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Quantifying Vinyl Monomer Coordination to Cu^I in Solution and the Effect of Coordination on Monomer Reactivity in Radical Copolymerization

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ABSTRACT: The association/dissociation equilibrium between vinyl monomers (M) and the complex [Cu^I(PMDETA)]BPh_4 (where PMDETA = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine) to form [Cu^I(PMDETA)(π-M)]BPh_4 was studied by variable temperature ^1H NMR. The enthalpy and entropy of coordination and the relative binding constants of methyl acrylate (MA), 1-octene (Oct), styrene (Sty), and methyl methacrylate (MMA) were determined. The affinity of the monomers to the Cu^I center decreased in the order MA > Oct > Sty > MMA with formation constants (at room temperature) equal to 760, 320, 250, and 6 M^{-1}, respectively. Quantification of this equilibrium process allowed the study of the effect that coordination has on the reactivity of the monomer in free radical polymerization. During these studies, an additional side reaction between free radical azo-initiators (AIBN and V-70) and the Cu^I complex was identified and analyzed. Additionally, the consequence of monomer coordination to Cu^I in atom transfer radical polymerization (ATRP) was examined. The reactivity of the monomers in conventional free and ATRP was not significantly affected by the coordination.

Introduction

The tolerance that radical polymerization shows toward polar functional groups, as opposed to traditional coordination and ionic polymerization, makes this technique attractive for polymerizing polar monomers. Nevertheless, a number of well-known drawbacks, including the inability to control molecular weight distribution or chain-end functionality and develop well-defined complex structures, make conventional radical polymerization less than ideal. Atom transfer radical polymerization (ATRP) has emerged in the past decade as a powerful technique for the synthesis of macromolecules with well-defined compositions, architectures, and functionalities. This controlled/living radical polymerization technique has produced a plethora of polymeric materials with predictable molecular weights and narrow molecular weight distributions.[1–6]

Mechanistic studies are crucial to any future developments of ATRP. Correlating reaction parameters including activation, deactivation, and initiation, rate constants, overall reaction rate, and evolution of molecular weight distribution[7–15] with catalyst, alkyl halide, and monomer structure, solvent composition, and temperature should ultimately lead to the development of more active catalysts.[16–21] Furthermore, concurrent reactions that may occur during ATRP and will affect its efficiency warrant further examination. Disproportionation of the Cu^I catalyst in aqueous media,[22] transfer reactions associated with the complexing ligand,[23–25] and solvent coordination[26] to the active catalyst have already been documented in this polymerization technique. This paper addresses the side reaction of monomer coordination to the Cu^I ATRP catalyst through the double bond of the vinyl monomer. Furthermore, this “side reaction” of monomer coordination to Cu^I was maximized in an attempt to affect the reactivity ratios of coordinated monomers in radical copolymerization. Indeed, the reactivity of polar monomers in a radical polymerization can be influenced by agents complexing with the monomer’s ester group functionalities.[27–31] This study investigated the effects of complexation through the vinyl double bond of several monomers, which include nonpolar α-olefins.

While radical polymerization techniques are well-suited for polar monomers, α-olefins typically do not polymerize via a radical mechanism. Recent work has shown the feasibility of incorporating small amounts of various 1-alkenes into copolymers with methyl acrylate under mild ATRP conditions.[32–35] However, the unfavorable reactivity ratios of these monomers in radical polymerizations have made statistical copolymers with a high degree of olefin incorporation difficult to attain and a high conversion difficult to reach. Recent advances toward the copolymerization of polar monomers and alkenes were made in the field of coordination polymerization with the introduction of rationally designed Pd- and Ni-based diimine polymerization catalysts.[36,37] Controlling these reactions still remains a challenge,[38,39] and detailed mechanistic studies concerning olefin coordination to transition metals will be necessary for any further advances made in this field. Moreover, combining concepts from two fields of polymerization by radically polymerizing coordinated monomers could provide a way of increasing olefin incorporation into copolymers with polar functional monomers.

Cu^I(PMDETA)X (PMDETA = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine and X = Cl or Br) is successfully used as an ATRP catalyst,[17] but complexes with coordinated monomer were only recently isolated with a weakly coordinating counterion that does not compete with monomer for coordination to the Cu^I center.[40] The compounds studied and characterized included the monomers methyl acrylate (MA), styrene (Sty), 1-octene

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(Oct), and methyl methacrylate (MMA) and had the general structure [Cu^I(PMDETA)(π-M)]BPh$_4$ (M = vinyl monomer), henceforth referred to as CuMA, CuSty, CuOct, and CuMMA, respectively.

Herein, quantification of this coordination process through variable temperature ^{1}H NMR and assessment of the stability of these complexes under polymerization conditions allowed the investigation of the effect that coordination has on the reactivity of the monomer in conventional radical copolymerization. Additionally, the consequence of monomer coordination on the performance of Cu^I(PMDETA)Br and [Cu^I(PMDETA)]BPh$_4$ as ATRP catalysts was examined, and the results were compared with those from conventional free radical polymerization.

Experimental Section

Materials. All reagents and solvents used in this study were obtained from commercial sources. Monomers were purified by passing the neat liquid through a column of aluminum oxide to remove the radical inhibitor. All monomers, ligands, and solvents were deoxygenated by purging with nitrogen for at least 1 h prior to usage. 2,2′-Azobis(isobutyronitrile) (AIBN) and 2,2′-azobis(2,4-dimethyl-4-methoxyvaleronitrile) (V-70) were recrystallized from methanol. Cu^I complexes of the form [Cu^I(PMDETA)(π-M)]BPh$_4$ were prepared according to published procedures.[40] All other reagents were used without further purification, unless otherwise specified.

