Macromol. Symp. **2003**, *199*, 483-497

Engineering with Metallo-Supramolecular Polymers: Linear Coordination Polymers and Networks

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Summary: Here we demonstrate the synthesis of telechelics with different spacer units and different numbers of metal-complexing units, like α-methoxy-ω-(2,2':6',2''-terpyrid-4'-yl)-poly(ethylenoxide)$_{78}$ (**1**), *bis*(2,2':6',2''-terpyrid-4'-yl) di(ethylene glycol) (**2**), *bis*(2,2′:6′,2′′-terpyrid-4'-yl)-poly(ethylene oxide)$_{180}$ (**3**) and *tris*[(2,2′:6′,2′′-terpyrid-4'-yl)-oligo (ethylenoxy-)$_{3.33}$]glycerin (**4**) utilizing 4-chloro-2,2':6',2''-terpyridine. The complexation behaviour of a variety of metal-salts towards the telechelics was studied and different supramolecular architectures were investigated, such as symmetric polymeric complexes and linear coordination polymers. Furthermore, attempts have been undertaken to prepare metallo-supramolecular cross-linked systems.

Keywords: supramolecular structures, telechelics

Introduction

The built-up of supramolecular architectures based on metal-ligand interactions is a very challenging and rapidly growing field of research.[1] Besides the straight forward methodology to create extended macromolecular architectures on the basis of metal complexing telechelics, the metal complex adds a structural as well as a functional benefit to the material. Depending on the utilized metal-salts different association constants and therefore different degrees of polymerization and reversibility are accessible. As a result materials can be synthesized with a tailor made response towards temperature,[2] chelating agents,[3] pH and redox agents.[4] Extended metallo-supramolecular coordination polymers[3, 5-9] can be prepared as well as defined block copolymers.[10] In particular, the utilization of functionalized polymers as supramolecular building blocks is an interesting approach towards high molecular weight polymers.[11-14] The application of *oligo*- or *poly*(ethylene oxides) results in water-soluble coordination polymers. Those systems might serve for applications such as water purification and wastewater treatment,[15] food processing and mining.[16] Water-soluble tailored polymers are also used in the manufacture of cosmetics, the stabilization of colloids and biomedicine.[17] On the basis of amphiphilic block copolymers

DOI: 10.1002/masy.200350940

metallo-supramolecular micelles[18] and reversible hydrogels can be synthesized. Intelligent microgels from cross-linked, hydrophilic polymers can undergo sudden sol-gel transitions under external influences such as temperature and pH changes.[19] In this way, such systems can release active substances under defined conditions or transmit chemo-mechanical signals.[20] A metallo-supromolecular approach towards cross-linked architectures might lead to enhanced materials for such kind of applications.

Experimental Part

Materials and Instruments

Basic chemicals were obtained from Sigma-Aldrich. Size exclusion chromatography was carried out on BioBeads SX1 columns (CH_2Cl_2). NMR spectra were measured on a Varian Mercury 400 NMR spectrometer. The chemical shifts were calibrated to the residual solvent peaks or TMS. UV/Vis spectra were recorded on a Perkin Elmer Lamda-45 (1 cm cuvettes). The applied solvents are indicated in the experimental section. The used 4'-chloro-2,2':6',2''-terpyridine was donated by the BASF-AG.

Preparation of α-methoxy-ω-(2,2'-6',2''terpyrid-4'-yl)-poly(ethylenoxide)$_{78}$ (1)

534 mg (0.178 mmol) of *α*-methoxy-*ω*-hydroxy-poly(ethylene oxide)$_{78}$ and 49 mg (0.87 mmol) KOH are dissolved in 40 mL of dry DMSO and stirred for 1 h at 60°C. After the addition of 50 mg (0.186 mmol) 4'-chloro-2,2':6',2''-terpyridine the reaction mixture is stirred for additional 24 h at 60°C. The solvent is removed *in vacuo*, 10 mL of water are added and the mixture is extracted four times with 100 mL of chloroform. The combined organic layers were dried over Na_2SO_4. After filtration and evaporation of the solvent, the residue is dissolved in THF and precipitated with diethyl ether. *α*-methoxy-*ω*-(2,2:-6',2''-terpyrid-4'-yl)-poly(ethylene oxide)$_{78}$ is yielded as a colorless solid. Yield: 423 mg, 0.131 mmol, (74%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H = 2.60 (t, 3H, J = 6.1 Hz, *H*-PEO), 3.40 (t, 4H, *H*-PEO), 3.64 (m, 410H, *H*-PEO), 4.42 (m, 3H, H-PEO), 7.35 (m, 2H, *H5,5''*), 7.83 (m, 2H, *H4,4''*), 8.07 (m, 2H, *H3',5'*), 8.66 (m, 2H, *H3,3''*), 8.69 (m, 2H, *H6,'6'*).

UV/Vis (CH_3OH): λ_{max}/nm (ε/10^4Lmol^{-1}cm^{-1}) = 239 (2.61), 276 (2.39).

MS (MALDI-TOF, dithranol): $\overline{M}_n$ = 3635, $\overline{M}_w$ = 3659, DPI = 1.01.

$C_{23}H_{27}N_3O$ (361.49): calcd. C 76.45, H 7.48, N 11.63; found C 76.20, H 7.40, N 11.60.

Preparation of bis(2,2':6',2''-terpyrid-4'-yl)-di(ethylene glycol) (2)

500 mg (4.7 mmol) di(ethylene glycol) and 2.60 g (47.11 mmol) KOH are heated in 10 ml dry DMSO 1h at 60°C under argon. 3.03 g (11.31 mmol) 4'-chloro-(2,2':6':2''-terpyridine) are added and heating is continued 50 h at 60°C. After cooling to room temperature the crude product is precipitated by addition of an excess of water. Washing with water and diethyl ether yields 2.60 g (4.57 mmol, 97%) of the product as a colourless powder. m.p. 185°C.
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.66 (d, 4H, *J* = 6.00, Hz, *H-6,6''*), 8.56 (d, 4 H, *J* = 8.0 Hz, *H-3,3''*), 8.05 (s, 4H, *H-3',5'*), 7.82 (m, 4H, *H-4,4''*) 7.30 (m, 4H, *H-5,5''*), 4.44 (m, 4H, -C*H₂*-O-C*H₂*), 4.04 (m, 4H, C_{ter}-O-C*H₂*).
UV/Vis (CH_3OH): λ_{max} (ε [10^4 l mol^{-1} cm^{-1})] = 244 nm (4.95), 279 nm (4.71).

