Soluble High-Molecular-Mass Poly(ethylene oxide)s via Self-Organization†

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ABSTRACT: High-molecular-weight poly(ethylene oxide)s are utilized for a wide variety of different applications. Here we present a new strategy for the large-scale synthesis of modified metallosupramolecular poly(ethylene oxide)s on the basis of the metal-induced self-assembly of bis(2,2′:6′,2″-terpyrid-4′-yl)-poly(ethylene oxide)$_{179}$. The influence of different metal ions (cadmium(II), copper(II), cobalt(II), nickel(II), iron(II)) on the degree of polymerization and the resulting molecular weight were evaluated. Elaborated reaction conditions allow easy access to high-molecular-weight iron(II) coordination polymers via self-organization. The polymers were characterized in detail utilizing ^{1}H NMR, UV/vis spectroscopy, MALDI-TOF-MS, and viscosity measurements. The molecular weight was estimated on the basis of concentration-dependent viscosity measurements to about 80 000 g/mol. Furthermore, the morphology of the utilized telechelic bis(2,2′:6′,2″-terpyrid-4′-yl)-poly(ethylene oxide)$_{179}$ and the corresponding coordination polymer was investigated using atomic force microscopy. In particular, the influence of complex formation on the morphology was investigated.

Introduction

Developing novel materials based on self-organizing systems has been a major goal in recent research aimed at organic−inorganic hybrid materials with interesting electronic, photophysical, magnetic, and catalytic properties.[1−4] In particular 2,2′:6′,2″-terpyridine-functionalized units were incorporated into a large variety of different architectures[5] such as block copolymers,[6] graft copolymers,[7] and metallosupramolecular micelles.[8] In addition, a wide range of linear coordination polymers have been synthesized, whose backbones are held together by transition-metal complexes (Scheme 1).[9−14] However, most of the systems described in the literature are built up from small organic entities that result in restricted molecular weights. Coordination polymers with short organic spacers have been reported mainly within mass ranges of about 11 000−15 000,[9a] 30 000−45 000,[9b−d] and 70 000.[11] Only a few systems have been reported utilizing polymeric spacers.[15] Moreover, only some of them provide water solubility.

Water-soluble high-molecular-weight poly(ethylene oxide)s are extensively utilized as functional ingredients in a variety of different applications such as flocculation processes, wastewater treatment, mining, food processing, cosmetics, and coagulation.[16−20] Reversible systems can serve as intelligent hydrogels and can be applied for drug delivery[21] or as smart materials (e.g., self-healing coatings).[22] The reversibility of coordination polymers can be achieved upon external stimuli such as UV irradiation, temperature, redox chemistry, and application of competitive ligands.[1,23,24] Recently, we prepared first water-soluble reversible model coordination polymers on the basis of di(ethylene glycol).[23] Here we present a multigram synthetic approach for high-molar-mass poly(ethylene oxide)s on the basis of metal-induced polymerization utilizing bis(2,2′:6′,2″-terpyrid-4′-yl)-poly(ethylene oxide)$_{179}$ as a building block.

Experimental Section

Instruments and Materials. Basic chemicals were obtained from Sigma-Aldrich. ^{1}H 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). Viscosity investigations were performed on a SCHOTT AVS350 system using SCHOTT 85310/I Ubbelohde viscosimeters. Each viscosity value was determined as an average of five independent measurements. MALDI-TOF mass spectrograms were obtained from a Voyager-DE PRO Biospectrometry workstation (Applied Biosystems) in linear operation mode. AFM images were measured on a Solver47H (NT-MDT, Moscow) equipped with a heating stage. DSC investigations were performed on a Perkin-Elmer Pyris-1 DSC system with a heating rate of 10 K/min (T_c and T_m) and 40 K/min (T_g).

Preparation of Bis(2,2′:6′,2″-terpyrid-4′-yl)-poly(ethylene oxide)$_{179}$ (1). A mixture of 20.00 g (2.18 mmol) of poly(ethylene oxide)$_{179}$ and 1.22 g of (21.77 mmol) KOH in 200 mL of DMSO (dry) was stirred for 1 h at 60 °C. 4′-Chloro-2,2′:6′,2″-terpyridine (1.40 g (5.23 mmol)) was added, and stirring was continued for 72 h at 60 °C. Subsequently, the solvent was removed in vacuo. The residue was dissolved in 75 mL of H_2O and extracted four times with 250 mL of $CHCl_3$ each time. The combined organic layers were dried over Na_2SO_4, the solvent was removed in vacuo, and the residue was dissolved in THF. Precipitation with diethyl ether yielded bis(2,2′:6′,2″-terpyrid-4′-yl)-poly(ethylene oxide)$_{179}$ as a colorless powder. Yield: 15.92 g, 1.72 mmol (79%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.48 (m, 4H, O−CH_2), 3.64 (m, 965H, O−CH_2), 3.75 (m, 4H, O−CH_2), 3.82 (m, 4H, O−CH_2), 3.94 (m, 4H, O−CH_2), 4.40 (m, 4H, O−CH_2), 7.33 (m, 4H, *H-5,5″*), 7.85 (ddd, 4H, J = 8.2, 8.2, 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 (4.94), 274 (4.59).

