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Kinetic Investigation of the Atom Transfer Radical Polymerization of Methyl Acrylate

Kelly A. Davis, Hyun-jong Paik, and Krzysztof Matyjaszewski*

Center for Macromolecular Engineering, Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

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ABSTRACT: The kinetics of atom transfer radical polymerization (ATRP) of methyl acrylate (MA) is discussed. MA polymerizations were carried out under homogeneous conditions using CuBr/4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy) as the catalyst. Plots of $\ln([M]_o/[M])$ vs time and molecular weight evolution vs conversion showed a linear dependence, indicating a constant number of propagating species throughout the polymerization as well as a negligible contribution of termination or transfer reactions. The dependence of the rate of polymerization on the concentrations of initiator, catalyst, Cu(II), and temperature are presented. The equilibrium constant between active and dormant species, $K_{eq} = 1.2 \times 10^{-9}$ at 90 °C is much smaller than in the ATRP of styrene or methyl methacrylate. On the basis of an Arrhenius plot, the apparent enthalpy of activation for homogeneous ATRP of MA $\Delta H^{\ddagger}_{app} = 27.5$ kcal/mol corresponds to an enthalpy of equilibrium $\Delta H^0_{eq} = 23$ kcal/mol, which is much higher than in the ATRP of styrene or methyl methacrylate. Because halides can potentially create a bridged structure between two copper centers, a Cu(I) species with a complex counteranion that cannot bridge was used, $Cu(CH_3CN)_4{}^+PF_6{}^-$ ($CuPF_6$). The resulting apparent rate constant of polymerization under homogeneous conditions was approximately 40 times that of the corresponding CuBr/dNbpy catalyzed reaction. The apparent enthalpy of activation for the $CuPF_6$/dNbpy system was $\Delta H^{\ddagger}_{app} = 10.3$ kcal/mol, in contrast to the larger value found for the CuBr/dNbpy system. Possible reasons behind these unexpected results are discussed.

Introduction

Free radical polymerizations are generally poorly controlled, leading to high molecular weights early in the polymerization, high polydispersities, and poorly defined products. With the advent of controlled radical polymerizations, it is possible to overcome these deficiencies.[1] Atom transfer radical polymerization[2] (ATRP) seems to be the most robust system to control radical polymerization of styrenes,[3−5] acrylates,[6,7] methacrylates,[8−12] and acrylonitrile,[13] especially when using the Cu-based catalytic system.

The ATRP of styrene (St) has been investigated both kinetically and mechanistically. The rate of the homogeneous bulk polymerization, employing a copper(I) halide/4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy) catalytic system and alkyl halide initiators, was first order with respect to monomer, initiator, and Cu(I) concentrations.[3] The relationship between the apparent rate constant of polymerization and Cu(II) was not inverse first order, as predicted by the rate law, but shows a decay behavior.[3] This was attributed to spontaneous formation of Cu(II) due to small amounts of termination at the beginning of the polymerization, resulting in a higher concentration of Cu(II) in the system than predicted by the added Cu(II). The fastest polymerization rate was observed with a ratio of ligand to metal of 2:1. Additionally, the polymerization was not affected by the presence of small amounts of water and alcohols, but in the presence of additives whose functional groups are strongly coordinating, such as pyridine or triphenylphosphine, lower polymerization rates and higher polydispersities were observed, presumably caused by deactivation of the catalyst through interaction with the additive.[3]

Similar results were obtained for the ATRP of methyl methacrylate (MMA) catalyzed by the CuCl/dNbpy system. The rate of polymerization was first order with respect to the concentrations of monomer, initiator and catalyst, and did not show an inverse first order dependence on the concentration of Cu(II), but the same decay behavior as in ATRP of styrene.[11] Unlike the ATRP of styrene, the fastest polymerization rates were obtained at a 1:1 ratio of dNbpy:CuBr; however, a 2:1 ratio was optimal when $CuPF_6$ was used as the Cu(I) species.

Results for the heterogeneous ATRP of methyl acrylate (MA) with the CuBr/4,4′-di(*tert*-butyl)-2,2′-bipyridine (dTbpy) catalytic system showed the polymerization to be first order with respect to the concentrations of monomer and initiator, approximately zero-order with respect to the Cu(I) concentration, and inverse order with respect to the concentration of Cu(II).[6]

This paper further explores the homogeneous ATRP of MA and includes detailed kinetic results on the effect of the concentrations of initiator, Cu(I), and Cu(II) on the rate of polymerization. The free energy of equilibrium, ΔG^0_{eq} is calculated through determination of the equilibrium constant of the activation/deactivation step and the apparent enthalpy of activation, $\Delta H^{\ddagger}_{app}$ and the enthalpy of equilibrium, ΔH^0_{eq} are estimated from the Arrhenius plots. Additionally, the effect of varying the counteranion on the Cu(I) species on the apparent rate constant of polymerization is reported and compared to the Cu^IBr/dNbpy catalyzed reaction.

Experimental Section

Materials. MA (Acros) was stirred over CaH_2 overnight and distilled under argon before use. Deoxygenating consisted of bubbling argon through the monomer for approximately 30 min before use. The initiator, methyl 2-bromopropionate (MBrP) (Aldrich), was distilled in vacuo before use. dTbpy was prepared through a coupling reaction of 4-(*tert*-butyl)pyridine

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* To whom correspondence should be addressed.

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using Pd/C as a catalyst.[14] dNbpy was prepared under the same coupling conditions as dTbpy, utilizing 4-(5-nonyl)-pyridine (Aldrich). The starting material was purified by vacuum distillation. The reaction mixture was filtered through Celite (Aldrich) to remove the Pd/C, vacuum distilled to remove unreacted starting material, and then distilled using a Kugelrohr apparatus at 180 °C to separate dimer from any higher oligomers. In some experiments, commercially prepared dNbpy was used (Reilly Chemicals). $Cu^{I}Br$ was purified according to literature.[15] $Cu(CH_3CN)_4PF_6$ ($CuPF_6$) was prepared using the method of Hathaway and recrystallized twice from CH_3CN.[16] $Cu^{II}Br_2$ and 1,4-dimethoxybenzene (DMB) were used as received.

General Procedure for Homogeneous Polymerizations. Into a dry Schlenk flask equipped with a stir bar were added 15.9 mg of CuBr (1.1×10^{-4} mol), 90.8 mg of dNbpy (2.22×10^{-2} mol), and 86.7 mg of DMB (~2% relative to monomer as an internal GC standard). The flask was covered with a rubber septum, evacuated, and back-filled with argon three times before leaving it under argon. A 4 mL (4.45×10^{-2} mol) sample of previously deoxygenated monomer was added via syringe to the flask, which was allowed to stir at room temperature until the catalyst was dissolved (30 min on average). Then 12.4 μL of MBrP was introduced via syringe, and the solution was allowed to stir to ensure even distribution of the initiator. A 3 mL aliquot of the solution was removed from the flask: 0.5 mL was distributed to each of five glass tubes, and 0.5 mL was kept as the standard to measure conversion. The tubes were attached to the Schlenk line and immediately frozen in liquid nitrogen. After three freeze/pump/thaw cycles, the tubes were sealed under vacuum. After thawing, the tubes were placed in an oil bath thermostated at the desired temperature, removed at timed intervals, and broken open and the contents dissolved in toluene to measure conversion by GC.

General Procedure for Addition of $CuBr_2$ (Using 5% as an Example). A concentrated monomer solution of $CuBr_2$/dNbpy was prepared. A 12.5 mg sample of $CuBr_2$ (5.55×10^{-5} mol) and 45.3 mg of dNbpy (1.11×10^{-4} mol) were added to a 15 mL round-bottom flask equipped with a stir bar. After the flask was covered with a rubber septum, the flask was degassed and back-filled with argon three times before the introduction of 4 mL (4.45×10^{-2} mol) of previously deoxygenated methyl acrylate via syringe. Then 0.4 mL of the 13.9 mM $CuBr_2$ solution was added to the stock solution (as prepared above with the amount of monomer adjusted accordingly for a final volume of 4 mL) after addition of the initiator.

