Controlled/"Living" Atom Transfer Radical Polymerization of Methyl Methacrylate Using Various Initiation Systems

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ABSTRACT: The homogeneous controlled/"living" free radical polymerization of methyl methacrylate (MMA) by atom transfer radical polymerization (ATRP) using a Cu¹X/4,4'-di(5-nonyl)-2,2'-bipyridine catalytic system (X = Cl, Br) with various initiators R-X was investigated. The rates of polymerization initiated by most of the systems exhibited first-order kinetics with respect to the monomer. A linear increase of number average molecular weight (M_n) versus monomer conversion was observed for most of these initiation systems. The benzhydryl chloride/Cu^ICl system yielded the lowest rate of polymerization, which could be increased by slow addition of the initiator. The reduced rate of polymerization was due the state of the polymerization was due to be added by a slow addition of the initiator. to an increase in the concentration of Cu^{II}Cl, which results from the coupling of benzhydryl radicals during initiation. The slow addition of benzhydryl chloride prevented the formation of a large amount of benzhydryl radicals in the initiation step, thereby reducing radical-radical termination and Cu^{II} formation, and led to an increase in the rate of polymerization. *p*-Toluenesulfonyl chloride/Cu^IBr gave better control of molecular weight and lower polydispersities than p-TsCl/Cu^ICl, possibly due to the faster deactivation step in ATRP. Ethyl 2-bromoisobutyrate/Cu^IBr gave the fastest rate of polymerization among all the initiation systems but showed some deviation in M_n at high conversions. The initiation efficiencies of diethyl 2-bromomalonate and diethyl 2-bromo-2-methylmalonate in the ATRP of MMA were examined. The latter can initiate polymerization efficiently, while the former gave no polymerization. This can be explained by the difference in the electronic nature of the two malonyl radicals generated during initiation. Such experimental observations, coupled with data from the literature, lead to some general "rules" by which successful initiation of ATRP can be achieved.

Introduction

One of the main goals in modern synthetic polymer chemistry is to prepare polymers with controlled molecular weight and well-defined architecture. Living polymerizations developed in the past forty years, including cationic, anionic, and group transfer polymerizations, provide the opportunity to reach that goal.¹ In living polymerizations, neither chain transfer nor chain termination processes occur. One of the major drawbacks of ionic living polymerizations that prevents them from wider industrial application is the stringent conditions required. Free radical polymerization is the most important industrial process to prepare high molecular weight polymers.² However, conventional free radical polymerization methods lack the control because of chain transfer and termination processes. This precludes conventional radical polymerization from synthesizing well-defined polymers with low polydispersities and complex architecture.

Gaining control over radical polymerization has become one of the most important topics in contemporary polymer chemistry. In a methodology similar to controlled/"living" cationic polymerization,³ free radical polymerization has been shown to be controlled under conditions in which a fast, dynamic equilibrium between the active and the dormant chains, and only a low and stationary concentration of the active species exist.⁴ Several examples of systems that have shown the ability to control radical polymerizations include nitroxyl radical-mediated polymerization of styrene,^{5–9} ruthenium-(II)/aluminum-based polymerization of methacrylates,¹⁰ Co^{II}-mediated polymerization of acrylates,¹¹ and polymerization of styrene using a degenerative transfer method.¹² Controlled/"living" free radical polymerization can also be obtained through atom transfer radical polymerization (ATRP).^{13–15} ATRP utilizes a transition metal, e.g., Cu/bipyridine complex, as a halogen atom transfer reagent between the dormant and the active polymer chains with the rate constants of activation and deactivation, k_{act} and k_{deact} , respectively (eq 1). The concent

$$P_{n} - X + Cu(I)/2L \xrightarrow{k_{act}} P_{n} + Cu(II)X/2L$$

$$(1)$$

$$Monomer \qquad P_{n+m}/P_{n} + P_{m}$$

tration of growing radicals, which propagate with the rate constant of propagation k_p , is sufficiently low to significantly reduce the contribution of radical–radical termination (with a rate constant k_t) and provide well-defined polymers with low polydispersities and novel architectures¹⁶ using various monomers, initiators, and ligands.^{17–22}

