Extended X-ray Absorption Fine Structure Analysis of the Bipyridine Copper Complexes in Atom Transfer Radical Polymerization

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Among the most efficient techniques for addition of alkyl halides across double bonds are atom transfer radical addition (ATRA)[1] and atom transfer radical polymerization (ATRP),[2] which are catalyzed by redox-active transition metal complexes. Successful ATRA and ATRP reactions require an appropriate control of the equilibrium constant, as well as dynamics of the exchange process (activation, k_a, and deactivation, k_d), which strongly affect the polydispersities of polymers prepared by ATRP and the proportion of chains involved in termination (k_t). Mechanistically, ATRA and ATRP presumably proceed via a reversible inner-sphere electron transfer (or atom transfer) process and the addition of the resulting radical to double bonds (k_p).[3]

The transition metal complexes play the most important role in ATRA and ATRP. They define the chemoselectivity of the radical addition, as well as the overall rate of the process. For example, ATRP catalyzed by CuBr or CuCl complexed by 4,4′-dialkyl-2,2′-bipyridines (dAbpy) allows formation of polystyrenes and polyacrylates with very low polydispersities of comparable or sometimes even better control than in anionic polymerization.[2b] For this, perhaps the most extensively studied system, the mechanism depicted in Scheme 1, based on the typical crystallographic structures of Cu^I and Cu^{II} complexes with bpy ligands, has been proposed.[2c] Since the catalyst plays such an important role in ATRA and ATRP systems, it is very important to know its precise structure in the reaction media. This understanding allows the catalyst structure to be better tuned to the reactivity of the system and helps enable the rational design of more efficient catalytic species.

There are several reports describing the solid-state crystalline structure of complexes of Cu^I halides with bipyridines and phenantrolines. Most of them show distorted tetrahedral cationic Cu^I species coordinated by two bpy molecules and the accompanying counterion (Br^-, Cl^-, I^-, or weakly coordinated anion such as PF_6^-, ClO_4^-, etc.).[4] When equimolar amounts of bpy and Cu^I halides were used, then either halogen-bridged dimeric species or a Cu^I/2bpy tetrahedral cation with $Cu^ICl_2^-$ anion was formed.[5] All of these species can potentially coexist in reaction mixtures in proportions dependent on the solvent (or monomer in ATRP),

Scheme 1
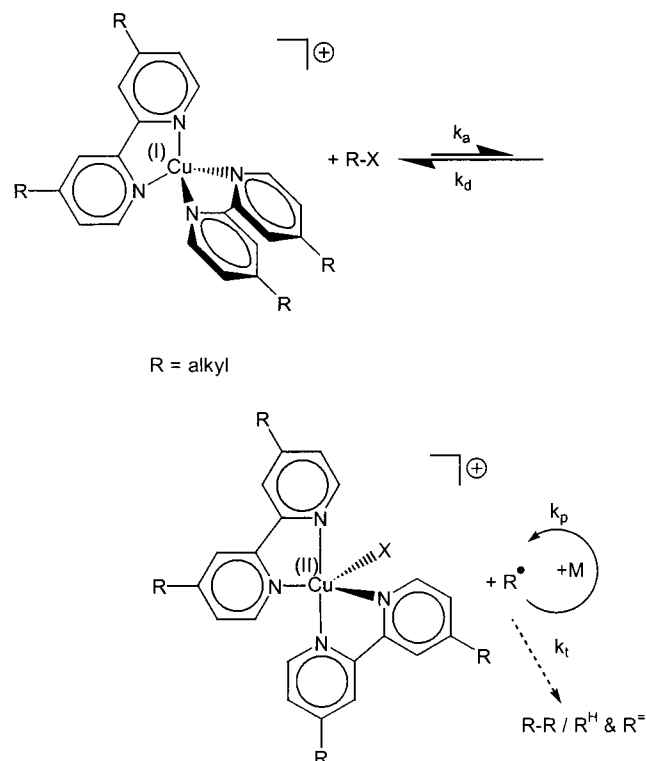
temperature, and concentrations.[6] The understanding of the structure of Cu^{II} species is also important because these species reversibly deactivate the radicals and convert them to the dormant structure. They are spontaneously formed via a persistent radical effect and have been directly detected by EPR.[7]

Since X-ray data can only refer to the isolated species in the solid state, we decided to use EXAFS (extended X-ray absorption fine structure) spectroscopy[8] under conditions typical for ATRP systems (monomers, temperature, and concentration) to get a deeper insight into the structures of Cu^I and Cu^{II} species coordinated by dAbpy. The structural characterization of such complexes in a nonpolar medium such as a typical monomer has never been attempted before because of the low solubility of complexes with unsubstituted bpy ligands.