General Procedure for Heterogeneous Polymerizations. Method I. Into a glass tube were added 8.0 mg of CuBr (5.6×10^{-5} mol) and 29.7 mg of dTbpy (1.11×10^{-4} mol), and the tube was sealed with a rubber septum. The tubes were evacuated and back-filled with argon three times via needles attached to the Schlenk line to ensure an inert atmosphere, prior to the addition of initiator. Then 12.4 μL of MBrP (1.11×10^{-4} mol) was added via syringe through the septum after which 1 mL (1.11×10^{-2} mol) of previously deoxygenated MA was added, also via syringe through the septum. The argon flow was stopped and the tubes were immersed in liquid nitrogen. After three freeze/pump/thaw cycles, the tubes were sealed under vacuum, placed in an oil bath thermostated at the desired temperature, and removed at timed intervals to measure kinetics of the polymerization. The tubes were broken open and the contents dissolved in a known volume of THF to determine conversion by GC. The same method was used for the polymerizations with added $CuBr_2$.

Method II. The procedure was as above, but the tubes were not degassed prior to the addition of initiator and monomer.

Temperature Study. A 4.1 mg sample of $CuPF_6$ (1.10×10^{-5} mol) and 9.1 mg dNbpy (2.20×10^{-5} mol) were added to a glass tube, which was sealed with a rubber septum, and the tube was degassed and back-filled with argon three times before addition of 0.5 mL of deoxygenated monomer. Then 2.7 μL of MBrP (2.42×10^{-5} mol) was added, and an additional 0.5 mL of monomer was added for a total volume of 1 mL (1.11×10^{-2} mol). Three freeze/pump/thaw cycles were performed, the tube was back-filled with argon, and a thermocouple was inserted through the septum. After reaching room temperature, the tube was placed in a 90 °C oil bath and the temperature recorded every 5 s until no changes were observed.

UV Studies. (All solutions were prepared in a drybox.) A 37 mg sample of $CuPF_6$ (1×10^{-4} mol) and 82 mg of dNbpy (2×10^{-4} mol) were added to a 10 mL volumetric flask and diluted to the line with MA. A small stir bar was added to help dissolve the complex. After approximately 45 min of stirring, 1.25 mL of the 1×10^{-2} M solution was added to a 25 mL volumetric flask and again diluted with MA. Then 3 mL of the 5×10^{-4} M solution was placed in a 50 mL Schlenk flask and capped with a 1 cm quartz cell modified with a ground glass joint. The apparatus was removed from the drybox and the UV spectrum measured against a MA reference. Subsequent dilutions were performed by adding a known volume of MA to the Schlenk flask through the sidearm. The same procedure was used for preparing the CuBr solutions. For those experiments performed at elevated temperatures, a fiber optic probe inserted into a modified Schlenk flask was utilized.

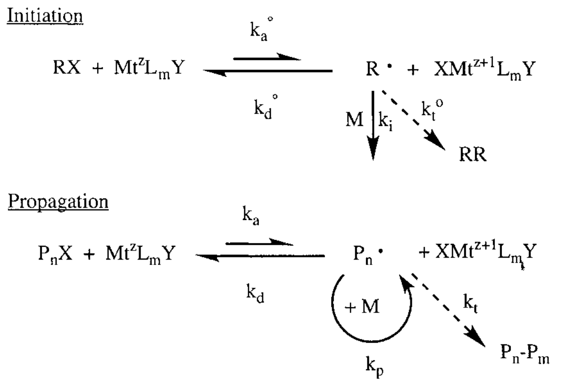
Characterization. Conversion of monomer was measured against an internal standard using a Shimadzu GC-14A gas chromatograph with a J&W Scientific DB−Wax 30m Megabore column. Molecular weight determinations were made using a GPC equipped with a Waters 712 WISP autosampler, Polymer Standards Service (PSS) columns (guard, 100 Å, 1000 Å, 10000 Å), and a Waters 410 RI detector against linear polystyrene standards. UV studies were performed on a Perkin-Elmer UV/VIS/NIR Lambda 900 spectrometer.

Background

Atom transfer radical polymerization (ATRP) proceeds through halogen (or pseudo-halogen) abstraction from an alkyl (pseudo)-halide by a metal in a lower oxidation state to produce an active radical and a higher oxidation state metal (k_a^0). The active radical can either add monomer (k_i) or deactivate to regenerate the metal in a lower oxidation state and a dormant species (k_d^0). Similar activation/deactivation of the dormant species occurs during reinitiation and propagation (k_a, k_d, and k_p). Although the stationary concentration of radicals has not yet been detected using a spectroscopic method, solving the kinetic expression for the concentration of active species indicates it is similar to that found in a conventional free radical polymerization (10^{-7} to 10^{-8} M). Negligible effects of CuBr/2dNbpy and $Cu(OTf)_2$/2dNbpy on molecular weights and polydispersities of conventional radical polymerizations of MA initiated by AIBN indicate there is no interaction of the radicals with copper, supporting the radical nature of ATRP.[17] Molecular weights in ATRP are significantly lower than in a conventional process. Therefore, although the concentration of terminated chains may be similar in both process (the rate constant of termination is presumably the same), the proportion of terminated chains relative to the total concentration of propagating chains (the sum of active and dormant species) in ATRP is relatively small (5−10%). This is in contrast to a conventional process where all chains are terminated. Deactivation is several orders of magnitude faster than radical−radical termination, and irreversible termination does not contribute significantly ($k_d[Cu^{II}][R^\bullet] \gg k_t[R^\bullet]^2$) ($k_t$o and k_t, Scheme 1). However, some early termination invariably occurs and leads to the formation of the Cu(II) species, which is needed for control via the persistent radical effect.[18]

The catalysts utilized in this report consist of Cu(I) salts combined with dNbpy as a solubilizing ligand, creating a homogeneous system. The ligand also may

Scheme 1



serve to adjust the oxidation potential of the catalyst through electronic[19] and steric effects.[20] This will in turn define the equilibrium constant, $K_{eq} = k_a/k_d$. The rate of polymerization should be dependent on the rate constant of propagation for the given monomer and the equilibrium constant of the activation/deactivation step as well as the concentrations of monomer, initiator (growing chains), catalyst, and deactivator (eq 1).

$$R_p = k_p K_{eq}[M][RX]_o \frac{[Mt^zL_m]}{[XMt^{z+1}L_m]} = k^{app}[M] \qquad (1)$$

I. Homogeneous ATRP of MA using CuBr/dNbpy. A. Kinetic Studies: Order with Respect to Initiator, Activator, and Deactivator. Results. Figure 1 shows the kinetic plot of $\ln([M]_o/[M])$ vs time for ATRP of MA catalyzed by CuBr/dNbpy initiated by MBrP at various initiator concentrations. The resulting slopes indicate the polymerizations proceeded with an approximately constant number of active species for the duration of the reaction, therefore the contribution of termination reactions could be neglected. As expected, increasing the initiator concentration increased the apparent rate constant of polymerization, k^{app}, as determined from the kinetic slopes.

Plotting $\ln k^{app}$ vs ln [MBrP] elucidated the dependence of the rate of polymerization on the concentration of initiator. For this system, the slope of the line indicated an apparent 0.8 order with respect to initiator (Figure 2). This differs slightly from the first-order dependence of the rate on the initiator concentration observed for ATRP of both St and MMA.

