Controlled/“Living” Radical Polymerization. Kinetics of the Homogeneous Atom Transfer Radical Polymerization of Styrene

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Abstract: The homogeneous atom transfer radical polymerization (ATRP) of styrene using solubilizing 4,4′-dialkyl substituted 2,2′-bipyridines yielded well-defined polymers with $M_n/M_w \leq 1.10$. The polymerizations exhibited an increase in molecular weight in direct proportion to the ratio of the monomer consumed to the initial initiator concentration and also exhibited internal first-order kinetics with respect to monomer concentration. The optimum ratio of ligand-to-copper(I) halide for these polymerizations was found to be 2:1, which tentatively indicates that the coordination sphere of the active copper(I) center contains two bipyridine ligands. The exclusive role for this copper(I) complex in ATRP is atom transfer, since at typical concentrations that occur for these polymerizations ($\approx 10^{-4}$ M), polymeric radicals were found not to react with the copper(I) center in any manner that enhanced or detracted from the observed control. ATRP also exhibited first-order kinetics with respect to both initiator and copper(I) halide concentration; however, the polymerization kinetics were not simple inverse first-order with respect to the initial copper(II) halide concentration. The latter observation was found to be due to the persistent radical effect, which resulted in an increase in copper(II) concentration during the initial stages of the polymerization. This phenomenon also has the effect of regulating the polymerization by ensuring that the rate of radical combination and/or disproportionation is sufficiently less than the rate of propagation.

Introduction

Free-radical polymerization is one of the most important commercial processes leading to high molecular weight polymers, because a wide variety of monomers can be polymerized and copolymerized under relatively simple experimental conditions.5 While free-radical polymerizations require the absence of oxygen, they can be conducted using water as a solvent or additive. A significant drawback to these polymerizations, however, is that they yield polymers with uncontrolled molecular weights and high polydispersities, which precludes the synthesis of well-defined polymers with low polydispersities and complex architectures.3

Termination by radical combination or disproportionation, which occurs at diffusion controlled rates, is unavoidable for radical chain reactions; however, the impact of this reaction upon the final product of radical polymerizations can be minimized. In analogy to controlled/“living” cationic polymerizations,4 radical polymerizations can become controlled under conditions in which a low, stationary concentration of the active species is maintained and a fast, dynamic equilibrium is established between the active and dormant species.5

One such controlled/“living” radical polymerization is atom transfer radical polymerization (ATRP).5,7 In this polymerization a copper(I) complex, $\text{CuX}/2\text{L}$ (X = Cl or Br, and L = 2,2′-bipyridine [bipy] or a 4,4′-disubstituted-2,2′-bipyridine) activates reversibly the dormant polymer chains via a halogen atom transfer reaction (eq 1), and it is this dynamic equilibrium which is responsible for the controlled behavior of the polymerizations. As reported, the homogeneous ATRP of styrene,

$$P_n-X + \text{CuX}/2\text{L} \xrightarrow{k_{\text{cat}}} P_n^* + \text{CuX}/2\text{L}$$ (1)

acrylates, and methacrylates can yield polymers with predetermined degrees of polymerization up to DP $\approx 100$ and polydispersities, $M_n/M_w$, as low as 1.04 and 1.05.7 Other well-established, controlled radical polymerization systems include the following: TEMPO/nitroxyl radical-mediated polymerizations of styrenes,8,9 ruthenium/aluminum-based polymerizations of methacrylates,10 and cobalt-mediated polymerizations of acrylates.11,12

The remarkable results found for homogeneous ATRP prompted us to investigate the system further in order to understand the reasons for the high degree of control. Initial kinetic studies on the ATRP of styrene using heterogeneous conditions (CuBr/2bipy) showed that the rate law for the polymerization had kinetics orders of 1, 0.4, and 0.6 with respect to initiator, copper(I) catalyst, and ligand, respectively.13 Most...
likely, the heterogeneity of the system was responsible for the fractional orders, and, therefore, it was difficult to explain their precise physical meanings. Here, we report a kinetic investigation of the homogeneous ATRP of styrene including the reaction orders of each component, the role of the deactivator in this system (CuII) halides), and the temperature dependence of the polymerization rate.

