

First synthesis of soluble, well defined coordination polymers from kinetically unstable copper(I) complexes

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Exclusion of competitive ligands is found to be the central requirement for obtaining solutions of constitutionally homogeneous, high-molecular-mass coordination polymers from kinetically unstable pseudo-tetrahedral complexes of copper(I) and *o*-phenanthroline derivatives.

Transition-metal coordination polymers, *i.e.* polymers whose main chains are held together only by coordinative bonds, are of considerable interest as magnetic, electronic or photooptical materials.¹ So far, most of the transition-metal complexes applied to the preparation of coordination polymers that are stable in solution are thermodynamically and kinetically stable.^{1,2} Coordination polymers from kinetically unstable metal complexes, on the other hand, are found either to be insoluble or to decompose in the presence of a potential solvent, exchanging some of their original ligands for solvent molecules, and their complete characterization is therefore prevented. Nevertheless, kinetically unstable coordination polymers could gain some importance as, for example, precursors of hitherto unrealized supramolecular structures such as polycatenanes,^{3,4} if the essential requirements are identified which must be fulfilled for obtaining derivatives of these metal-containing polymers that are stable in solution. Here, we study kinetically unstable copper(I)-*o*-phenanthroline complexes and demonstrate that soluble, high-molecular-mass coordination polymers of homogeneous constitution can be obtained if the solvents used for their preparation and dissolution cannot act as competitive ligands for copper(I).

The ligand monomer chosen for the present study was 4,4''-bis[(9-aryl)-2-*o*-phenanthroline]-2',5'-di-*n*-hexyl-*p*-terphenyl **5**. This contains two *o*-phenanthroline residues connected by a conformationally rigid *p*-terphenylene spacer. The latter was expected to prevent intramolecular complexation as well as formation of low-molecular-mass helicates.³⁻⁵ Furthermore, flexible *n*-hexyl side chains are attached to the central phenylene moiety of **5**. These side chains were found to be of crucial importance for the present strategy as they ensure the required solubility of polyelectrolyte **7** in non-coordinating and thus rather apolar solvents.⁶

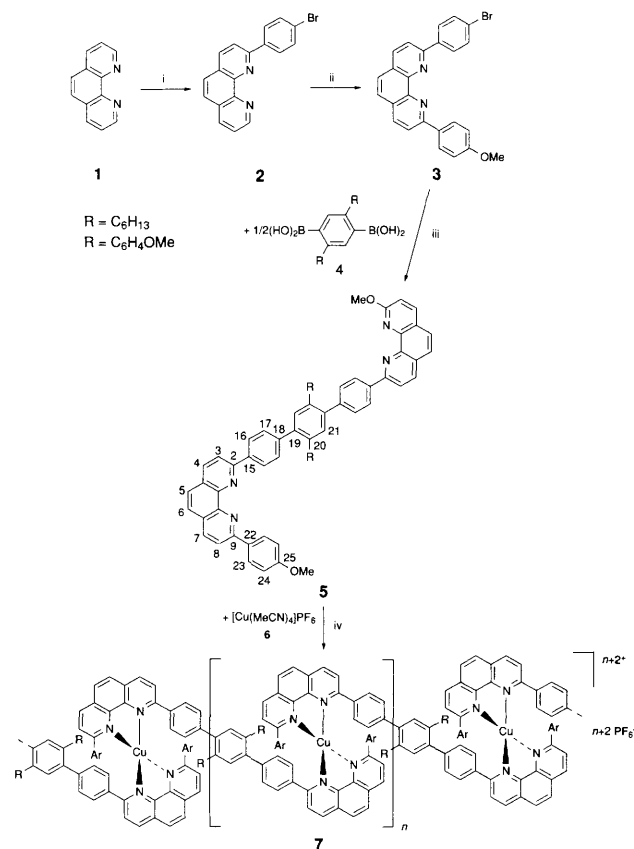
Ligand monomer **5** was prepared by analogy to known synthetic procedures (Scheme 1). *o*-Phenanthroline **1** was first reacted with *p*-bromophenyllithium,^{3,7} and after rearomatization, intermediate **2** was treated with *p*-methoxyphenyllithium.^{3,8} Diarylphenanthroline **3** was finally converted into monomer **5** via Pd-catalysed condensation with 2,5-dihexylbenzene-1,4-diboronic acid **4**.^{7,9} The molecular constitutions and the purities of compounds **2**, **3** and **5** were established by NMR spectroscopy and elemental analysis.

Prior to polymerization, model experiments were carried out in order to (i) develop appropriate reaction conditions for the conversion **5** → **7** in non-coordinating solvents, and (ii) show that ligand exchange processes do not occur in such solvents, or, if so, only to a very small extent. Silver(I) and copper(II) complexes **8** and **9** were prepared³ and, after isolation, were mixed together, dissolved in a variety of (deuteriated) solvents, and analysed by NMR spectroscopy.