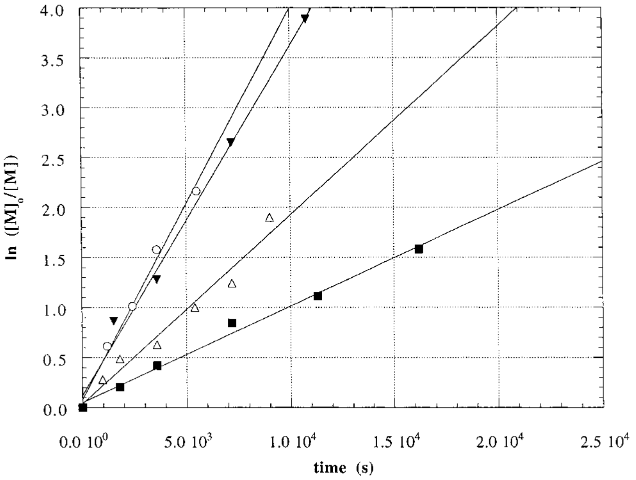


Figure 1. Effect of initiator concentration on kinetics of homogeneous ATRP of MA in bulk at 90 °C. $[MA]_o = 11.2$ M; $[CuBr]_o = [dNbpy]_o/2 = 0.028$ M. $[MBrP]_o = 0.083$ (○), 0.056 (▼), 0.028 (△), and 0.014 M (■).

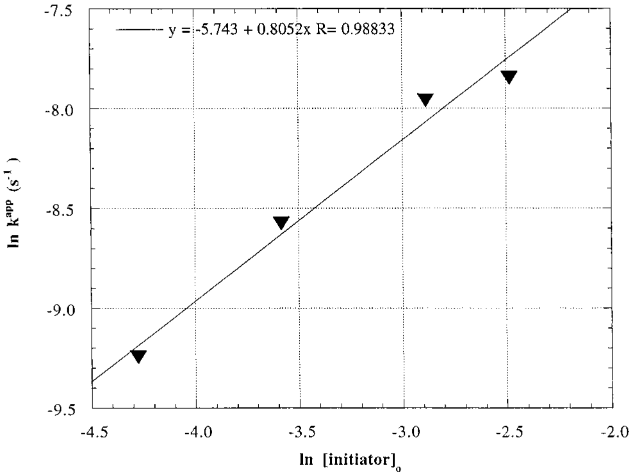


Figure 2. Dependence of the apparent rate constant of propagation (k^{app}) on the initiator concentration for homogeneous ATRP of MA in bulk at 90 °C. $[MA]_o = 11.2$ M; $[CuBr]_o = [dNbpy]_o/2 = 0.028$ M.

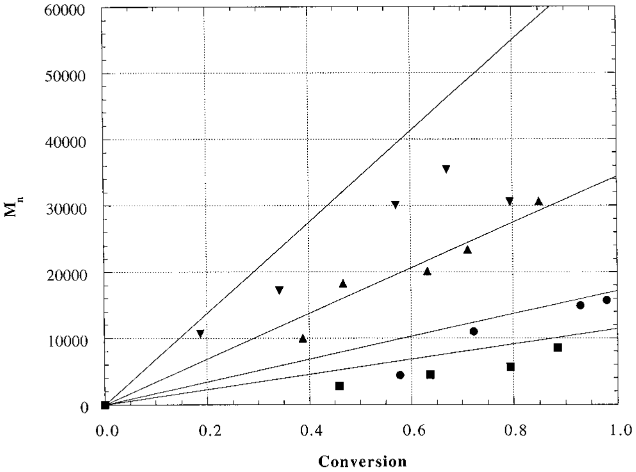


Figure 3. Plot of M_n vs monomer conversion for differing ratios of monomer:initiator for bulk ATRP of MA at 90 °C. $[MA]_o = 11.2$ M; $[CuBr]_o = [dNbpy]_o/2 = 0.028$ M; $[MBrP]_o = 0.083$ (■), 0.056 (●), 0.028 (▲), and 0.014 M (▼).

Figures 3 and 4 show the molecular weight evolution, M_n, and molecular weight distribution, M_w/M_n, as a function of conversion. The molecular weights determined by SEC against linear polystyrene standards generally agreed with the theoretical lines calculated from the degree of polymerization as predicted by the initial ratio of monomer:initiator. Deviation from the theoretical line at higher ratios of monomer:initiator may indicate transfer of some chains by undefined impurities, however, there may be some deviation due to differences in the hydrodynamic volumes of the poly(MA) vs the linear PS standards. Polydispersities followed the expected trend and decreased with increasing conversion, with final $M_w/M_n < 1.25$ for all polymerizations studied. The GPC traces showed a higher molecular weight shoulder with increasing conversion at low $[MBrP]_o$, suggesting some chain coupling (Figure 5).

The dependence of the rate of polymerization in the homogeneous ATRP of MA on the catalyst structure and concentration was also investigated. Figure 6 shows the apparent rate constant of polymerization as a function

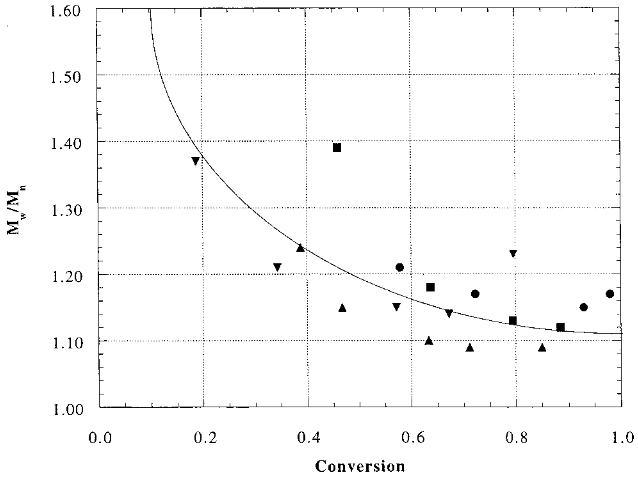


Figure 4. Plot of M_w/M_n vs monomer conversion for differing ratios of monomer:initiator for bulk ATRP of MA at 90 °C. $[MA]_o = 11.2$ M; $[CuBr]_o = [dNbpy]_o/2 = 0.028$ M. $[MBrP]_o = 0.083$ (▼), 0.056 (▲), 0.028 (●), and 0.014 M (■).

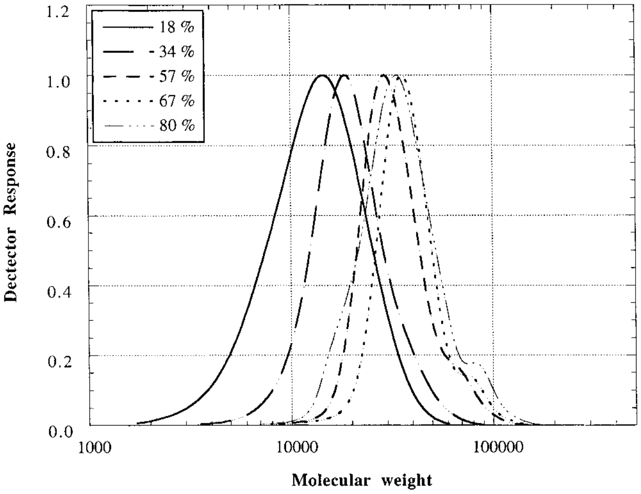


Figure 5. GPC traces for homogeneous ATRP of MA at various conversions in bulk at 90 °C. $[MA]_o = 11.2$ M; [MBrP] = 0.014 M; $[CuBr]_o = [dNbpy]_o/2 = 0.028$ M.