Preparation of bis(2,2′:6′,2′′-terpyrid-4'-yl)-poly(ethylene oxide)$_{180}$ (3)

20 g (2.177 mmol) poly(ethylene oxide)$_{180}$ and 1.22 g (21.77 mmol) KOH are dissolved in 200 ml dry DMSO and stirred for 1 h at 60°C. After addition of 1.40 mg (5.225 mmol) 4'-chloro-2,2':6',2''-terpyridin the reaction mixture is stirred additional 72 h at 60°C. The solvent is removed *in vacuo*, 75 mL of water are added and the mixture is extracted four times with 250 mL of chloroform. The combined organic layers are dried over Na_2SO_4. After filtration and evaporation of the solvent, the residue is dissolved in THF and precipitated with diethyl ether. *Bis*(2,2':6',2''-terpyrid-4'-yl)-poly(ethylene oxide)$_{180}$ is yielded as a colorless powder. Yield: 15.92 g, 1.716 mmol, (79%).
^{1}H-NMR (400 MHz, $CDCl_3$): δ_H = 3.48 (m, 4H, *H*-PEO), 3.64 (m, 965H, *H*-PEO), 3.75 (m, 4H, *H*-PEO), 3.82 (m, 4H, *H*-PEO), 3.94 (m, 4H, *H*-PEO), 4.40 (m, 4H, *H*-PEO), 7.33 (m, 4H, *H-5,5′′*), 7.85 (ddd, 4H, *J* = 8.2 Hz, 8.2 Hz, 2.0 Hz, *H-4,4′′*), 8.04 (m, 4H, *H-3′,5′*), 8.62 (m, 4H, *H-3,3′′*), 8.63 (m, 4H, H-6,6′′).
UV/Vis (CH_3CN): λ_{max}/nm (ε/10^4 L mol^{-1} cm^{-1}) = 238 (4.58), 274 (4.22).
MS (MALDI-TOF, dithranol): $\overline{M}_n$ = 9280 g/mol, $\overline{M}_w$: = 9380 g/mol, PDI = 1.01.

Preparation of tris[(2,2′:6′,2′′-terpyrid-4'-yl)-oligo(ethylenoxy-)$_{3.33}$]glycerin (4)

1.00 g (1.53 mmol) *tris*[oligo-(ethylenoxy)$_{3.33}$]glycerin and 1.00 g of KOH are dissolved in dry DMSO and stirred for 1 h at 60°C. After the addition of 1.47 g (5.51 mmol) of 4'-chloro-2,2':6',2''-terpyridine the reaction mixture is stirred for further 72 h at 60°C. The solvent is removed *in vacuo* and 10 mL of water are added and the mixture is extracted four times with 50 mL of chloroform. The combined organic layers are dried over Na_2SO_4. After filtration and evaporation of the solvent, the residue is dissolved in THF and precipitated with diethyl ether. *Tris*[*(*2,2′:6′,2′′-terpyrid-4’-yl)-*oligo*(ethylenoxy)$_{3.33}$]glycerin is yielded as a colorless oil. Yield: 1.94 g, 1.582 mmol, (84%).

^{1}H-NMR (400 MHz, CDCl$_3$): δ_H = 3.61 (m, 28H, *H*-PEO), 3.73 (m, 6H, *H*-PEO), 3.90 (m, 4H, *H*-PEO), 4.37 (m, 6H, *H*-PEO), (m, 6H, *H*-PEO), 7.32 (m, 6H, *H-5,5′′*), 7.84 (m, 6H, *H-4,4′′*), 8.04 (m, 6H, *H-3′,5′*), 8.60 (m, 6H, *H-3,3′′*), 8.67 (m, 6H, H-6,6′′).

Preparation of α-methoxy-ω-(2,2’:6’,2’’-terpyrid-4’-yl)-Fe(PF$_6$)$_2$-poly(ethylene oxide)$_{78}$ (5)

400 mg (116 µmol) of *α*-methoxy-*ω*-(2,2’:6’,2’’-terpyrid-4’-yl)-poly(ethylene oxid)$_{78}$ (**1**) and 10.1 mg (58.2 µmol) Fe(acetat)$_2$ are dissolved in 5 ml MeOH at 60°C under argon and stirred for 48 h. After cooling to room temperature, 37.9 mg (233 µmol) NH$_4$PF$_6$ are added. The formed purple precipitate is filtered off and washed consecutively with MeOH. The pure product is obtained after size exclusion chromatography. Yield: 320 mg, 44.3 mmol (on the basis of $\overline{M}_n$ = 7217 g/mol, 76%).

^{1}H-NMR (400 MHz, CD$_3$CN): δ_H = 3.35 (s, 6H, OC*H$_3$*), 3.63 (m, 546H, *H*-PEO), 4.12 (m, 4H, *H*-PEO), 4.76 (m, 4H, *H*-PEO), 7.09 (dd, 4H, *J* = 6.3 Hz, *H-5,5′′*), 7.18 (d, 4H, *J* = 5.06 Hz, *H-6,6′′*), 7.89 (psd. t, 4H, *J* = 7.6, *H-4,4′′*), 8.46 (d 4H, *J* = 8.2 Hz, *H-3,3′′*), 8.50 (m, 4H, *H-3′,5′*).

