Macromolecules **1997,** *30,* 6507−6512 **6507**

Kinetic Study of the Homogeneous Atom Transfer Radical Polymerization of Methyl Methacrylate

Jen-Lung Wang, Thomas Grimaud, and Krzysztof Matyjaszewski*

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

Received May 7, 1997; Revised Manuscript Received August 1, 1997[⊗]

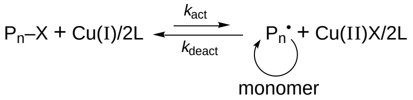
ABSTRACT: The homogeneous controlled/"living" radical polymerization of methyl methacrylate (MMA) using the atom transfer radical polymerization (ATRP) with CuCl/4,4′-di(5-nonyl)-2,2′-bipyridine catalytic system and diphenyl ether as the solvent generated well-defined polymers with polydispersities $M_w/M_n \leq 1.2$. The evolution of the molecular weights of the polymers follows the ratio of the mass of the consumed monomer to the initial initiator concentration. The rate of polymerization follows first-order kinetics with respect to the decrease of monomer concentration. The polymerization rate reaches a maximum when the ratio of ligand-to-Cu^ICl is one-to-one. ATRP of MMA shows first-order kinetics with respect to both Cu^ICl and the initiator, alkyl or sulfonyl chloride. The rate of polymerization did not obey simple negative first-order kinetics with respect to the concentration of $Cu^{II}Cl$, partially due to a persistent radical effect, which resulted in the increase of [$Cu^{II}Cl$] in the initial stage of polymerization. Thermodynamic data and activation parameters for the solution ATRP of MMA are reported.

Introduction

Free-radical polymerization is the most important commercial process for the preparation of high molecular weight polymers. A wide variety of monomers can be polymerized or copolymerized under simple experimental conditions.[1] One of the drawbacks of the conventional radical polymerization, however, is its lack of control in the molecular weights and polydispersities of the resulting polymers due to the chain termination and transfer processes. This excludes conventional radical polymerization from the synthetic methods for well-defined polymers with low polydispersities and complex architectures.[2]

In recent years, synthesis of well-defined polymers using radical polymerization has become a reality. Analogous to controlled/"living" cationic polymerization,[3] radical polymerization can also be controlled under conditions where a fast, dynamic equilibrium between the active and dormant species exists and only a low and stationary concentration of the active species is maintained in the reaction system.[4,5] Several well-controlled radical polymerization systems have been developed based on this concept, including nitroxyl radical-mediated polymerization of styrenes,[6,7] ruthenium/aluminum-based polymerizations of methacrylates,[8] and Co(II)-mediated polymerization of acrylates.[9]

One of such controlled/"living" radical polymerizations is atom transfer radical polymerization (ATRP).[10] In a similar fashion to atom transfer radical addition,[11] a copper(I) complex, CuX/2L (X = Cl or Br, and L = 2,2′-bipyridine or a 4,4′-disubstituted-2,2′-bipyridine) acts as a reversible halogen atom transfer reagent between the active and dormant polymer chains (eq 1). It is this dynamic equilibrium which is responsible for the control of the polymerization.



$$P_n\text{–}X + Cu(I)/2L \underset{k_{deact}}{\overset{k_{act}}{\rightleftarrows}} P_n^{\bullet} + Cu(II)X/2L \qquad (1)$$

monomer

It has been recently demonstrated that the homogeneous ATRP can be successfully applied to the synthesis of polystyrene[12] and poly(methyl methacrylate)[13] (PMMA) with well-controlled molecular weight and narrow molecular weight distribution. To continue our effort in understanding the mechanistic aspect of the polymerization process, we report here a kinetic investigation of the homogeneous ATRP of methyl methacrylate (MMA) including the reaction order of each component, the effect of Cu^I to ligand ratio on the rate of polymerization, the role of the deactivator (Cu^{II} halides), and the temperature dependence on the rate of polymerization.

Results and Discussion

The typical homogeneous ATRP of MMA using *p*-toluenesulfonyl chloride, benzhydryl or alkyl halide as initiator and Cu^IX (X = Cl, Br) as catalyst has been described previously.[13] The homogeneity of the system is achieved by using the ligand, 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy), which forms soluble Cu^I complexes in the solution.[12] Commercially available 2,2′-bipyridine has also been used as a ligand in ATRP of MMA. It leads to much broader polydispersity than does dNbpy, presumably due to the heterogeneous reaction condition.[14] In addition to solubility, the bipyridine ligands affect both Cu^I and Cu^{II} species electrochemically and sterically and therefore assure the appropriate position of the equilibrium for ATRP and the corresponding chemoselectivities. Polymerization of MMA proceeds through first-order kinetics with respect to monomer concentration as shown in Figure 1. The number-averaged molecular weight of the polymer increases with conversion (Figure 2). The molecular weight determined experimentally using GPC agrees with the theoretical molecular weight calculated by eq 2 and

$$M_n = ([M]_0 - [M]_t/[In]_0) \qquad (2)$$

polydispersities of the polymers remained low ($M_w/M_n < 1.2$) throughout the polymerization.