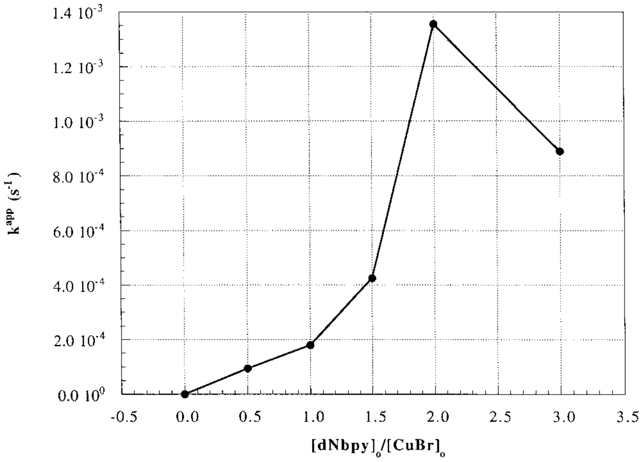


Figure 6. Plot of k^{app} vs equivalents of dNbpy used for bulk ATRP of MA using CuBr/dNbpy as the catalyst at 90 °C. $[MA]_o = 11.2$ M; $[MBrP]_o = 0.056$ M; $[CuBr]_o = 0.056$ M.

of the ratio of ligand:Cu(I). The maximum rate constant is observed at a 2:1 ratio of ligand:catalyst. This is consistent with X-ray crystal structures in which Cu(I) prefers a tetrahedral geometry, which can be achieved with two bidentate ligands.[21] However, solution structures may differ from those in the solid state. The reason behind the decrease of the rate constant in the presence of a 3:1 ratio is not clear, however, further coordination to the metal center may hinder the activity of the catalyst.

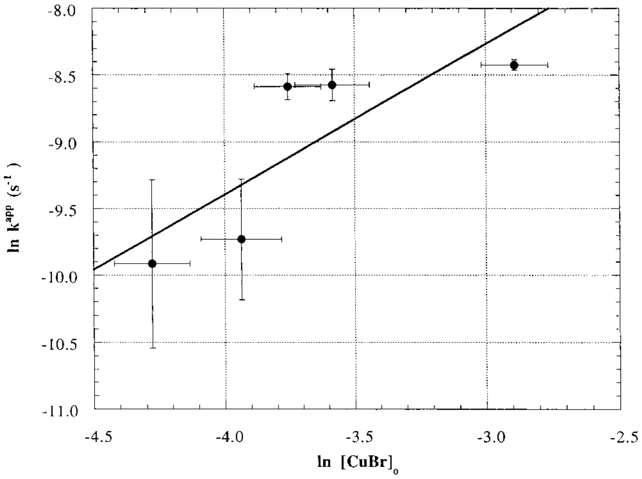


Figure 7. Dependence of the apparent rate constant of propagation (k^{app}) on the catalyst concentration for homogeneous ATRP of MA in bulk at 90 °C. $[MA]_o = 11.2$ M; $[MBrP]_o = 0.028$ M; ratio of ligand:metal = 2.

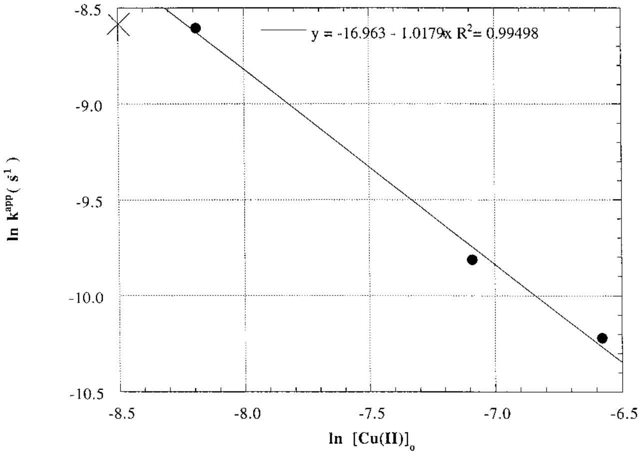


Figure 8. Dependence of the apparent rate constant of propagation (k^{app}) on the concentration of added Cu(II) for homogeneous ATRP of MA in bulk at 90 °C. $[MA]_o = 11.2$ M; $[MBrP]_o = [CuBr] = [dNbpy]/2 = 0.028$ M.

Figure 7 is a plot of ln k^{app} vs ln $[CuBr/2dNbpy]_o$. Due to some deviation from linearity, the error bars associated with the measurement of the apparent rate constants of polymerization and the catalyst concentration are present. The error in the apparent rate constant was found using a linear regression analysis of the individual experiments and for the catalyst concentrations from the additive error associated with weights and volumes. A linear fit is shown, however, the relationship between the catalyst concentration and the rate of polymerization in ATRP of MA does not appear to be this straightforward, and the line is only meant to show the deviation. These results deviate from those found for ATRP of St and MMA, which both showed a first order dependence on catalyst concentration.

The relationship between the rate of polymerization and the concentration of Cu(II) was determined. Figure 8 illustrates the dependence of ln k^{app} on ln $[Cu(II)]_{added}$. The slope of the line indicates an inverse first order dependence of the rate on the concentration of Cu(II) in the system. The cross on the *y*-axis corresponds to ln k^{app} of the reaction in the absence of any added Cu(II), showing 1% added $CuBr_2$ does not change the rate considerably. This is again different from the results of the ATRP of St or MMA where a nonlinear behavior of the rate on Cu(II) concentration was observed over a larger range of $[CuBr_2]_{added}$. At low concentrations of added Cu(II), there was no effect on the rate of polymerization, however, the rate began to drop significantly at higher concentrations.[3,11] This indicated the ATRP of St and MMA was less affected by small amounts of Cu(II) than the ATRP of MA. The reason for this may be that more Cu(II) is formed initially in the St and MMA systems through irreversible termination. This correlates with the higher concentration of Cu(II) detected by EPR in the polymerization of St or MMA compared to MA.[22,23]

Discussion. Recent data reported by Fischer have indicated that systems with persistent radicals, including atom transfer systems, may show an overall kinetic behavior that is a product of several different rate constants and that the dependence on various components, i.e., persistent radicals, initiator, and transient radicals, would not necessarily be expected to conform to a first order relationship.[18] From the results of the kinetic studies presented here, the dependence of the ATRP kinetics of MA with respect to initiator, activator, and deactivator concentrations cannot be simply explained. The dependence on the concentration of Cu(II) is perhaps the most important aspect to consider. There is an inverse first order dependence on the concentration of deactivator in this system. As the concentration of Cu(II) in the system increases, the overall polymerization rate is reduced considerably. In contrast to the St and MMA systems where small changes in the concentration of Cu(II) did not produce a noticeable effect on the polymerization rate, even small changes in the MA system affect the rate. This may account for the fractional order in initiator concentration. As the concentration of initiator increases, the concentration of radicals increases, potentially leading to more termination early in the polymerization and the irreversible production of Cu(II). The increase in [Cu(II)] shifts the equilibrium toward the dormant species, leading to a slower than expected polymerization at higher concentrations of initiator. Decreasing the $[\text{initiator}]_o$ decreases the concentration of radicals and less formation of Cu(II) occurs.

The results for the dependence on the concentration of Cu(I) can be similarly explained. Although the apparent rate constant of polymerization increases with increasing concentration of catalyst, there is some deviation from linearity. This again may be attributed to the formation of Cu(II) in the system. At higher concentrations of catalyst, the formation of more radicals will, as stated previously, increase the concentration of Cu(II) in the system through irreversible termination. The increased amount of deactivator will decrease the polymerization rate, contrary to what would be expected from an increased radical concentration. The converse is true at lower initial concentrations of catalyst. Additional effects may originate from any interaction between the Cu(I) and Cu(II) species and, in turn, vary their reactivities with concentration. For example, limited solubility of the Cu(II) species may lead to an observed non-first-order dependence on the initial concentrations of initiator and Cu(II).