It has been demonstrated that ATRP can synthesize poly(methyl methacrylate) (PMMA) with well-controlled molecular weights and narrow molecular weight distributions.^{17,22–30} We previously reported a mechanistic study of the ATRP of MMA, including the effect of the ligand/Cu^I ratio on the rate of polymerization, the dependence of polymerization rate on the concentrations of initiator, Cu^I and Cu^{II} species, and the effect of temperature on the polymerization.³⁰ Here we present a study on the ATRP of MMA using various initiation systems. In addition, we demonstrate how to improve the control of the polymerization by choosing the appropriate initiation systems and experimental procedures. Scheme 1

$$R - X + Cu(I)X/L \xrightarrow{K_{eq}^{\circ}} R \cdot + Cu(II)X_2/L$$

R · + monomer
$$\xrightarrow{k_i} P_1 \cdot$$

Propagation

Initiation

 $P_{n} X + Cu(I)X/L \xrightarrow{K_{eq}} P_{n} + Cu(II)X_{2}/L$ $P_{n} + monomer \xrightarrow{k_{p}} P_{n+1}$

Termination

$$P_{n}^{\bullet} + P_{m}^{\bullet} \xrightarrow{k_{i,d}} P_{m}^{=} + P_{n}^{H}$$

$$P_{n}^{\bullet} + P_{m}^{\bullet} \xrightarrow{k_{i,c}} P_{n+m}$$

Results and Discussion

The homogeneous ATRP using $Cu^{I}X/4, 4'$ -di(5-nonyl)-2,2'-bipyridine (dNbpy) (X = halide, such as Cl or Br) initiation systems has been proposed to occur by the mechanism illustrated in Scheme 1.³¹ It consists of (a) an atom transfer equilibrium at both the initiation and propagation steps, (b) addition of radicals to olefinic monomers at both the initiation and propagating steps, and (c) the termination step.

However, it was recently proposed³² that propagation in the Cu-based ATRP of MMA did not take place via a carbon-centered free radical, since no effect on the rates of polymerization or molecular weights was observed in the presence of phenols. While several earlier studies clearly demonstrated that although phenols do affect polymerization of styrene, their effect on the radical polymerization of (meth)acrylate is very weak. For example, less than 1% retardation was observed for MMA with 0.2 M hydroquinone.³³ The presence of 4-methoxyphenol even increased the rate of polymerization initiated by azobis(isobutyronitrile) (AIBN) at 45 °C. In the latter case, the transfer coefficient is $k_{\rm tr}/k_{\rm p}$ < 0.0005.³³ A similar observation was made for methyl acrylate, where the inhibition was again insignificant at 50 °C ($k_{tr}/k_p < 0.0002$).³⁴ Thus, the weak retardation/ transfer effect of phenols on the polymerization of (meth)acrylates does not contradict a radical mechanism. On the other hand, phenols may even accelerate polymerization by exchanging ligands at the Cu center. Similar effects were noticed for Cu^I carboxylate and Cu^I-PF₆.^{35,36}

Assuming fast initiation and a steady concentration of propagating radicals in Scheme 1, the following rate law is derived (eqs 2 and 3). While it is recognized that

$$K_{\rm eq} = \frac{k_{\rm act}}{k_{\rm deact}} = \frac{[\mathbf{P}_n][\mathbf{C}\mathbf{u}^{\rm I}\mathbf{X}]}{[\mathbf{C}\mathbf{u}^{\rm I}][\mathbf{P}_n\mathbf{X}]}$$
(2)

$$R_{\rm p} = k_{\rm app}[\mathbf{M}] = k_{\rm p}[\mathbf{P}_n][\mathbf{M}] = k_{\rm p}K_{\rm eq}[\mathbf{In}]_0 \frac{[\mathbf{Cu}^{\rm I}]}{[\mathbf{Cu}^{\rm II}\mathbf{X}]}[\mathbf{M}]$$
(3)

the concentration of growing radicals continuously



Figure 1. Semilogarithmic kinetic plot for the solution polymerization of MMA in diphenyl ether at 90 °C with various initiation systems. [Initiator]₀ = 0.023 M, $[CuX]_0$ = 0.0115 M, [dNbpy] = 0.023 M.

decreases due to radical-radical termination, after the initial nonstationary period the change in the concentration of the propagating radicals is insignificant.