Variable Temperature ^{1}H NMR. 0.02 M solutions of the four [Cu^I(PMDETA)(π-M)]BPh$_4$ compounds were prepared under a nitrogen atmosphere in separate NMR tubes in (CD$_3$)$_2$CO and were then flame-sealed under vacuum. Chemical shifts are given in ppm relative to the residual acetone solvent peak. The temperature dependence of the chemical shifts of all species was taken into account for any thermodynamic calculations. Errors in $\Delta H°$ and $\Delta S°$ were calculated from the standard deviations of the slope and intercept of Arrhenius plots.

Free Radical Polymerization (FRP) of MA and MMA. In a control copolymerization of MMA and MA, 5.4 μL (5.0 × 10^{-2} mmol) of MMA and 4.5 μL (5.0 × 10^{-2} mmol) of MA were injected into 0.60 mL of (CD$_3$)$_2$CO containing 1.4 × 10^{-3} g (4.5 × 10^{-3} mmol) of dissolved V-70. Toluene (10 μL) was used as the internal standard against which monomer conversion was measured by integration of all relevant proton peaks. The tube was immediately frozen in liquid nitrogen after all components were added and then flame-sealed under vacuum. An initial spectrum was taken upon thawing the reaction mixture, and the tubes were heated in an external thermostated oil bath set to 30 °C until the next spectrum was taken to monitor conversion. The same procedure was followed to copolymerize MA in the form of CuMA with MMA, except that 0.032 g (5.0 × 10^{-2} mmol) of the CuMA complex was dissolved in the NMR tube in place of free MA.

ATRP of MA and MMA. To a nitrogen-filled Schlenk flask containing 0.0130 g (0.0907 mmol) of Cu^{I}Br was added 2.0 mL of acetone, 0.2 mL of toluene as internal standard, 19.0 μL (0.0907 mmol) of PMDETA, 0.816 mL (9.07 mmol) of MA, and 0.970 mL (9.07 mmol) of MMA. The solution was warmed to the reaction temperature of 50 °C in a thermostated oil bath, and after a 0.1 mL initial sample was taken by nitrogen-purged syringe, 13.3 μL (0.0907 mmol) of ethyl 2-bromoisobutyrate (EBiB) initiator was injected into the solution. Conversion and molecular weights were determined from periodic aliquots taken from the solution. The same procedure was followed for the atom transfer radical copolymerization of MA and MMA catalyzed by 0.0583 g (0.0907 mmol) of the presynthesized [Cu^I(PMDETA)(π-MA)]BPh$_4$.

Spectrophotometric Determination of Formation Constants. To a Schlenk flask fit with a UV−vis quartz cuvette, filled with nitrogen, and containing 0.0281 g (0.196 mmol) of Cu^{I}Br was added 43.06 mL of acetone and 40.9 μL (0.196 mmol) of PMDETA. The solution stirred at room temperature (RT) for 2 h to ensure the complex was fully dissolved. After an initial spectrum was taken, increasing amounts of MA were added and spectra were collected. The spectra were monitored above 350 nm, where the solvent and excess MA do not absorb.

Analyses. All ^{1}H NMR spectra were obtained using a Bruker Avance DMX-500 (operating at 500.13 MHz) or a Bruker Avance AV-300 (operating at 300.13 MHz) variable temperature spectrometer. NMR probe temperatures below RT were calibrated using a 4% methanol sample in CD$_3$OD and above RT using neat ethylene glycol. Monomer conversion was either determined by ^{1}H NMR or by gas chromatography (GC) using a Shimadzu GC 14-A gas chromatograph equipped with a FID detector and J&W Scientific 30 m DB WAX Megabore column. The initial temperature was 40 °C (3 min hold) and final temperature 180 °C (1 min hold) with a heating rate of 40 °C/min. Before determination of molecular weights, the samples were diluted with THF and then filtered through a short column of neutral alumina followed by a 0.2 μm PTFE Acrodisc filter. Molecular weight distributions were determined on a gel permeation chromatography system consisting of a Waters 515 pump, a Waters 717plus autoinjector, Polymer Standards Service columns (styrogel 10^5, 10^3, 10^2 Å), and a Waters 2410 RI detector against poly(methyl methacrylate) standards using THF as the eluent at a flow rate of 1 mL/min. Absorption spectra were collected on a UV/vis/NIR Lambda 900 spectrophotometer.

Results and Discussion

A. Thermodynamic Study of π-Coordinated Monomers. Essential to our study of the effect that complexation has on monomer reactivity in polymerization was the accurate measure of the degree of monomer coordination under polymerization conditions. Because the four [Cu^I(PMDETA)(π-M)]BPh$_4$ complexes (CuMA, CuSty, CuOct, and CuMMA) undergo fast monomer exchange on the NMR time scale at room temperature according to the simple reaction

$$\mathrm{Cu} + \mathrm{M} \rightleftharpoons \mathrm{CuM}$$

where Cu represents Cu^I(PMDETA)$^+$, M the monomer, and CuM the complex [Cu^I(PMDETA)(π-M)]$^+$, the average signal for the protons of the free and coordinated monomers were observed. Methods for the determination of the formation constant

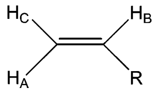
$$K_{\mathrm{M}} = \frac{[\mathrm{CuM}]}{[\mathrm{Cu}][\mathrm{M}]} \tag{1}$$

for such a reaction from solution NMR data are well-known.[41,42] The observed average chemical shift (δ_{obs}) can be expressed as the mole fraction (X) weighted average of the individual shifts for the free and complexed monomer.