Results and Discussion

When a solution of styrene and 1-phenylethyl bromide [1-PEBr] in a 100:1 mole ratio, 1 equiv of CuBr relative to initiator, and 2 equivs of 4,4′-dihydroxybipyrindine (dNbipy) per copper was heated at 110 °C, the ligand used was dNbipy or 4,4′-di-di-(5-nonyl)-2,2′-bipyridine (dTbipy) in diphenyl ether: [styrene]₀ = 4.3 M; [CuBr]₀ = [dNbipy]₀/2 = 0.045 M; [1-PEBr]₀ = 0.045 M. kₐ is 1.6 × 10⁻⁴ s⁻¹; kₐ (solution) = 3.9 × 10⁻⁵ s⁻¹.

In a previous report in which the ATRP of styrene was also conducted in various solvents, the conclusion was reached that no chain transfer-to-solvent occurs in ATRP. However, the transfer constants for the solvents used in that study (as well as this one) are quite low, and in the range of molecular weights studied one would not expect to observe transfer-to-solvent. Thus, the more appropriate conclusion is that the transfer coefficients for ATRP are not significantly higher than those found for conventional radical polymerization.

In order to assess the tolerance of ATRP toward functional groups, a series of polymerizations was performed in which equal amounts of various compounds were added to the polymerization mixture (Table 1). The resulting molecular weight and conversion data indicated that externally added polar protic and aprotic compounds, such as H₂O, CH₃OH, CH₃CN, and ethylene carbonate, had little effect upon the polymerization. When strongly coordinating compounds were used, such as pyridine and PPh₃, a large decrease in the polymerization rate and an increase in polydispersities was observed. Presumably these types of compounds can either saturate the coordination sphere of the copper(I) complex and render it inactive or bind to the copper(I) halide and form complexes that are not sufficiently active for atom transfer. Thus, a wide range of monomers with functional groups can be used in ATRP provided that the functional group is not a good ligand for copper(I).

Two equivs of ligand per copper center appears to be the kinetically optimum ratio for these polymerizations. As shown in Figure 3, when the concentration of ligand in a bulk polymerization was varied while the amounts of initiator and CuBr were kept constant, kₐ (vide infra) did not reach an appreciable value until a ratio of approximately 1:1 (ligand-to-copper) was reached; at this ratio, the CuBr dissolved completely in the polymerization medium at 110 °C. Then, kₐ increased until a ratio of 2:1 was reached, after which no increase in the apparent rate was observed.

These results were quite different from those found for heterogeneous ATRP, in which the polymerization rate was 0.6

Table 1. ATRP with Different Additives

<table>
<thead>
<tr>
<th>additive</th>
<th>time (h)</th>
<th>% conv</th>
<th>Mₐ expected</th>
<th>Mₐ GPC</th>
<th>Mₐ/Mₑ</th>
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<tr>
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</tr>
<tr>
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<td>60</td>
<td>5960</td>
<td>7740</td>
<td>1.09</td>
</tr>
<tr>
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<td>5950</td>
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</tr>
<tr>
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<td>63</td>
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<tr>
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<td>5340</td>
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<td>1970</td>
<td>1.34</td>
</tr>
</tbody>
</table>

*5% (v/v) relative to styrene. Two equivs relative to CuBr. All of the polymerizations were conducted in sealed tubes with bulk styrene at 110 °C. [1-PEBr]₀ = [CuBr]₀ = [dNbipy]₀/2 = 0.087 M.

Figure 1. Semilogarithmic kinetic plots for the bulk and solution ATRPs of styrene at 110 °C. Bulk: [styrene]₀ = 8.7 M; [CuBr]₀ = [dNbipy]₀/2 = 0.087 M; [1-PEBr]₀ = 0.087 M. 50% (v/v) solution in diphenyl ether: [styrene]₀ = 4.3 M; [CuBr]₀ = [dNbipy]₀/2 = 0.045 M; [1-PEBr]₀ = 0.045 M. kₐ (bulk) = 1.6 × 10⁻⁴ s⁻¹; kₐ (solution) = 3.9 × 10⁻⁵ s⁻¹.

Figure 2. The dependence of molecular weight, Mₐ, and molecular weight distribution, Mₐ/Mₑ, upon monomer conversion for the bulk ATRP of styrene at 110 °C: [CuBr]₀ = [1-PEBr]₀ = [dNbipy]₀/2 = 0.087 M.