MS (MALDI-TOF, dithranol): M_n = 9100 g/mol, M_w = 9200 g/mol, PDI = 1.01.

Preparation of [Bis(2,2′:6′,2″-terpyrid-4′-yl)-FeCl$_2$-poly(ethylene oxide)$_{179}$]$_n$. Procedure A: 300.0 mg (33.0 μmol) of bis(2,2′:6′,2″-terpyrid-4′-yl)-poly(ethylene oxide)$_{179}$ and 4.18 mg

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† Dedicated to Prof. Claus D. Eisenbach on the occasion of his 60th birthday.

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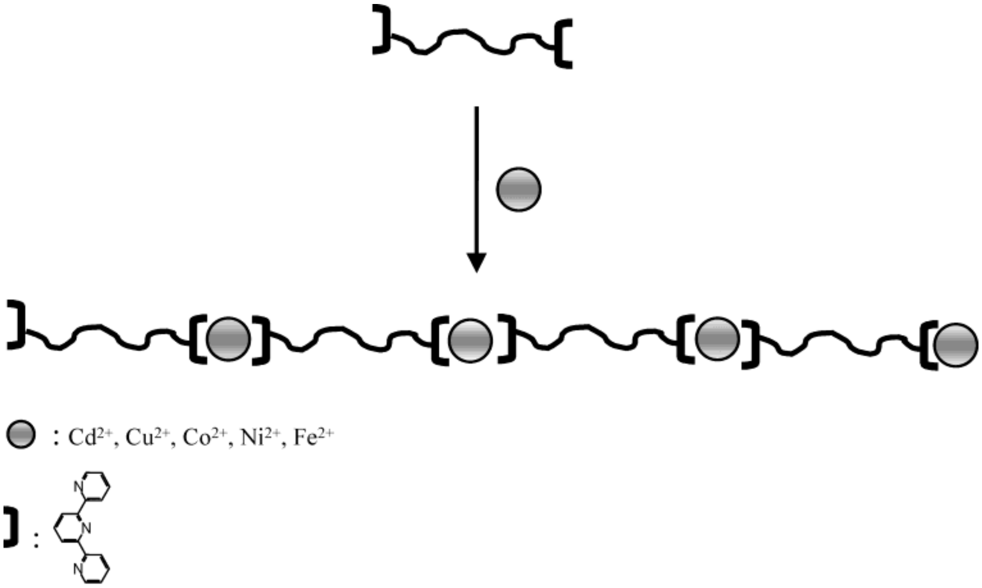
Scheme 1. Schematic Representation of the Metal-Induced Formation of Coordination Polymers



of (33.0 μmol) $FeCl_2$ were added to 10 mL of $CHCl_3$ and stirred at ambient temperature for 14 h. After the addition of a few drops of methanol, the reaction mixture was heated to 60 °C and stirred for an additional 28 h. The solvent was removed in vacuo, and the residue was washed several times with diethyl ether. The product was isolated as a purple solid. Yield: 280 mg (92%).

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.62$ (m, 1150H, O−C*H₂*), 4.18 (s, br, 4H, tpy−O−CH_2C*H₂*), 5.25 (s, br, 4H, tpy−O−C*H₂*-CH_2), 7.02 (s, br, 4H, *H-5,5″*), 7.10 (s, br, 4H, *H-6,6″*), 7.89 (s, br, 4H, *H-4,4″*), 9.11 (s, br, 4H, *H-3,3″*), 9.20 (s, br, 4H, *H-3′,5″*).

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

$\eta_{rel} = 2.41$ (methanol, $c = 20$ mg/mL, 20 °C).

Procedure B: $FeCl_2$ (6.96 mg (52.3 μmol)) was dissolved in 20 mL of methanol under argon. A solution of 250.0 mg (27.5 μmol) of bis(2,2′:6′,2″-terpyrid-4′-yl)-poly(ethylene oxide)$_{179}$ in 10 mL of $CHCl_3$ was slowly added at ambient temperature. After 4 h of stirring, another 250.0 mg (27.5 μmol) of bis(2,2′:6′,2″-terpyrid-4′-yl)-poly(ethylene oxide)$_{179}$ dissolved in 10 mL of $CHCl_3$ was added. The reaction mixture was stirred at 60 °C for 14 h. The solvent was removed in vacuo, and the product was isolated in quantitative yield as a purple solid. Yield: 490 mg (97%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.62 (m, 1150H, O−C*H₂*), 4.18 (s, br, 4H, tpy−O−CH_2C*H₂*), 5.25 (s, br, 4H, tpy−O−C*H₂*-CH_2), 7.02 (s, br, 4H, *H-5,5″*), 7.10 (s, br, 4H, *H-6,6″*), 7.89 (s, br, 4H, *H-4,4″*), 9.11 (s, br, 4H, *H-3,3″*), 9.20 (s, br, 4H, *H-3′,5″*).

UV/vis (CH_3OH): λ_{max}/nm (ϵ[10^4 L mol^{-1} cm^{-1}]) = 243 (4.37), 275 (5.29), 320 (3.64), 558 (1.11).

$\eta_{rel} = 2.74$ (methanol, $c = 20$ mg/mL, 20 °C).