$$\delta_{\mathrm{obs}} = \delta_{\mathrm{M}}X_{\mathrm{M}} + \delta_{\mathrm{CuM}}X_{\mathrm{CuM}} = \delta_{\mathrm{M}}X_{\mathrm{M}} + \delta_{\mathrm{CuM}}(1 - X_{\mathrm{M}}) \tag{2}$$

In this study, an equimolar amount of the products of dissociation ([Cu] = [M]) were present as only the isolated [Cu^I(PMDETA)(π-M)]BPh$_4$ was dissolved in solution. The formation constant K_{M} for the four CuM complexes could then be expressed in terms of the starting concentration of this complex ([CuM]$_{\mathrm{tot}}$), the known chemical shift of the free and coordinated monomer (determined in a separate experiment), and

Table 1. Chemical Shifts (500 MHz, $(CD_3)_2CO$) of Vinyl Protons in $[Cu^I(PMDETA)(\pi\text{-}M)]BPh_4$



complex^a	δH_A ($\Delta\delta H_A$)^b	δH_B ($\Delta\delta H_B$)	δH_C ($\Delta\delta H_C$)
CuMA	4.69 (1.65)^c	5.17 (0.97)^c	4.42 (1.45)^c
	4.59 (1.76)^d	5.09 (1.09)^d	4.32 (1.61)^d
CuSty	4.76 (1.04)^c	6.10 (0.66)^c	4.41 (0.82)^c
	4.78 (1.11)^d	6.07 (0.68)^d	4.28 (0.96)^d
CuOct	4.20 (0.78)^c	5.23 (0.58)^c	4.27 (0.64)^c
	4.10 (0.87)^d	5.10 (0.67)^d	4.15 (0.74)^d
CuMMA	4.65 (1.39)^c		4.38 (1.23)^c
	4.52 (1.52)^e		4.40 (1.30)^e

[a] Chemical shifts at all temperatures given relative to residual $(CH_3)_2CO$ peak set at 2.05 ppm. [b] $\Delta\delta H_A = \delta H_A$(free monomer) − δH_A(complexed monomer), ppm. [c] 30 °C, δH extrapolated. [d] −60 °C, δH measured. [e] −80 °C, δH measured.

the observed average chemical shift of a mixture of these species in equilibrium.

$$X_M = \frac{[M]}{[CuM] + [M]} = \frac{[M]}{[CuM]_{tot}} = \frac{\delta_{obs} - \delta_{CuM}}{\delta_M - \delta_{CuM}} \quad (3)$$

$$K_M = \frac{1 - X_M}{[CuM]_{tot}{X_M}^2} = \frac{(\delta_M - \delta_{obs})(\delta_M - \delta_{CuM})}{[CuM]_{tot}(\delta_{obs} - \delta_{CuM})^2} \quad (4)$$

The true chemical shifts of the free and coordinated monomers were accurately measured in $(CD_3)_2CO$, where the complexes were sufficiently soluble, and quantification of the degree of monomer coordination to the CuM complexes at various temperatures and concentrations in this solvent is provided hereafter. Any weak coordination of acetone to Cu^I in the absence of monomer will not affect calculations in eq 4, but it should be noted that K_M will likely be solvent dependent.

1. Variable Temperature ^{1}H NMR Studies of $[Cu^I(PMDETA)(\pi\text{-}M)]BPh_4$. The proton spectra of the four CuM complexes were taken at sufficiently low temperatures where distinct signals for the free and coordinated monomers could be seen. Because the observed chemical shifts of all species in solution are temperature dependent, including those for residual solvent peaks[43] and common internal standards such as TMS,[44] these changes in shift must be accounted for to ensure the accurate measurement of thermodynamic data. In this study, chemical shifts were measured for free monomers between 40 and −90 °C (where they showed a linear dependence with temperature) and for coordinated monomers between −60 and −90 °C where they could be directly observed (and where they also showed a linear dependence with temperature). From these data, the true chemical shifts of CuM at higher temperatures were extrapolated, and their drift over these temperatures can be observed in Table 1. All chemical shifts were referenced to the residual acetone solvent peak set to 2.05 ppm at every temperature, which adequately satisfies any calculations in eqs 3 and 4 where only the difference in chemical shifts of the free and coordinated monomer and observed average signal is important. Furthermore, when studying complex formation for the purpose of determining formation constants, the most accurate values for K_M are obtained when $0.2 < ([CuM]/[CuM]_{tot}) < 0.8$.[41] This tenet was adhered to in the study of all four CuM complexes, and $[CuM]_{tot}$ was chosen in such a fashion as to obtain measurements of K_M over a wide range of monomer complexation.

Table 2. Equilibrium Constants of Formation and Thermodynamic Information

complex	temp, °C	K_M,^{a} M^{-1}	$\Delta H°$, kJ/mol	$\Delta S°$, J/(mol K)
CuMA	40	385 ± 13	−30.2 ± 2.8	−46.0 ± 9.4
	30	650 ± 22		
	20	1040 ± 50		
	0	2170 ± 60		
CuSty	20	291 ± 26	−22.7 ± 0.4	−30.5 ± 1.6
	0	562 ± 61		
	−20	1270 ± 350		
CuOct	20	388 ± 9	−26.2 ± 0.8	−40.0 ± 2.8
	0	817 ± 7		
	−20	2120 ± 140		
CuMMA	20	7.0 ± 1.0	−25.4 ± 0.5	−70.2 ± 1.8
	0	15.6 ± 2.6		
	−20	38.5 ± 7.2		
	−40	102 ± 20		

[a] K_M was calculated from the chemical shift of each vinyl proton; the average value is reported.