For polymerizations under dilute conditions when the observed rate is slower, we have directly observed a slow side reaction that may be responsible for the upper limit of molecular weights that can be achieved in the ATRP of styrene. This will be the subject of a subsequent paper.

atom transfer activity in these polymerizations is L₂Cu,
copper, then the copper species most likely for the catalytic
Figure 3) indicates a 2:1 stoichiometry for bipy-to-
2:1 stoichiometry necessary for the most active catalyst (as
monomeric complexes of the formula, L₂Cu,
of a 2:1 stoichiometry between bipy or phen and copper(I) are
water with respect to ligand concentration. The difference was
most likely due to the difference in solubilizing abilities of the
ligands. In the case of bipy which poorly solubilizes copper(I)
halides in nonpolar media, increasing the concentration of ligand
solubilized more and more of the copper(I) halide. In the case of
dNBPb, only enough ligand to saturate the coordination
sphere of the copper(I) center or generate the active copper(I)
species was necessary, because the ligand could make the copper
halide completely soluble at this stoichiometry. These results
were, however, similar to a previous report on homogeneous
ATRP using arenesulfonyl chlorides as initiators, in which a
2:1 stoichiometry of ligand-to-copper(I) chloride was used. The
authors showed that at least a 1:1 stoichiometry of ligand-to-
copper(I) chloride was needed to obtain polymers with M_n/M_w < 1.5, but no rate data as a function of the stoichiometry was
provided so the kinetically optimum ratio was not found.
Copper(I) complexes with bipy or phenanthroline [phen] ligands
fall into two structural types depending upon the ligand-
to-copper stoichiometry. Complexes of a 1:1 stoichiometry
between bipy or phen and copper(I) halides are either halogen
bridged dimers, L₂Cu(μ-X)₂CuL, or 2:1 ligand-to-copper cations
with a dihalocuprate counteranion, L₂Cu⁺CuX₂⁻. Complexes of
a 2:1 stoichiometry between bipy or phen and copper(I) are
monomeric complexes of the formula, L₂Cu-X⁻, where X⁻
can be Cl⁻, Br⁻, or PF₆⁻ among other counteranions. Thus if the
2:1 stoichiometry necessary for the most active catalyst (as
shown in Figure 3) indicates a 2:1 stoichiometry for bipy-
copper, then the copper species most likely for the catalytic
atom transfer activity in these polymerizations is L₂Cu-X⁻. However, the solution chemistry could be more complex and
dynamic in that there could be several copper(I) species in rapid
equilibria with varying ligand stoichiometries that average to
CuBr/2dNBPb. For the purposes of the following discussion
the active copper(I) catalyst shall be described generally by “Cu-
(I)" or “Cu(I)/2L", and the corresponding copper(II) halide
complex formed after atom transfer shall be described generally by “Cu(II)X" or “Cu(II)X/2L" (X = Cl, Br).

A proposed mechanism for ATRP is shown in Scheme 1,
which contains eqs for the atom transfer equilibrium, the
propagation step, and radical termination. The exclusive role
for Cu(I) in these polymerizations is to abstract halogen atoms
from the inactive chains. This was shown by an experiment in

\[ R - X + CuX_2/2bpy \rightarrow K_{eq} \rightarrow \text{[Cu}X_2/2bpy \] (2)

\[ R + Cu(I)/2L \rightarrow k_{p} \rightarrow \text{[Cu}X_2/2bpy \] (3)

\[ P_{n} + \text{monomer} \rightarrow k_{p} \rightarrow P_{n+1} \] (4)

\[ P_{n} + \text{monomer} \rightarrow k_{p} \rightarrow P_{n+1} \] (5)

\[ P_{n} \rightarrow k_{p} \rightarrow P_{n} \rightarrow \left( k_{p} + k_{p}^\phi \right) \] (6)

Table 2. Data for the “Reverse ATRP” of Bulk Styrene at 110 °C

<table>
<thead>
<tr>
<th>time (s)</th>
<th>% conv</th>
<th>M_n GPC</th>
<th>M_w Expected</th>
<th>M_w/M_n</th>
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<td>1.10</td>
</tr>
</tbody>
</table>

