Utilizing Halide Exchange To Improve Control of Atom Transfer Radical Polymerization

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ABSTRACT: Halide exchange during atom transfer radical polymerization (ATRP) using mixed halide initiation systems, R-X/Cu-Y (X, Y = Cl or Br), was investigated. Model studies of mixed halide initiation systems (i.e., R-X/Cu-Y, $X \neq Y$) demonstrated that exchange occurs rapidly at 90 °C, and there is a clear preference for alkyl chlorides to be formed in over alkyl bromides. This was attributed mainly to the carbon-chlorine bond being stronger than the corresponding carbon-bromine bond. This implies that, in ATRP with a mixed halide initiator/catalyst system, the bulk of the polymer chain ends are terminated by chlorine if $[CuCl]_0 \ge [RBr]_0$. Examples of using this information to improve the control in ATRP of methyl methacrylate (MMA) are presented. It was shown that, when benzyl halides were used as the initiator in the ATRP of MMA, the rate of initiation was increased relative to the rate of propagation, thus providing better control by using the benzyl bromide/copper chloride mixed halide system. Better molecular weight control at high conversions of monomer to polymer was observed when using ethyl 2-bromoisobutyrate and copper chloride as initiator/catalyst in comparison to using ethyl 2-bromoisobutyrate provide, indicating that side reactions are less significant in the former.

Introduction

Radical polymerization is the most important industrial process used to prepare high molecular weight polymers.¹ One of the drawbacks of conventional radical polymerization, however, is the lack of control in both the molecular weight and the structure of the resulting polymers due to chain transfer and termination processes. In recent times, it has been demonstrated that controlled/"living" free radical polymerization techniques can be used to synthesize polymers with narrow polydispersities and predetermined molecular weights.² There are a number of methods that can be utilized to gain such control. These include atom transfer radical polymerization (ATRP) of a variety of monomers, nitroxide-mediated polymerization of styrene, ruthenium(II)/aluminum based polymerizations of methacrylates, and cobalt(II)-mediated polymerization of acrylates.²

Of these methods, ATRP appears to be the most versatile. This technique has been successfully applied to prepare poly(methyl methacrylate) (PMMA),³⁻⁶ as well as acrylates⁷ and styrene(s),⁸⁻¹⁰ with well-controlled molecular weights and well-defined structures. In a typical ATRP, a transition metal complex, e.g., a Cu^I/bipyridine complex, behaves as a halogen atom transfer agent between the active and dormant chains. By using an activated alkyl halide as an initiator, all of the chains can start growing at the same time. Furthermore, the equilibrium between the active and the dormant chains ensures a low concentration of propagating radicals and thus reduces the probability of termination (eq 1).⁸ A similar equilibrium between dormant and active chains is established in the other methods of controlled/"living" polymerization.

$$P_{n}-X + Cu^{l}-Y/2L \xrightarrow{k_{act}} P_{n} + X-Cu^{ll}-Y/2L$$
(1)
$$\underbrace{k_{deact}}_{Monomer} P_{m} + R_{n+m}/P_{n} + P_{m}$$

While the basic premise of controlled/"living" ATRP is accepted, exact details of the role of the deactivator and the kinetics within the exchange reactions remain sketchy. In copper-based ATRP, the deactivating species is generally a Cu^{II} -XY (X, Y = Cl or Br) species. Our previous communications have noted that using a system comprised of an alkyl bromide as initiator with a CuCl catalyst (i.e., a mixed halide system) generally gives better control of the polymerization of methyl methacrylate (MMA) than a R-X/CuX system.⁶ Furthermore, preliminary results indicated that, within the mixed halide system (e.g., R-Br/CuCl), a mixture of both bromine and chlorine atoms caps the polymer chain during the polymerization. In this paper, we examine the halide exchange reaction and the effect that this process has on the ATRP of MMA.

Results and Discussions

The mechanism for homogeneous ATRP using Cu^IX/ 4,4'-di-(5-nonyl)-2,2'-bipyridine (dNbpy) has been proposed in earlier publications from this group.^{8,10} To obtain good control over the molecular weight and molecular weight distribution in ATRP, several criteria must be fulfilled. The rate of initiation must be faster than, or comparable to, propagation to ensure efficient generation of polymer chains. The position of the equilibrium in both the initiation and propagation steps should be strongly shifted to the side of dormant species. Fast deactivation of active species to dormant polymer chains is necessary to minimize the contribution of chain termination and leads to a narrow molecular weight distribution. Finally, the degree of polymerization should be predetermined by the ratio of Δ [monomer]/ [initiator]₀.