Using eq 4 and the data in Table 1, the formation equilibrium constants could now be calculated over a range of temperatures, and the thermodynamic information for these systems obtained from plots of ln(K_M) vs $1/T$ is provided in Table 2. The importance of the steric properties of these olefins in determining the stability of these complexes is apparent in a comparison of those constants calculated for the electronically similar CuMA and CuMMA (Table 2); the formation constant of the former complex is 2 orders of magnitude greater at RT than that of the latter. While the complex formation in all cases was exoentropic, the biggest loss of entropy was observed for the disubstituted alkene (MMA), presumably a consequence of the greater physical restraint to free rotation of this monomer around the metal−olefin bond imposed by two α-substituents.

It has been observed with d^{10} metals that for Ni^0−olefin complexes, π (metal to olefin) back-donation is more important in the formation of a stable complex than σ (olefin to metal) bond formation, as evident from the observed increase in stability and enthalpy of the complexes with an increase in the electron-withdrawing ability of the substituent on the olefin double bond. In contrast, the π character of Ag^I−olefin complexes is relatively small, and electron-withdrawing substituents on the olefin destabilize these complexes.[45] While formation of all four CuM complexes was exothermic, no clear trend in formation enthalpy was observed in Table 2. This relative insensitivity to the alkene substituent groups has previously been observed for Cu^I−olefin complexes, for which the bonding nature was described as intermediate between those complexes with Ni^0 and Ag^I.[46] It is generally difficult to separate the steric and electronic influences of the olefin substituents, and these complexes are no exception as the formation enthalpies in Table 2 differ by less than 2 kcal/mol. However, monomer coordination did prove most exothermic with the most electrophilic alkene (MA). This suggests, when considered together with the extent of the upfield shift of the vinyl proton resonances and the downfield shift of the complexing PMDETA ^{1}H NMR signals upon monomer coordination to the Cu^I center (which have been thoroughly discussed in a previous publication[40]), that π-back-donation is very significant in the stabilization of these metal−olefin complexes.

The formation constants of the CuM complexes presented in this table decrease with increasing temperature. Less monomer will thus be coordinated to Cu^I under typical radical polymerization temperatures than will be coordinated at room temperature, an observation which had implications on our choice of polymerization temperatures for an experiment described in a later section. The relative binding constants for the different monomers can also be calculated from the data in Table 2; i.e., MA binds approximately 2 orders of magnitude stronger to Cu^I than MMA at 0 and 20 °C. In this investigation of the reactivity of free and coordinated monomers in a copolymerization, information on the relative binding constants of the comonomers to the metal is essential for the selection of a suitable polymerization system and for the accurate interpretation of the results attained thereafter.

2. Competition for Coordination with Halogen. Under typical ATRP conditions where Cu^I is used in catalytic concentrations to polymerize neat monomer, the equilibrium in eq 1 would be strongly shifted toward formation of the complex. However, unlike the $[Cu^I(PMDETA)(\pi\text{-}M)]BPh_4$ system described above, free monomer competes for the open coordination site on $Cu^I(PMDETA)^+$ in ATRP with a halide anion that has a much stronger affinity for the cationic metal complex. Thus, quantifying the degree of monomer coordination to Cu^I in ATRP requires knowledge of a Cu^IBr formation constant, or

$$K_{Br} = \frac{[CuBr]}{[Cu][Br]} \tag{5}$$

where Cu represents $Cu^I(PMDETA)^+$ and CuBr the complex $Cu^I(PMDETA)Br$. Equimolar amounts of $Cu^I(PMDETA)Br$ and free monomer were initially employed in an attempt to determine by ^1H NMR the relative binding strength of the Br^- ion over the monomer by measuring K_{obs} defined as

$$K_{obs} = \frac{[CuM][Br]}{[CuBr][M]} = \frac{K_M}{K_{Br}} \tag{6}$$

from which K_{Br} could be determined with previous knowledge of K_M (Table 2).

Only a slight upfield shift (0.03 ppm) of the vinyl protons of MA was observed when 0.1 M of this monomer, which binds the strongest to Cu^I and competes the most effectively with Br^- of the monomers used in this study, was reacted with an equimolar amount of $Cu^I(PMDETA)Br$ in $(CD_3)_2CO$. Limited by the freezing point of the solvent, the solution was taken to −90 °C, at which temperature distinct resonances for the free and coordinated monomer could be seen with chemical shifts very similar to those of CuMA (see Figure 2), justifying the assumption in our calculations using eq 6 that the vinyl protons of $[Cu^I(PMDETA)(\pi\text{-}MA)]^+$ have the same chemical shifts in the presence of BPh_4^- and Br^-. Integration of these MA proton resonances in this slow exchange region at −90 °C revealed approximately 17% of the MA was coordinated to Cu^I at this temperature compared to 2% at room temperature determined by the observed average chemical shift, outside the range of $0.2 < ([CuM]/[CuM]_{tot}) < 0.8$. The excess free monomer required to further shift the equilibrium affected the observed average chemical shifts to the extent that the subtle shifts could not be accurately measured in the ^1H NMR spectra. Therefore, UV−vis spectroscopy was employed to determine the relative binding constants of Br^- and MA, as a large excess of free MA did not absorb in the same wavelength region as the Cu^I complexes.