UV/Vis (CH$_3$CN): λ_{max}/nm (ε/10^4 L mol^{-1} cm^{-1}) = 244 (3.03), 273 (3.21), 315 (1.92), 360 (0.31), 556 (0.59).

Preparation of bis(2,2’:6’,2’’-terpyrid-4’-yl)-FeCl$_2$-di(ethylene glycol) (6)

250 mg (0.44 mmol) of *bis*(2,2’:6’,2’’-terpyrid-4’-yl)-di(ethylene glycol) are dissolved in 20 mL MeOH under argon and 55.7 mg (0.44 mmol) of FeCl$_2$ are added slowly at room temperature. The reaction mixture is heated 48 h at 60°C, the solvent is removed *in vacuo* and the product is isolated in quantitative yield.

^{1}H-NMR (400 MHz, methanol-d6): δ = 8.88 (s, 4H, *H-3′,5′*), 8.75 (d, 4H, J = 8.0 Hz, *H-3,3′′*), 7.96 (m, 4H, *H-4,4′′*), 7.32 (d, 4H, J = 8.0 Hz, *H-6,6′′*) 7.21 (m, 4H, *H-5,5′′*), 4.99 (m, 4H, -C*H$_2$*-O-C*H$_2$*), 4.42 (m, 4H, C$_{ter}$-O-C*H$_2$*).

UV/Vis (CH$_3$OH): λ_{max} (ε [10^4 l mol^{-1} cm^{-1})] = 244 nm (4.39), 275 nm (5.25), 319 nm (3.66), 559 (1.10).

η_{rel} = 1.82 (methanol, c = 20 mg/ml, approx. 2 weight-%).

Preparation of bis(2,2':6',2''-terpyrid-4'-yl)-$FeCl_2$-poly(ethylene oxid)$_{180}$ (7)

300 mg (32.97 μmol) *Bis*(2,2':6',2''-terpyrid-4'-yl) poly(ethylenoxid)$_{180}$ and 4.17 mg (32.97 μmol) $FeCl_2$ were dissolved in 10 mL chloroform and stirred for 14 h at ambient temperature. After the addition of a view drops of methanol the reaction mixture is refluxed for additional 28 h. The solvent is removed *in vacuo* and the product is yielded as a purple solid. Yield: 280 mg, (92%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.63 (m, 1150H, *H*-PEO), 4.18 (m, 4H, *H*-PEO), 5.82 (m, 4H, *H*-PEO), 7.02-7.90 (m, 8H, *H-5,5'', H-6,6''*), 9.12-9.23 (m, 8H, *H-3,3'', H-3',5'*).

UV/Vis (CH_3OH): λ_{max}/nm (ε [10^4 $Lmol^{-1}cm^{-1}$)] = 244 (4.39), 275 (5.25), 319 (3.66), 559 (1.10).

UV/Vis (CH_3OH): λ_{max}/nm (ε [10^4 $Lmol^{-1}cm^{-1}$)] = 245 (4.41), 274 (5.07), 559 (0.97).

MS (MALDI-TOF, dithranol): [*bis*(2,2':6',2''-terpyrid-4'-yl) FeCl poly(ethylene oxide)$_{180}$]$^+$, 2x[*bis*(2,2':6',2''-terpyrid-4'-yl) FeCl poly(ethylene oxide)$_{180}$]$^+$, 3x[*bis*(2,2':6',2''-terpyrid-4'-yl) FeCl poly(ethylene oxide)$_{180}$]$^+$, 4x[*bis*(2,2':6',2''-terpyrid-4'-yl) FeCl poly(ethylene oxide)$_{180}$]$^+$, 5x[*bis*(2,2':6',2''-terpyrid-4'-yl) FeCl poly(ethylene oxide)$_{180}$]$^+$, 6x[*bis*(2,2':6',2''-terpyrid-4'-yl) FeCl poly(ethylene oxide)$_{180}$]$^+$.

η_{rel} = 2.41 (methanol, c = 20 mg/ml, approx. 2 weight-%).

Results and Discussion

Synthesis of Telechelics

Herein we demonstrate the preparation of the 2,2':6',2''-terpyridine functionalized telechelics α-methoxy-ω-(2,2'-6',2''terpyrid-4'-yl)-poly(ethylenoxide)$_{78}$ (**1**), *bis*(2,2':6',2''-terpyrid-4'-yl) di(ethylene glycol) (**2**), *bis*(2,2′:6′,2′′-terpyrid-4'-yl)-poly(ethylene oxide)$_{180}$ (**3**) and *tris*[(2,2′:6′,2′′-terpyrid-4'-yl)-oligo(ethylenoxy-)$_{3.33}$]glycerin (**4**). The substitution of several hydroxy-functionalized telechelics with terpyridine moieties was performed applying a literature procedure based on a Williamson type reaction (see Figure 1).[20-24]

The hydroxy-functionalized telechelics were deprotonated applying potassiumhydroxyd in dimethyl sulfoxide. The addition of 4-chloro-2,2':6',2''-terpyridine resulted in a quantitative functionalization. The desired products were characterized via ^{1}H-NMR spectroscopy, UV/Vis and GPC. Complete functionalization could especially be proven by MALDI-TOF-MS.