A fast equilibrium between the active and the dormant polymer chains is a necessary condition to observe low polydispersities in controlled/"living" polymerization. In ATRP, both effective initiation and good control of the polymerization rely heavily on the position of the equilibrium in both the initiation and propagation steps, and also on the reactivities of the radicals generated in the initiation step. Thus, choosing suitable organic halides and Cu^I halides in the reaction is necessary for controlled polymerization. For example, the initiation step must be faster than, or equal to, the propagation step to ensure efficient generation of polymer chains. Therefore, the C-X bond in the initiator must be weak enough for effective generation of radicals. Deactivation must also be fast to ensure a high concentration of dormant species (relative to active species) and prevent irreversible radical-radical chain termination. This is mainly governed by the dissociation energy of the Cu^{II}–X bond and the radical affinity toward the halogen atom. The importance of these factors will be discussed in terms of the effectiveness of various initiation systems.

We have reported that the rate of ATRP polymerization of MMA using Cu^I halide/R–X systems reaches a maximum when the ligand/Cu^I ratio equals approximately 1.³⁰ However, the reaction mixture may require nearly 1 h to become homogeneous for an equimolar ratio of ligand-to-Cu^I, while Cu^I halides dissolve much faster when an excess of ligand is used. Therefore, a ligand/Cu^I ratio of 2 has been used in the experiments discussed below. The typical reaction condition used in these studies is [initiator]₀/[Cu^IX]₀/[dNbpy]₀/[MMA]₀ = 1/0.5/1/200 in diphenyl ether (v/v = 1/1) at 90 °C.

ATRP of MMA using initiators such as ethyl 2-bromoisobutyrate (Br-iB), *p*-toluenesulfonyl chloride (*p*-TsCl), benzhydryl chloride (Ph₂CHCl), 1-phenylethyl chloride (1-PECl), and 1-phenylethyl bromide (1-PEBr) along with Cu^IX catalysts (X = Cl and Br) was investigated, and the results are shown in Figures 1–3.

As shown in Figure 1, the polymerization of MMA proceeds through approximately first-order kinetics with respect to monomer concentration for all the initiation systems. The number average molecular weight (M_n)



Figure 2. Dependence of molecular weight on conversion in the solution polymerization of MMA in diphenyl ether at 90 °C using various initiation systems. [Initiator]₀ = 0.023 M, $[CuX]_0 = 0.0115$ M, [dNbpy] = 0.023 M.



Figure 3. Dependence of polydispersities on conversion in the solution polymerization of MMA in diphenyl ether at 90 °C. [Initiator]₀ = 0.023 M, [CuX]₀ = 0.0115 M, [dNbpy] = 0.023 M.

increases (except for 1-PECI/Cu^ICl) with the monomer conversion (Figure 2), which indicates a constant concentration of growing chains throughout the reaction. The small deviation observed for the Br-iB/CuBr system will be discussed later.

The experimental M_n determined by gel permeation chromatography (GPC) was in agreement with the theoretical molecular weight calculated by eq 4, and the

$$DP = ([M]_0 - [M]_t)/[In]_0$$
(4)

polydispersities (= M_w/M_n , where M_w = weight average molecular weight) of the polymers remained low during the polymerization, except for the 1-PECl/Cu^ICl initiation system. Apparently, the rate of initiation with 1-PECl is much slower than propagation, resulting in inefficient initiation. This has a much larger effect on polydispersities and evolution of molecular weights with conversion than on the polymerization rate. The latter depends strongly on the concentration of Cu^{II} species, which is relatively low when initiation is slow. Using 1-PEBr/CuCl provides faster initiation, and hence lower polydispersities and better agreement with the theoretical molecular weight. For example, when a M_n of 22 000 was targeted (i.e., M_n at 100% conversion) using various 1-PEX and CuY/2dNbpy, the 1-PEBr/CuBr system led to $M_n = 22\ 000$ and $M_w/M_n = 1.28$, whereas 1-PECl/CuCl led to $M_n = 40\ 000$ and $M_w/M_n = 1.75$. The worst results were found for 1-PECl/CuBr, which yielded $M_n = 76\ 000$ and $M_w/M_n = 3.20$ (cf. subsequent discussion on the effect of halogen exchange).