The importance of the initiator/catalyst system in ATRP of MMA has been discussed in a recent article from our group.⁶ All the R–Br/CuBr initiation systems used in our study, ethyl 2-bromoisobutyrate (Et-2-BriB)/ $Cu^{I}Br$ for example, showed a deviation from an idealized controlled/"living" system at high monomer conversion,

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indicating the presence of some side reactions. However, when *p*-TsCl/CuBr or 1-PEBr/CuCl was used, for example, experimental molecular weights agreed well with theoretical values.⁶ This is an indication that mixed halogen systems may improve molecular weight control. Ando et al.¹¹ have also observed that halide exchange occurs during the ATRP of MMA with a Ru^{II} complex; however, there was no attempt to quantify the effects of the exchange.

Model reactions were performed in order to better quantify the amount of halide exchange and to obtain some correlation between the rate of exchange, the position of the exchange equilibrium, and the structure. Such information is difficult to obtain via polymeric structures from the MALDI-TOF MS technique, for example, because the halide end groups are easily lost during the ionization process. Therefore, the model reactions may provide an avenue to understanding the factors affecting the halide exchange process, and from this knowledge extrapolations to the polymerization systems can be made.

Model Studies. An equimolar solution (0.1 M in most cases) of various activated halides R-X (Chart 1) and CuY ($X \neq Y$; X, Y = Cl or Br) was degassed, sealed in a NMR tube, and heated at the desired temperature. The progress of the exchange reaction (eq 2) was monitored by gas chromatography (GC) for each system and also by ¹H NMR spectroscopy for the BzX and 1-PEX systems for comparison. The relative concentra-

$$RBr + CuCl/2L \xrightarrow{K_{eq}^{exch}} RCl + CuBr/2L$$
(2)

tions of R–Br and R–Cl in the GC analysis were determined by using an internal standard and checked by calibrating the relative GC response for each compound (where commercially available). ¹H NMR determination of R–Br and R–Cl for the BzX and 1-PEX systems involved comparing the intensities of their individual benzylic protons. For the other systems, overlap of the α -protons of R–Br and R–Cl in the ¹H NMR spectrum precluded the use of this technique.

Table 1 contains the relative percentage of R-Cl from each system at various time intervals from the GC analysis. The most striking feature is that most of the alkyl groups are chlorinated, even when no R-Cl was added initially. Furthermore, the R-Cl reached an equilibrium concentration quickly, usually within 30 min at 90 °C (BzX is the exception). Starting from an R-Cl/CuBr system results in equilibrium concentrations quite similar to that obtained with an R-Br/CuClsystem. For comparison, the results of the NMR analysis of some systems are presented in Table 2. These data show excellent agreement with the results

Table 1. Percentage of R-Cl as a Function of Time in R-X/Cu-Y Halide Exchange Reactions As Monitored by Gas Chromatography (GC)^a

	% R–Cl			
system (R-X/Cu-Y)	10 min	25 min	40 min	90 min
BzBr/CuCl ^b	66	78	81	
BzCl/CuBr ^b	94	90	87	82
1-PEBr/CuCl ^b	87	91	91	
1-PECl/CuBr ^b		90	88	89
Et-2-BriB/CuCl ^c	91	91	91	
MeBrP/CuCl ^c	79	84	85	

^{*a*} [R-X] = 0.1 M, [Cu-Y] = 0.1 M, [dNbpy] = 0.2 M, [internal standard] = 0.05 M, solvent = benzene, temperature = 90 °C. ^{*b*} GC internal standard = chlorobenzene. ^{*c*} GC internal standard = dimethoxybenzene.