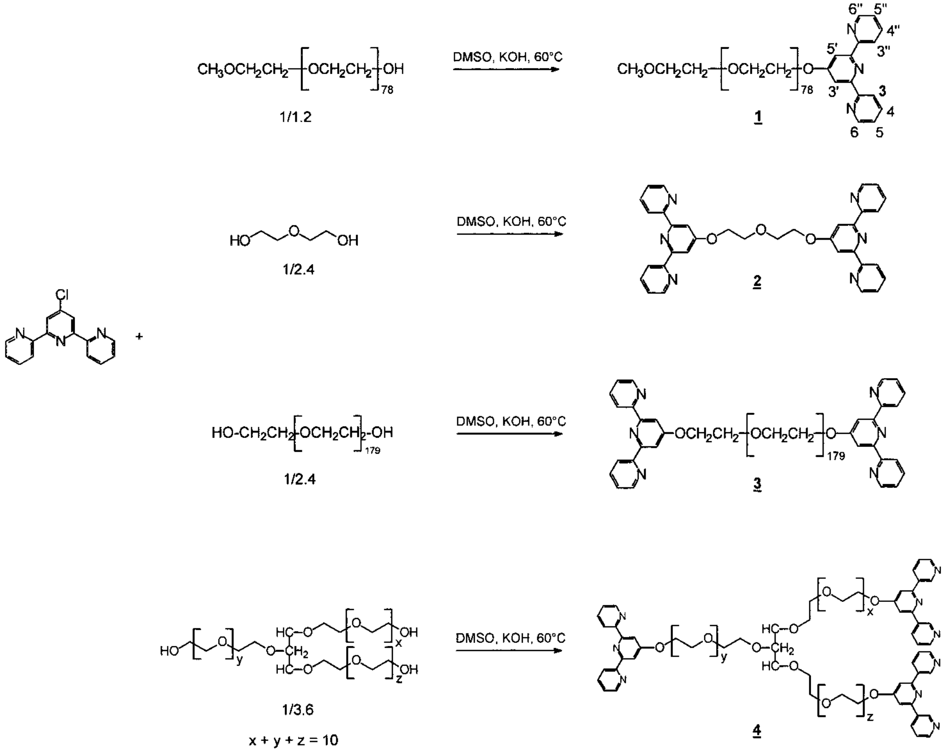
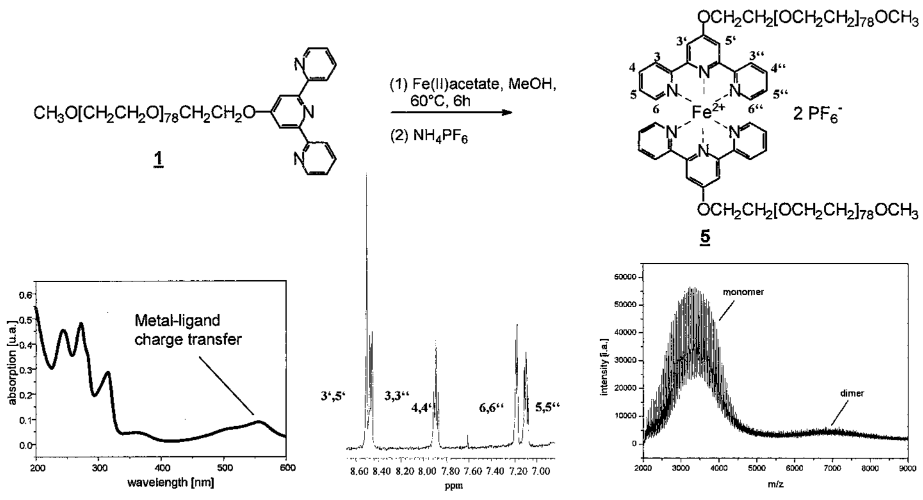


Fig. 1. Synthesis of different 2,2':6',2''-terpyridine-functionalized telechelics: *α-methoxy-ω-(2,2'-6',2''terpyrid-4'-yl)-poly(ethylenoxide)*$_{78}$ (**1**); *bis*(2,2':6',2''-terpyrid-4'-yl)-di (ethylene glycol) (**2**); *bis*(2,2′:6′,2″-terpyrid-4'-yl) poly (ethylene oxide)$_{180}$ (**3**); *tris*[(2,2′:6′,2″-terpyrid-4'-yl)-oligo(ethylenoxy-)$_{3.33}$]glycerin (**4**); and *bis*(2,2':6',2''-terpyrid-4'-yl)-poly(propylene oxide)$_{80}$ (**5**).

Synthesis of Model-Complexes

To elaborate suited reaction condition for the formation of metallo-supramolecular coordination polymers on the basis of *bis*(2,2':6',2''-terpyrid-4'-yl)-di(ethylene glycol) and *bis*(2,2′:6′,2″-terpyrid-4'-yl)-poly(ethylene oxide)$_{180}$ and model complexes were synthesized. In particular iron(II) complexes of the polymeric ligand α-methoxy-ω-(2,2'-6',2''-terpyrid-4'-yl) poly(ethylene oxid)$_{78}$ (**1**) have been under investigation. Iron(II) was chosen due to the non-toxicity, the low cost, the considerably high binding constants towards 2,2':6',2''-terpyridine and the redox properties of iron(II) that facilitates the "switchability" of the systems.



a) b) c)

Fig. 2. top: Schematic representation of the formation of the model-complex α-methoxy-ω-(2,2':6',2''-terpyrid-4'-yl)-Fe$(PF_6)_2$-poly(ethylene oxide)78 (5); bottom: Characterization of 5: a) the aromatic region of the ^{1}H-NMR spectrum ($CDCl_3$) shows the typical signals of the complexed terpyridine-unit; b) the UV/Vis spectra shows the typical metal-ligand charge transfer band; c) besides the mass of the monomer, the MALDI-TOF-MS shows the peak with a mass corresponding to the complex.

Addition of $FeCl_2$ under inert conditions to a solution of 1 in methanol resulted in an immediate complex formation, indicated by a colour change. An inert atmosphere was applied in order to avoid an oxidation to Fe^{3+}. After completion of the reaction the chloride counter-ions were exchanged by hexafluorophosphate. The crude product could be successfully purified utilizing size exclusion chromatography (Figure 2).