When benzhydryl chloride (Ph₂CHCl) was added rapidly to the reaction mixture consisting of Cu^ICl, ligand, and monomer, the rate of polymerization was slow (monomer conversion $\sim 10\%$ after 18 h). In fact, the color of the solution turned from brown (Cu^I species) to green (Cu^{II} species) immediately after the initiator was added, which indicated the formation of a large quantity of Cu^{II}X₂. Increasing [Cu^{II}] has been shown to decrease the rate of polymerization dramatically.³⁰ It appears that a large amount of Cu^{II} species is produced during the initiation process, which hinders the progress of polymerization. The C-Cl bond in benzhydryl chloride is easily activated by the Cu^I complex to form benzhydryl radicals in relatively high concentrations. Therefore, radical-radical termination occurs at a significant rate early in the polymerization, irreversibly generating an excess of Cu^{II}Cl₂. This results in much slower polymerization. A ¹H NMR study, under the same reaction conditions as described above except 15 min at 70 °C and benzene as solvent, showed that 1,1,2,2-tetraphenylethane is formed (a singlet at 4.75 ppm from the $(C_6H_5)_2CH_2$ proton in CDCl₃) in smaller quantities if the benzhydryl chloride is added slowly to the polymerization mixture. A model study without added monomer also supports this proposal. One equivalent of benzhydryl chloride and 3 equiv of Cu^ICl/2dNbpy were heated at 90 °C in C₆D₆ and the reaction was monitored by ¹H NMR. Benzhydryl chloride was quantitatively converted to 1,1,2,2tetraphenylethane at 90 °C within 15 min.

The low rate of polymerization for the benzhydryl chloride/Cu^ICl-initiated polymerization can be improved by slow addition of initiator (during the first 5 min of the reaction) when monomer conversion is less than 5%. The kinetic plot of benzhydryl chloride/Cu^ICl-initiated polymerization shown in Figure 1 was obtained with the slow addition of initiator. Slow addition of benzhydryl chloride generates lower concentrations of benzhydryl radicals and thus reduces the rate of termination between radicals. The rate of polymerization and the evolution of molecular weights for slow and fast addition of Ph₂CHCl are compared in Figures 4 and 5. With slow addition of initiator into the reaction system, the rate of polymerization increased by approximately 5 fold (Figure 4) and molecular weight evolution agreed well with that predicted by eq 4 (Figure 5). The color of the solution remained brown throughout the slow addition experiment, indicating that Cu^IX/dNbpy complex is active in the reaction mixture.

Other Cl-based initiation systems (R–Cl/CuCl) have also been investigated, and the results are shown in Figure 6 with a comparison with the *p*-TsCl/CuCl system. 1-Phenylethyl chloride/Cu^ICl has been demonstrated to be an effective initiation system for the ATRP of styrene.³¹ For the ATRP of MMA, however, it gave poor molecular weight control during polymerization (Figure 6). It appears that for the 1-PECl/CuCl system, the product of the equilibrium constant and rate constant for addition in the initiation step ($k_i^{obs} = k_i K_{eq}^{\circ}$)



Figure 4. Semilogarithmic kinetic plot for the solution polymerization of MMA in diphenyl ether at 90 °C for slow and fast addition of benzhydryl chloride. For slow addition, the initiator was added over 5 min. [Benzyhydryl chloride]₀ = 0.023 M, [CuCl]₀ = 0.0115 M, [dNbpy] = 0.023 M.



Figure 5. Dependence of molecular weight on conversion in the solution polymerization of MMA in diphenyl ether at 90 °C for slow and fast addition of benzhydryl chloride. [Benzyhydryl chloride]₀ = 0.023 M, [CuCl]₀ = 0.0115 M, [dNbpy] = 0.023 M.



Figure 6. Dependence of molecular weight on conversion in the solution polymerization of MMA in diphenyl ether at 90 °C using Cl-based (R–Cl/CuCl) initiation systems. [Initiator]₀ = 0.023 M, [CuCl]₀ = 0.0115 M, [dNbpy] = 0.023 M.

is much smaller than the observed propagation rate constant ($k_p^{obs} = k_p K_{eq}$). The result is inefficient initiation, and therefore high molecular weight polymer is continually formed throughout the experiment, much the same as in a conventional radical polymerization. A similar observation is made for the methyl 2-chloroacetate (MeClAc)/CuCl system, in which the molecular weight increases continuously with monomer conversion

and deviates significantly from the calculated molecular weight.