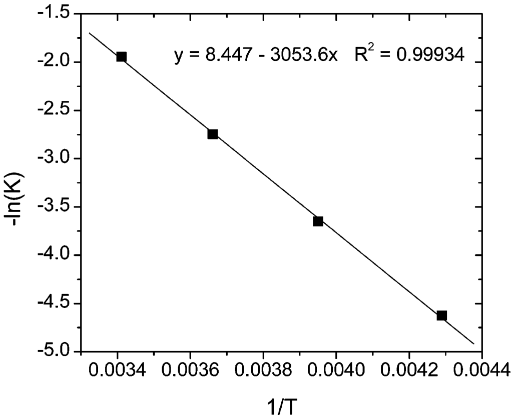


Figure 1. Arrhenius plot for K_M of CuMMA.

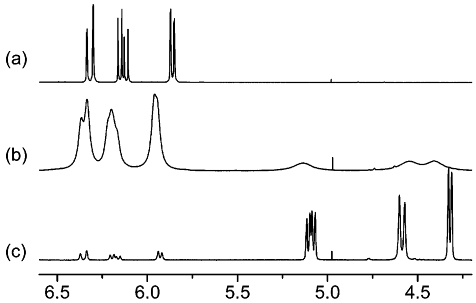


Figure 2. Comparison of 500 MHz ^1H NMR spectra of 0.1 M $Cu^I(PMDETA)Br$ + 0.1 M MA at 30 °C (a) and −90 °C (b) and 0.02 M CuMA at −60 °C (c).

All measurements were made in acetone above 350 nm to ensure no absorbance was due to free monomer or residual impurities in the solvent. The binding strength of $Cu^I(PMDETA)^+$ to Br^- was much greater than to MA, and this experiment ultimately revealed a large excess of the monomer could not entirely displace the anion. Because the spectrum of purely complexed monomer could not be measured in acetone in the presence of Br^-, the molar absorbance of $[Cu^I(PMDETA)(\pi\text{-}MA)]^+$ was measured by titrating a solution of $[Cu^I(PMDETA)(\pi\text{-}MA)]BPh_4$ with MA until there was no further change in absorbance (i.e., until all Cu^I was bound to form the MA complex). A solution of $Cu^I(PMDETA)Br$ (for which the extinction coefficients were also measured) was then titrated with MA. The relative proportions of $Cu^I(PMDETA)^+$, $[Cu^I(PMDETA)(\pi\text{-}MA)]^+$, and $Cu^I(PMDETA)Br$ were calculated from these observed spectra (shown in Figure 3), with more details provided in the Supporting Information.

The amount of $Cu^I(PMDETA)^+$ present in the above experiment was found to be negligible; thus, eq 6 was used to calculate K_{obs}. Knowing the formation constant of $[Cu^I(PMDETA)(\pi\text{-}MA)]^+$ at RT from Table 2 (760 M^{-1}), K_{Br} could be calculated as $(3.80 \pm 0.50) \times 10^6\ M^{-1}$ from this spectrophotometric data where $[CuM]/[CuM]_{tot}$ ranged from 0 to 0.15. No concentration dependence was observed for these calculated equilibrium constants, justifying our assumption that $[Cu(PMDETA)(\pi\text{-}MA)]^+$ has the same extinction coefficient with either BPh_4^- or Br^- as the counterion. Initial calculations based upon these formation constants suggest that under typical

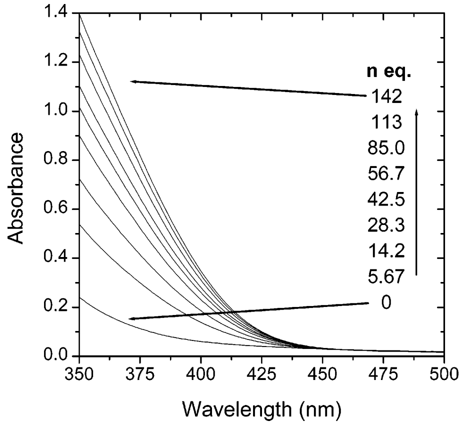


Figure 3. Addition of n equivalents of MA to 4.55×10^{-3} M $Cu^I(PMDETA)Br$ in acetone at 25 °C.

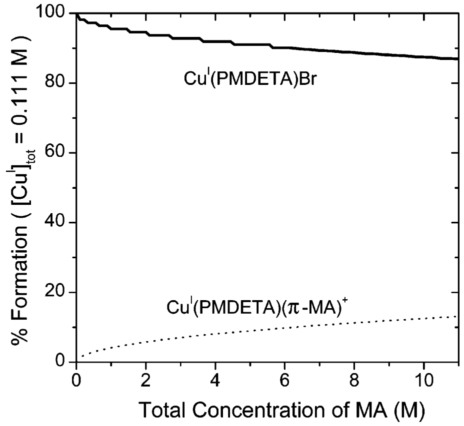


Figure 4. Calculated species distribution of $Cu^I(PMDETA)$-Br and $Cu^I(PMDETA)(\pi\text{-MA})^+$ relative to 0.111 M $[Cu^I]_{tot}$ in acetone at 25 °C where $K_{MA} = 760\ M^{-1}$ and $K_{Br} = 3.80 \times 10^6\ M^{-1}$.

ATRP conditions ($[MA]_0 = 11.1$ M and $[Cu^IBr/PMDETA]_0 = 0.111$ M) less than 15% of the Cu^I complex will be coordinated with MA at 25 °C (see Figure 4).