Different model systems for the catalysts in solution of the monomers, as well as real polymerizations, were determined at

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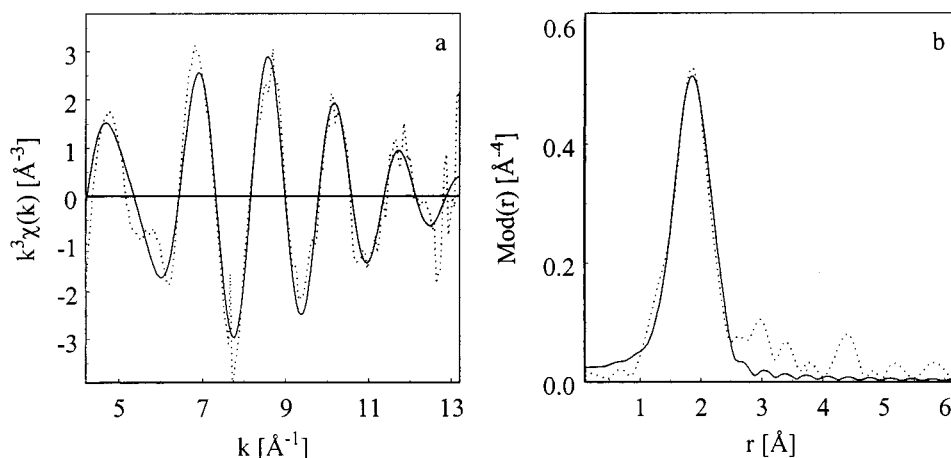
Figure 1. Experimental (dotted line) and calculated (solid line) $k^3 \chi(k)$ functions and the corresponding Fourier transformations mod(r) for a mixture of 1 equiv of CuBr and 1 equiv of dNbpy in styrene at room temperature, measured at the Cu K-edge ($k = 4.2-13.2$ Å^{-1}; energy shift $\Delta E_0 = 18.2$ eV).

Table 1. Comparison of Experimental Bonding Distances [pm] from EXAFS Measurements at Room Temperature with Distances in Single-Crystal X-ray Structures

	Cu−N EXAFS	Cu−N crystal	Cu−Br EXAFS	Cu−Br crystal
[(bpy)$_2$Cu][ClO$_4$]	198	202.0, 202.1[9]		
[(bpy)$_2$CuBr][BF$_4$]	201	199.5, 199.6, 206.8, 211.4[10]	241	241.9[10]
[N(Bu)$_4$][CuBr$_2$]			225	222.6[11]
[CuBr(bpy)]$_2$	210	208.3, 209.9[5]	244	242.8, 246.3[5]

the copper and bromine K-absorption edge. We used the solid-state samples [Cu^I(bpy)$_2$]$^+$[ClO$_4$]$^-$ for tetrahedral Cu^I complexes, [Cu^{II}(bpy)$_2$Br]$^+$[BF$_4$]$^-$ [10] for trigonal bipyramidal Cu^{II} complexes, the bridged Cu^I complex [CuBr(bpy)]$_2$,[9] and the anionic Cu^I complex [N(Bu)$_4$]$^+$[Cu^{I}Br$_2$]$^-$.[11] The crystals were prepared according to literature procedures and determined by single-crystal diffractometry before use in the measurements. The use of unsubstituted bpy complexes as the standards instead of the dAbpy complexes was not expected to display any relevant influence on the Cu−N bond length. A comparison of the bond length from EXAFS and X-ray structures of all standards is shown in Table 1. EXAFS data displayed a good agreement with the X-ray data. The evaluation of the EXAFS data was performed according to standard procedures.[8] For the nitrogen atoms, only one backscatterer at a mean distance could be found in all systems. The coordination numbers were fixed at the known values for the curve fitting.

Measurements in solution were carried out with styrene and methyl acrylate as solvents (typical ATRP monomers) under an argon atmosphere with the 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy) complexes. The results of the measurements are shown in Table 2. The first experiments were carried out to reveal whether ratios of CuBr to dNbpy of 1:1 or 1:2 would alter the structure of the catalyst. The 1:1 ratio was originally thought to form a bridged structure in solution as proposed by Skelton et al.,[5] but the elongated Cu−N and the bridging Cu−Br bond lengths (see Table 1) could not be found in the analysis of our data. In both cases, the predominant structure is a copper species surrounded by four nitrogen atoms and a second copper species surrounded by two bromine atoms. The experimental distances obtained agree very well with those distances of crystal struc-