The general conclusions from Figures 1 and 2 are that the polymerization is fastest with ethyl 2-bromoisobutyrate (iBuBr)/CuBr as the catalytic system and slowest with benzhydryl chloride Ph_2CHCl/CuCl as the catalyst in ATRP of MMA. Molecular weights follow approximately the theoretical values; however, RBr/CuBr as

---

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.

S0024-9297(97)00636-0 CCC: $14.00

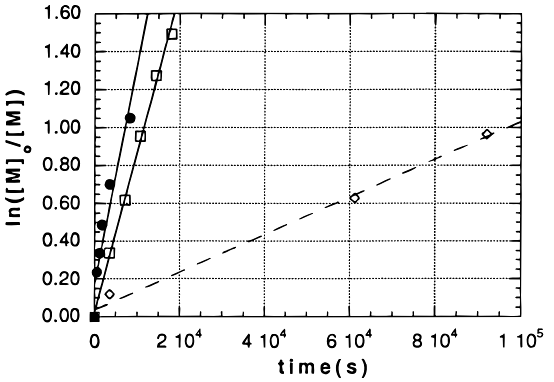


Figure 1. Conversion and ln($[M]_0/[M]$) plots versus time in solution polymerization of MMA in diphenyl ether at 90 °C with $[R-X]_0 = 0.023$ M, $[CuX]_0 = 0.0115$ M, and $[dNbpy] = 0.023$ M. Initiation System (●): R−X = Ethyl 2-Bromoisobutyrate, CuX = Cu(I)Br. (□): R−X = *p*-Toluenesulfonyl Chloride, CuX = Cu(I)Cl. (◇): R−X = Benzhydryl Chloride, CuX = Cu(I)Cl.

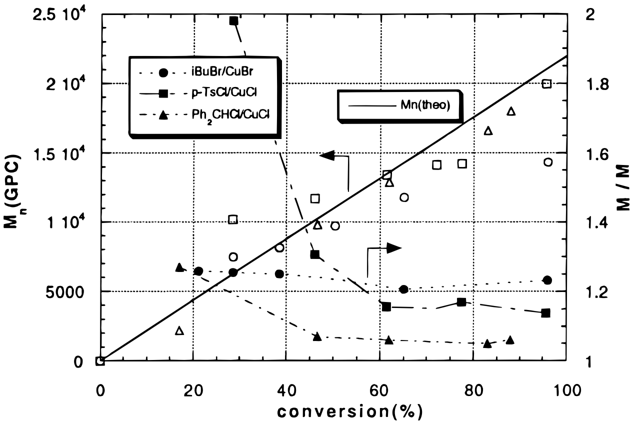


Figure 2. Dependence of molecular weight and polydispersities on conversion in solution polymerization of MMA in diphenyl ether at 90 °C with $[R-X]_0 = 0.023$ M, $[CuX]_0 = 0.0115$ M, and $[dNbpy] = 0.023$ M. Initiation system (○): R−X = ethyl 2-bromoisobutyrate, CuX = Cu(I)Br. (□): R−X = *p*-toluenesulfonyl chloride, CuX = Cu(I)Cl. (△): R−X = benzhydryl chloride, CuX = Cu(I)Cl. Open symbols represent M_n(GPC) and filled symbol represents polydispersities.

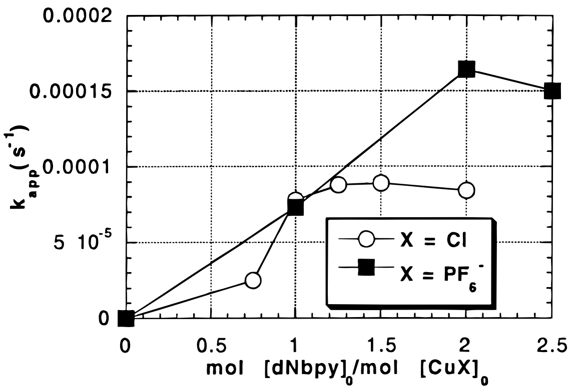
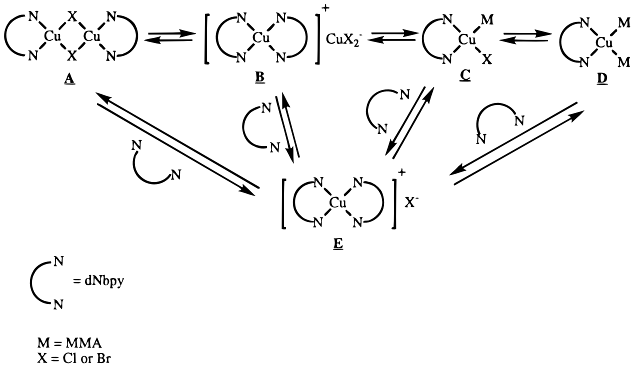


Figure 3. Plot of k_{app} as a function of increasing ligand concentration (dNbpy) at constant CuX (X = Cl or PF_6) concentration for the solution ATRP of MMA in diphenyl ether at 90 °C. $[p\text{-TsCl}]/2 = [CuCl] = 0.0115$ M.