which CuBr/2dNBPb was added to free-radical polymerizations of styrene (dicumyl peroxide initiator at 110 °C). Within
experimental error, no effect upon the kinetics or molecular
weights of the polymerization was observed. Thus, at the radical
concentrations of ATRP, Cu(I)/2L does not react with the
intermediate radicals in such a way that contributes to or detracts
from the observed control of the polymerization. One can also
show that the Cu(II)X/2L, the proposed species after atom transfer,
does lie along the mechanistic pathway of the polymerization.
When 1 equiv of CuBr/2dNBPb was added to bulk free-radical
styrene polymerizations initiated by one-half an equiv of AIBN
at 110 °C (essentially entering ATRP from the right side of the
equilibrium), controlled radical polymerization behavior was
observed (eq 7). The observed polymerization rate was
somewhat slower (k_{app} = 7.7 \times 10^{-5} s^{-1}), and the resulting

\[ 1/2 \text{AIBN} + \text{CuBr/2dNBPb} \rightarrow \text{styrene} \rightarrow \text{controlled/“living” radical polymerization} \] (7)

cellular molecular weights were somewhat higher (Table 2) than found
for the corresponding bulk styrene ATRP, which can be ascribed
to the limited efficiency of radical generation from AIBN (f < 1).
This “reverse ATRP” was also observed for heterogeneous
systems using CuBr/2bipy catalyst.

From the initiation and propagation eqs in Scheme 1 the
following rate laws were derived assuming a fast preequilibrium,
a necessary condition to observe low M_n/M_w in controlled/
“living” free-radical polymerizations (eqs 8 and 9).

\[ K_{eq} = \frac{k_{act}}{k_{deact}} = \frac{[P]^{2} [\text{Cu} (\text{II}) X]}{[\text{Cu} (\text{I})] [\text{PX}]} \] (8)

\[ R_p = k_{app} [M] = k_{p} [P]^{2} [M] = k_{p} K_{eq} [\text{In}] \frac{[\text{Cu} (\text{I})]}{[\text{Cu} (\text{II}) X]} [M] \] (9)

As shown before, plots of ln([M]/[M]) versus time were linear,
which confirmed that the polymerization rate was first-

(17) (a) Hathaway, B. J. In Comprehensive Inorganic Chemistry;
1987; Vol. 5, pp 533–593. (b) Healy, P. C.; Pakawatchai, C.; White, A. H.
(18) (a) Reference 17a. (b) Munakata, M.; Kitagawa, S.; Asahara, A.; Masuda, H.

for the ATRP of styrene in diphenyl ether: [styrene]₀ = 4.34 M; [CuX]₀ = [dNbipy]₀/2 = 0.045 M. Slope (Br) = 0.99; Slope (Cl) = 1.03.

Figure 5. Reaction orders for CuBr (110 °C) and CuCl (130 °C) for the ATRP of styrene in diphenyl ether: [styrene]₀ = 4.34 M; [1-PEX]₀ = [dNbipy]₀/2. Slope (Cl) = 0.87; Slope (Br) = 1.03.

order with respect to monomer concentration and that the concentration of radicals was constant throughout the polymerization. Equation 9 in combination with the values of \( k_{\text{app}} \) from Figure 1 (bulk: \( 1.6 \times 10^{-4} \text{ s}^{-1} \); solution: \( 3.9 \times 10^{-5} \text{ s}^{-1} \)) and the known rate constant of radical propagation for styrene \( k_p = 1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \) at 110 °C\(^2\)) can be used to estimate the steady-state concentration of radicals in the polymerization. In this case, the calculated concentrations of radicals are \( 1.0 \times 10^{-2} \text{ M} \) and \( 2.4 \times 10^{-8} \text{ M} \), bulk and solution, respectively, which are sufficiently low for a minimal number of chains to undergo termination during the timespan in which the polymerization can go to high conversion. The bulk polymerization value (10\(^{-7} \text{ M} \) at 110 °C) can be compared to that found for the corresponding TEMPO-mediated styrene polymerizations at 130 °C (10\(^{-8} \text{ M} \)).\(^{20,22}\)

A plot of \( \ln(k_{\text{app}}) \) versus \( \ln([\text{initiator}]_0) \) (for both 1-PEBr and 1-PECl, Figure 4) showed that the rate of polymerization was first-order with respect to the concentration of both initiators. A plot of \( \ln(k_{\text{app}}) \) versus \( \ln([\text{CuX}]_0) \) (for both CuBr and CuCl, Figure 5) showed that the rate of polymerization was first order with respect to the concentration of copper(I). This result is in contrast to a previous report\(^{15} \) on ATRP using arenensulfonyl chlorides as initiators in which it was reported that the rate of polymerization decreased with an increase in soluble catalyst concentration. The authors used \( M_R/M_S \) as an indicator of catalyst efficiency; however, this parameter is mainly indicative of the relative rate of exchange between dormant and active species in the polymerization. Information on the rates of polymerization and molecular weights in combination with the \( M_R/M_S \) provides a better way to assess the efficiency of the catalyst system. The reaction orders thus determined help to explain why the observed rates of polymerization in bulk are approximately four times greater than those conducted in 50% monomer solution: a reduction in the concentration of both copper(I) and initiator by a factor of two should result in a reduction of the overall rate by a factor of four.