The characteristic absorptions of the methoxy protons allowed precise assessment of whether ligand exchange had

occurred in a given solvent (Scheme 2). It was found that in coordinating solvents such as acetonitrile, ligand exchange occurs instantaneously, as manifested by the appearance of absorptions due to complexes **10** and **11**; acetonitrile thus strongly promotes ligand exchange.¹⁰ On the other hand, no evidence of ligand exchange was observed, even after several hours, with 1,1,2,2-tetrachloroethane (TCE) as solvent. Only after one week was formation of some **10** and **11** evident, caused presumably by the small amount of water present. Consequently, ligand exchange between kinetically unstable complexes can be slowed dramatically by avoiding solvents that may act as auxiliary ligands in such processes.¹⁰

It was expected that this rationale may also be valid with complexes incorporated in a polymer such as **7**. Therefore, TCE was used as the solvent of choice for the subsequent polymerizations. First, an appropriate quantity of monomer **5** was weighed into an NMR tube and dissolved in [2H₂]TCE. Then, the required amount of metal monomer [Cu(MeCN)₄]PF₆ **6** was added gradually. After each addition, NMR spectra were recorded for the resulting mixture. In the obtained sequence of spectra, the characteristic absorptions of the inner-chain repeat



Scheme 1 Reagents and conditions: i, *p*-bromophenyllithium, diethyl ether, -10 °C, MnO₂, 80%; ii, *p*-methoxyphenyllithium, diethyl ether, -10 °C, MnO₂, 80%; iii, toluene/1M aqueous Na₂CO₃, [Pd(PPh₃)₄], 90%; iv, 1,1,2,2-tetrachloroethane, 25 °C

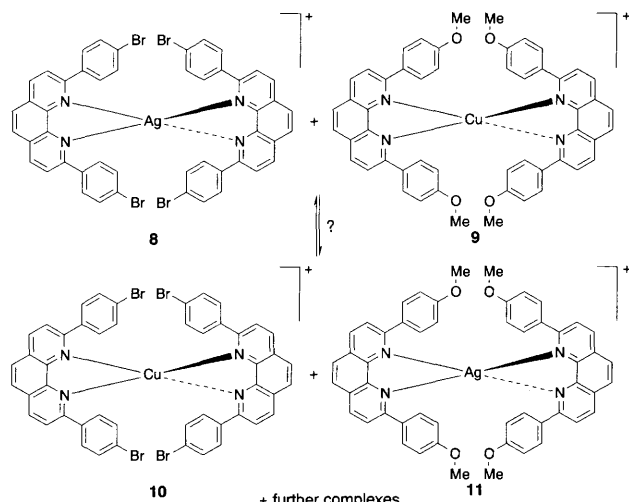
units of **7** increased systematically while the corresponding absorptions of free ligands and end groups decreased. At exactly 1 : 1 stoichiometry, only the broad absorptions of the polymer repeat units remained (Fig. 1). While the formation of a constitutionally homogeneous product was evident from both the signal assignments and intensities, the lack of end-group absorptions implied a degree of polymerization of $P_n \geq 30$.

This considerable P_n achieved for a coordination polymer from kinetically unstable complexes was also reflected by the high viscosities of homogeneous solutions of **7**. For systematic viscosimetry, gram quantities of polymer **7** were prepared in dry TCE, and the formed polymers were precipitated in hexane to completely remove even the small amount of acetonitrile introduced through application of $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ as the

metal monomer. Polymers **7** precipitated as red-brown, fibrous materials and were dried *in vacuo*. They readily and completely redissolved in pure TCE, and NMR showed that neither isolation nor redissolution caused defect structures or chain degradation. Also, complete removal of acetonitrile was evident. For the polymers **7** thus available, intrinsic viscosities of $[\eta] \approx 11 \text{ ml g}^{-1}$ were determined. This value is in excellent agreement with recent results obtained for ruthenium(II) coordination polymers where $[\eta] = 12 \text{ ml g}^{-1}$ was found for a sample of $P_w \approx 45\,000 \text{ g mol}^{-1}$ (determined by small-angle X-ray scattering, SAXS).¹¹ We therefore conclude that soluble, high-molecular-mass coordination polymers **7** from kinetically unstable copper(I) complexes can be obtained when coordinating solvents are avoided.

Currently, we are extending our studies to further kinetically unstable metal complexes. Furthermore, a direct determination of the absolute P_w values of **7** by SAXS and light scattering is under way.

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Scheme 2

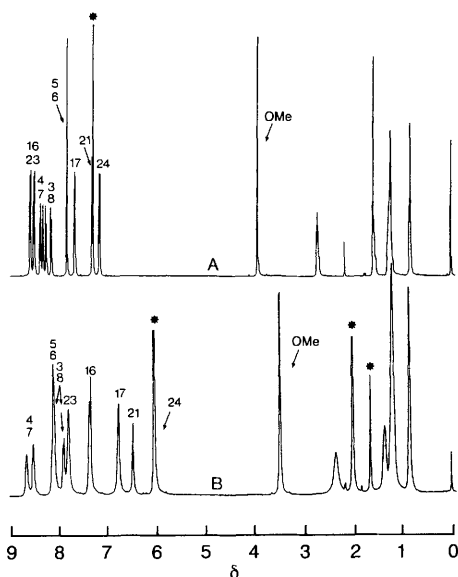


Fig. 1 400 MHz ^1H NMR spectra of (a) ligand monomer **5** and (b) coordination polymer **7**, recorded in CDCl_3 and $[\text{D}_2\text{O}]\text{TCE}$, respectively, at room temperature; the signal assignment is made according to the numbering given for monomer **5** in Scheme 1; solvent absorptions are assigned by asterisks

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