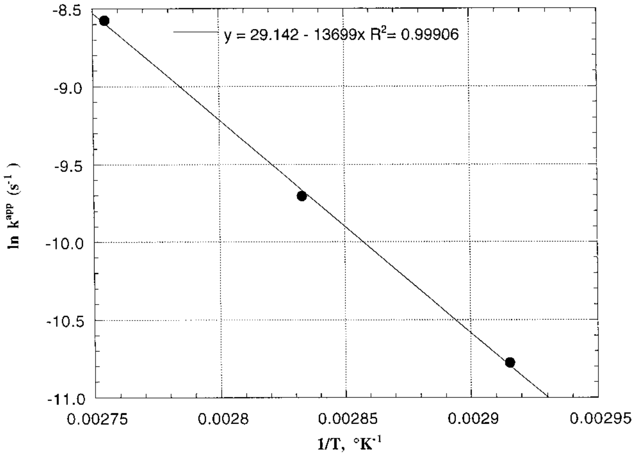


Figure 9. Plot of ln(k ^{app}) vs 1/*T* for bulk ATRP of MA. $[MA]_o = 11.2$ M; $[MBrP]_o = 0.028$ M; $[CuBr]_o = [dNbpy]_o/2 = 0.028$ M.

B. Determination of K_{eq} and $\Delta G^0{}_{eq}$. To calculate the equilibrium constant, assuming a free radical mechanism,[24] a reliable value for the rate constant of propagation of MA must be used, however only values acquired using the rotating sector method are available. Literature reports suggest pulsed laser polymerization (PLP) techniques combined with SEC analysis may furnish more reliable values of rate constants of propagation.[25] Further PLP studies found there was not a significant difference in the enthalpy of propagation between methacrylates with various alkyl side groups.[26] It was assumed this trend would hold for acrylates as well and the activation parameters determined by PLP for butyl acrylate could be applied to MA and used for estimating the equilibrium constant, the free energy of equilibrium, and the enthalpy of equilibrium for ATRP of MA.

Calculation of the equilibrium constant was based on experiments where 5% $CuBr_2$ relative to CuBr was added to a standard polymerization in order to avoid a potential effect of variation in the concentration of $CuBr_2$ with time. The apparent rate constant of polymerization for this reaction was $k^{app} = 3.6 \times 10^{-5}\ s^{-1}$. Based on a rate constant of propagation for butyl acrylate (assumed to be similar to MA) of $k_p = 5.6 \times 10^4\ M^{-1}\ s^{-1}$ at 90 °C,[27] the equilibrium constant determined from Equation 1 is $K_{eq} = 1.2 \times 10^{-9}$. Using the relationship between free energy and the equilibrium constant, the free energy of equilibrium is $\Delta G^0{}_{eq} = 14.4$ kcal/mol. This value is higher than the values found for St or MMA because the equilibrium constant for ATRP of MA is smaller than for either St ($K_{eq} = 2 \times 10^{-8}$ (Br)) or MMA ($K_{eq} = 7.0 \times 10^{-7}$ (Cl)) at 90 °C. This may be ascribed to differences in the radical structure of the different systems. The tertiary nature of the MMA radical and the phenyl substituent on the styryl radical stabilize the radical species, or destabilize the covalent species, increasing the concentration of the active species during the polymerization and, as a result, increasing the equilibrium constant.

The Arrhenius plot for the CuBr/dNbpy catalyzed polymerization of MA is plotted in Figure 9. Based on the slope, an apparent enthalpy of activation, $\Delta H^{\ddagger}{}_{app} = 27.2$ kcal/mol was calculated. According to eq 2, with

$$\Delta H^0{}_{eq} = \Delta H^{\ddagger}{}_{app} - \Delta H^{\ddagger}{}_{prop} \quad (2)$$

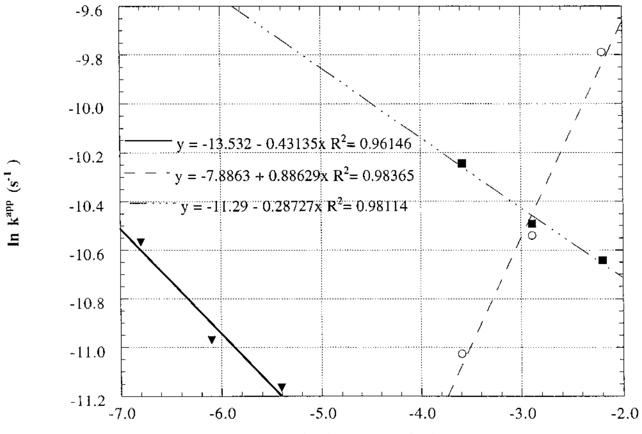


Figure 10. Dependence of the apparent rate constant of propagation (k^{app}) on initiator concentration (○), catalyst concentration (■), and Cu(II) concentration (▼) for heterogeneous ATRP of MA in bulk at 90 °C. $[MA]_o = 11.2$ M; $[dTBbpy]_o/[CuBr]_o = 2$.

an $\Delta H^{\ddagger}_{prop} = 4.2$ kcal/mol for butyl acrylate,[27] $\Delta H^0_{eq} = 23$ kcal/mol was calculated for Br-mediated ATRP of MA. This value is much higher than the corresponding values for St ($\Delta H^0_{eq} = 11.9$ kcal/mol for the Br-mediated system and 13.4 kcal/mol for Cl-mediated) or MMA ($\Delta H^0_{eq} = 9.7$ kcal/mol for Cl-mediated). This difference seemed to be too large to be attributed solely to substituent effects on the energy associated with cleavage of the carbon−halogen bonds and may originate in the variation of the catalyst structure with solvent and temperature (vide infra).

II. Heterogeneous ATRP of MA Using CuBr/dTbpy. Kinetic Studies: Order with Respect to Initiator, Activator, and Deactivator. The results obtained from the homogeneous studies lend themselves to comparison with the results obtained from the heterogeneous ATRP of MA (prepared according to Method II) using dTbpy as the ligand. Figure 10 is a compilation plot of ln k^{app} vs $[MBrP]_o$ and ln $[catalyst]_o$ as previously reported.[6]

From the slopes, the rate of polymerization is 0.9 order with respect to the concentration of MBrP and −0.3 order with respect to the concentration of catalyst. In contrast to the homogeneous ATRP systems, the rate of polymerization appears to be much less dependent on the catalyst concentration in the heterogeneous system. The slightly negative dependence may be explained by solubility effects. The observation that the rate of polymerization is relatively independent of the catalyst concentration indicates the solubility limit of the Cu(I) complex is reached. However, the slightly negative behavior could suggest that increasing the catalyst concentration increases the concentration of Cu(II), which manifests itself in decreasing the rate of polymerization. This is reasonable when considering that the concentration of Cu(II) is approximately 2 orders of magnitude smaller than the concentration of Cu(I), allowing for the increase without reaching any solubility limits. Additionally, the rate of polymerization shows a −0.4 order dependence on the concentration of added Cu(II), also shown in Figure 10.