The formation of the complex could be demonstrated via UV/Vis- and ^{1}H-NMR-spectroscopy and MALDI-TOF-MS. The UV/Vis spectrum of 5 shows a typical metal-ligand-charge transfer band at 556 nm. The bathochromic shift of the π-π^* band also indicates the complex formation (Figure 2a). The shift of the terpyridine signals in the aromatic region in the ^{1}H-NMR-spectrum gives further evidence for the formation of the complex. Due to the formation of an octahedral complex geometry the pyridine rings flip from an antiperiplanar into a synperiplanar conformation. Therefore in particular the protons in 6,6'' position are shifted to higher fields and the protons in 3',5' position are shifted to lower fields (Figure 2b). The MALDI-TOF-MS spectrogram of the product shows to different peaks. One corresponds with the molecular weight of the desired complex, the other one with the mass of the uncomplexed ligand (Figure 2c). The latter one is of higher intensity. In particular ^{1}H-NMR-spectroscopy revealed, that there is no free ligand present in the metal complex. Therefore a rupture of the complex under MALDI-TOF-MS measurement conditions seems to be likely.

Synthesis of Linear Coordination Polymers

Reaction at Room Temperature

The complexation behavior of *bis*(2,2′:6′,2′′-terpyrid-4’-yl)-poly(ethylene oxide)$_{180}$ (**3**) towards a wide range of metal-salts were investigated at ambient temperature. Viscosity measurements revealed for all utilized metal-ions (bivalent) a maximum value after the addition of an equivalence of metal-ions. (Figure 3). However, the absolute values for the maximum vary for different ions. The relative viscosity reaches values of η_{rel} = 1.55 with cadmium(II)actetate, η_{rel} = 2.22 with copper(II)actetate, η_{rel} = 2.37 with cobalt(II)acetate, η_{rel} = 2.60 with nickel(II)acetate and η_{rel} = 2.75 with iron(II)acetate. The different maximum values of the viscosities are in agreement with available data for the thermodynamic stability of the formed *bis*complexes. The LogK values for the complex formation of the iron(II)*bis*complex is 13.8, for the nickel(II)*bis*complex is 11.1 and for the Co(II)*bis*complex is 9.9.[25] For other metal-ions there are no data available for the *bis*complexes.

The behaviour of the polymer solutions upon addition of an excess of metal ions are significantly different. It results in an immediate decrease of the viscosity in the cases of cadmium(II)acetate, copper(II)acetate and cobalt(II)acetate. For iron(II)acetate the decrease is much less pronounced and for nickel(II) a plateau is reached, that is almost independent from the amount of added metal-salt. In part, the experimental findings correlate with the thermodynamic stability of the *bis*complexes and available kinetic data. Iron(II)*bis*complexes are known to be kinetically more stable towards ligand exchange (k = 60 min^{-1}), than nickel(II) (k = 780 min^{-1}) and cobalt(II) (k = 9800 min^{-1}) complexes.[26] Therefore, especially the viscosity drop upon addition of an excess of metal-ions for the kinetically very labil cobalt(II)terpyridine coordination polymer is in agreement with the data.

Moreover, for cadmium(II)acetate, copper(II)acetate and cobalt(II)acetate the slope seems to be almost linear, whereas for nickel(II)acetate and iron(II)sulfate a exponential increase of the viscosity can be obtained. Even more striking is the difference between iron(II)chloride and iron(II)sulfate (Figure 4). The complexation or polymerization behaviour respectively seems to be strongly influenced by the utilized counter-ion. For chloride as counter-ion a linear increase of the viscosity with rising metal-ion content can be obtained, whereas for sulfate an exponential increase can be obtained. A strong influence of the counter-ions on the rates of formation as well as the stabilities of *mono-* and *bis*complexes can be derived from that observation. However, those phenomena have to be investigated further in detail.