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Table 2. Results of Room Temperature EXAFS Measurements of Different Ligand to Copper Halide Mixtures, Number of Backscattering Atoms, and Their Distances[a]

mixture	monomer	Cu−N no. N atoms	Cu−N distance, pm	Cu−Br no. Br atoms	Cu−Br distance, pm
CuBr + dNbpy	St	3.8	200	1.4	225
CuBr + 2 dNbpy	St	3.4	201	1.3	227
CuBr + dNbpy	MA	3.8	200	1.4	226
CuBr + 2 dNbpy	MA	3.6	199	1.2	226
CuBr$_2$ + 2 dNbpy	MA	4.4	204	3.6	237
CuBr + 2 dNbpy, polymerization @ 95 °C	St	3.4	202	1.7	226
CuBr + 2 dNbpy, polymerization @ 80 °C	MA	3.6	202	1.3	227

[a] Inherent errors are 20% for coordination numbers and 1% for distances.

ture data from the tetrahedral [Cu^I(dNbpy)$_2$]$^+$ cation, which shows a Cu−N distance of 201.0 and 201.2 pm.[9] The experimental Cu−Br distances correspond to the bond length in a [Cu^{I}Br$_2$]$^-$ anion, which is 222.6 pm.[11] Figure 1 shows a comparison between the experimental and calculated $k^3 \chi(k)$ functions together with the corresponding Fourier transform for a mixture of 1 equiv of CuBr and 1 equiv of dNbpy in styrene at room temperature. The smaller peak at 3 Å and the residual peaks up to 6 Å originate from the backscattering of carbon atoms of the bpy ligands. Because of the weak backscattering properties of these atoms and the problem distinguishing between them, they were neglected in the fitting. Similar structures were obtained using 2 equiv of dNbpy. Therefore, it seems that 1 equiv of the ligand is sufficient for the catalytic activity of ATRA and ATRP systems. Since it is known that [Cu^{I}Br$_2$]$^-$ has essentially no ATRP catalytic activity,[2c] the fitted structures support the proposed mechanism of Cu/bpy ATRP shown in Scheme 1. Changing the monomer from styrene to methyl acrylate has no significant influence on the structures of the complexes.

A solution of Cu^{II}Br$_2$ and 2 equiv of dNbpy in methyl acrylate displays, as expected, a different arrangement at the copper centers. A comparison between the experimental and calculated $k^3 \chi(k)$ functions with the corresponding Fourier functions is shown in Figure 2. The analysis shows that in this case the coordination sphere around the copper can be described best by four nitrogen atoms at 204.0 pm and four bromines at 237.0 pm. Although there is no clear evidence for a [Cu^{II}(dNbpy)$_2$Br]$^+$ cation with a Cu−Br bond length of 242 pm[10] (Table 1), we believe that this species is present in the solution together with [Cu^{II}Br$_3$]$^-$ as a counterion that has a bond length of about 235 pm.[12] Because
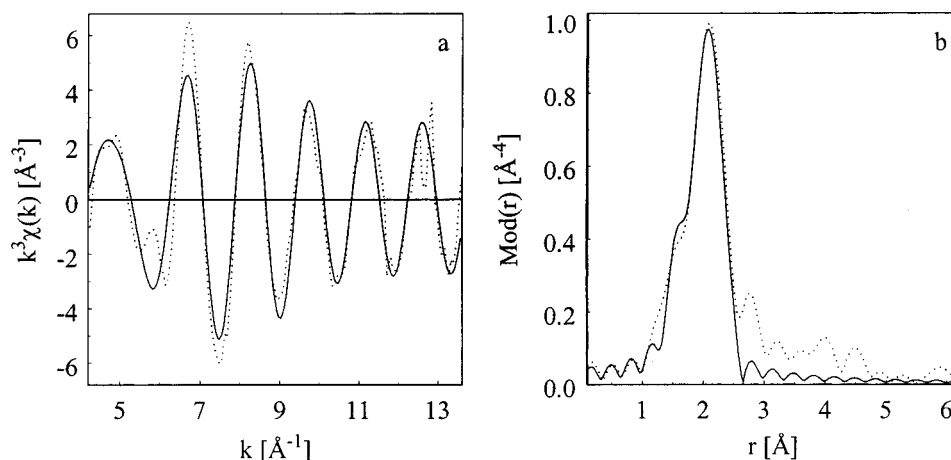
Figure 2. Experimental (dotted line) and calculated (solid line) $k^3 \chi(k)$ functions and the corresponding Fourier transformations mod(r) for a mixture of 1 equiv of CuBr$_2$ and 2 equiv of dNbpy in methyl acrylate at room temperature, measured at the Cu K-edge ($k = 4.2-13.6$ Å^{-1}; energy shift $\Delta E_0 = 22.2$ eV).