Determining the reaction order with respect to [Cu(II)X] was not as straightforward. A series of polymerizations was performed in which a known amount of CuBr\(_2\)/2dNbipy was added to the polymerization mixture. Plots of \( \ln(k_{\text{app}}) \) vs. ln-[CuBr\(_2\)]\(_{\text{added}} \) (Figure 6) were not linear with a slope of -1 but instead reached a constant value of \( k_{\text{app}} \) at low added copper(II) concentrations.\(^{23} \) Evidently the reaction rate is not simple inverse first-order with respect to the initial, added CuBr\(_2\) concentration. There are several possible explanations for this observation, but one that is borne out by experiment is that Cu(II)X is formed irreversibly during the initial stages of the polymerization, and, therefore, the actual concentration of Cu(II)X in the polymerization is not the same as the added concentration of Cu(II)X.

The rate law of the model mechanism (eq 9) is not consistent with the observations in this case, because in formulating the rate law, we explicitly omitted termination by radical coupling. It turns out that even though radical coupling is a negligible reaction during the majority of the polymerization and does not affect the controlled/“living” behavior, it plays a very important regulatory role during the very initial stages of the polymerization (cf. eq 12).

To investigate the incipient stage of the polymerization, we studied a model reaction between the initiator, 1-PEBr, and a well-defined copper(I) complex of the structural type that has been implicated in the catalytic activity of Cu(I)/2L catalyst mixture, [(dNbipy)\(_2\)Cu\(^{+}\)]\(^{2+}\) PF\(_6\)\(^{-}\). When 2 equivs of 1-PEBr were heated with 1 at 110 °C in \( C_6D_6 \) and the reaction was monitored using \(^1H\) NMR, in less than 30 min signals for the two diastereomers of 2,3-diphenylbutane were observed in the


\(^{23} \)It was reported by Voříš, Asscher, and Orocho (J. Chem. Soc., Perkin II 1973, 1000) that CuBr\(_2\) can react with styrene to form (1,2-dibromoethyl)benzene and CuBr. The dichalide thus formed in ATRP could act as an initiator, and this reaction could account for the nonlinear behavior observed in Figure 8. However, when CuBr\(_2\)/2dNbipy (or 2 bipy) and styrene were heated at reflux for 1 week and monitored using \(^1H\) NMR spectroscopy, no formation of (1,2-dibromoethyl)benzene was observed. Furthermore, independently prepared (1,2-dibromoethyl)benzene was shown to be a very inefficient initiator for ATRP, presumably due to the deactivating effect of the \( \beta \)-bromo substituent.
Fisher, H.

The amount of 2,3-diphenylbutane formed could not be quantitated due to overlap of the dNbipy ligand signals; however, the intensity of the signals did not appear to change with an increased time of heating. The formation of this product was observed more clearly for the reaction between CuBr/2bipy and 1-PEBr under identical conditions, but the reaction proceeded at a much slower rate due to the insolubility of the copper complex. When a sample of the former NMR reaction proceeded at a much slower rate compared to the latter, facts that are consistent with the formation of the two diastereomers of 2,3-diphenylbutane. Thus, the dimer of 1-phenylethyl radical clearly was formed during the initial stages of the reaction. According to the stoichiometry of the preequilibrium (Scheme 2), 2 equivs of Cu(II)X must be formed irreversibly along with the radical dimer. Due to the differences in extinction coefficients between the corresponding copper(I) and (II) complexes (ε of [dNbipy]2CuBr+PF6− ≈ 10 times ε of [dNbipy]2CuBr+PF6−), it was difficult to detect the UV-visible spectrum of the few percent of the copper(II) complex formed in the presence of the copper(I) complex. However, when the above reaction was forced to completion by increasing the temperature to 130 °C and by increasing the heating time to 24 h, the UV-visible spectrum of the resulting solution showed an absorption at λ = 750 nm that matched the spectrum of an independently synthesized sample of [(dNbipy)2CuBr]2PF6−.