Figure 1 also shows that the Br-iB/CuBr initiation system produced the fastest rate of polymerization among all the systems. The weaker C-Br bond in $-CH_2C(CO_2CH_3)(CH_3)$ -Br than the corresponding C-Cl bond in $-CH_2C(CO_2CH_3)(CH_3)-Cl$ is responsible for the faster rate of polymerization in R-Br/Cu^IBr systems since more radicals are generated during the activation process. The initial low polydispersities in the Br-iB/ CuBr system (Figure 3) are rationalized by fast deactivation, since the Cu^{II}–Br bond is weaker than the Cu^{II}-Cl bond. Nevertheless, the Br-iB/Cu^IBr-initiated polymerization showed some deviation in molecular weight from the theoretical $M_{\rm n}$, and instead of a continuing decrease in polydispersity with conversion (as often observed in other ATRP systems), a slight increase in polydispersity occurred at higher conversions (Figure 2 and Figure 3). The deviations are presumably due to an unidentified transfer process and slower initiation. Slow initiation with Br-iB can be related to the back strain effect,³⁷ i.e., the release of steric strain of dormant species during the rehybridization from sp³ to sp² configurations (e.g., carbocations or radicals). Recently, Mayr et al.³⁸ explained the differences in the apparent initiation rates between tert-butyl and 2,4,4trimethyl-2-pentyl halides in the cationic polymerization of isobutylene by this effect. A similar approach can be used to explain the slow initiation observed in the Br-iB/CuBr system. The radical 1, generated in the



reaction between CuBr and Br-iB, can add to MMA quickly, forming the propagating radical **2**. The reactivity of the propagating radical **2** toward MMA, however, should be lower than that of **1** due to the steric strain effect imposed by the substituent groups on carbon 4. The decrease in the rate of initiation due to the back strain effect, therefore, may lead to the observed deviation from the theoretical molecular weight at lower conversion. Apparently, dimeric halide, which generates the corresponding dimeric radical **2**, is an efficient initiator in Ru-catalyzed systems.³⁹

The higher reactivity of radical **1** should correlate with a lower equilibrium constant and lower overall initiator efficiency. It must also be stressed that back strain effect operates only for tertiary but not for secondary radicals/carbocations.

Two bromomalonate derivatives $(C(R)(Br)(CO_2Et)_2, R = Me, H)$ were used together with Cu^IBr as initiators for the ATRP of MMA. The results are shown in Figure 7.

The diethyl 2-bromo-2-methylmalonate (dEBMM)/ CuBr system behaves similarly to ethyl 2-bromoisobutyrate/CuBr initiation and produced polymers with low polydispersities. Some deviation of experimental molecular weights was noticed at high conversion, which can be attributed to the earlier discussed transfer reaction for R–Br/CuBr systems. The diethyl 2-bromomalonate (dEBM)/CuBr system gave essentially no polymerization (less than 5% conversion after 24 h). The color of the reaction mixture changed instantly from brown (Cu^I species) to green (typical for Cu^{II} species in



Figure 7. Dependence of molecular weight on conversion in the solution polymerization of MMA in diphenyl ether at 90 °C with bromomalonate derivatives as initiation systems. [Initiator]₀ = 0.023 M, [CuBr]₀ = 0.0115 M, [dNbpy] = 0.023 M.

the presence of Cu^I) with the addition of the initiator, regardless of the mode of addition. The diethyl 2-bromomalonate/CuBr system, however, does initiate ATRP of styrene and shows good control of polymerization when the catalyst was slowly added to the initiator/ monomer solution. The unsuccessful polymerization of MMA may be attributed to the different reactivities for malonyl radical toward styrene and MMA. Carboncentered radicals that contain two electron-withdrawing groups, such as nitriles or esters, possess relatively lowlying SOMOs and react preferentially with electron-rich olefins that contain high-energy HOMOs.⁴⁰ Giese et al.⁴¹ have demonstrated that the relative rates for addition of the malonyl radical to α -substituted styrenes depends on the electronic nature of the substituent. The rate of addition of malonyl radicals to an alkene with an electron-donating methyl group is approximately 4 times faster than that to an alkene with an electronwithdrawing ester group. In the ATRP of styrene, malonyl radicals are generated at the initiation step, add to the monomer, and start the polymerization. In the ATRP of MMA, however, initiating radicals formed cannot add to the monomer fast enough because of the electron-deficient nature of MMA. The malonyl radicals are therefore consumed by some side reactions, presumably by a redox reaction, leading to the formation of a malonyl anion and Cu^{II} species. The presence of a methyl group in dEBMM changes the radical to a less electron-deficient species, which adds to MMA efficiently and successfully initiates polymerization.