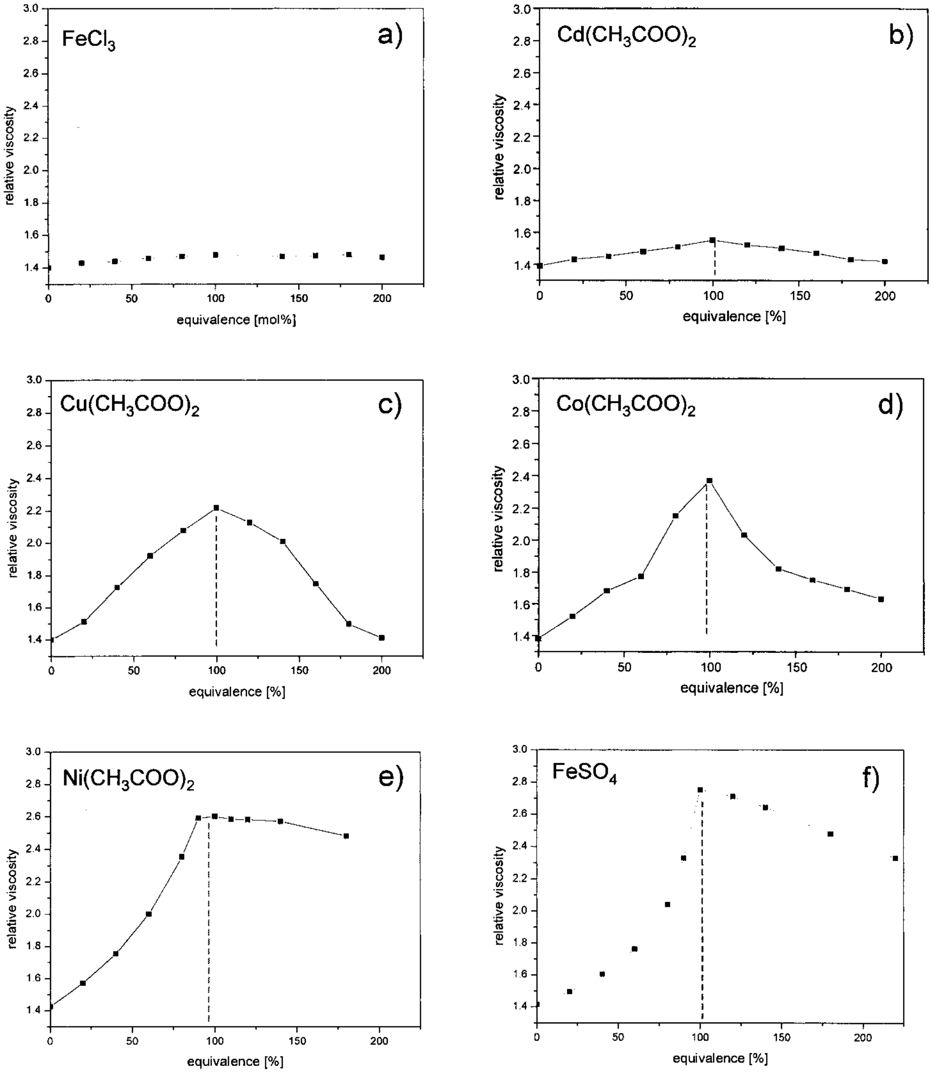


Fig. 3. Viscosimetry experiments: The stepwise addition of a) Cd(II)acetate, b) Cu(II)acetate, c) Co(II)acetate, d) Ni(II)acetate and Fe(II)acetate to a polymer solution (c=100 mg/5 mL methanol) leads to different maximum values of the relative viscosity for an equivalent addition of the metal salt; f) the addition of Fe(III)chloride does not result in a significant increase of the relative viscosity.

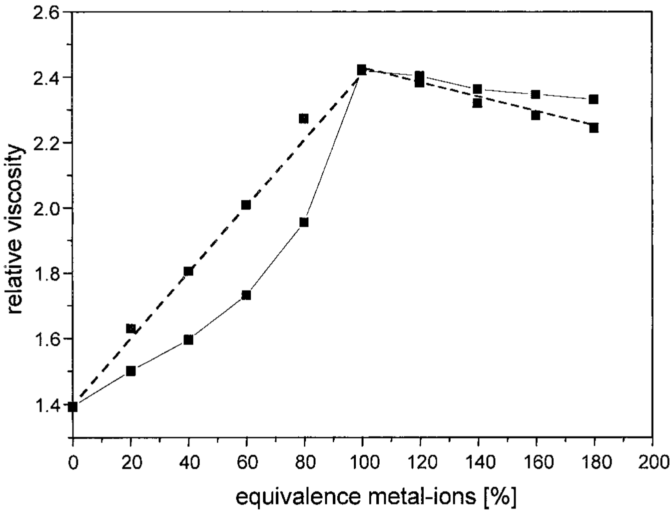
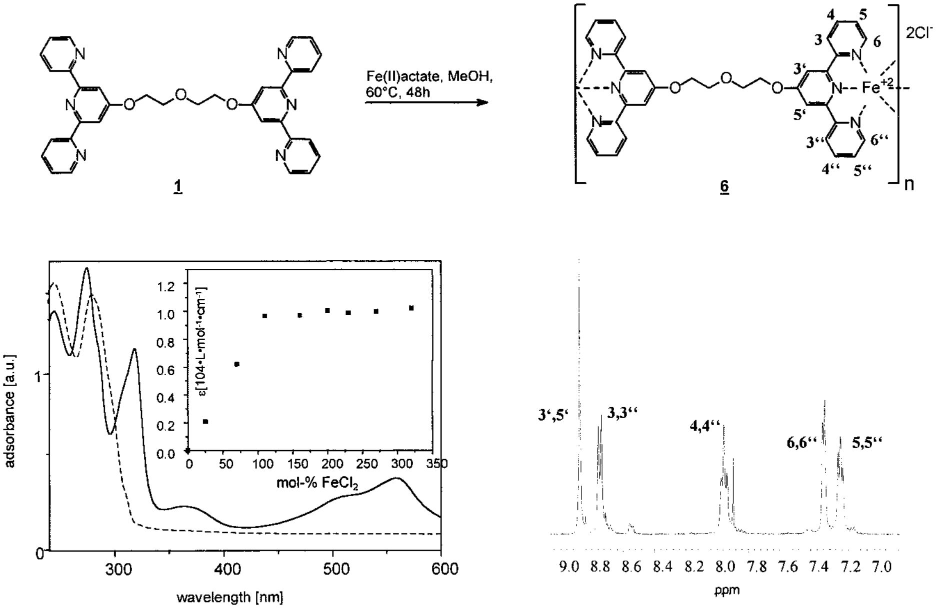


Fig. 4. Influence of the counter-ion onto the complexation/polymerization behaviour of *bis*(2,2′:6′,2′′-terpyrid-4'-yl)-poly(ethylene oxide)$_{180}$: linear increase of the viscosity for chlorine (dotted line) and exponential increase of the viscosity for sulfate (straight line) as counter-ion.

Reaction at Elevated Temperature (Short Spacer and Long Spacer)

The elaborated reaction conditions for the synthesis of the model complex 5 were applied to the synthesis of Fe^{2+} coordination polymers on the basis of the telechelic *bis*(2,2':6',2''-tepyrid-4'-yl) di(ethylene glycol) (2) (see Figure 5). In order to obtain water-soluble coordination polymers an exchange of the chloride counter-ions was not undertaken. The quantitative formation of the complex was proven via UV/Vis-, ^{1}H-NMR-spectroscopy and MALDI-TOF-MS. The UV/Vis spectrum shows a metal-ligand-charge transfer-band as well as a bathochromic shift of the π-π^* band (see Figure 5a). In addition, the complex formation was monitored by UV/Vis-titration experiments. They show a linear growth of the extinction coefficient of the metal ligand charge transfer (t_{2g}-π^*) band at 559 nm with increasing metal-ion content. After addition of 100 mol% Fe^{2+} a maximum for ε is reached, which demonstrates the full conversion. Moreover, that experiment gives evidence of a complete *bis*functionalization of telechelic **1**.