Scheme 1



catalysts give some deviation at higher conversion, presumably due to the transfer process. Polydispersities decrease with conversion for RCl/CuCl systems, but they are the lowest for Ph_2CHCl system. The iBuBr/CuBr system gives initially the lowest polydispersities which become highest at the end of the reaction, again presumably due to some side reaction.

Although the detailed discussion of these trends is beyond the scope of this paper, the phenomena observed in Figures 1 and 2 can be explained by the energetics of C−X and Cu−X bonds, equilibrium and termination reactions at the initiation stage, and some side reactions for C−Br species. Both *p*-toluenesulfonyl chloride and Ph_2CHCl are easily activated to form high concentrations of radicals. However, *p*-toluenesulfonyl radicals do not terminate bimolecularly, since the formation of α,α-disulfones is relatively slow.[15] Thus, they can only add to the monomer and initiate polymerization. On the other hand, benzhydryl radicals generated during the initiation step can couple quickly to form tetraphenylethanes, reducing the initiator efficiency, leading to deviation of the molecular weight of polymers. Simultaneously, an excess of the $Cu^{II}Cl_2$ is formed, resulting in a slower polymerization. Both undesired effects can be corrected by slow addition (in approximately 5 min) of the initiator to the reaction mixture. The slow addition of Ph_2CHCl generated a small amount of radicals which can add to the monomer without significant dimerization. The rate of polymerization, molecular weight, and polydispersity shown in Figures 1 and 2 were obtained by the slow addition of the initiator. Ethyl 2-bromoisobutyrate seems to be an efficient initiator. Since the bond strength of the C−Br bond is weaker than that of the C−Cl bond, the polymerization rate with the iBuBr/CuBr system is the fastest. Nevertheless, there are chain transfer/termination processes for RBr/CuBr systems which reduce the molecular weights of polymers at high conversion and also increase the polydispersities.

Beyond the initiation step, both of the Cl-based systems *p*-TsCl and Ph_2CHCl behave in a similar fashion in ATRP of MMA since the only difference is in the end group. Therefore, most of the results presented here for *p*-TsCl also apply to other efficient alkyl chloride initiators. Detailed effects of the structure of R−X on the efficiency of initiation for MMA polymerization will be presented in a future publication.[16]

The effect of the dNbpy/Cu^ICl ratio on the rate of polymerization has been investigated, and the result is shown in Figure 3. It appears that the rate of polymerization reaches the maximum with the ratio ligand/Cu^ICl = 1. The apparent rate constant of polymerization ($k_{app} = -d\ln[M]/dt$, *vide infra*) increases sharply as the $[L]_0/[Cu^ICl]_0$ ratio approaches 1. For ATRP of styrene, 2 equiv of ligand/CuBr or CuCl is necessary to achieve the maximum rate of polymerization.[17] As a result, a monomeric copper complex $L_2Cu^+X^-$ was proposed as the active catalyst in ATRP of styrene. Figure 3 suggests a different structure of the CuCl/dNbpy complex in MMA polymerization and deserves an explanation.

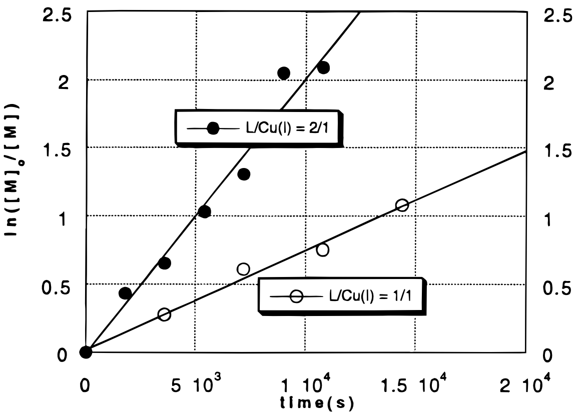
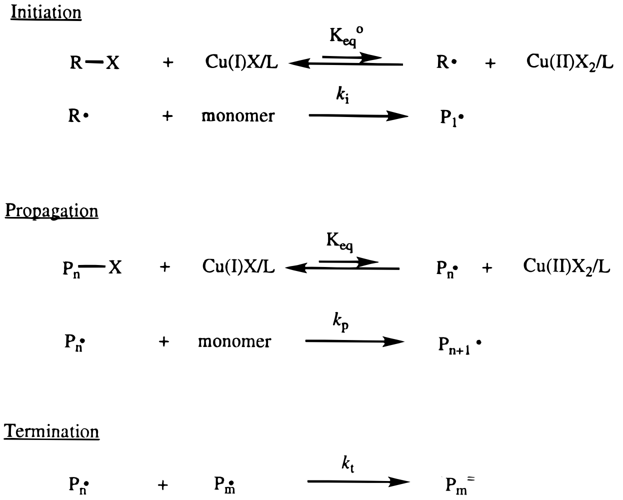


Figure 4. Semilogarithmic kinetic plots for the solution ATRPs of methyl methacrylate at 90 °C using different ratios of [$CuPF_6(CH_3CN)_4$]/[dNbpy]. [MMA] = 4.67 M, [p-TsCl]$_0$ = 0.023 M, and [$CuPF_6(CH_3CN)_4$] = 0.0115 M. Slopes for [$CuPF_6(CH_3CN)_4$]/[dNbpy] = 1 (open) and 2 (filled) are 7.30×10^{-5} and 2.1×10^{-4} s^{-1}, respectively.