Some other initiators that generate radicals with high electron affinities also failed to provide controlled polymerization of MMA using homogeneous Cu-based ATRP. These initiators include 2-bromoisobutyrophenone, 2-bromopropiophenone, and carbon tetrachloride. The latter can be used successfully under heterogeneous conditions and also provides well-defined polystyrenes with homogeneous catalyst if the (CuBr/2dNbpy) is added slowly to the reaction mixture. Apparently, the electrophilic radicals Cl₃C[•], PhC(O)C[•]H(CH₃) and PhC- $(O)C^{\bullet}(CH_3)_2$ are rapidly reduced by Cu^{I} species, perhaps in an outer sphere electron transfer process, and produce the corresponding carbanions and Cu^{II}species. The characteristic green color of the Cu^{II} species in the presence of Cu^I is formed immediately after mixing the solutions of alkyl halides with CuBr/2dNbpy. The fast



Figure 8. Dependence of molecular weight and polydispersities on conversion in the solution polymerization of MMA in diphenyl ether at 90 °C using *p*-TsCl/CuBr and *p*-TsCl/CuCl initiation systems. [Initiator]₀ = 0.023 M, $[CuX]_0 = 0.0115$ M, [dNbpy] = 0.023 M.

reaction can also indicate a direct outer sphere electron transfer to the alkyl halides and formation of the radical anions, which decompose in the presence of adventitious moisture, rather than an inner sphere electron transfer (atom transfer). More successful initiation of styrene polymerization can be ascribed either to faster reaction of the intermediate radicals with styrene than with MMA, or to some differences in redox chemistry in less polar styrene in comparison with MMA. It must be stressed here that the redox chemistry and electron transfer processes depend very strongly on the metal and ligands. For example, 2-bromoisobutyrophenone, 2-bromopropiophenone, carbon tetrachloride, and some other haloketones were successfully used in Ru-catalyzed ATRP of MMA.³⁹ Ru-mediated reactions proceed approximately 100 times slower than Cu-mediated ATRP under similar conditions (temperature, concentrations of all reagents) and 5 times slower when activated by Al(OR)₃. This indicates that the equilibrium between Mt^n and $X-Mt^{n+1}$ species (Mt = Cu or Ru) is much more shifted toward higher oxidation state metal centers for Cu than for Ru. This roughly correlates with the redox potentials and with more facile reduction of the organic radicals by Cu^I than by Ru(II) species.

Comparison between the initiation systems *p*-TsCl/ Cu^IBr and *p*-TsCl/Cu^ICl show that *p*-TsCl/Cu^IBr gave better control of the polymerization (Figure 8).

For the *p*-TsCl/Cu^IBr system, the molecular weights followed the theoretical values very well, indicating an efficient initiation process. The observed low polydispersities throughout the polymerization also suggest a more effective deactivation process for *p*-TsCl/Cu^IBr than for *p*-TsCl/Cu^ICl. This is due to the Cu^{II}–Br bond being weaker than the Cu^{II}–Cl bond, resulting in faster deactivation of the propagating radicals, in agreement with earlier results on the inhibition of radical polymerization of MMA by CuCl₂ and CuBr₂ in DMF solution.^{42,43} The initial higher polydispersities in the *p*-TsCl/Cu^ICl system suggest a less efficient deactivation process.