Procedure C: Bis(2,2′:6′,2″-terpyrid-4′-yl)-poly(ethylene oxide)$_{179}$ (2000.0 mg (22.0 μmol)) was dissolved in a minimum amount of $CHCl_3$ under argon. A solution of 27.86 mg (22.0 μmol) of $FeCl_2$ in methanol was added at once with vigorous stirring. Gel formation immediately took place. The solvent was removed in vacuo, and the product was isolated in quantitative yield. Yield: 1970 mg (97%).

^{1}H NMR (400 MHz, methanol-d_6): δ 3.66 (m, 1150H, O−C*H₂*), 4.20 (m, 4H, tpy−O−CH_2C*H₂*), 4.83 (m, 4H, tpy−O−C*H₂*CH_2), 7.24 (m, 4H, *H-5,5″*), 7.30 (m, 4H, *H-6,6″*), 8.00 (m, 4H, *H-4,4″*), 8.72 (m, 4H, *H-3,3″*), 8.84 (s, br, 4H, *H-3′,5′*).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.62 (m, 1150H, O−C*H₂*), 4.18 (s, br, 4H, tpy−O−CH_2C*H₂*), 5.25 (s, br, 4H, tpy−O−C*H₂*-CH_2), 7.02 (s, br, 4H, *H-5,5″*), 7.10 (s, br, 4H, *H-6,6″*), 7.89 (s, br, 4H, *H-4,4″*), 9.11 (s, br, 4H, *H-3,3″*), 9.20 (s, br, 4H, *H-3′,5′*).

UV/vis (CH_3OH): λ_{max}/nm (ϵ[10^4 L mol^{-1} cm^{-1}]) = 244 (4.36), 274 (5.30), 319 (3.65), 559 (1.12).

MS (MALDI-TOF, dithranol): $M_n = 18\,900$ [bis(2,2′:6′,2″-terpyrid-4′-yl)-FeCl-poly(ethylene oxide)$_{179}$]$^+$; $M_n = 29\,070$ [bis(2,2′:6′,2″-terpyrid-4′-yl)-FeCl-poly(ethylene oxide)$_{179}$]$_2$$^+$; $M_n = 39\,250$ [bis(2,2′:6′,2″-terpyrid-4′-yl)-FeCl-poly(ethylene oxide)$_{179}$]$_3$$^+$; $M_n = 48\,790$, [bis(2,2′:6′,2″-terpyrid-4′-yl)-FeCl-poly(ethylene oxide)$_{179}$]$_4$$^+$; M_n= 57 820 [bis(2,2′:6′,2″-terpyrid-4′-yl)-FeCl-poly(ethylene oxide)$_{179}$]$_5$$^+$; $M_n = 67\,490$ [bis-(2,2′:6′,2″-terpyrid-4′-yl)-FeCl-poly(ethylene oxide)$_{179}$]$_6$$^+$.

$\eta_{rel} = 5.51$ (methanol, $c = 20$ mg/mL, 20 °C).

Preparation of [Bis(2,2′:6′,2″-terpyrid-4′-yl)-MeX$_2$-poly-(ethylene oxide)$_{179}$]$_n$: Viscosity Measurements at Room Temperature. Bis(2,2′:6′,2″-terpyrid-4′-yl)-poly(ethylene oxide)$_{179}$ (100.0 mg (11.0 μmol)) was dissolved in 5 mL of methanol. The respective metal salts (cadmium(II) acetate, copper(II) acetate, cobalt(II) acetate, nickel(II) acetate, iron(II) sulfate, and iron(III) chloride) were added stepwise in 100-μL portions (corresponding to 20 mol % steps) from a stock solution (0.22 mmol in 10 mL of methanol) at ambient temperature. The relative viscosity of the solution was determined after each addition of the metal salt after a waiting period of 30 min.

Sample Preparation for the AFM Measurements. Solutions of bis(2,2′:6′,2″-terpyrid-4′-yl)-poly(ethylene oxide)$_{179}$ and [bis(2,2′:6′,2″-terpyrid-4′-yl)-$FeCl_2$-poly(ethylene oxide)$_{179}$]$_n$ in methanol ($c = 20$ mg/mL) were drop-casted on a silica wafer. The samples were annealed at 70 °C for 30 min utilizing the heating stage of the AFM. The annealed samples were measured at room temperature.

Results and Discussion

The terpyridine-modified poly(ethylene oxide) was synthesized on a 20-g scale by a Williamson-type reaction. In the first step, poly(ethylene oxide)$_{179}$ was deprotonated in a DMSO/KOH suspension, followed by an addition of 4′-chloro-2,2′:6′,2″-terpyridine. Bis(2,2′:6′,2″-terpyrid-4′-yl)-poly(ethylene oxide)$_{179}$ (**1**) (Figure 1) could be isolated in 79% yield after precipitation (proven by ^{1}H NMR, MALDI-TOF-MS, UV/vis, and GPC). To evaluate the capability of the spontaneous formation of extended coordination polymers at room temperature, the complexation behavior of **1** toward a wide range of metal salts was investigated and monitored by measurements of the relative viscosity. However, to exclude any nonspecific complexation with the utilized metal ions (see, for example, refs 25 and 26), reference experiments were undertaken. The addition of iron(II)