3. Decomposition of $[Cu^I(PMDETA)(\pi\text{-M})]BPh_4$. The general stability of the four CuM complexes under polymerization conditions was monitored qualitatively. A 0.02 M solution of CuSty in acetone became dark yellow and heterogeneous after 90 min of stirring at 60 °C due to decomposition of the complex. While a similar color change was observed at RT over the course of 24 h, the solution remained homogeneous. The average chemical shifts of the vinyl protons of free and complexed Sty in this solution of CuSty were monitored by NMR over 24 h, and they shifted slightly downfield (approximately 0.1 ppm). The ratio of free to coordinated monomer had increased due to the slow decomposition of the Cu^I complex. All CuM complexes were quite stable over several days in solution at −20 °C, as determined by the absence of any change in the ^1H NMR spectra. Additionally, these complexes decompose into a black precipitate when irradiated with UV light of similar intensity required to break down azo-initiators that initiate polymerization. All of these observations prompted the use of a low-temperature azo-initiator in the following polymerization experiments to ensure a significant amount of the complex did not decompose over the course of the reaction.

B. Effect of Monomer Coordination on Polymerization. ATRP originates and is mechanistically similar to atom transfer radical addition (ATRA), a widely used reaction in organic synthesis.[47,48] The nature of the active species in these reactions has been debated, and it has even been proposed that for some systems the radicals produced are not free but under the influence of the metal center.[49,50] The nature of the propagating species under typical ATRP conditions has already been investigated; the similarities between the reactivity ratios in conventional free radical and atom transfer radical copolymerization,[51,52] the similar rates of racemization, exchange, and trapping reactions,[53] the identical reactivities of radicals in metal-catalyzed and conventional free radical addition reactions,[54] and also the direct ESR observation of radicals during ATRP gelation experiments[55] all provide convincing evidence that the dominant intermediates in these processes are truly free radicals. Despite recent suggestions that copper-mediated living radical polymerization is not a simple free radical process,[56] current studies revealed indistinguishable ^{13}C kinetic isotope effects between free radical polymerization initiated by AIBN and ATRP initiated by ethyl 2-bromoisobutyrate using $Cu^IBr/2,2'$-bipyridine as the catalyst, further reinforcing a free radical mechanism of chain extension in ATRP.[57] Our demonstration that a fraction of vinyl monomer is coordinated with the $Cu^I(PMDETA)Br$ ATRP catalyst under polymerization conditions does suggest, however, that the reactivity of the coordinated monomers could be altered during polymerization.

1. $[Cu^I(PMDETA)]BPh_4$-Catalyzed ATRP. To adequately study the effect of monomer coordination to Cu^I in ATRP, $[Cu^I(PMDETA)]BPh_4$ was used as the catalyst instead of $Cu^I(PMDETA)Br$ such that monomer coordination during the polymerization would be maximized. Monitoring the relative incorporation of MA and MMA into a copolymer in such a system, for which the equilibrium constants of formation for CuMA and CuMMA were known (Table 1), could reveal whether π-coordination to Cu^I alters a monomer's reactivity in a radical polymerization. As MA binds 2 orders of magnitude stronger to Cu^I than MMA, approximately 98% of the Cu^I was calculated to be coordinated with MA under the initial polymerization conditions when no halogen was present ($[MMA]:[MA]:[[Cu^I(PMDETA)(\pi\text{-MA})]BPh_4]:[EBiB] = 100:100:1:1$; 50 °C, 10% toluene, 50% acetone), although during the polymerization the alkyl bromide initiator provides a source of halogen. Regardless, any enhanced incorporation of MA into the copolymer in this experiment relative to a control experiment catalyzed by $Cu^I(PMDETA)Br$ would demonstrate whether this π-coordination influenced monomer reactivity.

In a copolymerization catalyzed by $Cu^I(PMDETA)Br$ at 50 °C (where $[MMA]:[MA]:[Cu^IBr]:[PMDETA]:[EBiB] = 100:100:1:1:1$; 10% toluene, 50% acetone), 46% conversion was reached in 7 h, yielding a copolymer that had a M_n of 11 000 g/mol and $M_w/M_n = 1.15$. Comparatively, that catalyzed by $[Cu^I(PMDETA)]BPh_4$ was significantly faster, reaching 45% conversion in 1.5 h and producing a copolymer that had a similar M_n of 12 700 g/mol but $M_w/M_n = 1.76$. The relative incorporation of MMA to MA into the copolymer at low conversion was virtually the same within experimental error in both experiments (2.3 molar ratio for $Cu^I(PMDETA)Br$ compared to 2.1 for $[Cu^I(PMDETA)]BPh_4$ catalyzed ATRP at approximately 15% overall conversion) and is in good agreement with reported literature reactivity

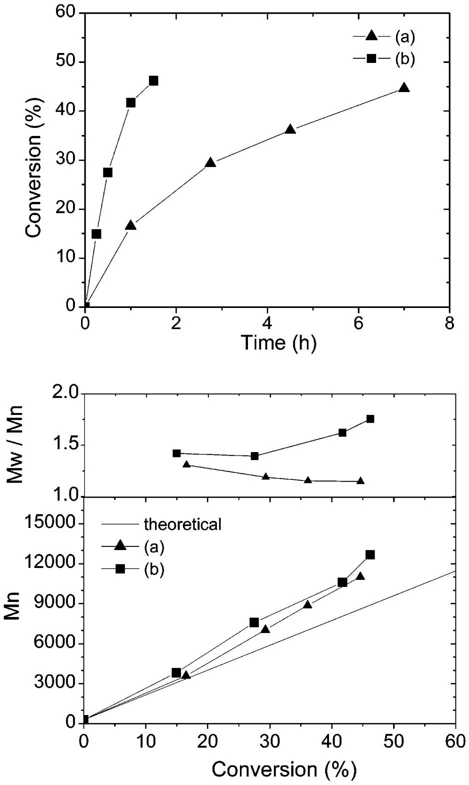


Figure 5. (a) [MMA]:[MA]:[Cu$^{\mathrm{I}}$Br]:[PMDETA]:[EBiB] = 100:100:1:1:1; 50 °C, 10% toluene, 50% acetone. (b) [MMA]:[MA]:[[Cu$^{\mathrm{I}}$(PMDETA)(π-MA)]BPh$_4$]:[EBiB] = 100:100:1:1; 50 °C, 10% toluene, 50% acetone.

ratio values.[58] Thus, no significant enhancement of incorporation of MA into the copolymer was observed in the [Cu$^{\mathrm{I}}$(PMDETA)]BPh$_4$-catalyzed polymerization.