Table 2. Percentage of R-Cl as a Function of Time in R-X/Cu-Y Halide Exchange Reactions As Monitored by ¹H NMR Spectroscopy (Solvent = Benzene-d₆)

system (R-X/Cu-Y)	temp (°C)	reaction time	% R–Cl
BzBr/CuCl ^a	100	120 min	83
BzCl/CuBr ^b	100	120 min	82
1 PECI/CuBr	90	21 min	89
BzBr/CuCl ^d	room temp	50 h	83

^{*a*} [BzBr] = 0.2 M, [CuCl] = 0.2 M, [dNbpy] = 0.4 M. ^{*b*} [BzCl] = 0.15 M, [CuCl] = 0.15 M, [dNbpy] = 0.3 M. ^{*c*} [1-PEX] = 0.1 M, [Cu-Y] = 0.1 M, [dNbpy] = 0.2 M. ^{*d*} [BzBr] = 0.1 M, [Cu-Cl] = 0.1 M, [dNbpy] = 0.2 M.



Figure 1. ¹H NMR spectra obtained from the model study of BzBr/CuCl at room temperature at the times indicated (last entry in Table 2). [BzBr] = 0.1 M, [CuCl] = 0.1 M, [dNbpy] = 0.2 M solvent = benzene- d_{6} .

from the GC experiments. The experiment performed at room temperature has an equilibrium concentration for the BzBr/CuCl system that is identical to that obtained at 90–100 °C. Figure 1 shows the ¹H NMR spectrum of the halogen exchange process in the BzBr/CuCl system at room temperature. The spectra showed that BzBr ($\delta = 4.00$ ppm, singlet) was converted to BzCl ($\delta = 4.11$ ppm, singlet). Actually, it was found that, even at time zero, a small amount of BzCl was formed. This was also observed during GC analysis for each system at both room and higher temperatures.

The general position of the equilibrium (i.e., % R–Cl \approx 80–90%) indicates that there are differences in energies between the C–Cl and C–Br bonds and/or the association between Cu–Cl and Cu–Br. For example, the bond energy of the C–Cl bond in benzyl chloride is estimated to be 284.7 kJ/mol at 298 K, while the C–Br

bond in benzyl bromide is 213.5 kJ/mol.¹² An equilibrium constant (K_{eq}^{exch}) of approximately 80 ($\sim 0.9^2/0.1^2$) would lead to a change in free energy ($\Delta G_{\rm e}$) of around 10–15 kJ/mol (ln $K_{eq}^{exch} = -\Delta G_e/RT$). Since the position of the equilibrium appears temperature insensitive (in the range studied here), the changes in enthalpy (ΔH) are negligible, and therefore the equilibrium concentrations are primarily determined by entropy. However, the partial ionic nature of the Cu-X bonds in $Cu(bpy)_2+X^$ complexes and the indication that some other structures, such as halogen-bridged dimers observed earlier,^{13,14} are present in these systems make for a complex system. As such, we expect that other ATRP catalytic systems (e.g., different ligands, metals) would show different equilibrium positions and halide exchange behavior.

The equilibrium concentrations of the alkyl halides are slightly different from each other, as is the rate at which the exchange equilibrium is established. The general trend for the position of the equilibrium, although not great, is toward the formation of R–Cl as the amount of substitution on the carbon bearing the halogen increases. The differences in the rates at which the equilibrium is reached are more marked. Tertiary halides (Et-2-BriB) exchange faster than secondary halides (1-PEX, MeBrP), which exchange faster than primary halides (BzX). A comparison of the two secondary halides reveals that the benzyl substituent provides a greater inductive effect than the carbonyl, as would be expected.

The results of the model study indicate that the mixed halogen initiation systems R–Br/Cu^ICl potentially possess several advantages over the R-Br/Cu^IBr or R-Cl/ Cu^ICl systems in initiating ATRP. Initiation is faster in R-Br/CuCl than that in R-Cl/CuCl due to a weaker C–X bond in the former. Although halide exchange occurs relatively rapidly, during the initiation step there is not enough Cu^{II} species formed to ensure substantial exchange, and so initiator is consumed before exchange is significantly completed (i.e., $k_i[M] > k_d[Cu^{II}]$). Furthermore, assuming that the polymer chain behaves in a manner similar to the alkyl initiator, after a short time the end group of the dormant polymer chain is Clcapped instead of Br-capped. This may have two effects on the efficiency of ATRP. First, the stronger C–Cl bond in the polymer end group means that the concentration of the active propagating chains during ATRP will be lower than that in R-Br/Cu^IBr initiated polymerization, resulting in slower propagation. The mixed halogen system R-Br/CuCl has faster initiation than the R-Cl/CuCl system and slower propagation than R-Br/CuBr. A fast rate of initiation relative to the rate of propagation is essential for a successful controlled radical polymerization. Second, the previously observed deviation of molecular weights as a function of conversion in R-Br/Cu^IBr-initiated ATRP of MMA was attributed to some side reactions which could originate from the more labile C-Br bond end group. In R-Br/ CuCl systems, however, the side reactions could be minimized since most of the polymer chains contain a chloride end group (i.e., the system converts to mostly P_n -Cl/CuBr).