Scheme 1 illustrates the possible structures for Cu^I halide/dNbpy complexes during polymerization. It has been reported that complexes of a one-to-one Cu^I halide with bidentate ligands such as bpy or phenanthroline are either halogen-bridged dimers, $LCu(\mu{-}X)_2CuL$ (**A**), or a two-to-one ligand-to-copper(I) with a dihalocuprate counteranion, $(L_2Cu^+)CuX_2^-$ (**B**).[18-20] CuX_2^- should not be the active catalyst during polymerization since ATRP using $N(n{-}Bu)_4{}^+CuX_2^-$ shows no control of polymerization. Munakata has suggested that the structures of Cu^I halide/bpy complexes in solution depend on the polarity of the solvent.[21] For example, in a polar solvent such as ethanol, the monomeric form $L_2Cu^+X^-$ (**E**) predominates while the bridged dimer $LCu(\mu{-}X)_2CuL$ exists in a less polar solvent such as acetone. To evaluate if the bridged dimer is the active species, a different Cu^IX catalyst, $CuPF_6$/dNbpy, was used in ATRP of MMA. Cu^IPF_6 cannot form a bridged dimer; therefore, the rate of polymerization is expected to increase for the Cu^I/ligand up to 2 since only half of the CuL_2 could be generated for a $[dNbpy]_0/[Cu^I]_0$ ratio of 1. The result is shown in Figure 4. The rate of polymerization for $[L]_0/[CuPF_6(CH_3CN)_4]_0 = 2/1$ is approximately 2 times higher than that for 1/1. This implies that for $Cu^I = CuPF_6$, $L_2Cu^+X^-$ (**E**) is the active form while $LCu(\mu\text{-}X)_2CuL$ is the possible active catalytic species for $Cu^I = CuCl$. However, one cannot rule out the possible coordination of one or two MMA molecules with Cu^I species so that only 1 equiv of dNbpy is sufficient to satisfy the coordination sphere of Cu^I species (**C** and **D** in Scheme 1) or rather stable CuX_2^- anion in MMA solution (**B**).

The colors of the reaction mixtures also indicate that different species are involved when polymerizations of various monomers are catalyzed by $CuPF_6$ and CuCl, respectively. When Cu^I halides are used as the catalyst in ATRP of styrene or MMA, the color of the Cu^I halide/dNbpy complex is light reddish brown at room temperature, while in the acrylate monomer, the solution shows yellowish color at ambient temperature. The colors of all these solutions containing Cu^I complexes turn to dark red-brown at reaction temperatures (≥90 °C). When $CuPF_6$ is used as a catalyst in ATRP of the three monomers mentioned above, the color of the solution is dark red-brown already at room temperature at comparable concentration. A detailed spectroscopic study on the structures of active metal complexes in ATRP using UV spectroscopy and electron paramagnetic resonance (EPR) spectroscopy is currently conducted in our group and will be reported in the future.

Scheme 2



The discussion on the rate of polymerization as a function of the ligand/Cu^I ratio only provides an apparent picture for the active structures of the catalysts, and the solution chemistry of the Cu^I species could be far more complicated. For example, the rate acceleration using $CuPF_6$ as the catalyst depends on the monomer used. For styrene and MMA, the acceleration is approximately two-fold while the rate of polymerization increases by 30 times for methyl acrylate.[22] The different solubilities of Cu^I/dNbpy and Cu^{II}/dNbpy species in various monomers will also affect the rate of polymerization. The less Cu^{II}/dNbpy complex is solubilized in the solution, the faster the rate of polymerization will be (*vide infra*). The proportion of structures **A**–**E** therefore depends on Cu–X bond strength, solvent, monomer, temperature, and concentrations of all the components in the solution. A complete discussion concerning the structures of Cu^I complexes in ATRP is beyond the scope of this paper, and we shall use "Cu^I" or "Cu^I/L" to describe the active catalyst in the following discussion. For an L/Cu^I ratio of 1, the solution may take an hour to become homogeneous while Cu^I halide dissolves much faster when an excess amount of ligand is used. Therefore, we used an L/Cu^I ratio of 2 in the following experiments to accelerate the dissolution process and used the same condition as for polymerization of styrene and methyl acrylate.

