

# Metallo-Supramolecular Polymers: Towards New Functional Materials with Controlled Nanostructures

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Supramolecular polymers are of great interest in modern material research. Within this field, the construction of coordination polymers by complexation of oligomeric precursors bearing metal-coordinating groups at the chain ends is a promising approach. In the present contribution, we report on the synthesis of linear coordination polymers constructed from poly(ethylene glycol) and terpyridine metal complexes. Well-soluble high molecular weight polymers were prepared by complexing a low-molecular weight  $\alpha,\omega$ -bisterpyridinyl poly(ethylene glycol) with iron(II) and ruthenium(II) ions, respectively. The resulting compounds were characterized by UV-vis and NMR spectroscopy. In addition, the viscosity of the materials was investigated. Moreover, the thermal stability of the polymers was investigated utilizing TGA. Finally, AFM imaging was performed to study the morphology of thin films of the material.

Key words: coordination polymer, metal complex, polyelectrolyte, poly(ethylene glycol), terpyridine

## 1. INTRODUCTION

In the last few years, the study of supramolecular polymers became one of the most important fields in modern polymer chemistry due to the possibility of fine-tuning the material properties or the prospect of reversible polymers. Eventually, "smart materials" for use in coating applications or reversible glues may be feasible. One major type of supramolecular polymers are linear coordination polymers that are assembled from oligomeric precursors bearing supramolecular binding moieties at the chain end. Such kind of polymers have already been reported for self-complementary quadruple hydrogen bonding<sup>[1]</sup> and metal coordination systems.<sup>[2]</sup> A well-suited moiety for metal complexation is the chelating ligand 2,2':6',2''-terpyridine,<sup>[3]</sup> which forms stable coordinative bonds with a variety of transition metal ions (e.g. Fe(II), Zn(II), Ru(II)). Linear terpyridine coordination polymers have so far been reported with Ru(II), Fe(II), Zn(II) or Co(II) ions<sup>[4-6]</sup>. Rigid<sup>[7-9]</sup> as well as flexible<sup>[5]</sup> precursors have been employed. Well-soluble metalopolymers based on poly(ethylene glycol) have been reported for iron and ruthenium.

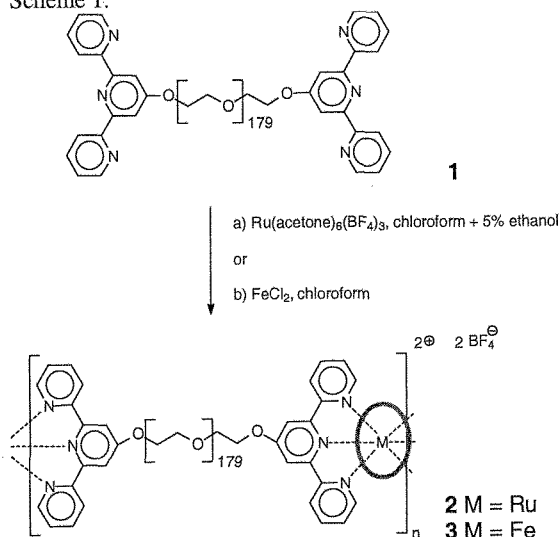
The most interesting feature of metal coordination polymers is the reversibility of the complexation under certain conditions.<sup>[4,5,10,11]</sup> An example is the thermal switching of an iron(II) terpyridine complex in a poly(ester) material.<sup>[12]</sup>

Ruthenium is one of the most favorable ions in the engineering of coordination polymers, since it allows both the directed synthesis of asymmetric complexes as well as symmetric systems. In addition, ruthenium complexes possess interesting optical and photophysical properties.

## 2. SYNTHESIS AND CHARACTERIZATION

The synthesis and characterization can be found in the corresponding literature for the ruthenium<sup>[13]</sup> and iron polymers.<sup>[14]</sup> TGA measurements have been performed

on a Perkin Elmer Pyris 6 with a heating rate of 5 °C/min. The general reaction scheme is shown in Scheme 1.