The above data suggest the following overall picture for the polymerization. At the start of the polymerization the concentrations of radicals and Cu(II)X are zero, and, as Cu(I) reacts with the initiator, the concentration of the former two species increases. Because of the form of the equilibrium expression (eq 8) and the fact that the concentrations of Cu(I) and R−X are constant to within a few percent, the product of the concentrations of Cu(II)X and R should also be constant. Therefore, during the initial stages of the polymerization the concentration of radicals is sufficiently large that the rate at which the radicals revert to the dormant state (rate = kdeact * [Cu(II)X] [R*]) is much slower than the rate at which they undergo termination (rate = k* [R*]2). With each termination event, the concentration of Cu(II)X increases, and because the product [Cu(II)X][R*] is constant, the concentration of radicals decreases. Therefore, the rate at which the radicals terminate decreases until a sufficiently high concentration of Cu(II)X is formed, at which point the rate of termination is slow enough for a controlled “living” polymerization to occur. This “self-adjustment” process during the initial stages of the polymerization is also called the “persistent radical effect” and has been observed previously for organic radical reactions.

The persistent radical effect accounts for the observed initial formation of 2,3-diphenylbutylate under model reaction conditions, and because Cu(II)X was formed irreversibly along with the 2,3-diphenylbutylate, this effect demonstrates why the actual concentration of Cu(II)X in the polymerization could not be predetermined (the effect as seen in Figure 6). If the amount of added Cu(II)X was not sufficient to ensure the proper steady-state concentration of radicals (∼10−7−10−8 M), then more would be generated from Cu(I) and the initiator/dormant chains by radical coupling. The concentration of Cu(I) and the initiator/dormant chains in the polymerizations is always much greater than the concentration of Cu(II)X, so the decrease in the concentration of Cu(I) and the initiator/dormant chains upon the initial formation of Cu(II) is relatively small. Because this change is small, its effect upon the kinetics is not observed. Thus, radical coupling only shows an effect when determining the reaction order with respect to species that are present in low concentrations.

The temperature dependence of the rate of polymerization was studied using both the bromide- and chloride-mediated ATRP systems in which 10 mol % of CuX2/2L (X = Br, Cl) was added (Figure 7).

The temperature dependence of the rate of polymerization was studied using both the bromide- and chloride-mediated ATRP systems in which 10 mol % of CuX2/2L (X = Br, Cl) was added. The excess of CuX2 was needed to ensure that its concentration remained constant to within a few percent error under different polymerization conditions. Otherwise, variations in the amount of CuX2 formed could have lead to variations in the determination of both kapp and the preequilibrium constant.

From the slopes of the plots, the apparent activation enthalpies (∆Happ) were measured at 11.9 kcal mol−1 for the bromide-mediated ATRP of styrene and 13.4 kcal mol−1 for the chloride-mediated ATRP of styrene. The activation enthalpy for styrene propagation is known (∆Hprop = 7.1 kcal mol−1). Equation 13 shows how the enthalpy of the preequilibrium and the apparent activation enthalpy of propagation are related to the apparent activation enthalpy, so we could calculate the the enthalpies of the preequilibrium: ∆H0 = 4.8 kcal mol−1 and ∆H0 = 6.3 kcal mol−1 for the ATRP of styrene initiated by 1-PEBr and 1-PECI, respectively.

(24) Simultaneously, styrene formation was also observed (ref 14).

The preequilibrium constants for both the 1-PEBr/CuBr- and 1-PECI/CuCl-initiated ATRPs of styrene at 110 °C were calculated using eq 9 and kinetic data from polymerizations in which 10 mol % of CuX2/2L (X = Br, Cl) was added initially. In these polymerizations, the amount of Cu(II) generated from the persistent radical effect would be small compared to the large added concentration of Cu(II) and therefore [Cu(II)]_f ≈ [Cu(II)]_i. Thus, for 50% (v/v) styrene polymerizations performed using diphenyl ether solvent and with 1 mol % initiator and 1 mol % Cu(I/II), the apparent rate constants were 2.5 × 10^{-3} s^{-1} (X = Br) and 1.4 × 10^{-3} s^{-1} (X = Cl), and the calculated equilibrium constants were 3.9 × 10^{-8} (X = Br) and 2.1 × 10^{-8} (X = Cl). These values correspond to free energies of equilibrium (ΔG°) at 110 °C of 13.0 kcal mol^{-1} (X = Br) and 13.5 kcal mol^{-1} (X = Cl). The differences in the equilibrium constants and free energies of polymerization for the bromide- and chloride-mediated ATRPs of styrene reflect the smaller difference in bond strengths between the carbon-bromine and copper(II)-bromine bonds relative to the carbon-chlorine and copper(II)-chlorine bonds.