III. Factors Affecting the Rate of ATRP. As discussed above, the rate of polymerization is affected by the concentration of deactivator in solution, whether using a homogeneous catalytic system or a heterogeneous one. When Method I, a more rigorous method, was used for the preparation of the heterogeneous reaction mixtures, the apparent rate constants of polymerization were roughly six times larger than the reported values obtained using Method II.[6] When air was carefully eliminated from the system prior to the introduction of initiator, the polymerizations were faster and the molecular weight distributions broader, presumably due to a lower initial concentration of deactivator in solution. Method II was also used for the preliminary reports on homogeneous ATRP of MA, which, again, have lower rate constants of polymerization compared to the results reported here. The stock solution method used to prepare the homogeneous reactions in this report not only decreases the level of oxygen in the system, but the catalyst is dissolved before polymerization begins, which was not the case with Method II. Consequently, the molecular weight distributions are broader for polymerizations with higher rate constants of polymerization because the concentration of deactivator in solution is lower (see eq 3).

$$M_w/M_n = 1 + \frac{k_p[RX]_o}{k_d[XCu(II)]}\left(\frac{2}{p} - 1\right) \qquad (3)$$

In addition to the preparation method, the source of ligand can also affect the polymerization rate. The initial reports on homogeneous ATRP of MA utilized ligand obtained from Reilly Industries that was not purified further. A yellow tint to the ligand indicated the presence of some impurity when compared to the nearly colorless ligand prepared later in our labs by the coupling of 4-(5-nonyl) pyridine and purified by Kugelrohr distillation. The presence of impurities in the ligand could slow the polymerization.

It follows from the differences between the ATRP of MA and the ATRP of St or MMA with respect to the catalyst that the nature of the catalyst species comes into question. Temperature-dependent color changes of catalyst-containing monomer solutions were observed. For example, the catalyst solution in MA is yellow at low temperatures, orange/red at room temperature, and deep red at high temperature, indicating the nature of the catalyst may be temperature dependent. According to literature, these color changes may be associated with a structural change from a monomeric Cu(I) species to a dimeric halogen bridged species.[28]

Kitagawa and Munakata investigated the solution behavior of Cu(I)halides complexed by 2,2′-bipyridine and found the extinction coefficients of these complexes in acetone were significantly smaller than when ethanol was used as a solvent. The extinction coefficients in ethanol were similar to those found for Cu(I) complexes containing ClO_4^- as a counteranion, which do not bridge, suggesting the observed differences in acetone may result from the presence of the dimeric species in solution.[28] This led us to conduct similar UV studies on a Cu(I)/dNbpy complex containing a nonbridging counteranion, $Cu(dNbpy)_2^+PF_6^-$, and $CuBr(dNbpy)_2$ using MA as a solvent to compare the absorption spectra. While the $CuPF_6$ spectra recorded at 25 °C contained an absorption maximum at $\lambda = 442$ nm and an extinction coefficient $\epsilon_{\lambda=442} = 3570$ M^{-1} s^{-1} calculated from the slope of a Beer's law plot, the absorption maximum disappeared in the CuBr spectrum, indicating the structure of the complex in solution may be different (Figure 11). Spectra of the CuBr complex in MA were also recorded at 90 °C to simulate polymerization

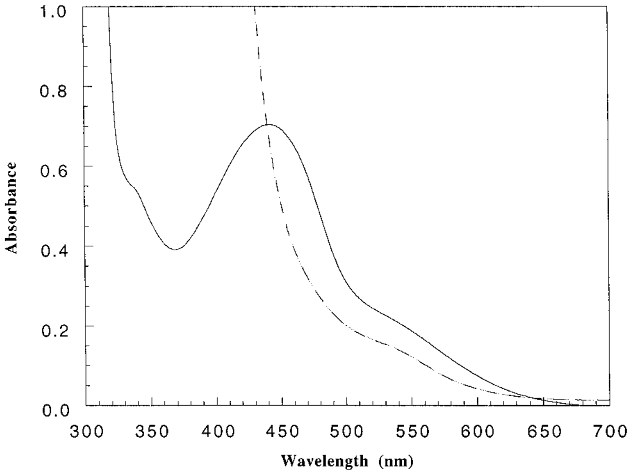


Figure 11. Plot of absorbance vs wavelength for Cu(I) complexes in MA at room temperature. [CuBr]=[dNbpy]/2 = 0.01M (dotted line), $[CuPF_6]$=[dNbpy] = 2.5 × 10^{-4} M (solid line); path length = 1 cm.

conditions. It was expected that an absorption maximum would be visible and the spectra similar to the $CuPF_6$ complex, but while there was a shift in the wavelength due to color changes that occurred upon dilution, the spectra obtained were similar to those collected at room temperature without a distinct absorption maximum. This indicates the two complexes may have different structures in MA solution, the exact nature of which is still under investigation. Because of the difference in the UV spectra of the two complexes, $CuPF_6$ was used as the Cu(I) species for ATRP of MA to determine if changing the counteranion had an effect on the overall rate of polymerization.

IV. Homogeneous ATRP of MA Using $CuPF_6$/dNbpy. A. Kinetic Studies. Initially, polymerizations using $CuPF_6$/dNbpy as the catalyst were attempted under the same conditions as the CuBr/dNbpy catalyzed reactions, however, this catalyst resulted in faster polymerizations than those catalyzed by the homogeneous CuBr system. Reactions performed at high catalyst concentrations were exothermic and the polymerizations reached high conversion (>90%) within minutes when started at room temperature. At lower catalyst concentrations, the polymerization was controlled and the kinetic behavior could be investigated.

Figure 12 is a kinetic plot of $\ln([M]_o/[M])$ vs time for the ATRP of MA using $CuPF_6$/dNbpy as the catalyst (closed symbols). The apparent rate constant of polymerization is much larger in this reaction than in the CuBr/dNbpy system. Again, the highest rate constants were found with a 2:1 ratio of ligand:metal (Figure 13). The molecular weights increased with conversion and agreed well with the theoretical line, but the molecular weight distributions were broader than for the CuBr/dNbpy catalyzed reactions (Figure 14).

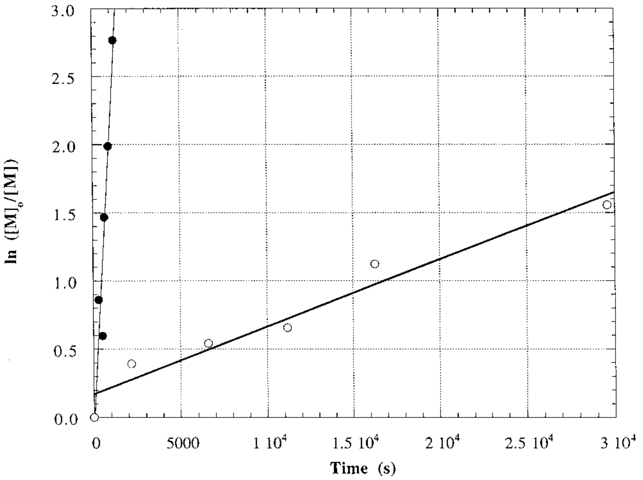


Figure 12. Plot of $\ln([M]_o/[M])$ vs time for $CuPF_6$/dNbpy and CuBr/dNbpy catalyzed bulk ATRP of MA at 90 °C. $[MA]_o$ = 11.2 M; $[MBrP]_o$ = 0.024 M. $[CuPF_6]_o$ (●) = $[CuBr]_o$; (○) = $[dNbpy]_o/2$ = 0.011 M.

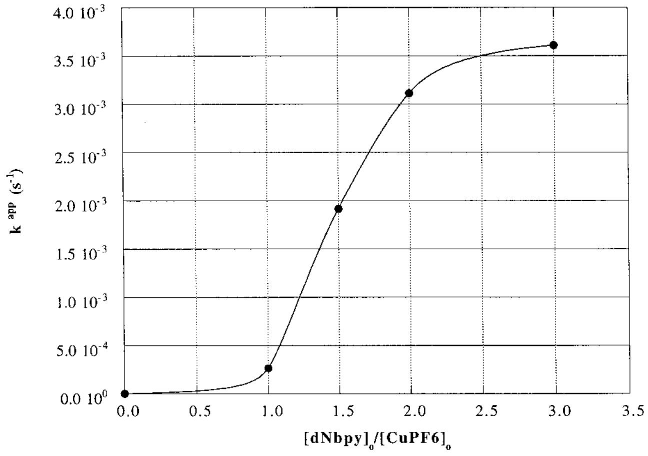


Figure 13. Plot of k^{app} vs equivalents of dNbpy used for bulk ATRP of MA using $CuPF_6$/dNbpy as the catalyst at 90 °C. $[MA]_o$ = 11.2 M; $[MBrP]_o$ = 0.024 M; $[CuPF_6]_o$ = 0.011 M.