Scheme 1. Synthesis of the coordination polymers.

## 3. RESULTS AND DISCUSSION

### 3.1 Synthesis

A telechelic poly(ethylene glycol)<sub>180</sub><sup>[6]</sup> **1** ( $M_n = 8000$ ), which has been functionalized with terpyridine units at both chain ends, was complexed with various metal ions to result in the coordination polymers. The ruthenium metalopolymer **2** has been prepared by reacting **1** with hexaacetone ruthenium(III) tetrafluoroborate ( $\text{RuCl}_3$  has been treated with  $\text{AgBF}_4$  in refluxing acetone) and a reduction of ruthenium(III) to ruthenium(II). The corresponding iron polymer **3** was obtained by adding equimolar amounts of  $\text{FeCl}_2$  to a solution of the precursor. In order to obtain high-molecular weight polymers and to reduce the

possibility of ring formation, high concentrations of the reactants were applied in both cases.

Film-like materials were obtained after filtration and evaporation of the reaction solutions. The appearance of the precursor and the resulting ruthenium polymer is shown in Figure 1.

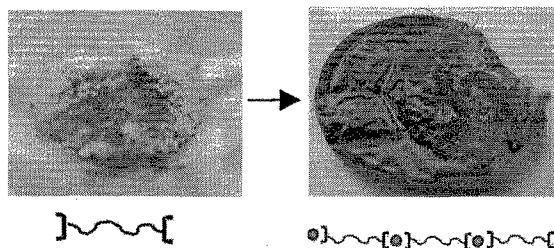


Fig. 1. Film formation of coordination polymer 2.

### 3.2 NMR

<sup>1</sup>H-NMR spectroscopy demonstrated the successful complexation of the telechelics (Figure 2).

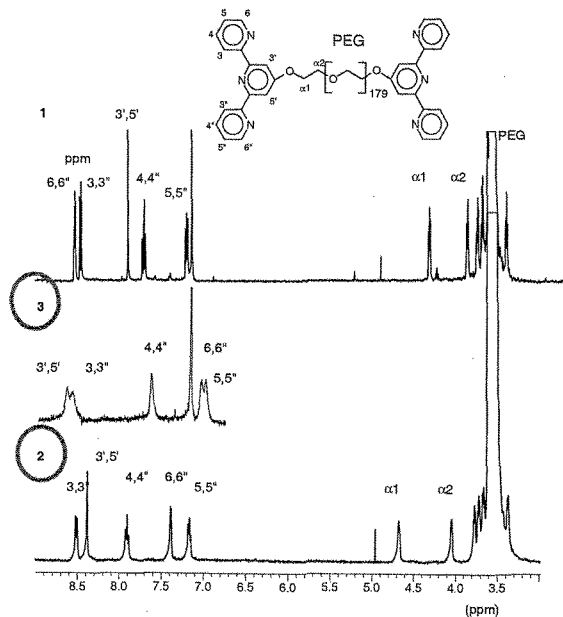


Fig. 2. <sup>1</sup>H-NMR spectra of 1, 3 (CHCl<sub>3</sub>) and 2 (CH<sub>3</sub>CN).

The signals in the aromatic region could be assigned to the complexed terpyridine protons and the chemical shifts were in accordance with the model complexes: In particular the upfield shift of the 6,6''-signal is characteristic for bisterpyridine complexes, due to the different chemical environment of the 6,6''-protons compared to the free ligand. No signals of uncomplexed terpyridines were found within the detectability of the NMR. The signals between 4 and 5 ppm could be attributed to the proton signals of the methylene groups next to the terpyridines ( $\alpha$ -methylenes) and the large signal around 3.5 to the other methylene protons of the poly(ethylene glycol) chain. The signals from the 3',5'-protons in the iron polymer are shifted more downfield compared to the ruthenium case.