Polymerization Systems Based on Mixed Halogen Initiators. As an example of how a mixed halide initiator/catalyst system can have an effect on ATRP, we present results from polymerizations using benzyl halides and copper halides. While benzyl halides have



Figure 2. Dependence of molecular weights (filled symbols) and polydispersities (open symbols) of PMMA on monomer conversion for solution ATRP of MMA in diphenyl ether at 90 °C using BzCl/Cu¹X initiation systems, where $X = Cl (\bigcirc, \bullet)$ and Br (\Box, \bullet) . Line is predicted molecular weight based on $M_n^{\text{th}} = 100.12(\Delta[M]/[In]_0)p$, where $[In]_0 = \text{initial initiator}$ concentration and p = fractional conversion. [BzCl]₀ = 0.021 M, [CuX]₀ = 0.011 M, [dNbpy] = 0.021 M.



Figure 3. Dependence of molecular weights (filled symbols) and polydispersities (open symbols) of PMMA on monomer conversion for solution ATRP of MMA in diphenyl ether at 90 °C using BzBr/Cu¹X initiation systems, where $X = Cl (\bigcirc, \bullet, \triangle, \triangle)$ and $Br (\Box, \blacksquare)$. Line is predicted molecular weight based on M_n th = 100.12(Δ [M]/[In]₀)p, where $[In]_0 =$ initial initiator concentration and p = fractional conversion. For $(\bigcirc, \bullet, \Box, \blacksquare)$, [BzBr]₀ = 0.021 M, [CuX]₀ = 0.011 M, [dNbpy] = 0.021 M; for $(\triangle, \blacktriangle)$, [BzBr]₀ = 0.021 M, [CuCl]₀ = 0.021 M, [dNbpy] = 0.042 M.

been efficient initiators in ATRP of styrene and acrylates,¹⁵ our initial results with BzCl/CuCl indicated that they are inefficient for methacrylates. To improve this situation, the halides within the initiator/catalyst system were varied, and the results of these ATRP experiments are shown in Figures 2–4. For BzCl/CuCl- and BzCl/CuBr-initiated systems (Figure 2), poor control of molecular weight and molecular weight distribution is observed. In contrast to these systems, the BzBr/CuX systems (Figure 3) gave relatively better control of molecular weight (although incomplete initiation is still observed at low conversions) and polymers with lower polydispersity indexes. Furthermore, BzBr/CuCl-initiated ATRP provided the best control of molecular weight and the lowest polydispersities among all four systems.



Figure 4. Semilogarithmic kinetic plot for solution ATRP of MMA in diphenyl ether at 90 °C using BzX/Cu^IX (X = Cl and Br) initiation systems. Inset shows the same data but including high conversion data points. $[BzX]_0 = 0.021$ M, $[CuX]_0 = 0.011$ M, [dNbpy] = 0.021 M, except BzBr/CuCl (1/1) where $[BzBr]_0 = 0.021$ M, $[CuCl]_0 = 0.021$ M, [dNbpy] = 0.042 M.

Increasing the amount of CuCl relative to BzBr to a 1/1 ratio, to promote further exchange, increases slightly the molecular weight control compared with the BzBr/CuCl = 2/1 case (Figure 3). The polydispersities also decreased slightly.

The kinetic plots in Figure 4 show that all these polymerizations of MMA do not exactly proceed through first-order kinetics with respect to monomer concentration, indicating some termination is occurring during the polymerization, although the precision of measuring conversion above 90% may not be adequate. The rate of polymerization in ATRP depends on the concentration of propagating radicals and is a function of both the initiation efficiency and the concentration of deactivator in the system (e.g., Cu^{II} halides).¹⁴ For the BzCl/CuX systems, poor initiation efficiency leads to smaller amounts of both propagating radicals and Cu^{II} species than that in the BzBr/CuX systems. The effect of lowering the concentrations of both propagating radicals and Cu^{II} is that the rates of polymerization for the BzCl/ CuX systems is similar to the rates for the BzBr/CuX systems, as indicated in Figure 4.