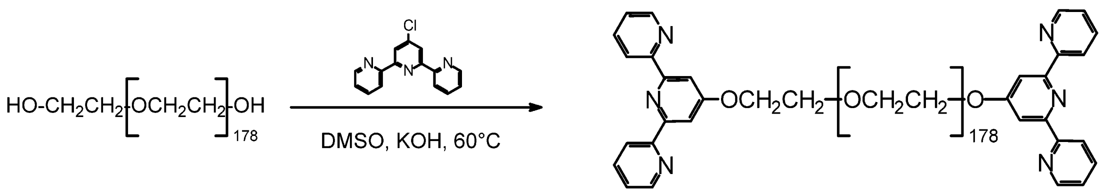


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Figure 1. Synthesis of the telechelic bis(2,2′:6′,2″-terpyrid-4′-yl)-poly(ethylene oxide)$_{179}$ (**1**).

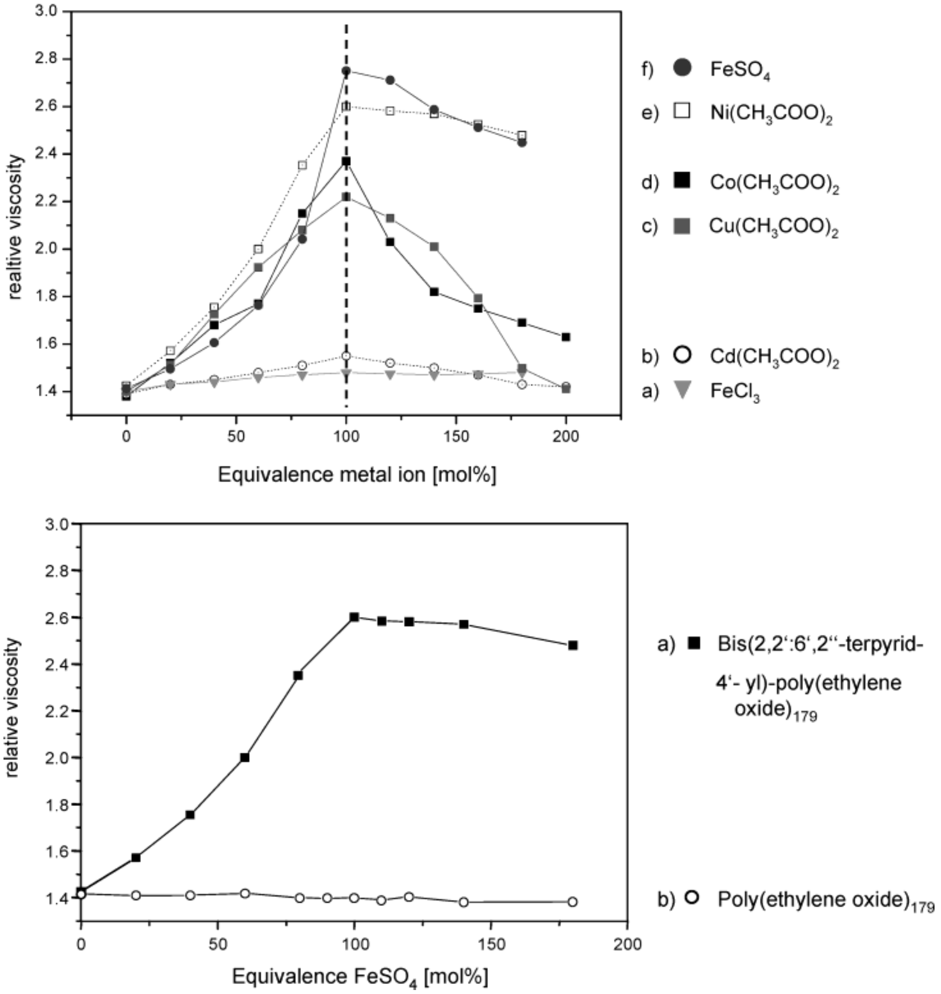
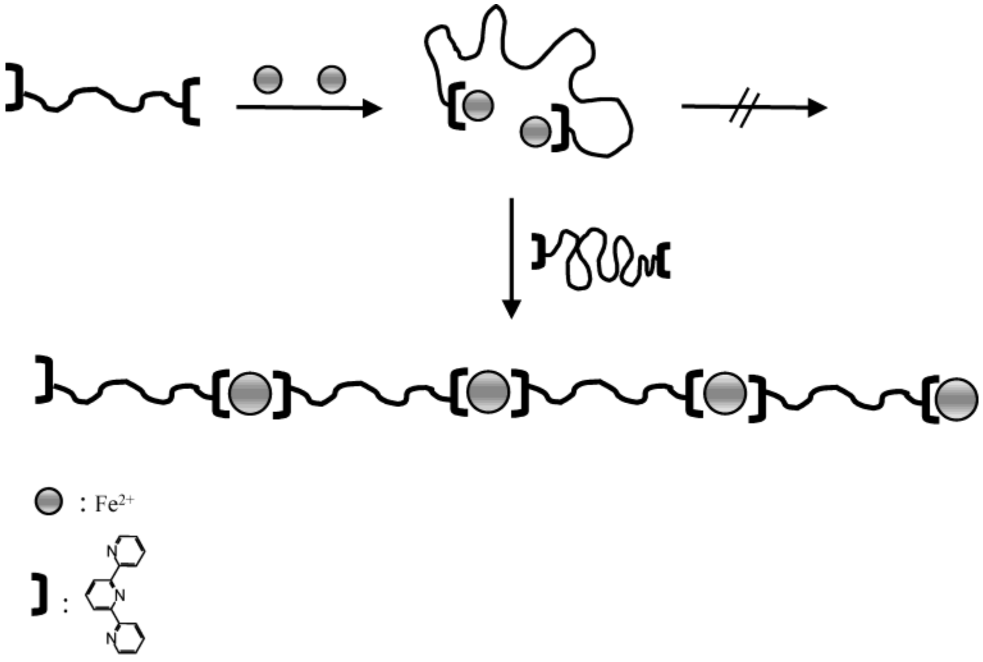