### 3.3 UV-vis

UV-vis spectroscopy for the complexed species revealed the characteristic red-shift for the

$\pi$ - $\pi^*$ -absorption bands of the ligands to 267 and 303 nm. Furthermore, the appearance of the metal-to-ligand charge transfer (MLCT) band for the ruthenium complex at 486 nm and 568 for the iron polymer was detected (Figure 3).

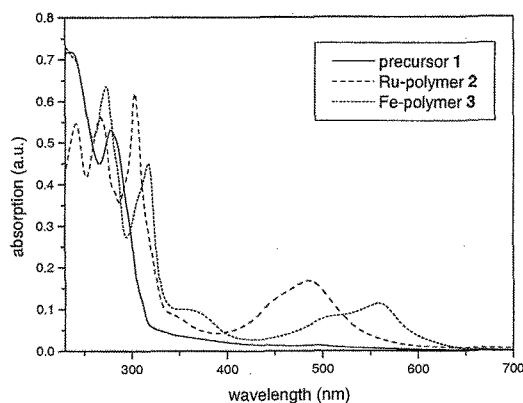


Fig. 3. UV-vis spectra of 1-3 (CH<sub>3</sub>CN).

### 3.4 TGA

The decomposition in inert atmosphere (nitrogen) as well as under oxidative conditions (air) was investigated using TGA (Figure 4 and Table 1).

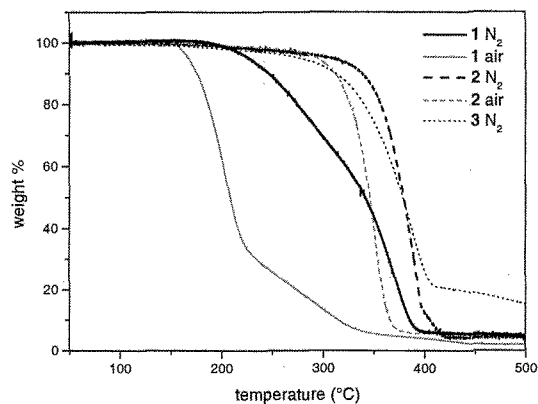


Fig. 4. TGA traces of polymers 1 and 2 in nitrogen and air atmospheres.

Table 1. 5%-onsets (°C) by TGA for compounds 1 and 2 in nitrogen and air atmospheres

	nitrogen	air
1	227	168
2	307	295
3	278	

In nitrogen atmosphere, precursor 1 revealed the fastest decomposition with a 5% weight loss at 227 °C (Table 1), while the corresponding coordination polymers 2 and 3 showed increased stabilities (5% onsets at 307 °C for 2 and 278 °C for 3). Repetition of the TGA measurements in air (for 1 and 2) showed that compound 1 is oxidized more easily with a 5%-onset of 168 °C (59 K less than the nitrogen-measurement) than ruthenium coordination polymer 2 (295 °C, 12 K less than in N<sub>2</sub>). The metallopolymers possess an increased stability towards thermal and oxidative decomposition, suggesting a stabilization of the polymers by the terpyridine ruthenium(II) complex units.

### 3.5 Viscosity

A suitable method to obtain an indication about the molecular weight of the polymers is solution viscosimetry, which has been performed in Ubbelohde viscosimeters. Compared to the precursor, the ruthenium as well as the iron coordination polymer revealed relatively high relative viscosities and the values are similar for both polymers (Figure 5).

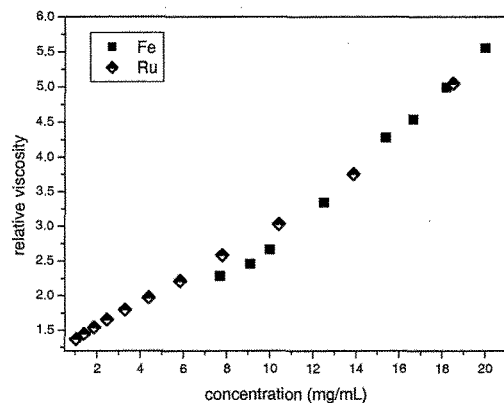


Fig. 5. Viscosity of polymers 2-3 (methanol).

