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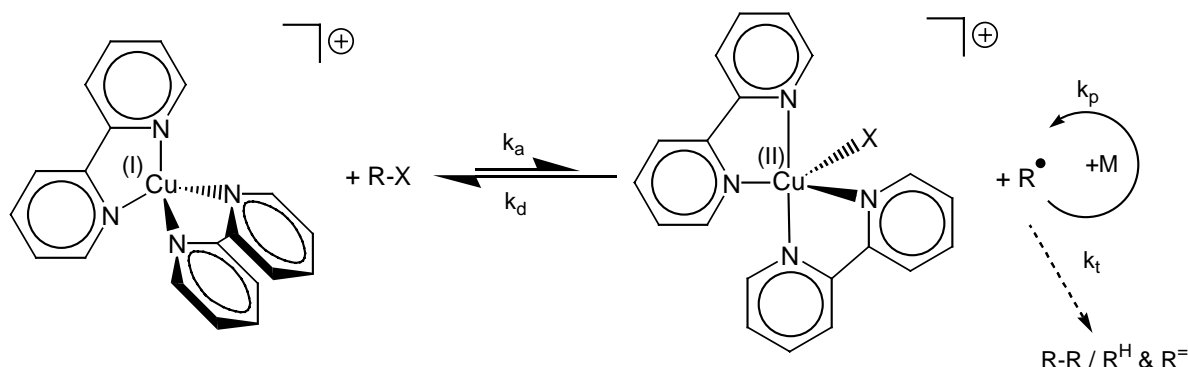
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Transition metal mediated atom transfer radical polymerization (ATRP) is one of the most interesting developments in controlled radical polymerization processes in the last couple of years. Especially due to the fact that compared to other controlled radical polymerization techniques it accepts a broad variety of monomers. [1] The proposed mechanism is based on the ability of a transition metal complex to abstract a halogen from an organohalogen bond by a homogeneous cleavage of that bond and hence the formation of a radical. The halogen abstracted should form a Cu(II) complex (scheme 1). Due to the fact that only a very low concentration of radicals is formed, side reactions like terminations are minimized and the polymerization could be specified controlled.



Although a lot of different transition metal complexes have potential applications in this reaction the amine-substituted copper system is the most commonly used. From all possible ligands bipyridyl (bpy) is the most applied one. Unfortunately, there was no structural information on the catalytic active species up to now so the mechanism of the polymerization is not yet fully understood.

In order to obtain insight into the structure of the species occurring in the solutions, we studied the systems copper halide + bipyridine + monomer in a first step. The measurements were carried out under an argon atmosphere with the 4,4'-di(5-nonyl)-2,2'-bipyridine (dNbpy) complexes, dissolved in styrene and methyl acrylate, respectively. Both substances are typical ATRP monomers. The results are shown in Table 1. 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 fit very well with those distances of crystal structure data from the tetragonal $[\text{Cu}^{\text{(I)}}(\text{bpy})_2]^+$ cation which shows Cu-N distance of 201.0 pm and 201.2 pm. Experimental Cu-Br distances correspond to the bond length in a $[\text{CuBr}_2]^-$ anion, which is 222.6 pm. This is consistent with the following scheme:



The amine ligand coordinates to the copper ion generating a copper amine complex and a second, anionic species.

All measurements were performed at the beamline A1 of HASYLAB at the Cu K-edge (8980.5 eV). Data were analysed with the program packages, described in [2] and [3]. The EXCURV92 module of CERIUS2 was used additionally for curve fitting. Figure 1 shows the experimental and calculated $k^3\chi(k)$ functions and their Fourier transforms for the system CuBr + dNbpy in the ratio 1:1, dissolved in styrene. For the ratio 2:1 and for methyl acrylate as solvent, almost identical spectra were found. The results have been published in [4].

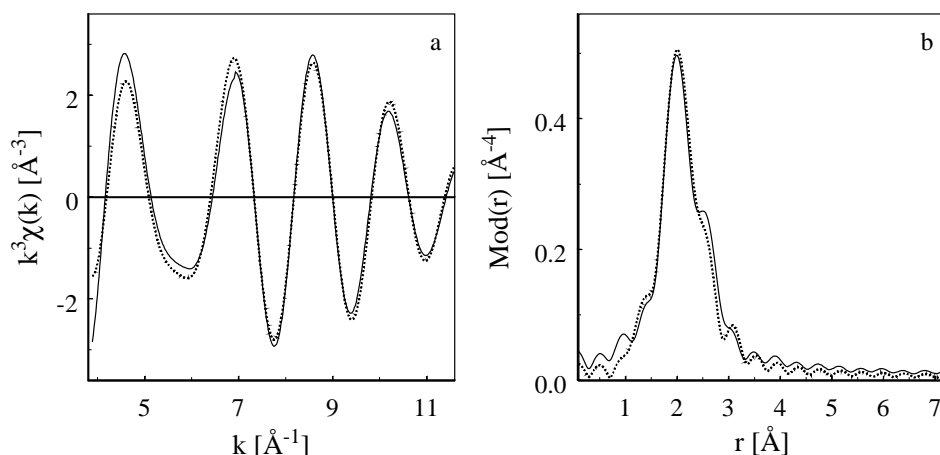


Figure 1: Fourier-filtered experimental (dotted line) and calculated (solid line) $k^3\chi(k)$ functions (a) and their Fourier transforms (b) for CuBr + dNbpy + styrene

Styrene	N	r [Å]	• [Å]	MA	N	r [Å]	• [Å]
Cu-N	4	2.01	0.110	Cu-N	4	2.03	0.103
Cu-Br	2	2.25	0.110	Cu-Br	2	2.29	0.110

Table 1: Structural parameter absorber-backscatterer distance r, coordination number N and Debye-Waller factor σ for CuBr + dNbpy + styrene or methyl acrylate (ratio 1:1)

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