As mentioned above, the C-Cl bond is stronger than that of C-Br bond, leading to a smaller concentration of benzyl radicals from benzyl chloride than from benzyl bromide. For the BzCl/CuX systems, the lack of molecular weight control is mainly due to the much smaller product of the equilibrium constant and addition rate constant in the initiation step $(k_i^{obs} \approx k_i K_{eq,i})$ than that of propagation $(k_p^{obs} \approx k_p K_{eq,p})$, in the ATRP of MMA. Inefficient initiation is the result. Values of k_i and k_p do not depend on the halogen since the rate constants reflect only the addition of benzyl radicals to MMA, and poly(MMA) radicals to MMA, respectively. However, equilibrium constants depend strongly on the halogen in R-X and P_n-X and are much higher for alkyl bromides than for alkyl chlorides. Thus, the observed initiation rate increases for the BzBr/CuCl system (where only R-Br is present) in comparison with the observed propagation radical chain (predominantly P_n -Cl). A similar explanation was made previously for the poor control of polymerization with 1-phenylethyl chloride (1-PECI)/CuCl or methyl chloroacetate/CuCl initiation systems.⁶ BzBr/CuX systems, with a weaker C-Br



Figure 5. Dependence of molecular weights of PMMA on monomer conversion for solution ATRP of MMA in diphenyl ether at 90 °C using Et-2-BriB/Cu^IX initiating systems, where X = Cl (\bullet) and Br (\Box). Line is predicted molecular weight based on M_n th = 100.12 (Δ [M]/[In]₀)p, where [In]₀ = initial initiator concentration and p = fractional conversion. For Et-2-BriB/CuBr system (ref 6), [Et-2-BriB]₀ = 0.023 M, [CuBr]₀ = 0.0115 M, [dNbpy] = 0.023 M, [CuBr]₀ = 0.023 M, [dNbpy] = 0.046 M.

bond, can generate initiating radicals more efficiently than BzCl/CuX systems and yield molecular weights of polymers closer to theoretical values.

The narrower molecular weight distribution yielded by the BzBr/CuX initiation system is worth noting. The Cu^{II}-Br bond is weaker than that of Cu^{II}-Cl, resulting in faster deactivation of the propagating radical and lower polydispersity. This result is in accordance with the earlier results on the inhibition of radical polymerization of MMA by Cu^{II}Cl₂ and Cu^{II}Br₂ and trapping of alkyl radicals.^{16,17}

ATRP of MMA using Et-2-BriB/CuCl as the initiation system was carried out to reduce the deviation in the molecular weight dependence on conversion observed in the Et-2-BriB/CuBr system.⁶ The results are compared in Figure 5. In the Et-2-BriB /CuCl system, [initiator]/[Cu^ICl] ratio was increased to 1/1 in order to promote nearly complete halogen exchange and improve the control of polymerization. For Et-2-BriB/CuClinitiated ATRP of MMA, the evolution of molecular weight agrees well with the theoretical value and reduces the deviation of the molecular weight at high conversion, which suggests that the side reaction associated with the Et-2-BriB/CuBr system was minimized by employing the mixed halogen initiation system. Furthermore, the molecular weight distribution using the Et-2-BriB/CuCl system remained quite narrow throughout the polymerization, indicating a sufficiently fast deactivation process in the mixed halogen system. Additionally, as discussed in our previous paper,⁶ isobutyrate is not the best model of PMMA growing chains due to back-strain effects. A similar observation was recently reported for Ru-catalyzed ATRP systems.¹¹

R-Cl/CuX-initiated ATRP generally leads to an uncontrolled polymerization; however, *p*-TsCl/CuX are efficient initiation systems for ATRP of MMA.^{5,6} This can be attributed to the fact that *p*-TsCl/CuX initiates ATRP fast enough due to the very labile S-Cl bond in the initiator and, therefore, leads to well-controlled polymerization. In this system, the high reactivity of

RSO₂Cl compensates for the unfavorable R–Cl/CuBr composition of the initiating system.