Furthermore, this polymerization was faster and worse controlled than that catalyzed by Cu$^{\mathrm{I}}$(PMDETA)-Br (Figure 5), and the reaction mixture was much darker blue, indicating an increased presence of Cu$^{\mathrm{II}}$. These observations would be consistent with the presence of a strongly activating Cu$^{\mathrm{I}}$ complex and/or a poorly deactivating Cu$^{\mathrm{II}}$ complex, but recent studies have shown that the activation rate constant of [Cu$^{\mathrm{I}}$(PMDETA)]BPh$_4$ under ATRP conditions is not significantly different from that of Cu$^{\mathrm{I}}$(PMDETA)Br.[15] This suggests that [Cu$^{\mathrm{II}}$(PMDETA)Br]BPh$_4$ may be a poor deactivating species and is responsible for the increase in polymerization rate in [Cu$^{\mathrm{I}}$(PMDETA)]BPh$_4$-catalyzed ATRP. The solid-state structures of Cu$^{\mathrm{II}}$(PMDETA)Cl$_2$ [59] and Cu$^{\mathrm{II}}$(PMDETA)Br$_2$ [60] support this notion. Both of these complexes have a distorted square-pyramidal geometry; one halogen is located at the apical position, and the other halogen and three nitrogens are found on the basal plane. In both complexes, the apical Cu$^{\mathrm{II}}$−X bond is elongated by approximately 0.2 Å, and cleavage of a Cu$^{\mathrm{II}}$−X bond during the deactivation process of ATRP is therefore expected to occur at this energetically more favorable position.[61] This further suggests that the Br$^-$ in [Cu$^{\mathrm{II}}$(PMDETA)Br]BPh$_4$ would likely be more difficult to cleave than the Br$^-$ in Cu$^{\mathrm{II}}$(PMDETA)Br$_2$, which would give rise to a slower deactivation rate in ATRP.

Another plausible explanation for the observed increase in polymerization rate and loss of control in the [Cu$^{\mathrm{I}}$(PMDETA)]BPh$_4$ catalyzed ATRP is that the Br$^-$ anion coordinated to [Cu$^{\mathrm{II}}$(PMDETA)Br]BPh$_4$ may further equilibrate with the remaining excess of [Cu$^{\mathrm{I}}$(PMDETA)]BPh$_4$ and form some Cu$^{\mathrm{I}}$(PMDETA)Br and a [Cu$^{\mathrm{II}}$(PMDETA)](BPh$_4$)$_2$ complex, which would be unable to deactivate radicals during the polymerization. This proposed equilibrium is currently under investigation.

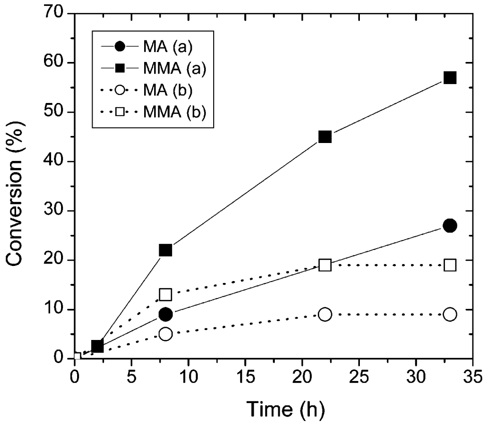


Figure 6. Conversion of MMA and MA in (a) [MMA]:[MA]:[V-70] = 12.5:12.5:1 and (b) [MMA]:[CuMA]:[V-70] = 12.5:12.5:1. 30 °C, 10 μL internal toluene standard, (CD$_3$)$_2$CO solvent.

2. Monomer Coordination in FRP. While no significant enhancement of incorporation of MA into the copolymer was observed when [Cu$^{\mathrm{I}}$(PMDETA)]BPh$_4$ was used as the ATRP catalyst to maximize monomer coordination, the fact that a significant but undetermined amount of Cu$^{\mathrm{I}}$(PMDETA)Br was likely generated in this polymerization rendered these findings inconclusive. To determine whether monomer coordinated to the Cu$^{\mathrm{I}}$ catalyst is significantly involved in propagation in ATRP, a FRP system in the absence of halide was examined where stoichiometric amounts of the CuM complex could be used.