Figure 2. Viscosimetry experiments. (Top) Stepwise addition of (a) iron(III) chloride, (b) cadmium(II) acetate, (c) copper(II) acetate, (d) cobalt(II) acetate, (e) nickel(II) acetate and (f) iron(II) acetate to a solution ($c = 20$ mg/mL methanol) of bis(2,2′:6′,2″-terpyrid-4′-yl)-poly(ethylene oxide)$_{179}$ leads to different maximum values of the relative viscosity for an equivalent addition of the metal salt. The addition of iron(III) chloride does not result in an increase in the relative viscosity. (Bottom) As demonstrated for the example of iron(II) sulfate, the addition of metal salt to unfunctionalized poly(ethylene oxide)$_{179}$ does not result in an increase in the relative viscosity.

sulfate to unfunctionalized poly(ethylene oxide)$_{179}$ up to a molar ratio of 1.6:1 (typical range of the performed viscosity measurements) did not result in any change of the relative viscosity (Figure 2, bottom). In contrast to these findings, the stepwise addition (in 20 mol % portions) of different metal salt solutions in methanol (cadmium(II) acetate, copper(II) acetate, cobalt(II) acetate, nickel(II) acetate, iron(II) sulfate) to a solution of **1** in methanol (20 mg/mL) resulted for all salts in an increase in the relative viscosity up to a maximum value at a metal ion-to-telechelic ratio of 1:1, followed by a decrease in viscosity for higher ratios (Figure 2, top). Considering the reference measurement, this change in the relative viscosity can be exclusively attributed to the formation of coordination polymers. Similar to polycondensation reactions, small amounts of only partially functionalized monomers should lead to a drastic decrease in the degree of polymerization for the formation of metallosupramolecular coordination polymers. This would also lead to maximum relative viscosity values below the 1:1 ratio. Therefore, this point can serve as additional proof of the quantitative bisfunctionalization.

As can be seen from Figure 2, the absolute values for the maximum viscosities vary for the different metal ions. The relative viscosity reaches values of $\eta_{\text{rel}} = 1.55$ with cadmium(II) acetate, $\eta_{\text{rel}} = 2.22$ with copper(II) acetate, $\eta_{\text{rel}} = 2.37$ with cobalt(II) acetate, $\eta_{\text{rel}} = 2.60$ with nickel(II) acetate, and $\eta_{\text{rel}} = 2.75$ with iron(II) sulfate. The relative viscosity is directly related to the molecular weight of the linear coordination polymers and therefore to the degree of polymerization. The latter

Scheme 2. Schematic Representation of the Iron(II) Induced Formation of Monocomplexes and Further Polymerization upon the Addition of Free Telechelics without the Formation of Monocycles



depends on the stability constants of the monocomplexes and biscomplexes. For all metal complexes discussed here, the stability constants of the biscomplexes are higher than those of the corresponding monocomplexes (e.g., log K (iron(II) monocomplex) = 7.1, log K (iron(II) biscomplex) = 13.8, log K (nickel(II) monocomplex) = 10.7, log K (nickel(II) biscomplex) = 11.1, log K (cobalt(II) monocomplex) = 8.4, log K (cobalt(II) biscomplex) = 9.9[27,28]). Therefore, the relative viscosity values can be qualitatively correlated to the thermodynamic stability of the biscomplexes. The maximum values of the viscosities for the different complexing metal ions in the coordination polymers (iron(II) > nickel(II) > cobalt(II) > copper(II) > cadmium(II)) are in agreement with available literature data for the stability constants of the formed biscomplexes (see above-mentioned values for iron(II), nickel(II), and cobalt(II), kinetic considerations are not taken into account).[27,28] Furthermore, the viscosity behavior upon addition of an excess of metal ions also varies significantly depending on the metal ions utilized (Figure 2): the relative viscosity immediately decreases in the cases of cadmium(II), copper(II), and cobalt(II). For iron(II), the decrease is much less pronounced, and for nickel(II), a plateau is reached that is almost independent of the amount of added metal salt. These observations also correspond qualitatively to the thermodynamic stability of the biscomplexes.