Another class of good initiators for Cu-based ATRP of MMA are 2-halopropionitriles (XPN, X = Cl or Br). Figure 9 presents the evolution of molecular weights and polydispersities with conversion for CH₃CH(CN)-Br/CuBr and CH₃CH(CN)Cl/CuCl systems. In both cases well-defined polymers with low polydispersities



Figure 9. Dependence of molecular weight and polydispersities on conversion in the solution polymerization of MMA in diphenyl ether at 90 °C using ClPN/CuCl and BrPN/CuBr initiation systems. [Initiator]₀ = 0.023 M, $[CuX]_0 = 0.0115$ M, [dNbpy] = 0.023 M.

are formed; however, at high conversions some deviations in molecular weight behavior are observed for RBr/ CuBr and at low conversions higher polydispersities are noticed for the RCl/CuCl system. These phenomena agree well with some side reactions for pure bromidebased systems and for slower deactivation with CuClcatalyzed systems.

Halogen atoms exchange rapidly between the carbon and copper centers. For mixed-halide systems (R-X, Cu–Y, where $X \neq Y$), preliminary model studies show that, at equilibrium concentrations, Cu-Br predominates over Cu-Cl and, conversely, C-Cl is formed in preference to C-Br. For example, an equimolar reaction of benzyl bromide and CuCl/dNbpy reached the equilibrium concentration of 17% R-Br and 83% R-Cl $(\mathbf{R} = \text{benzyl})$ after 30 min at 110 °C. A similar observation was noticed for the 2-bromopropionate/CuCl initiation system. In the polymerization of MMA initiated by p-TsCl/CuBr (2/1), approximately 90% of the PMMA chains were capped by a Cl atom according to MALDI-TOF MS and ES-MS analysis. Ando et al.³⁹ have also demonstrated through NMR analysis that halogen atoms exchange in mixed-halide systems. The exchange of halogens additionally improves the efficiency of initiation with 1-phenylethyl derivatives (cf. Figures 2 and 3).

Comparison between the R-X/Cu-Y ATRP reactions discussed above and other systems using Cu or different metal centers can be made. Percec et al.⁴⁴ have recently described sulfonyl chloride derivatives as successful ATRP initiators. Our results indicate that combining TsCl with CuBr can further improve control over polymerization. Uegaki et al²⁴ have used alkyl chloride and bromide initiators for MMA ATRP using a Ni^{II}X₂ complexed with triphenylphosphine as catalysts. It was found that, with Cl as an exchanging halide, controlled/ "living" polymerization did not occur. However, Granel et al.²³ have shown that alkyl chloride initiators can be successfully used in controlled/"living" polymerization with a bis(ortho chelated) diaminoarylnickel(II) complex. From these observations, one can conclude that the success of ATRP is sensitive to a variety of factors, not-the-least the initiator. Our results here indicate that using a mixed-halide system can be beneficial, as a R-Br/CuCl system can provide fast initiation and reduced side reactions. More work is required, however, to investigate the mechanism(s) of halide exchange within ATRP in detail.

It is useful to correlate the behavior of various initiators with their structures. This discussion is mostly based on the data reported in this paper, but is additionally supplemented with data reported in the literature.

Two parameters are important for successful ATRP initiating systems: first, initiation should be fast in comparison with propagation, and second, it should minimize the probability of side reactions. In an analogous way to many new "living" systems based on equilibria between active and dormant species, the apparent (observed) initiation rate constant should be larger or at least comparable to the observed propagation rate constant, $k_i^{obs} \ge k_p^{obs}$ (i.e., $k_i K_{eq}^{\circ} \ge k_p K_{eq}$).

If we assume some similarities with carbocationic systems, the main factor determining the observed rate constants are equilibrium constants rather than the absolute rate constants of addition.³ This means that K_{eq}° should be larger than K_{eq} . This can be accomplished by careful structural adjustment of both the alkylating part (R) and leaving group (X) in order to make the bond R–X more labile than P_n –Y (if Y = X, only R structure matters).

There are two general "rules" for the initiator choice.

1. Tertiary alkyl halides are better initiators than secondary ones, which are better than primary alkyl halides.

2. The stabilizing group order is roughly $CN > C(O)R > C(O)R \approx Ph > Cl > Me$. This order also effects the possibility of cross-propagation and is important for block copolymer synthesis.

There are, however, some additional peculiarities that should be taken into account for finer manipulation of the initiating system.