The ^{1}H-NMR-spectrum (Figure 5b) shows the significant shifts of protons 3',5' and 6',6'' after complexation as they are described above. Based on UV/Vis- and ^{1}H-NMR-spectroscopy a quantitative complex formation can be concluded. Attempts were undertaken to determine the molecular weight of the metallo-supramolecular coordination polymer with MALDI-TOF-MS. The main fragments were the free ligand [*bis*(2,2':6',2''-terpyrid-4'-yl) di(ethylene glycole)]$^+$ and a *mono*complex with one counter-ion attached to it [*bis*(2,2':6',2''-terpyrid-4'-yl) FeCl di(ethylene glycole)]$^+$. No higher oligomers could be detected. The observed fragmentation is in agreement with the results of the model-complex α-methoxy-ω-(2,2':6',2''-terpyrid-4'-yl)-Fe$(PF_6)_2$-poly(ethylenoxide)$_{78}$ (5).



a) b)

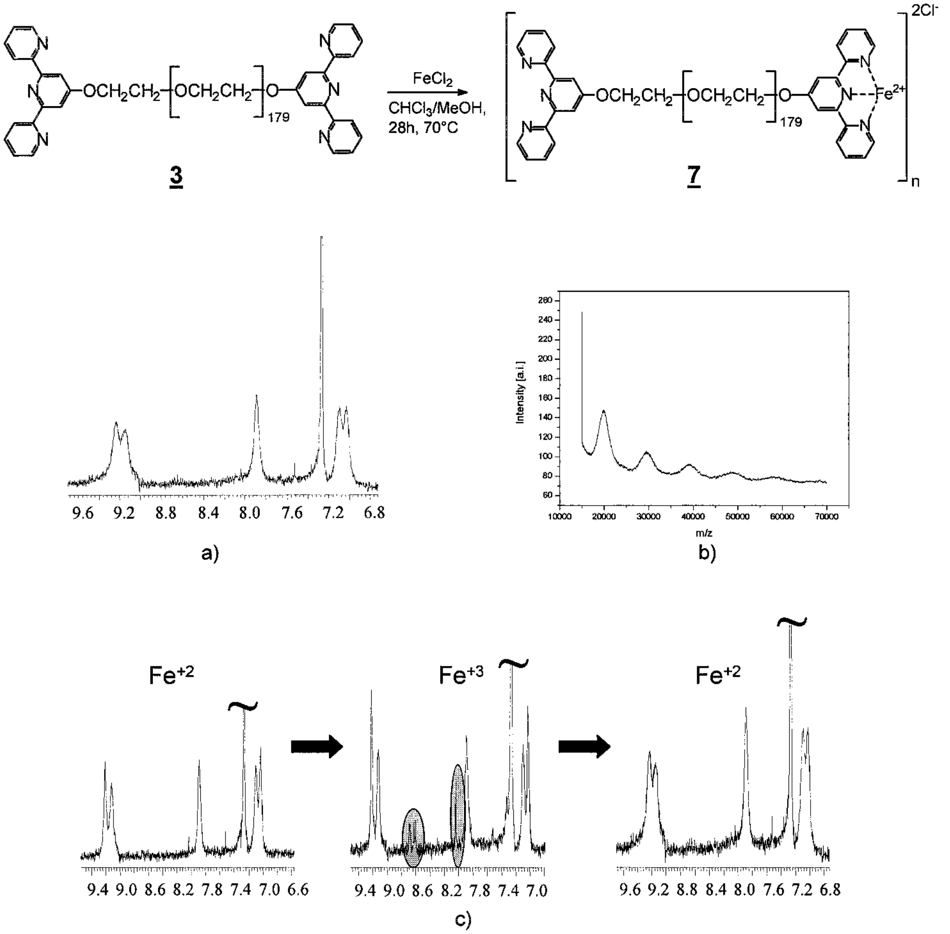
Fig. 5. top: Schematic representation of the complexation of telechelic 1 to form the coordination polymer 6; a) the UV/Vis spectra shows the typical metal-ligand charge transfer band; inset: UV/Vis titration experiments reveal a maximum value for the extinction coefficient after an equimolar addition of $FeCl_2$; b) the aromatic region of the ^{1}H-NMR spectrum (CD_3OD) shows the typical signals of the complexed terpyridine-unit.

In order to investigate the capability of opening and closing the metal-ligand bond and therefore the reversibility of the coordination polymers several parameters were investigated, such as temperature and the influence of chelating agents. The experimental outcome was monitored via ^{1}H-NMR, UV/Vis spectroscopy and AFM measurements.

First investigations on the temperature sensitivity of Fe^{2+} *bis*(2,2':6',2''-tepyrid-4'-yl) di(ethylene glycol) coordination polymers were undertaken. Upon heating the purple colour of a drop-casted film of 2 slightly fades at about 210°C. Heating to 270°C does not results in a complete disappearance of the colour, but it leads to the degradation of the polymer. For other terpyridine-containing polymers a cleavage of the Fe^{2+}-ligand bond could be already obtained at temperatures of about 160°C.[2] The higher stability of the coordination polymer 6 might be due to the high charge density that might lead to very stable, net ionic structures in the bulk material. Heating up to 210°C and cooling down to room temperature within 30 min, does not lead to the reappearance of the purple colour of the metal-complexes. After 12 h at room temperature the opened complexes reform, which can be monitored by the reappearance of the purple colour. Experiments with a competitive ligand HEDTA revealed the full reversibility of the polymer formation.[3]

A similar reaction procedure as for 5 and 6 has been applied for the complexation/polymerization of *bis*(2,2′:6′,2′′-terpyrid-4'-yl)-poly(ethylene oxide)$_{180}$ (Figure 6, top image). Chloroform was used as solvent to achieve an exposed position of the complexing moieties in solution rather than an integration into the coiled polymer matrix. To avoid oxidation to iron(III) the reaction was performed under inert conditions. The complexation/polymerization could be demonstrated by UV/Vis measurements and ^{1}H-NMR spectroscopy. Besides the typical chemical shifts of the octahedral terpyridine complexes the broadening of the signals reveal the formation of extended coordination polymers (Figure 6a). Moreover, the MALDI-TOF-MS spectrogram shows peaks matching to the masses of oligomers up to six repeating units (Figure 6b). Higher oligomers could not be obtained for similar reason as stated for the compounds 5 and 6. The low values of the relative viscosities of $\eta = 2.41$ for 7 in comparison with $\eta = 1.85$ for the coordination polymer *bis*(2,2':6',2''-terpyrid-4'-yl)-iron(II)-chloride-di(ethylene glycol) (6) are in agreement with other randomly coiled polymers. The film forming properties of the material from methanol solution (in contrary to the free telechelic 3) reveals as well its polymeric character.