Because of the high viscosities obtained for the iron(II) coordination polymers and their nontoxicity, the formation of [bis(2,2′:6′,2″-terpyrid-4′-yl)-$FeCl_2$-poly(ethylene oxide)$_{179}$]$_n$ was investigated for different reaction conditions in more detail. Chloroform was applied as a solvent in all cases. It provides better solubility for the (2,2′:6′,2″-terpyrid-4′-yl) moieties, which leads to improved accessibilty. As can be seen from Figure 2 (graph a), the addition of iron(III) chloride does not lead to an increase in viscosity. To avoid oxidation to iron(III), the reaction was performed under an argon atmosphere. Procedure A facilitates the slow dissolution of iron(II) chloride over the course of 18 h and was chosen to guarantee a more defined build up of the coordination polymer. Higher concentrations (30 mg/mL) were applied to prevent intramolecular complexation (ring formation). The synthetic strategy of procedure B aimed at an initial formation of monocomplexes applying a 2:1 ratio (iron(II) chloride/**1**), followed by polymerization by an additional feed of **1** (Scheme 2). For procedure C, high concentrations (about 150 mg/mL) and a fast addition of iron(II) chloride at room temperature were applied.

For all reaction conditions, quantitative complex formation could be demonstrated by means of ^{1}H NMR and UV/vis spectroscopy. UV/vis revealed the typical MLCT band for iron(II)-bisterpyridine complexes at 559 nm and a bathochromic shift of the $\pi-\pi^*$ band (Figure 3). The extinction coefficient of the MLCT band correlates with values obtained for model complexes and similar coordination polymers.[23] The signals of the terpyridine protons in the ^{1}H NMR spectrum are shifted (Figure 4). The formation of octahedral complexes

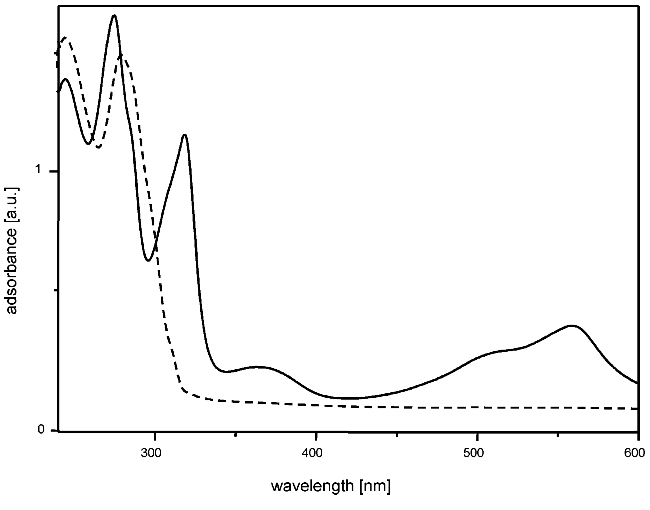


Figure 3. UV/vis spectrum (methanol) of telechelic **1** (dotted line) and coordination polymer [bis(2,2′:6′,2″-terpyrid-4′-yl)-$FeCl_2$-poly(ethylene oxide)$_{179}$]$_n$ (straight line).

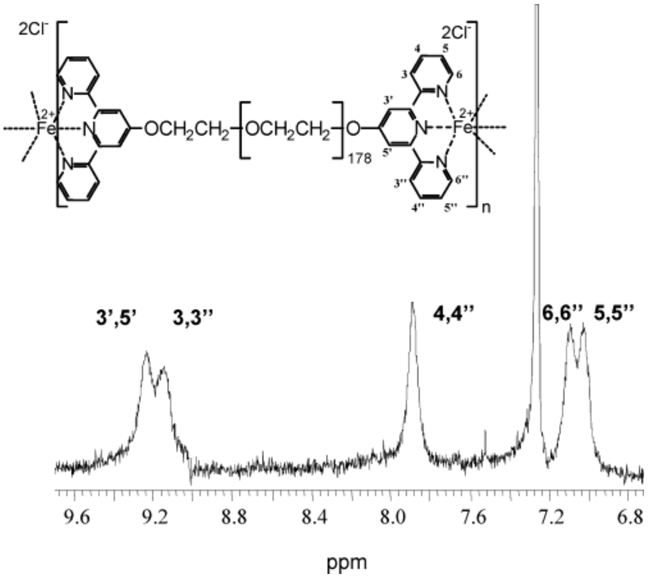


Figure 4. Aromatic region of the ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of coordination polymer [bis(2,2′:6′,2″-terpyrid-4′-yl)-$FeCl_2$-poly(ethylene oxide)$_{179}$]$_n$.

results in a change from an antiperiplanar (uncomplexed state) to a synperiplanar conformation (complexed state). The protons in the 6,6″ position are shifted to higher fields, and the protons in 3′,5′ position are shifted to lower fields. Furthermore, the absence of the signals of the free ligand in the spectra demonstrates quantitative complex formation. Finally, the broadening of the signal peaks indicates the formation of extended coordination polymers.