With the free energies and enthalpies of the preequilibrium thus determined, we calculated the changes of entropy at equilibrium at 110 °C, which tentatively indicates that the coordination sphere of the active copper(I) center contains two bipyridine ligands. The exclusive role for this copper(I) complex in ATRP is atom transfer, since at typical concentrations that occur for these polymerizations (∼10^{-7} – 10^{-8} M), polymeric radicals were found not to react with the copper(I) center in any manner that enhanced or detracted from the observed control. ATRP also exhibited first-order kinetics with respect to both initiator and copper(I) halide concentration; however, the polymerization kinetics were not simple inverse first-order with respect to the initial copper(II) halide concentration. The latter observation was found to be due to the persistent radical effect, which resulted in an increase in copper(II) concentration during the initial stages of the polymerization. This phenomenon also has the effect of regulating the polymerization by ensuring that the rate of radical combination and/or disproportionation is sufficiently less than the rate of propagation. The temperature dependence of the rate of ATRP was measured, and the apparent activation enthalpies were found to be ΔH°_app = 11.9 kcal mol^{-1} for the bromide-mediated ATRP of styrene and ΔH°_app = 13.4 kcal mol^{-1} for the chloride-mediated ATRP of styrene. Estimates of the enthalpies and entropies of equilibrium for the preequilibrium step were calculated at ΔH° = 4.8 and ΔH° = 6.3 kcal mol^{-1} for the ATRP of styrene initiated by 1-PEBr and 1-PECI, respectively, and ΔS° = −22 and ΔS° = −20 cal mol^{-1} K^{-1} for the ATRP of styrene initiated by 1-PEBr and 1-PECI, respectively.

Experimental Section

Materials. Styrene was stirred over CaH₂ overnight and vacuum distilled before use. CuBr (98%, Aldrich) and CuCl (98%, Aldrich) were purified according to the procedure of Keller and Wycoff. The initiators, 1-phenylethyl bromide and 1-phenylethyl chloride, were distilled from CaSO₄ before use. Diphenyl ether (ACROS) was stirred over anhydrous CuSO₄ for 24 h and then distilled onto P₄O₁₀. The CH₃CN was stirred over P₂O₅ for 24 h, after which time it was distilled and stored under argon. Tetrahydrofuran (THF) and toluene were distilled from Na/benzophenone before use. Disopropylamine was distilled from CaH₂ before use. tBippy, 4′,4′-di-tert-butyl-2,2′-bipyridine, was prepared according to the procedure of Hadda and Bozec. Unless specified, all other reagents were purchased from commercial sources and used without further purification.

General Procedures and Characterizations. Monomer conversion was determined by GC using THF or diphenyl ether (when present) as an internal standard. Molecular weights and molecular weight distributions were measured using a Waters 712 WISP autosampler and the following Phenogel GPC columns: guard, linear, 1000 Å and 100 Å. Molecular weights were calibrated using polystyrene standards. Experiments requiring an inert atmosphere were performed using standard Schlenk and drybox techniques.