3. Tertiary alkyl halides, though electronically similar to propagating species, are less active due to smaller back strain effect; this is not observed for the secondary structures. Thus, secondary species mimicking growing chains are efficient initiators (styrene, acrylates, acrylonitrile), ^{14,19,31,36} but tertiary species are not (methacrylates, methacrylonitrile). ^{39,45}

4. Multiple functional groups may increase the activity of the alkyl halide, e.g., carbon tetrachloride, benzhydryl derivatives, malonates, propiophenones.

5. Electron-withdrawing groups may increase the electron affinity of the initiating radical or parent molecule to a level that an outer sphere electron transfer occurs and leads to side reactions. In some cases, electron-donating groups (Me) may reduce side reactions, e.g., 2-methylmalonates vs malonates. Additional improvement is possible by slow addition of the catalyst and by using less reducing catalysts (e.g., RuCl₂ instead of CuCl).

6. Some initiating radicals may add relatively slowly to monomers and couple/disproportionate, leading to low initiator efficiency (higher molecular weights) and an excess of Cu^{II} species (slower polymerization). Slow initiator addition may improve initiator efficiencies, e.g., benzhydryl halides in MMA polymerization.

7. Some special initiators may not mimic structures of growing species but may be very efficient if coupling is less probable, e.g., sulfonyl halides^{20,44} and 2-meth-ylmalonates.

8. Additional manipulation of the initiator efficiency is possible by halogen exchange between the growing chains and the metal center. The general order of bond strength in alkyl halides is R-Cl > R-Br > R-I. Thus,

alkyl chlorides should be least efficient initiators and alkyl iodides most efficient. In addition, the affinities toward metal catalysts are important. Thus, if the relative affinity of chlorine is higher toward carbon, then even potentially inefficient alkyl bromides can be used successfully, as demonstrated for the 1-phenylethyl bromide/CuCl initiating system for MMA.

9. The use of bromides as initiators or salts has additional advantages because of the faster exchange reaction and can result in polymers with lower polydispersities. However, some side reactions occur more readily for RBr/CuBr than for the mixed halogen systems.

10. Use of alkyl iodides requires special precautions due to their light sensitivity, the low affinity of iodine toward most metals, and the possibility of heterolytic cleavage of the R-I bond.¹⁸

The above 10 "rules" may serve as general guidelines for the selection of the efficient initiators, but more work is required to quantify the observed phenomena.

Conclusion

Initiator efficiency is of prime importance for successful controlled/"living" polymerization through ATRP. Suitable initiators require an observed initiation rate constant greater than (or at least equal to) the observed propagation rate constant. These initiators also need to show little or no tendency to undergo side reactions. The homogeneous controlled/"living" ATRP of MMA using Cu^IX/4,4'-di(5-nonyl)-2,2'-bipyridine catalytic systems (X = Cl, Br) with various initiators R-X provides examples of how structural differences of the initiators affect the energetics of the C-X bonds, the electrochemistry of the initiating radicals, and therefore the efficiency of the initiation step. It is found that a variety of factors play a role in determining initiator efficiency (e.g., steric, polar, redox properties). These factors, however, provide a handle by which an ATRP system can be fine-tuned, and hence some general observations are given regarding the choice of appropriate initiators/ catalysts for successful ATRP.

Experimental Section

Materials. Methyl methacrylate was passed through an alumina column, dried over molecular sieves, deaerated by bubbling argon, 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 the literature procedure.⁴⁶ All the initiators were purchased from Aldrich and used as received. 4,4'-Di(5-nonyl)-2,2'-bipyridyl (dNbpy) was prepared by the procedure described previously.³¹

General Procedures and Characterization. Monomer conversion during the solution ATRP was determined by GC using diphenyl ether as an internal standard. Molecular weights and molecular weight distributions were measured using a Waters 510 LC pump, Waters 712 WISP autosampler, Waters 410 refractometer, and the following Phenogel GPC columns: guard, linear, 1000, and 100 Å. Molecular weights were calibrated using poly(methyl methacrylate) standards.

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 Cu¹X and ligand. The Cu¹/ligand solution was purged with argon flow for 15 min to deplete oxygen from 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 of 90 °C. The desired amount of initiator in 1 mL of deaerated methyl methacrylate was dissolved in a 5 mL round-bottom flask. The initiator/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 a reference for GC analysis. At timed intervals, 0.5 mL of the solution was withdrawn under an argon atmosphere and added to 1 mL of THF.

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

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