The reaction mechanism for ATRP is proposed in Scheme 2, which consists of the atom transfer equilibrium followed by the addition of radicals to olefinic monomers at both initiation and propagation steps and the termination step. Assuming a fast initiation, insignificant termination reactions and a steady concentration of propagating radicals in Scheme 2, the following rate laws were derived (eqs 3 and 4). A fast

$$K_{eq} = \frac{k_{act}}{k_{deact}} = \frac{[P^\bullet][Cu(II)X]}{[Cu(I)][PX]} \tag{3}$$

$$R_p = k_{app}[M] = k_p[P^\bullet][M] = k_pK_{eq}[In]\frac{[Cu(I)]}{[Cu(II)X]}[M] \tag{4}$$

equilibration is a necessary condition to observe the low polydispersity in controlled/"living" free-radical polymerization.[17]

As shown in Figure 1, ln($[M]_0/[M]$) remained a linear relationship with time which demonstrates that the

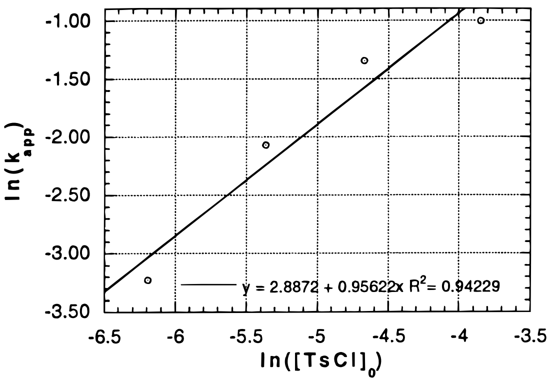


Figure 5. Dependence of k_{app} on the concentration of the initiator *p*-toluenesulfonyl chloride for the solution ATRP of methyl methacrylate in diphenyl ether. [MMA] = 4.67 M; $[CuCl]_0 = [dNbpy]_0/2 = 0.0115$ M. Slope = 0.96.

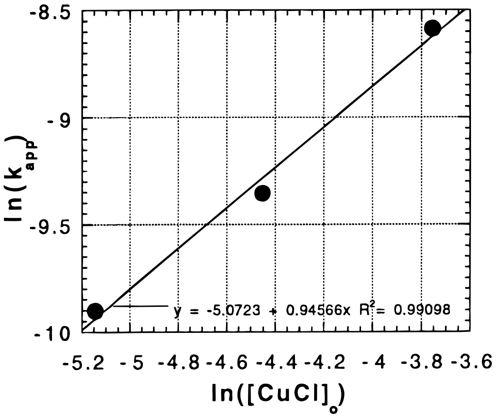


Figure 6. Dependence of k_{app} on the concentration of CuCl for the ATRP of methyl methacrylate in diphenyl ether: [MMA] = 4.67 M, [*p*-TsCl] = 0.023 M, and $[CuCl]_0 = [dNbpy]_0/2$. Slope = 0.94.

polymerization was first order with respect to monomer concentration and that the concentration of radicals during the polymerization was constant. The steady-state concentration of the propagating radicals during the solution polymerization can then be estimated by combining the value of k_{app} in eq 4 ($k_{app} = d\ln[M]/dt = 8.6 \times 10^{-5}$ s^{-1}) and the known rate constant of radical propagation for methyl methacrylate ($k_p = 1.616 \times 10^3$ M^{-1}s^{-1} at 90 °C).[23] The calculated concentration of propagating radicals is 5.3×10^{-8} M in 1/1 (v/v) MMA/diphenyl ether solution which is sufficiently low to prevent a significant chain termination.

A plot of $\ln(k_{app})$ versus $\ln[RX]_0$ showed that the rate of polymerization is first order (slope = 0.96) with respect to the concentration of the initiator (Figure 5). A plot of $\ln(k_{app})$ vs $\ln[CuCl]_0$ (Figure 6) showed that the rate of polymerization also follows first order (slope = 0.95) with respect to the concentration of the Cu^I catalyst. The results agree with our earlier report that the rate of ATRP for styrene is first order in $[Cu^IX]_0$ and $[RX]_0$.[17]