Conclusions

The homogeneous atom transfer radical polymerization (ATRP) of styrene using solubilizing 4,4′-diaryl substituted 2,2′-bipyridines yielded well-defined polymers with M Yö/M Yö ≤ 1.10. The polymerizations exhibited an increase in molecular weight in direct proportion to the ratio of the monomer consumed to the initial initiator concentration and also exhibited internal first-order kinetics with respect to monomer concentration. The kinetically optimum ratio of ligand-to-copper(I) halide for these polymerizations was found to be 2.1, which tentatively indicates that the coordination sphere of the active copper(I) center contains two bipyridine ligands. The exclusive role for this copper(I) complex in ATRP is atom transfer, since at typical concentrations that occur for these polymerizations (∼10^{-7} – 10^{-8} M), polymeric radicals were found not to react with the copper(I) center in any manner that enhanced or detracted from the observed control. ATRP also exhibited first-order kinetics with respect to both initiator and copper(I) halide concentration; however, the polymerization kinetics were not simple inverse first-order with respect to the initial copper(II) halide concentration. The latter observation was found to be due to the persistent radical effect, which resulted in an increase in copper(II) concentration during the initial stages of the polymerization. This phenomenon also has the effect of regulating the polymerization by ensuring that the rate of radical combination and/or disproportionation is sufficiently less than the rate of propagation. The temperature dependence of the rate of ATRP was measured, and the apparent activation enthalpies were found to be ΔH°_app = 11.9 kcal mol^{-1} for the bromide-mediated ATRP of styrene and ΔH°_app = 13.4 kcal mol^{-1} for the chloride-mediated ATRP of styrene. Estimates of the enthalpies and entropies of equilibrium for the preequilibrium step were calculated at ΔH° = 4.8 and ΔH° = 6.3 kcal mol^{-1} for the ATRP of styrene initiated by 1-PEBr and 1-PECI, respectively, and ΔS° = −22 and ΔS° = −20 cal mol^{-1} K^{-1} for the ATRP of styrene initiated by 1-PEBr and 1-PECI, respectively.

1-bromohexane (9.2 mL, 65.5 mmol) was added. The mixture was allowed to warm to room temperature overnight and was then poured into cold brine (250 mL). The aqueous phase was extracted with anhydrous Na2SO4, filtered, and concentrated under vacuum. Purification by activated neutral aluminum oxide chromatography (ether/hexane, 1/2, Rf = 0.29) afforded 4.0 g (75% combined yield) of a white solid. Further purification can be achieved by recrystallization in acetonitrile to give white needles: mp 52.0–53.3 °C; 1H NMR (CDCl3, δ ppm): 8.5 (d, 2H), 8.2 (s, 2H), 7.1 (d, 2H), 2.6 (t, 4H), 1.6 (m, 4H), 1.2 (m, 20H), 0.8 (t, 6H).

6.98 (d, 2H) into cold brine (250 mL). The aqueous phase was extracted with a purged syringe and added to 5.00 mL of THF. The THF solutions were injected into the GC, and percent conversions were calculated relative to the time = 0 data points. The samples were then filtered through a small column of alumina and a 0.2 micron filter and then injected into the GPC for analysis.

Procedure for Conducting Free-Radical Polymerizations in the Presence of Copper Compounds. Under an inert atmosphere, the following stock solutions were prepared: (1) blank: 13 mg (3.8 mM) of dicumyl peroxide in 10.00 mL of styrene; (2) well-defined copper(I) compound: 0.894 g (87.0 mM) of [(dNbipy)2 Cu]PF6, 1.38 g (3.33 mM) of dicumyl peroxide in 10.00 mL of styrene; (3) ATRP catalyst: 0.125 g (87.0 mM) of CuBr, 0.721 g (176 mM) of [CuBr2·2.75 H2O], and 13 mg (3.8 mM) of dicumyl peroxide in 10.00 mL of styrene; (4) ATRP homo-catalyst: 0.125 g (87.0 mM) of CuBr, 0.721 g (176 mM) of dNbipy, and 13 mg (3.8 mM) of dicumyl peroxide in 10.00 mL of styrene. Several samples (1.00 mL) of each solution were added to individual glass tubes. While maintained under an inert atmosphere, each tube was attached to the vacuum line, “freeze—pump—thaw” degassed once, and sealed under vacuum. The tubes were placed in an oil bath thermostatted at 110 ± 1 °C. At timed intervals, the tubes were removed from the oil bath and cooled to room temperature by washing the tube with hexanes. Afterwards, the individual tubes were broken, and the contents were dissolved in 10.0 mL of THF.

Procedure for Homogeneous “Reverse ATRP”. The procedure used here was the same as that used for the bulk ATRP of styrene. The quantities of reagents used for each glass tube were as follows: 3.7 mg (2.3 × 10–2 mmol) of AIBN, 10.1 mg (4.5 × 10–2 mmol) of CuBr2, 37.1 mg (9.1 × 10–2 mmol) of dNbipy, and 0.500 mL (0.454 g, 4.4 mmol) of styrene. After polymerization, the contents of each tube were dissolved in 5.0 mL of THF, and the polymer solutions were analyzed as described above.

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