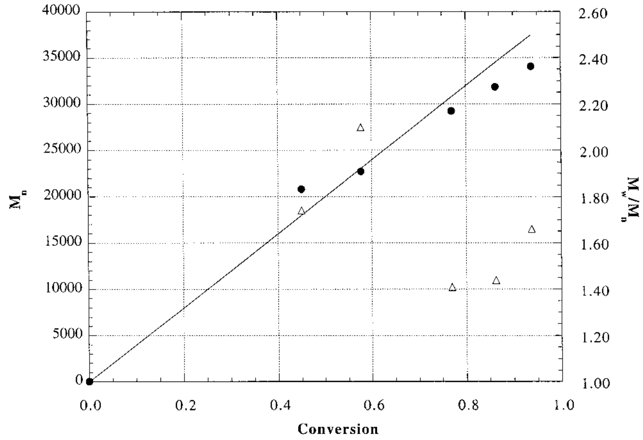


Figure 14. Plot of M_n (closed symbols) and M_w/M_n (open symbols) vs monomer conversion for bulk ATRP of MA using the $CuPF_6$/dNbpy catalyst system at 90 °C. $[MA]_o$ = 11.2 M; $[MBrP]_o$ = 0.024 M; $[CuPF_6]_o$ = $[dNbpy]_o/2$ = 0.011 M.

According to eq 3, M_w/M_n should decrease with increasing conversion, p.[29] This expression assumes, however, that the Cu(II) species formed is an effective deactivator and that k_d is large relative to k_p. A smaller rate constant of deactivation for a given Cu(II) species will necessarily result in higher polydispersities at the same conversion. EPR data for ATRP of MA catalyzed by the $CuPF_6$/dNbpy system showed approximately 10% of the Cu(I) is oxidized to Cu(II). In a comparable CuBr/dNbpy catalyzed polymerization, only 3% of the Cu(I) was oxidized to Cu(II) (MA:MBrP:CuX:dNbpy, 464:1:0.47:0.94, T=90 °C, 50% toluene solution).[23] The majority of the build-up of Cu(II) is attributed to termination arising from inefficient deactivation and a high concentration of active radicals, producing the broad molecular weight distributions.

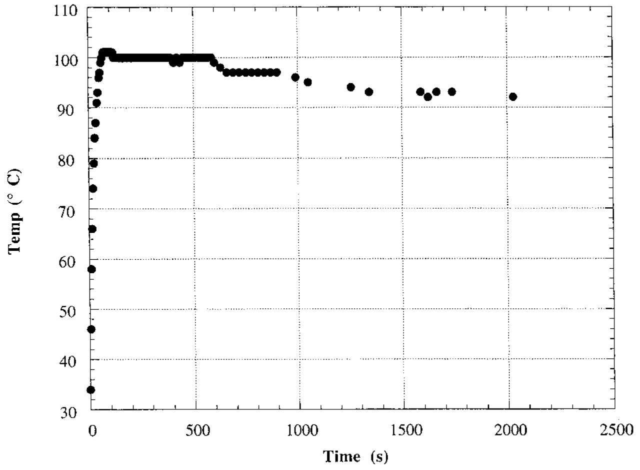


Figure 15. Plot of temperature vs time for bulk ATRP of MA catalyzed by $CuPF_6$/dNbpy. $[MA]_o = 11.2$ M; $[MBrP]_o = 0.024$ M; $[CuPF_6]_o = [dNbpy]_o/2 = 0.011$ M; oil bath temp = 90 °C.

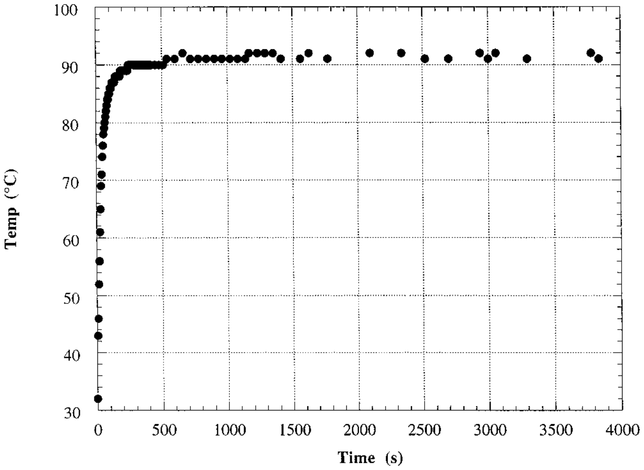


Figure 16. Plot of temperature vs time for bulk ATRP of MA catalyzed by CuBr/dNbpy. $[MA]_o = 11.2$ M; $[MBrP]_o = 0.024$ M; $[CuBr]_o = [dNbpy]_o/2 = 0.024$ M; oil bath temp = 90 °C.

B. Temperature Studies. Figure 12 plots $\ln([M]_o/[M])$ vs time for the two catalytic systems under comparable conditions. The $CuPF_6$/dNbpy system has an apparent rate constant of polymerization approximately 40 times greater than the CuBr/dNbpy system. Although this can be primarily ascribed to a larger equilibrium constant, the exothermic polymerizations at higher catalyst concentrations led us to monitor the reaction temperature during a typical polymerization. Polymerization of MA is exothermic ($\Delta H = 13$ kcal/mol [30]) and the heat exchange through the glass wall of 2 mm thickness without stirring may not be immediate and could result in the apparent temperature increase. Indeed, in an oil bath thermostated at 90 °C, the temperature of the solution reached approximately 100 °C within 2 min, remained at 100 °C for 5 min, then gradually decreased to the temperature of the oil bath as higher conversion was reached (Figure 15). Although this polymerization was performed under an inert atmosphere rather than in sealed tubes as when kinetics are monitored, the results suggest that the large increase in the apparent rate constant of polymerization when $CuPF_6$/dNbpy was used as the catalyst may partially be ascribed to the apparently higher reaction temperature. Figure 16 shows an equivalent CuBr/dNbpy polymerization which yielded no evidence of an exotherm. The polymerization proceeded at the temperature of the oil bath.

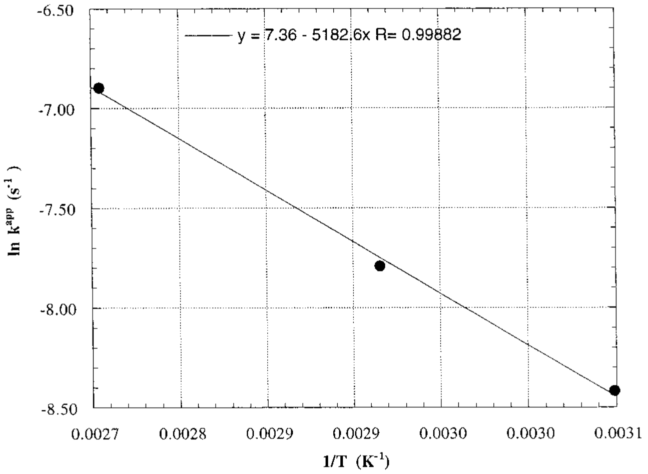


Figure 17. Plot of $\ln(k^{app})$ vs $1/T$ for bulk ATRP of MA. $[MA]_o = 11.2$ M; $[MBrP]_o = 0.024$ M; $[CuPF_6]_o = [dNbpy]_o/2 = 0.011$ M.