The kinetic relationship between k_{app} and $[Cu^{II}X_2]_0$ was studied by adding a known amount of $CuCl_2$/2dNbpy to the sample mixture before polymerization, and the results are shown in Figure 7. The result is similar to the study on the effect of $[Cu^{II}X_2]_0$ on the rates of ATRP of styrene,[17] only the effect of $[Cu^{II}]$ on the rate is even greater. A plot of $\ln(k_{app})$ vs $[Cu^{II}Cl_2]$ is not linear with the slope of −1, but instead reduces the value of k_{app} only slightly when $[Cu^{II}Cl_2] \leq 10$ mol % of Cu^ICl. Not until $[Cu^{II}Cl_2]_0 > 10\%$ that the rate of polymerization decreases dramatically and becomes very small as $[Cu^{II}Cl_2]_0$ equals 40%. This observation can be rationalized by the same argument that the radical coupling is an important process in the initial stage of the polymerization even though it is negligible during the polymerization process. At the start of the polymerization, the concentrations of $Cu^{II}X$ species and the radicals are zero. As Cu^I reacts with the initiator, the concentrations of both $Cu^{II}X$ and radicals increase. Therefore, during the initial stage of polymerization, the concentration of the radicals is large enough that the rate of deactivation ($=k_{deact} \times [Cu^{II}Cl][R^\bullet]$) is much slower than the rate of termination ($=k_t[R^\bullet]^2$). As termination proceeds, the concentration of Cu^{II} increases which leads to the decrease in concentration of radical $R^\bullet$ since the product of $[Cu^{II}Cl][R^\bullet]$ should be nearly constant ($=K_{eq}[RX][Cu^ICl]$). The rate of termination for the radicals continues to decrease until the concentration of $[Cu^{II}X]$ reaches a maximum where the termination of the radicals is negligible and controlled/living polymerization starts to occur. This “persistent radical effect” has been described by Fischer[24] and applied to organic radical reactions. The “self-adjustment” process could explain why the rate of polymerization is nonlinear with respect to $[Cu^{II}X]_0$ (Figure 7). If the amount of added $[Cu^{II}X]$ is not sufficient to reach the steady-state concentration of radicals (10^{-7}–10^{-8} M), more $Cu^{II}X$ species are generated at the expense of Cu^I and the initiator/active chain radicals. Since the concentrations of Cu^I species and the initiator/dormant chain are always much greater than the concentration of $Cu^{II}X$, the decrease in concentration of Cu^I and initiator/dormant chains due to the formation of $Cu^{II}X$ initially is relatively small. Therefore the effect on the kinetics due to the small change of $[Cu^{II}X]$ is not observed. Thus, the radical coupling only affects the reaction order of $Cu^{II}X$ when it is present in low concentration.

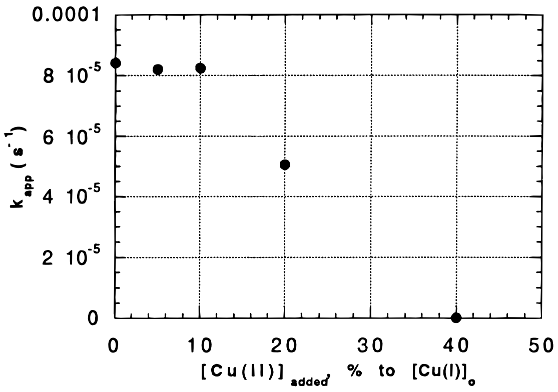


Figure 7. Plot of k_{app} as a function of added $CuCl_2$ for the solution ATRP of methyl methacrylate in diphenyl ether at 90 °C. [MMA] = 4.67 M, [*p*-TsCl] = 0.023 M, and $[CuCl]_0 = [dNbpy]_0/2 = 0.0115$ M.

The large decrease in the rate of polymerization caused by the addition of $[Cu^{II}]$ is also worth noting. In ATRP, the effect of $[Cu^{II}]_{added}$ on the rate of polymerization appears to be dependent on the monomer used. For MMA, as shown in Figure 7, the rate deceleration is larger than 10-fold as $[Cu^{II}]_{added}$ reaches 40% of the initial $[Cu^I]_0$. In the ATRP of styrene, the rate of polymerization decreases by a factor of 2 to 3 as $[Cu^{II}]_{added}$ increases to approximately 20% of $[Cu^I]_0$. ATRP of methyl acrylate[25] shows that the rate of polymerization follows inverse first order with respect to $[Cu^{II}]_{added}$ while in acrylonitrile, $[Cu^{II}]_{added}$ does not affect the rate of polymerization as $[Cu^{II}]_{added}$ reaches up to 25% of $[Cu^I]_0$. Our preliminary UV studies on the

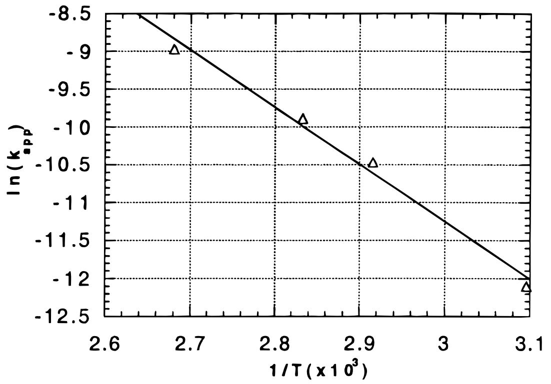


Figure 8. Effect of temperature on k_{app} for the *p*-TsCl/CuCl-mediated ATRPs of methyl methacrylate in diphenyl ether. [*p*-TsCl] = 0.023 M and $[CuCl]_0 = [dNbpy]_0/2 = 0.0115$ M. Slope = −7.56.

Cu^{II} halide/dNbpy complex in toluene in the presence of a Cu^{I} halide shows that the addition of Cu^{I} species to a Cu^{II} halide/dNbpy solution reduces the Cu^{II}/dNbpy complex absorption at $\lambda_{max} = 550$ nm significantly. An EPR study also suggests that Cu^{II} species interact with Cu^{I} species and lead to a possible mixed valence Cu^{II}/Cu^{I} complex with one or more structures. The formation of these possible Cu^{II}/Cu^{I} complexes depends on the monomer used. These observations suggest that the Cu^{II} species at high concentrations in the polymerization of MMA not only reduces the rate according to eq 4 but also deactivates the active Cu^{I} catalyst. The role of mixed valence Cu^{II}/Cu^{I} dimers in activation and deactivation of ATRP is currently under investigation.

