet + X{-}Mt^{z+1}L_n \quad (5)$$

**Effect of Ligand**. The ligands tune the electronic, steric, and solubility properties of ATRP catalysts. The data obtained here are for three ligands having different structures and coordinating atoms (Figure 1). The relative rates of activation of alkyl bromides for the three ligands follow order PMDETA (8) > BDMAEE (2) > bpy (1) (Table 2). The activation rate constant was decreased 4 times by substituting one "N" by "O" coordinating atom. The ligand with three nitrogen atoms (PMDETA) activates the ATRP process 4 times faster compared to ligands having two "N" atoms and one "O" atom (BDMAEE). The complex with bpy ligand was 8 and 2 times less active than PMDETA and BDMAEE complexes, respectively. Furthermore, the value of $k_{act}$ was 1.8 times larger for $PF_6^-$ than $Br^-$ counterion when bpy was used as the coordinating ligand. For PMDETA ligand, the values of $k_{act}$ were 1.1 times larger for $PF_6^-$ compared to $Br^-$ counterions. Notably, the effect of counterion on $k_{act}$ was less significant for PMDETA ligand. The activity of copper complexes having different ligand/counterion in acetonitrile decreased in the following order: PMDETA/$PF_6^-$ > PMDETA/$Br^-$ > BDMAEE/$Br^-$ > bpy/$PF_6^-$ > bpy/$Br^-$ (Table 2).

**Effect of Alkyl Bromides.** The activation rate constants of alkyl bromides decreased in the following order: EBriB ≫ MBrP > t-BBrP (Figure 1). The relative ratios of $k_{act}$ showed that EBriB and MBrP were ~35 ± 5 and 3 times, respectively, more reactive than t-BBrP. Irrespective of the solvent polarity, monomer, ligands, and counterions (Table 3), the rates of activation of alkyl bromides primarily depend on two factors: (1) the stability of the formed redicals 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, the *tert*-butyl group slows down the activation 3 times in comparison with the methyl groups. This suggest that the rate-determining step should involve the bimolecular process of the Br atom transfer from alkyl halide to copper (eq 5) through an inner-sphere electron transfer (ISET). However, in more polar reaction media there may be some contribution of the OSET process or free ions may be more reactive than ion pairs.

## Conclusions

A detailed investigation on the effect of [PMDETA]/[Cu(I)] ratio, monomer, solvent polarity, counterion, ligand, and alkyl bromide on the $k_{act}$ revealed that it is necessary to adjust the reaction condition for the successful ATRP. To achieve the maximal values of $k_{act}$, the [PMDETA]/[Cu(I)] ratio ~1/1 should be maintained for $Br^-$ in polar and for $PF_6^-$ in more polar and less polar and monomer media. However, it may be sufficient to maintain the ratio of [PMDETA]/[Cu(I)Br] between 0.5/1 and 1/1 in the presence of monomer to avoid chain-transfer reactions of propagating radicals to free PMDETA ligands.[49,50] The values of $k_{act}$ increased with polarity of the reaction medium. The formation of the $[Cu(\pi\text{-MA})(PMDETA)]^+PF_6^-$ complex was anticipated by the monomer coordination through the open coordination site of the $[Cu(PMDETA)]^+Y^-$ (Y = $PF_6$/$BPh_4$) complex. The values of $k_{act}$ were higher for ligands with three nitrogen atoms compared to the ligands containing two nitrogen atoms and one oxygen atom. The relative rates of $k_{act}$ of alkyl bromides decreased in the following order: EBriB (30) ≫ MBrP (3) > t-BBrP (1) irrespective of the nature of solvent polarity, monomer, counterions, and ligands. In the absence of monomer, the $k_{act}$ for different ligand/counterion decreased in the following order: PMDETA/$PF_6^-$ > PMDETA/$Br^-$ > BDMAEE/$Br^-$ > bpy/$PF_6^-$ > bpy/$Br^-$. Similar studies at different temperatures for various alkyl halides and ligands on $k_{act}$, $k_{deact}$, and $K_{eq}$ are necessary to comprehend the controlled ATRP process.

## Experimental Section

**Materials.** Cu(I)Br (99.999%, Aldrich) was purified according to the published procedure.[51] 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. $CuPF_6$ was synthesized using the procedure reported earlier.[52] Ethyl 2-bromoisobutyrate (EBriB) (99%, Aldrich), methyl 2-bromopropionate (MBrP) (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), bis(2-dimethylaminoethyl) ether (BDMAEE) (98+%, TCI America), and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) (99+%, Aldrich) were used as received. Acetonitrile (Aldrich, 99+%, HPLC grade), ethyl acetate (99+%, Aldrich), and toluene (99+%, Aldrich) were distilled before use. Methyl acrylate (MA) (99%, Aldrich) and *tert*-butyl acrylate (t-BA) (99%, Aldrich) were distilled under reduced pressure over $CaH_2$ and stored at −10 °C before use.

**Activation Rate Constant Measurements.** Stock solutions of EBriB, MBrP, and t-BBrP were prepared by adding 1 mmol/L of the corresponding reactant along with trichlorobenzene (5 mmol/L) and 10 mmol/L of TEMPO in acetonitrile in a 10 mL volumetric flask. Similarly, a 20 mmol/L stock solution of PMDETA/BDMAEE was prepared in acetonitrile. In a Schlenk flask, 20 mmol/L of Cu(I)Br was taken and the flask was degassed and back-filled with $N_2$ three times. 20 mmol/L of PMDETA/BDMAEE stock solution 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, EBriB, MBrP, and tBBrP, trichlorobenzene, 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 the GC analysis for time zero. The reaction was carried out at 35 °C under constant stirring. The sample was taken at timed intervals, and the consumption of alkyl bromide with time was analyzed by gas chromatography (GC). Similar experiments were conducted for $Cu^+PF_6^-$ systems and in the presence of solvents of different polarity and monomer. The activation rate constant measurement for $Cu(I)BPh_4$ was executed in situ by adding $NaBPh_4$ (20 mmol/L) to the homogeneous solution of Cu(I)Br/PMDETA (20 mmol/L). The mixture was stirred for 5 min before adding solutions of alkyl bromides. 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 (electron capture detector, ECD) detector. The ECD detector is very sensitive to alkyl halides and governed by radiation ($\beta$-ray) from the $^{63}Ni$ source sealed in the ECD cell ionized by an inert gas ($N_2$). The injector and detector temperature was kept constant at 250 °C. The temperature program for the GC column was as follows: initial temperature, 45 °C, 0 min; ramp, 5 °C/min; final temperature, 200 °C.

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