C. Determination of ΔH^0_{eq}. Temperature monitoring of ATRP of MA catalyzed by the $CuPF_6$/dNbpy system with additional solvent and adequate stirring provided conditions under which the temperature of the reaction remained constant and the enthalpy of activation could be measured. Addition of 25 wt % DMB relative to monomer and small stir bars to each of the glass tubes created an isothermal environment. Figure 17 is the Arrhenius plot constructed from polymerizations performed at 90, 70, and 55 °C. The apparent enthalpy of activation $\Delta H^{\ddagger}_{app} = 10.3$ kcal/mol, as determined from the slope. According to eq 2, using $\Delta H^{\ddagger}_{prop} = 4.2$ kcal/mol for butyl acrylate,[27] $\Delta H^0_{eq} = 6$ kcal/mol for Br-mediated ATRP of MA catalyzed by the $CuPF_6$/dNbpy system. This is much lower than ΔH^0_{eq} calculated for the CuBr/dNbpy system (23 kcal/mol), but in better agreement with the values for St ($\Delta H^0_{eq} = 11.9$ kcal/mol (Br) and 13.4 kcal/mol (Cl)) and MMA ($\Delta H^0_{eq} = 9.7$ kcal/mol (Cl)). Since the $CuPF_6$/dNbpy catalytic system does not appear to exhibit the strong temperature dependence found for the CuBr/dNbpy catalyst, this again suggests the nature of the catalyst in the CuBr system may vary with temperature and explain the unusually large enthalpy of equilibrium found.

Further results from our laboratory on the ATRP of *n*-butyl acrylate using the CuBr/2,2′-bipyridine (bpy) catalytic system also suggest the nature of the catalyst may change based on the solvent.[31] Using ethylene carbonate (EC) as a solvent, it was expected the rate of polymerization would decrease because of dilution; however, the apparent rate constant of polymerization increased 4 times over that of the bulk reaction.[31] The rate of the CuBr and $CuPF_6$ catalyzed reactions in EC were similar, indicating the structure of the CuBr catalyst in polar media may resemble the $CuPF_6$ catalyst. This suggests the observed rate difference between the CuBr and $CuPF_6$ systems in MA may also be due to the existence of the bridged species in the CuBr catalytic system that is not present in the $CuPF_6$ system, resulting in a more active catalyst in the $CuPF_6$ case. This increased activity may result from a change in the nature of the Cu(I) species and increase the rate constant of activation or a change in the nature of the Cu(II) species, resulting in slower deactivation and an overall rate enhancement. This may not be the only

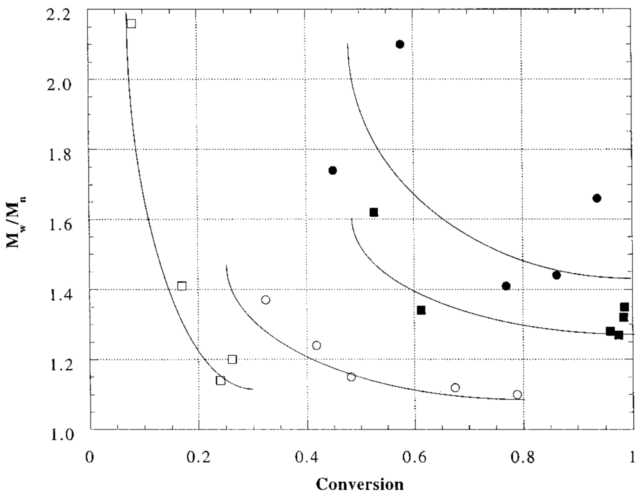


Figure 18. Effect of adding deactivator on M_w/M_n in $CuPF_6$/dNbpy catalyzed ATRP of MA at 90 °C; ratio of ligand:metal = 2; $[MA]_o = 11.2$ M; $[MBrP]_o = 0.024$ M; $[CuPF_6]_o = 0.011$ M (●). $[CuPF_6]_o = 0.011$ M; $[CuBr]_o = 0.00011$ M (■). $[CuPF_6]_o = 0.011$ M; $[CuBr_2]_o = 0.00011$ M (□). $[CuPF_6] = 0$ M; $[CuBr]_o = 0.024$ M (○).

reason for the large rate increase, however, and further investigation into the nature of the catalyst is underway.

D. Improving the $CuPF_6$/dNbpy Catalytic System. Upon addition of 1% CuBr relative to $CuPF_6$ to the polymerization, which will form the deactivator $CuBr_2$ in situ, the rate of polymerization and molecular weight evolution were not affected significantly, but the molecular weight distribution narrowed (Figure 18). When $CuBr_2$ is added directly, the molecular weight evolution followed the theoretical line and the polydispersities decreased as when CuBr was added ($M_w/M_n < 1.15$), but the rate of polymerization drops dramatically, reaching only 25% conversion after 1 h, compared to >95% conversion in the other two reactions after the same time period. Even though the addition of 1% of CuBr to the $CuPF_6$ system does not produce polymers with molecular weight distributions as narrow as in the CuBr/dNbpy only catalyzed reaction ($M_w/M_n < 1.15$), the molecular weight distribution in the $CuPF_6$/dNbpy polymerization decreased from $M_w/M_n > 1.7$ to $M_w/M_n < 1.3$ with the added CuBr. Based on the results of adding either CuBr or $CuBr_2$ to the $CuPF_6$ catalyzed polymerization, this again implies that the Cu(II) species formed from $CuPF_6$ is a less efficient deactivator, but, by adding small amounts of a more effective deactivator, the system can be improved to yield better defined polymers.

The temperature of the system must also be controlled. Addition of a solvent along with efficient stirring results in more efficient heat exchange where the rate of the reaction is reasonable and the system can be investigated.

Conclusions

MA was polymerized by ATRP under homogeneous conditions using a CuBr/dNbpy catalytic system. Kinetic results showed an apparent 0.8 order dependence of the rate of polymerization on the concentration of initiator, while the dependence on the catalyst concentration seemed to be more complex. An inverse first order dependence on the concentration of added Cu(II) was observed. This differed from the results of the ATRP of St and MMA which were both first order in initiator and catalyst concentrations, and showed a nonlinear dependence on the concentration of added Cu(II). Using the observed equilibrium constant, $K_{eq} = 1.2 \times 10^{-9}$, the free energy of equilibrium $\Delta G^0_{eq} = 14.4$ kcal/mol at 90 °C was calculated. The apparent enthalpy of polymerization was $\Delta H^{\ddagger}_{app} = 27.2$ kcal/mol, which led to an enthalpy of equilibrium, $\Delta H^0_{eq} = 23$ kcal/mol for the Br-mediated ATRP of MA. This was significantly higher than those calculated for the ATRP of St or MMA. In addition to CuBr, where the halides can potentially form a bridge between two copper centers, a Cu(I) species containing a counteranion that cannot bridge, $CuPF_6$, was used for homogeneous ATRP of MA. The resulting apparent rate constant of polymerization was approximately 40 times larger than a comparable CuBr/dNbpy catalyzed polymerization. The build-up of Cu(II) in this system implied a smaller rate constant of deactivation for the Cu(II) species formed. This potentially increased K_{eq} and enhanced the rate of polymerization. The apparent enthalpy of polymerization was $\Delta H^{\ddagger}_{app} = 10.3$ kcal/mol, leading to an enthalpy of equilibrium $\Delta H^0_{eq} = 6$ kcal/mol. This agreed with the values for St or MMA and supported the idea that the nature of the catalyst in the CuBr/dNbpy system may be temperature dependent. Addition of Cu^IBr to the $CuPF_6$/dNbpy system formed the better deactivator $Cu^{II}Br_2$ in situ, thus reducing the polydispersities and producing more well-defined products without sacrificing the rate of polymerization.

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