of the small difference of the Cu−Br distances, only one peak occurs in the Fourier transformation for the bromine atoms. The bromine backscatterers from the anion dominate the spectrum; therefore, the resulting distance is strongly shifted toward the Cu−Br distance from [Cu^{II}Br$_3$]$^-$. Another possible explanation would be a pairing of the ions leading to equalization of the Cu−Br distances. However, the resulting bridging should lead to a Cu−Cu distance of about 3.3 Å, which could not be found. Again, the smaller peaks above 3 Å caused by the carbon atoms of the bpy ligands were neglected in the fitting.

The analysis of the data for the polymerization reactions revealed that in these systems only the tetrahedral Cu^I structure accompanied by the [Cu^{I}Br$_2$]$^-$ anion could be detected. The amount of Cu^{II} species formed during polymerization is relatively small and usually does not exceed 6% from the initial Cu^I species.[7b] This value apparently was too low to get any structural information about the Cu^{II} complex by EXAFS. This is a clear indication that the equilibrium has shifted strongly toward the Cu^I side in the equilibrium between Cu^I and Cu^{II} in solution (Scheme 1).

All the above experiments from the copper K-absorption edge were confirmed by analysis of data from the bromine K-edge. Distances differed only 2 pm at most. Although the fitting of the experimental data with the simulation from model systems gave good agreements, the inherent problem of the EXAFS method is determination of the exact proportions and amounts when there are several different species in the system. Especially in the case of the anions we cannot be sure that the [Cu^{I}Br$_2$]$^-$ anion for the Cu^I case and the [Cu^{II}Br$_3$]$^-$ for the Cu^{II} case are the only anions present in the system. The EXAFS analysis shows that they are the predominant species, but it is also possible that anion Br$^-$, which cannot be detected by EXAFS, and [Cu^{II}Br$_4$]$^{2-}$, which shows distances similar to those of [Cu^{II}Br$_3$]$^-$, are also present to some extent. Furthermore, free bpy molecules existing in the mixtures with Cu/dNbpy = 1:2 ratio could coordinate to the anions, generating species like [Br$_2$Cu(dNbpy)]$^-$ and [Br$_3$Cu(dNbpy)]$^-$ with tetrahedral and trigonal bipyramidal coordination of Cu, respectively. However, if such species should exist in solutions to a higher extent, this would at least lead to changes in the Cu−N coordination number. We found the same

coordination numbers and distances regardless of the dNbpy content of the solutions, leading to the conclusion that [Cu^{I}Br$_2$]$^-$ and [Cu^{II}Br$_3$]$^-$ are the dominating anionic species in solutions of the ATRP monomers.

In summary, our study shows that the predominant Cu^I species in atom-transfer radical polymerization is a Cu^I cation surrounded by four nitrogen atoms, presumably tetrahedral [Cu^I(dNbpy)$_2$]$^+$. This cation in a nonpolar media such as monomers in ATRP is accompanied by the [Cu^{I}Br$_2$]$^-$ anion. The results obtained in this report were also supported by a recent study of silyl-substituted ATRP catalysts in which a tetrahedral bpy-substituted Cu^I complex was found to be accompanied by a [Cu^{I}Br$_2$]$^-$ anion.[13] The EXAFS of isolated Cu^{II} species indicates the possibility of the presence of a [Cu^{II}(dNbpy)$_2$Br]$^+$ cation and a [Cu^{II}Br$_3$]$^-$ anion. Thus, it appears that in nonpolar media, a bare halide anion coordinates to CuBr more strongly than bpy. In polar and protic solvents the halide anions are better stabilized and [Cu^I(dNbpy)$_2$]$^+$Br$^-$ or [Cu^{II}(dNbpy)$_2$Br]$^+$Br$^-$ species may dominate. These results also indicate that the 1:1 ratio of bpy to Cu species can be sufficient for both ATRA and ATRP. The earlier determined optimal kinetic ratio of 2:1 for styrene ATRP could be related to the slow formation of CuBr or CuCl/dAbpy complexes in nonpolar solvents that can be accelerated in the presence of an excess of the ligand. The catalytic activity in these systems is related to the cationic bpy complexes because reactivity of the anionic species is much lower.[2c]

We are further investigating the structures by EXAFS to determine the proportion of various species and the structures of the mixed Cu^I/Cu^{II} systems as well as the solution structures of complexes with different ligands and different solvents.

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