Comparing the reduced viscosities, a polyelectrolyte behavior (increase of the reduced viscosities at low concentrations) was found for **2** (which could be suppressed by the addition of salt), but not for **3**. An explanation could be the different counterions used.

The capability of a formation of extended coordination polymers at room temperature has been studied for a variety of different transition metal ions in viscosity titration experiments. Starting from a methanolic solution (20 mg/mL) of the telechelic **1**, solutions of metal salts (Cd(II)-, Co(II)-, Ni(II)-acetate, Fe(II) sulfate and Fe(III) chloride) in methanol were added stepwise to the solution and the viscosities were measured after each step (Figure 6).

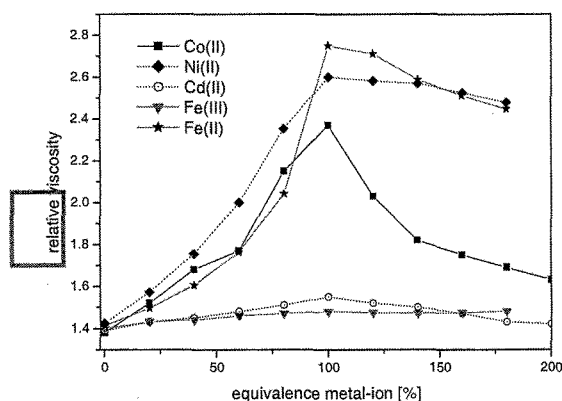


Fig. 6. Viscosity titration of telechelic **1** with metal salts (methanol).

An increase of the viscosity was observed for all metal(II) salts with a maximum value being reached at a metal ion/**1** ratio of 1:1, indicating a quantitative complexation. Only in the case of Fe(III) chloride, no viscosity increase was observed. Also a reference experiment was performed to exclude unspecific coordination of the metal ions to the polymeric backbone: The addition of iron(II) sulfate to unfunctionalized poly(ethylene glycol)<sub>180</sub> did not result

in a change of viscosity. Therefore, the change of the solution viscosity can be exclusively attributed to the formation of coordination polymers. As can be seen from Figure 6 and Table 2, the absolute values for the maximum viscosities vary for the different metal ions.

Table 2. Maximum values for the viscosity titrations

metal	Cd(OAc) <sub>2</sub>	Co(OAc) <sub>2</sub>	Ni(OAc) <sub>2</sub>	FeSO <sub>4</sub>
$\eta_{rel}$	1.55	2.37	2.60	2.75

The relative viscosity is directly related to the molecular weight of the linear coordination polymers and therefore to the degree of polymerization, which depends on the stability of the *bis*complexes compared to the *mono*complexes. For all metal(II) complexes discussed here, the stability constants of the *bis*complexes are comparably higher than the ones of the corresponding *mono*complexes.<sup>[15]</sup> Therefore, the obtained viscosity values can be qualitatively correlated to the thermodynamic stability of the *bis*complexes. The maximum values of the viscosities for the different complexing metal ions in the coordination polymers (Fe(II) > Ni(II) > Co(II) > Cd(II)) are in agreement with available literature data for the stability constants of the formed *bis*complexes. On the other hand, Fe(III) forms mainly *mono*complexes, thus no increase of viscosity was observed.

A different behavior was found for the different metal ions after overtitration. Whereas a plateau was observed for nickel(II) and only a slight decrease for iron(II), a strong decrease was found in the case of cobalt and cadmium. These observations could also be explained by the thermodynamic stability of the *bis*complexes. In the case of the less-stable *bis*complexes, the formation of *mono*complexes is more likely by adding an excess of metal ions. This, as consequence, will result in a cleavage of the chains.