At a macroscopic level, the complexed material revealed polymeric character with film-forming properties from methanol and chloroform. These films swell in water and dissolve only after 20 h at room temperature. In organic solvents (such as methanol or chloroform), the films can be redissolved only in the ultrasonic bath at 50 °C after 30 min. Furthermore, the material was investigated utilizing MALDI-TOF mass spectrometry, viscosity measurements, scanning probe microscopy (morphology investigations), and DSC (thermal investigations). The MALDI-TOF-MS spectrogram showed different distributions corresponding to the masses of oligomers of up to seven repeating units (Figure 5). The absence of mass fractions of higher-molecular-weight oligomers or polymers can be explained by the opening of the iron(II)-terpyridine complexes under the MALDI conditions or insufficient desorption. Similar results were obtained for model complexes (α-methoxy-ω-(2,2′:6′,2″-terpyrid-4′-yl)-Fe(PF_6)$_2$-poly(ethylene oxide)$_{78}$ and comparable dimers.[10,23,29]

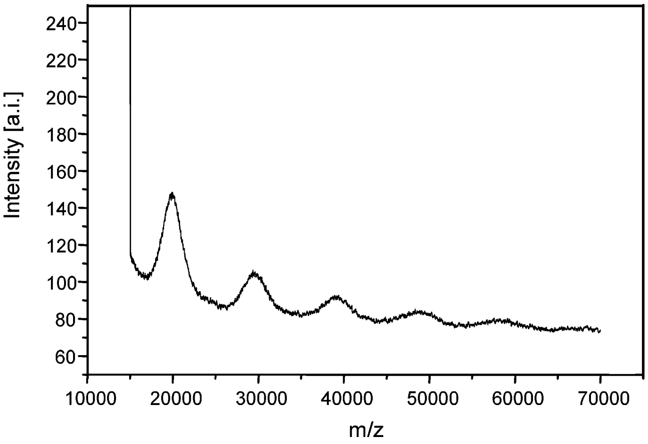


Figure 5. MALDI-TOF spectrogram (matrix: 2,5-dihydroxybenzoic acid) of the linear coordination polymer [bis(2,2′:6′,2″-terpyrid-4′-yl)-$FeCl_2$-poly(ethylene oxide)$_{179}$]$_n$. The observed distributions with the *m/z* maxima of 18 900, 29 070, 39 250, 48 790, 57 820, and 67 490 correspond to oligomers with degrees of polymerization of 2, 3, 4, 5, 6, and 7, respectively.

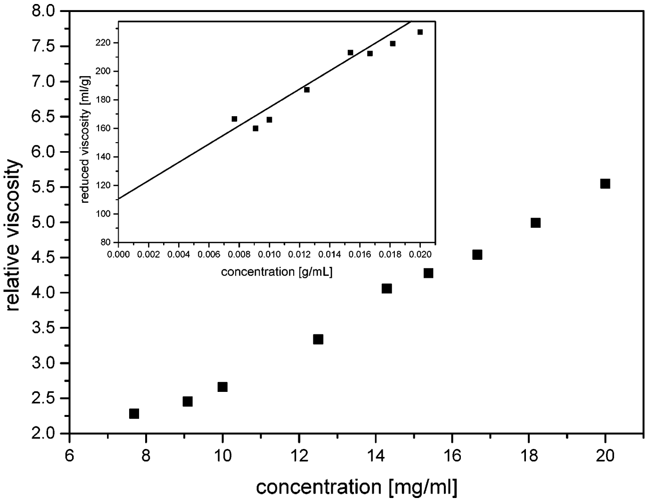


Figure 6. Plot of the relative viscosity of coordination polymer [bis(2,2′:6′,2″-terpyrid-4′-yl)-$FeCl_2$-poly(ethylene oxide)$_{179}$]$_n$ in methanol in a concentration range between 7 and 20 mg/mL. (Inset) Plot of the reduced viscosity against the concentration. Extrapolation to zero concentration reveals an intrinsic viscosity of $[\eta] = 113$.

The observed values of the relative viscosities differed depending on the applied reaction procedures: $\eta_{rel} = 2.41$ for procedure A and $\eta_{rel} = 2.74$ for procedure B. Procedure C yielded materials with the highest relative viscosity of $\eta_{rel} = 5.51$ (all measurements were performed in methanol with a concentration of $c = 20$ mg/mL). Assuming quantitative complex formation, several reasons for the different values of the relative viscosity can be discussed. One of them is the formation of cyclic oligomers (most probably monocycles). The results of the polymerizations following the described conditions allow us to draw two principal conclusions: (1) High concentrations favor the intermolecular complexation and therefore the formation of extended coordination polymers rather than cyclic structures. (2) The mode of metal salt addition strongly influences the polymerization. Point 1 is obvious. Regarding the latter argument, it must be pointed out that 2,2′:6′,2″-terpyridine is known to form monocomplexes with iron(II).[30] Starting with an excess of metal salt (procedure B) is expected to result in the preformation of monocomplexes, which avert the formation of monocycles. Therefore, even if applying lower concentrations (procedure A: $c = 30$ mg/mL, procedure B: $c = 12.5$ mg/mL), procedure B leads to higher relative viscosity values due to an optimized metal salt addition. Monomer concentrations of about 150 mg/mL applied in procedure C facilitates an instant and quantitative complexation at room temperature.