The temperature effect on the rate of polymerization for a solution of the ATRP of methyl methacrylate was investigated, and the result is shown in Figure 8. As mentioned in the previous section, the concentration of $Cu^{II}X$ may have varied due to the radical coupling at the initial stage of polymerization and led to uncertainty in the determination of activation parameters. Therefore, 20% of $CuCl_2/2L$ was added prior to the reaction mixture to ensure the concentration of $Cu^{II}X$ remains constant under the polymerization conditions.

On the basis of the Arrehnius plot in Figure 8, the apparent activation energy was calculated $E^{\neq}_{app} = 15.0$ kcal/mol for *p*-TsCl/CuCl-initiated ATRP of methyl methacrylate. The activation energy for MMA propagation is known to be $E^{\neq}_{p} = 5.3$ kcal/mol.[23] The relation between the enthalpy of the equilibrium, the activation energy of propagation, and the apparent activation energy is shown in eq 5. The enthalpy of the equilibrium was therefore estimated to be $\Delta H° = 9.7$ kcal/mol for R-Cl/CuCl-initiated ATRP of methyl methacrylate.

$$\Delta H^{\circ}_{eq} = \Delta E^{\neq}_{app} - \Delta E^{\neq}_{prop} \qquad (5)$$

The equilibrium constant for R-Cl/CuCl-initiated ATRP of MMA at 90 °C was calculated using eq 4 and the kinetic data from polymerization in which 20 mol % of $Cu^{II}Cl_2/2L$ to $Cu^{I}Cl/2L$ was added to the sample before reaction. Thus, for a solution of the ATRP of MMA in diphenyl ether (50% v/v) with 0.5 mol % initiator and 1 mol % of $Cu^{I}Cl/2L$, the apparent rate constant was 8.6×10^{-5} s^{-1} and the calculated equilibrium constant was 7.0×10^{-7}. This leads to the estimated free energy of equilibrium $\Delta G° = 10.2$ kcal/mol at 90 °C. The free energy of equilibrium for phenylethyl chloride/CuCl-initiated ATRP of styrene has been estimated approximately $\Delta G° = 13.5$ kcal/mol at 110 °C.[17] The difference in equlibrium constants between these two different systems may be attributed to the differences between the energetics of -$CH_2C(CO_2CH_3)(CH_3)-Cl$ and $-CH_2CH(Ph)-Cl$ and respective radicals. However, the variation of structures of Cu^{I} and Cu^{II} species with monomers/solvents can also affect values of K_{eq}. The change of entropy of equilibrium can be calculated from values of the free energy and enthalpy of the equilibrium. For a solution of the ATRP of MMA, the calculated $\Delta S°$ is equal to −1.4 cal/mol·K.

Conclusions

The homogeneous atom transfer radical polymerization (ATRP) of methyl methacrylate using CuCl/R-X/4,4′-di(5-nonyl)-2,2′-bipyridine catalytic system yielded well-controlled polymers with polydispersities less than 1.2. The molecular weights of the resulting polymers are directly proportional to the ratio of the consumed monomer-to-initiator. The polymerization follows a first-order kinetics with respect to the decrease of monomer concentration. The rate of polymerization reaches a maximum when the ligand-to-metal ratio reaches 1 for CuCl but 2 for $CuPF_6$ using the dNbpy ligand. First-order kinetics are also observed with respect to $[Cu^{I}Cl]_0$ and $[initiator]_0$. A deviation from negative first-order kinetics with $[Cu^{II}Cl_2]_0$ is noticed and can be partially explained by a persistent radical effect, which resulted in an initial increase in $[Cu^{II}Cl_2]$ during the polymerization. The large decrease in the rate of polymerization by the addition of Cu^{II} species can originate in a possible deactivation of Cu^{I} species by a Cu^{II} halide. The apparent activation energy ($E^{\neq}_{app}$) for ATRP of MMA in 50% (v/v) diphenyl ether is found to be $E^{\neq}_{app} = 15.0$ kcal/mol, and the enthalpy of the equilibrium is estimated to be $\Delta H° = 9.7$ kcal/mol. The change of entropy ($\Delta S°$) for a solution ATRP of MMA is estimated to be $\Delta S° = -1.4$ cal/mol/K. The free energy of equilibrium for ATRP of MMA is calculated to be $\Delta G° = 10.2$ kcal/mol which is ∼3 kcal/mol less than that for the ATRP of styrene. It is rationalized by the differences between the bond energies of $CH_2C(CO_2CH_3)(CH_3)-Cl$ and $CH_2CH(Ph)-Cl$.