Conclusions

In conclusion, mixed halogen initiation systems were investigated in both model reactions and ATRP of MMA experiments. Model studies of different initiation systems demonstrated that, for the mixed halogen system R-Br/CuCl, halogen exchange occurred rapidly and showed that alkyl chlorides were preferentially formed over alkyl bromides. The results implied that the mixed halogen system R–Br/CuCl should give faster initiation, slower propagation, and therefore better control of molecular weight. This was subsequently verified through the ATRP of MMA, where the mixed Bz-X/ Cu-Y initiator/catalyst systems were used. For example, the BzCl/Cu^IX (X = Br and Cl) initiation systems gave essentially uncontrolled polymerization, which was attributed to the strong C-Cl bond and inefficient initiation. However, when BzBr/Cu^ICl was used as the initiator/catalyst, polymerization gave polymers with molecular weights closer to the theoretical values with much narrower polydispersities than those initiated by R-Cl/CuX. ATRP of MMA using the Et-2-BriB/CuCl initiation system also led to better molecular weight control than the Et-2-Br-iB/CuBr system. Thus, it is generally beneficial to initiate ATRP with an R-Br/Cu^I-Cl system, which features fast initiation and fast deactivation and can, therefore, improve the molecular weight distribution of the resulting polymer without introducing undesired side reactions observed in R-Br/ Cu^IBr initiation systems.

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.¹⁸ All the initiators were purchased from Aldrich and used as received. 4,4'-Di-(5-nonyl)-2,2'-bipyridyl (dNbpy) was prepared according to the procedure described in previous articles from this group.⁸

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 differential 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 Cu^IX (typically, if X = Cl, 10.5 mg, 1.06×10^{-4} mol; if X = Br, 15.2 mg, 1.06×10^{-4} mol) and ligand (dNbpy; $87.1 \text{ mg}, 2.13 \times 10^{-4} \text{ mol}$). The Cu^I/ligand solution was purged with argon flow for 15 min to deplete oxygen from the solution. Methyl methacrylate (4 mL, 37.4×10^{-3} mol, 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 preset temperature of 90 °C. The desired amount of initiator (for BzCl, 24.4 μ L; for BzBr, 25.3 μ L, 2.13 imes 10⁻⁴ mol) was dissolved in deaerated methyl methacrylate (1 mL, 9.35×10^{-3} mol) in a 5-mL roundbottom 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. At timed intervals, 0.5 mL of the solution was withdrawn under argon atmosphere and added to 1 mL of THF. This

procedure was followed for the Et-2-BriB (34.3 $\mu L,$ 2.34 \times 10⁻⁴ mol)/CuCl (23.4 mg, 2.36 \times 10⁻⁴ mol)-initiated polymerization with dNbpy (190.9 mg, 4.67 \times 10⁻⁴ mol).

The THF solutions were injected onto 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 onto the GPC for analysis.

General Procedure for Halogen Exchange Model Study. Cu^I halides (Cu-Y; if Y = Br, 21.6 mg, 1.5×10^{-4} mol, 0.1 M; if Y = Cl, 14.8 mg, 1.5×10^{-4} mol, 0.1 M) and dNbpy (122 mg, 3.0×10^{-4} mol, 0.2 M) were dissolved in benzene (benzene- d_6 for the NMR studies) (1.5 mL) in a small round-bottom flask under an Ar atmosphere. Alkyl halides (R–X, 1.5 \times 10 $^{-4}$ mol, 0.1 M) were introduced into the flask, the solution was stirred for approximately 1 min, and then 0.5 mL of this solution was placed in an NMR tube and immediately frozen. The reaction mixtures were degassed by three cycles of freeze-pump-thaw and were then sealed under vacuum. The tube was then placed in an oil bath with preset temperature of 90 °C (unless noted otherwise). For ¹H NMR analysis of the BzX and 1-PEX systems, the sample tubes were withdrawn from the oil bath at certain time intervals and cooled to room temperature, and the progress of the exchange reaction was monitored by ¹H NMR spectroscopy. For GC analysis, the sample tubes were broken at certain time intervals, followed by the addition of THF to deactivate Cu^I catalyst. The concentration of each component was determined by integration of peak heights relative to an internal standard (either dimethoxybenzene or chlorobenzene) and checked against an independently generated calibration curve.

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