### 3.6 AFM

The morphology of the telechelic **1** and the coordination polymers **2** and **3** were investigated by atomic force microscopy (Figure 7). Samples were prepared by drop-casting methanolic solutions on silicon wafers. While height images showed uniform flat surfaces, the phase images of **1** and of the metallopolymers **2-3** revealed a lamellar structure due to poly(ethylene glycol) chain folding, revealing sizes of the lamellae of about 14 - 18 nm for **1**, 13 - 18 nm for **2** and around 16 nm for **3**. Subsequently, samples of **1** and **3** were annealed (70 °C for 30 min), leading to a double lamella structure for the metallopolymer **3**. For the annealed compound **1**, no double lamella structure was found. In literature, double lamella structures were reported for unfunctionalized, low molecular weight poly(ethylene glycol)s<sup>[16]</sup> and explained by an uneven number of chain foldings. The folding is believed to result from hydrogen bonding of the free hydroxy end groups of the polymer. In consequence, the absence of hydrogen bonding units due to end-of-chain functionalization hinders chain folding and a multiple lamella structure. This has, e.g., been already reported for  $\alpha,\omega$ -bismethoxy functionalized poly(ethylene glycol)s.<sup>[17]</sup> In contrary, the metal-induced polymerization of the telechelic provides these secondary interactions in form of the iron(II)-

*bis*(2,2':6',2''-terpyrid-4'-yl) complexes and lead to the built-up of double lamella structures (see Figure 7).

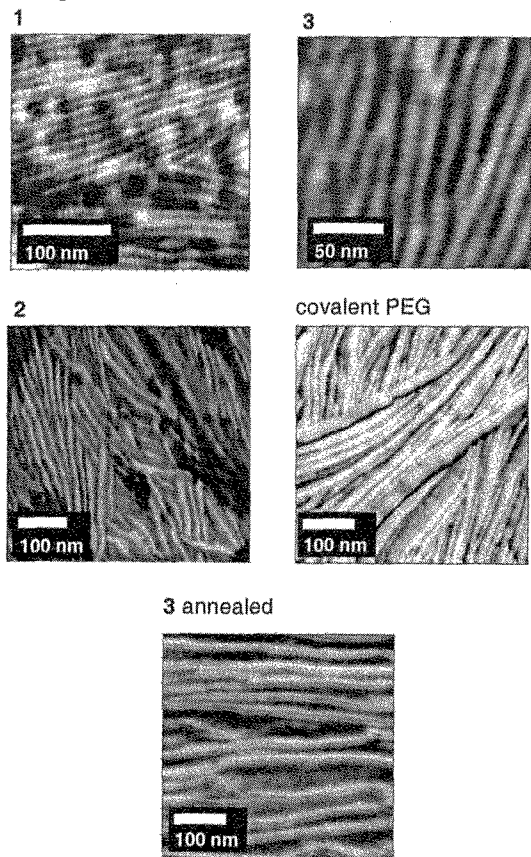


Fig. 7. AFM images of 1-3 and covalent PEG.

Furthermore, the model of a once-folded chain for poly [*bis*-(2,2':6',2''-terpyrid-4'-yl)-poly(ethylene glycol)<sub>180</sub>] iron(II) chloride is in agreement with the experimental finding, that the size of the lamellae does not differ between 1 and the coordination polymer. The extended chain crystals and the double folded structure have comparable sizes. A comparison of the lamella domain size with literature data is critical due to the strong dependence on the crystallization conditions (e.g. temperature). Nevertheless, the lamellae dimensions of the telechelic *bis*-(2,2':6',2''-terpyrid-4'-yl)-poly(ethylene glycol)<sub>180</sub> 1 seem to be considerably small (compared to covalent PEG), indicating that the bulky terpyridine unit could act as a defect that inhibits larger crystalline domains.

#### 4. CONCLUSIONS

Functional polymeric telechelics with terpyridine moieties could be successfully subjected to metal complexation, resulting in coordination polymers. Solution viscosimetry indicated the formation of high molecular weight polymers for strongly coordinating metals. An increased thermal stability was found by TGA, and AFM revealed a lamellar morphology.

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