As known from literature and indicated by viscosity measurements (see Figure 4a), iron(III) tends to form *mono*complexes. Oxidation of the metal centers of 7 therefore should result in a degradation of the formed polymer and reduction should on the other hand lead to anew complexation/polymerization. Attemps were undertaken to switch between the metallo-supramolecular coordination polymer and monomers units purely by oxidizing the complex bound iron(II) at air upon heating. The process was monitored by ^{1}H-NMR spectroscopy (Figure 6c). After fourteen hour of refluxing under air clearly the signals of the free ligand (approx δ – values 8.65 and 8.10) are approaching which corresponds to the breaking-up of the iron(II) terpyridine *bis*complexes upon oxidation. Utilizing *N*-ethylmorpholine as a reducing agent the reformation of the complexes/polymers can be achieved (see dissapearance of the free ligand peaks in the ^{1}H-NMR). The experimental data demonstrate the feasibility of the concept. However, different methodologies for the redox processes have to be investigated in order to achieve a quantitative "switching" under milder conditions.



a) b)

c)

Fig. 6. top: Schematic representation of the complexation of telechelic 3 to form the coordination polymer 7; a) the aromatic region of the ^{1}H-NMR spectrum ($CDCl_3$) shows the typical signals of the complexed terpyridine-unit; the broadening of the peaks reveal the polymeric character of the material; d) MALDI-TOF-MS spectrogram shows oligomers up to six repeating units; c) appearance/disappearance of the signals of the free ligand in the aromatic region of the ^{1}H-NMR spectrum ($CDCl_3$) upon oxidation/reduction of the central metal-ion.

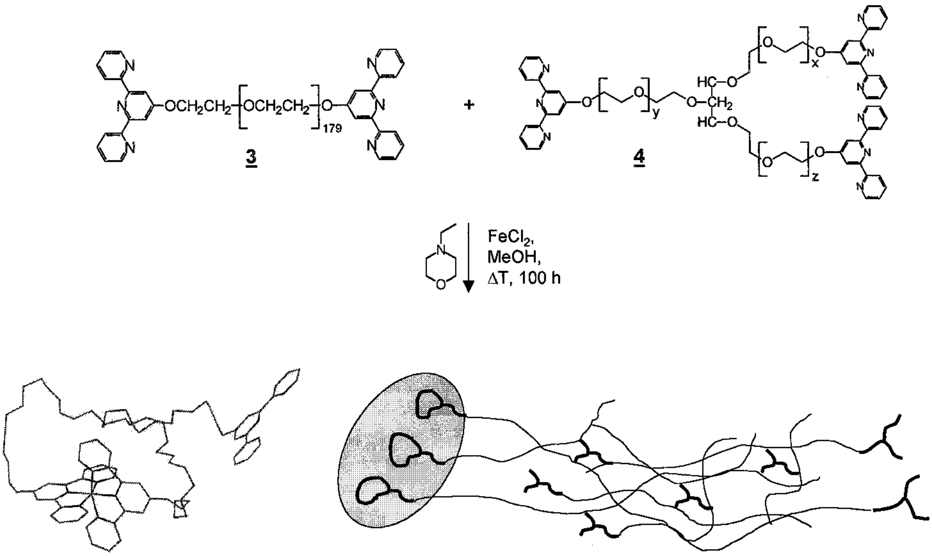


Fig. 7. Schematic representation of the formation of a metallo-supramolecular cross-linked architecture (bottom right) utilizing *bis*(2,2′:6′,2″-terpyrid-4'-yl) poly(ethylene oxide)$_{180}$ (3) and *tris*[(2,2′:6′,2″-terpyrid-4'-yl) oligo (ethylenoxy-)$_{3.33}$]glycerin (**4**). Molecular modeling of the intramolecular complexed cross-linker (bottom left).

In order to create metallo-supramolecular cross-linked architectures, attempts were undertaken to incorporate the *tris*functionalized cross-linker 4 into the polymer-matrix of *bis*(2,2':6',2''-terpyrid-4'-yl)-iron(II)-chloride-poly(ethylene oxid)$_{180}$. Initial experiments revealed that a built-in at room temperature is not feasible. However, a quantitative cross-linking can neither be obtained at elevated temperatures (Figure 7). During the reaction only a small quantity of cross-linked material precipitates from the methanol solution. From molecular modeling data a strong tendency of the cross-linker to form intramolecular complexes could be derived (Figure 7c). Therefore they act as chain stopper rather than cross-linker. Stiffer *multi*functional ligands might lead to enhanced cross-linking.

Conclusion

We have demonstrated the synthesis and full characterization of several 2,2':6',2''-terpyridine functionalized metallo-supramolecular building units and could prove their feasibility to form polymeric complexes and coordination polymers. Applying different metal-ions, metallo-supramolecular polymers with different stability ratios between monomeric and polymeric complexes could be synthesized in an self-assembly manner. Therefore, depending on the metal-ion and the metal ion content, solutions with tailor made and tuneable viscosities are easily accessible. However, due to the randomly coiled character of the polymers the range of viscosity values seems to be limited. Furthermore, the reversibility of iron(II) polymers *bis*(2,2':6',2''-terpyrid-4'-yl)-$FeCl_2$-di(ethylene glycol) (**6**) and *bis*(2,2':6',2''-terpyrid-4'-yl)-$FeCl_2$-poly(ethylene oxid)$_{180}$ (**7**) upon the increase of temperature, addition of chelating ligands (HEDTA) and the application of oxidizing/reducing conditions could be demonstrated.

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