Experimental Section

Materials. Methyl methacrylate was passed through an alumina column, dried over molecular sieves, deaerated by argon bubbling, and stored under argon. Diphenyl ether was dried over molecular sieves and degassed with argon for 15 min before use. CuCl (98% Aldrich) and CuBr (98% Aldrich) were purified according to literature procedure.[26] $CuPF_6(CH_3CN)_4$ was synthesized according to the procedure by Hathaway.[27] *p*-Toluenesulfonyl chloride (Aldrich) was used as received. 4,4′-Di-(5-nonyl)-2,2′-bipyridyl [dNbpy] was prepared by the procedure described in previous articles from this group.[17]

General Procedures and Characterization. Monomer conversion during the solution of ATRP was determined by GC using diphenyl ether as the internal standard. Molecular weights and molecular weight distributions were measured using a Water 712 WISP autosampler and the following Phenogel GPC column: guard, linear, 1000 Å, and 100 Å. Molecular weights were calibrated using a poly(methyl methacrylate) standard.

General Procedure for the Solution ATRP of Methyl Methacrylate in Diphenyl Ether. A 25 mL Schlenk flask was charged with diphenyl ether (5 mL) and the appropriate amounts of $Cu^{I}X$ and ligands. The Cu^{I}/ligand solution was purged with argon for 15 min to deplete oxygen in the solution. Methyl methacrylate (4 mL, degassed by purging with argon for 15 min before use) was then added to the Schlenk flask via an argon-washed syringe, and the flask was immersed in an oil bath with a preset temperature at 90 °C. In a 5 mL round-bottom flask, the desired amount of *p*-toluenesulfonyl chloride was dissolved in 1 mL of deaerated methyl methacrylate. The TsCl/MMA solution was then cannulated to the Schlenk flask, and 0.5 mL of the reaction solution was withdrawn, mixed with THF, and used as the reference solution. At timed intervals, 0.5 mL aliquots of the solution were withdrawn under argon atmosphere and added to 1 mL of THF.

The THF solutions were injected into the GC and the percent conversions were calculated relative to the reference solution. The samples were then filtered through a small column of alumina and a 0.2 μm filter and then injected into the GPC for analysis.

Acknowledgment. Support by the Industrial Sponsors of ATRP Consortium at CMU is gratefully acknowledged. T.G. acknowledges additional support from Elf Aquitaine.

References and Notes

(1) Moad, G.; Solomon, D. H. *The Chemistry of Free-Radical Polymerization*; Pergamon: Oxford, 1995.
(2) Webster, O. *Science* **1991**, *251*, 887.
(3) Matyjaszewski, K. *Cationic Polymerizations*; Marcel Dekker: New York, 1996.
(4) Greszta, D.; Mardare, D.; Matyjaszewski, K. *Macromolecules* **1994**, *27*, 638.
(5) Matyjaszewski, K. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 769.
(6) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Trends Polym. Sci.* **1994**, *2*, 66.
(7) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11185.
(8) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.
(9) Wayland, B. B.; Poszmik, G.; Mukerjee, S. L.; Fryd, M. *J. Am. Chem. Soc.* **1994**, *116*, 7943.
(10) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.
(11) Curran, D. P. *Synthesis* **1988**, 489.
(12) (a) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866. (b) Percec, V.; Barboiu, B.; Neuman, A.; Ronda, J. C.; Zhao, M. *Macromolecules* **1996**, *29*, 3665.
(13) (a) Percec, V.; Barboiu, B. *Polym. Prepr.* (*Am. Chem. Soc. Div. Polym. Chem.*) **1997**, *38* (1), 733. (b) Grubbs, R. B.; Hawker, C. J.; Dao, J.; Frechet, J. M. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 270. (c) Matyjaszewski, K.; Grimaud, T. *Macromolecules* **1997**, *30*, 2216.
(14) Wang, J. S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901.
(15) da Silva Correa, C. M. M.; Waters, W. A. *J. Chem. Soc.* (*C*) **1968**, 1874.
(16) Wang, J.-L.; Grimaud, T.; Matyjaszewski, K. *Macromolecules*, in press.
(17) Matyjaszewski, K.; Patten, T. E.; Xia, J. *J. Am. Chem. Soc.* **1997**, *119*, 674.
(18) Hathaway, B. J. In *Comprehensive Inorganic Chemistry*; Pergamon: Oxford, 1987; Vol. 5.
(19) Healy, P. C.; Englehart, L. M.; Patrick, V. A.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1985**, 2541.
(20) Pallenberg, A. J.; Koenig, K. S.; Barnhart, D. M. *Inorg. Chem.* **1995**, *34*, 2833.
(21) Munakata, M.; Kitagawa, S.; Asahara, A.; Masuda, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1927.
(22) Davis, K.; O'Malley, J.; Paik, H.-J.; Matyjaszewski, K. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1997**, *38* (1), 687.
(23) Gilbert, R. G. et al. *Pure Appl. Chem.* **1996**, *68*, 1491.
(24) Fischer, H. *J. Am. Chem. Soc.* **1986**, *108*, 3925.
(25) Paik, H.-J.; Matyjaszewski, K. (*Am. Chem. Soc., Polym. Prepr. Div. Polym. Chem.*) **1996**, *37* (2), 274.
(26) Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1946**, *2*, 1.
(27) Hathaway, B. J.; Holah, D. G.; Postlethwaite, J. D. *J. Chem. Soc.* **1961**, 3215.

MA970636J