Because MA binds so much stronger to Cu$^{\mathrm{I}}$ than MMA, the FRP of MMA with MA mostly in the form of CuMA is possible and would permit a more precise determination of the effect that coordination to Cu$^{\mathrm{I}}$ has on monomer reactivity. Initiated by the low-temperature azo-initiator V-70 at 30 °C where the CuM compounds are relatively stable, these polymerizations were run in acetone-d_6 and monitored by ^{1}H NMR spectra periodically over 33 h. Indeed, the average chemical shift of the vinyl protons of the monomers at the start of the polymerization showed that approximately 90% of the MA was bound to Cu$^{\mathrm{I}}$ (when [CuMA]$_{\mathrm{Tot}}$ = 0.083 M) compared to 2.5% of MMA, in good agreement with the data from Table 1. The relative incorporation of MMA to MA was 2.2 at 13% conversion, reached in 20 h (Figure 6). Surprisingly, the ^{1}H NMR spectra of this reaction taken at 22 h showed no V-70 proton signals, indicating initiator decomposition was complete and the polymerization had ceased after reaching 13% overall conversion.

In the control copolymerization of free MA and MMA, approximately 30% overall conversion was reached after 33 h, and V-70 resonances could still be observed in the ^{1}H NMR spectra, signifying that initiator decomposition was not complete. The relative incorporation of MMA to MA was 2.4 at 15% conversion, reached in 10 h. While these results suggested that coordination to Cu$^{\mathrm{I}}$ had no significant effect on monomer reactivity, the qualitative observation that the rate of azo-initiator decomposition was greatly accelerated in the presence of excess Cu$^{\mathrm{I}}$ warranted further examination.

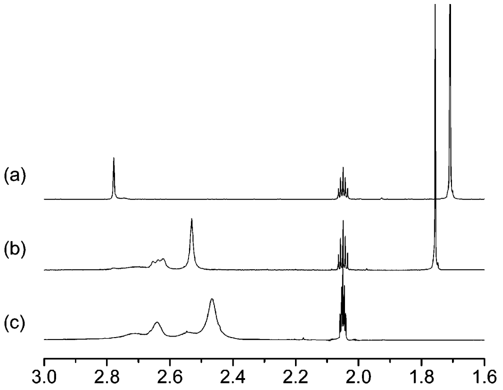


Figure 7. Comparison of RT 300 MHz ^{1}H NMR spectra of AIBN (a), 0.02 M [Cu^I(PMDETA)]BPh$_4$ and 1 equiv AIBN (b), and 500 MHz spectra of 0.02 M [Cu^I(PMDETA)]BPh$_4$ (c).

3. Coordination of Azo-Initiators to Cu^I. A qualitative look at the proton resonances of V-70 in the presence of the large excess of Cu^I in the above experiment revealed that the signals for the azo-initiator in the ^{1}H NMR spectra were slightly shifted during the polymerization, indicating that the V-70 also interacted or coordinated to the metal. Additionally, the disappearance of any V-70 proton signals in the polymerization with CuM after 20 h (in contrast to the control experiment) suggested Cu^I had catalyzed the decomposition of the azo-initiator. However, quantification of this accelerated decomposition in the above experiment was complicated by the presence of copolymer ^{1}H NMR signals and competition for coordination with monomer. (A change in the degree of shift of the V-70 signals with monomer conversion was observed.) This phenomenon was investigated further in a separate experiment with another more thermally stable azo-initiator (AIBN) to provide clear evidence of the interaction between Cu^I and these initiators.

In the ^{1}H NMR spectra of 0.02 M AIBN and 1 equiv of [Cu^I(PMDETA)]BPh$_4$, the methyl resonance of the azo-compound was shifted downfield approximately 0.05 ppm from 1.71 ppm (see Figure 7). The PMDETA protons were similarly shifted downfield, indicating there was coordination of the AIBN to Cu^I (either through the nitrile or azo groups of the initiator). When [Cu^I(PMDETA)]BPh$_4$ was added to a solution of partially decomposed AIBN, the resonance of the coupled product of AIBN decomposition was shifted as well from 2.78 ppm, presumably to overlap with the PMDETA protons. Furthermore, when 0.02 M AIBN in acetone-d_6 was heated for 10 h at 50 °C, approximately 10% of the AIBN decomposed. In the presence of just 1 equiv of [Cu^I(PMDETA)]BPh$_4$, the rate of AIBN decomposition increased approximately 3-fold.

In the above free radical copolymerization of MA (in the form of CuMA) and MMA, the reaction between Cu^I and V-70 increased the rate of initiator decomposition, yet the overall rate of polymerization had significantly decreased relative to the control experiment in the absence of Cu^I. This rapid decomposition of the initiator may have resulted in a greater radical concentration that would increase the rate of radical termination. The decomposition may involve a combination of a cage effect of the solvent and an attraction between Cu^I and the nitrile groups of the products of the azo-initiator decomposition that could promote the coupling of the two radicals (the extent of which is still under investigation), thus decreasing initiator efficiency.

But despite this side reaction, approximately 90% of MA was still coordinated to Cu^I (as observed in the ^{1}H NMR spectra) during the polymerization. The reactivity ratios of the monomers in this study were, surprisingly, not significantly affected one way or the other upon coordination to Cu^I during radical polymerization. However, the reactivity of other monomers that experience a stronger π-interaction with a different transition-metal complex could still potentially be influenced, and the search for such a combination is currently underway.

Conclusions

The thorough investigation of four CuM complexes has yielded valuable information concerning the degree of monomer coordination to Cu^I under polymerization conditions. Quantification of the relative binding constants of the monomers provided grounds for the determination that monomer reactivity was not significantly affected by π-coordination to Cu^I(PMDETA)$^+$ in radical copolymerization and furthermore that this coordination plays no significant role in the chain extension step of ATRP.

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Supporting Information Available: Plots of ln(K_M) vs 1/T for the CuM complexes from which all thermodynamic information in Table 1 was calculated; details concerning calculation of K_{Br} from spectrophotometric data. This information is available free of charge via the Internet at http://pubs.acs.org.

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