Concentration-dependent viscosity measurements were performed with the coordination polymer [bis(2,2′:6′,2″-terpyrid-4′-yl)-$FeCl_2$-poly(ethylene oxide)$_{179}$]$_n$ synthesized according to procedure C. The measurements were performed in methanol within a concentration range of 2×10^{-2} to 7×10^{-2} g mL^{-1} (Figure 6). The relative viscosity value dropped from 5.51 initially to 2.12. By extrapolating to concentration zero, the intrinsic viscos-

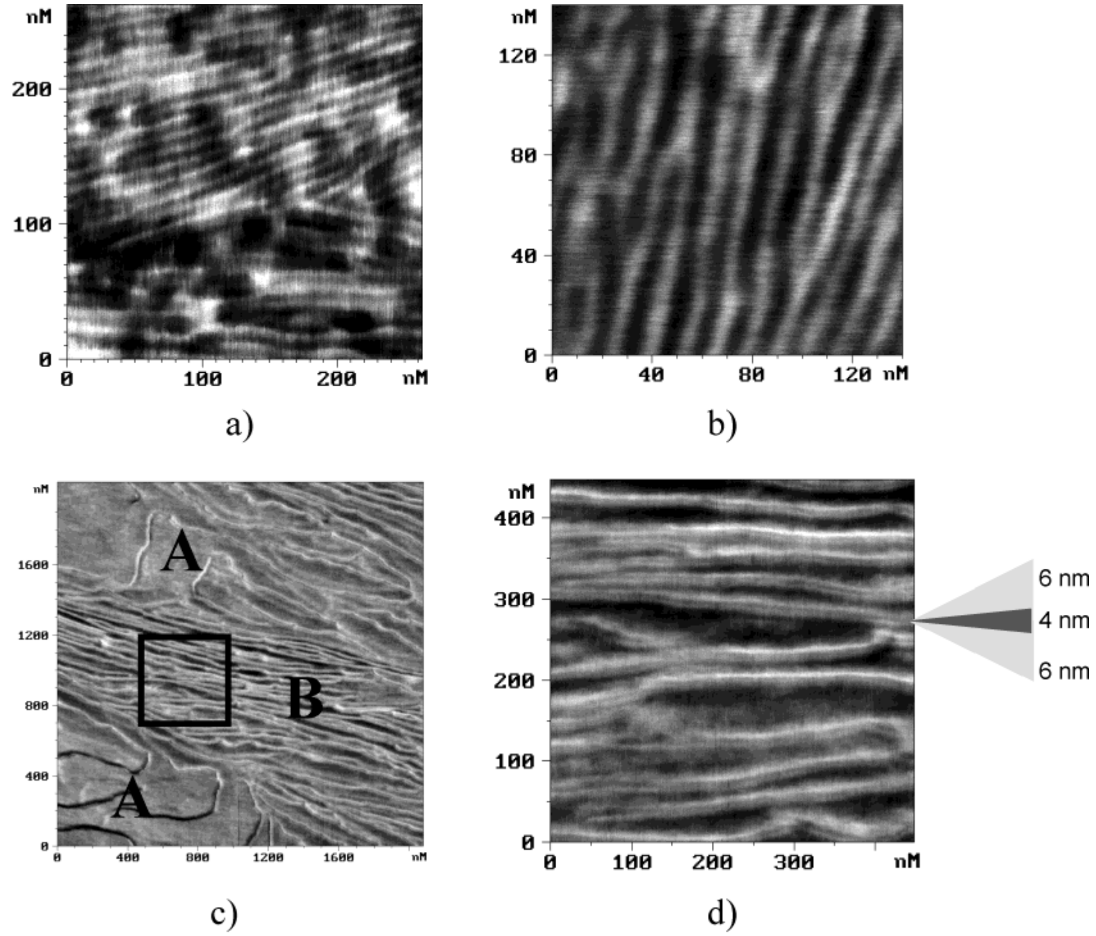


Figure 7. Comparison of the AFM images (phase image, film preparation: drop casting of a 0.1% solution in methanol) of (a) bis(2,2′:6′,2″-terpyrid-4′-yl)-poly(ethylene oxide)$_{179}$ and (b) coordination polymer [bis(2,2′:6′,2″-terpyrid-4′-yl)-FeCl$_2$-poly(ethylene oxide)$_{179}$]$_n$. Both images reveal a typical lamellar structure. (c) AFM phase images of an annealed sample (70 °C, 30 min) of [bis(2,2′:6′,2″-terpyrid-4′-yl)-FeCl$_2$-poly(ethylene oxide)$_{179}$]$_n$. Lamella are seen face-on (A) and edge-on (B). d) Single lamella reveals a double line feature consisting of two phase domains of about 6 nm separated by a domain (having the opposite phase) of about 4 nm.

ity could be determined ($[\eta] = 113$). Using the equation $[\eta] = K_{[\eta]} \times M^a$ and applying $K_{[\eta]}$ and a values for pure poly(ethylene oxide),[31] a molecular weight of about $M_n = 80\,000$ could be estimated for the coordination polymer. To the best of our knowledge, only one iron(II) coordination polymer has been reported with a similar high molecular weight of 70 000. However, the reported coordination polymer was not soluble in water, methanol, or chloroform.[11]

The morphology of the telechelic **1** and the iron(II) coordination polymer (synthesized according procedure C) has been investigated using atomic force microscopy. The first set of samples was prepared by drop-casting from solutions in methanol ($c = 20$ mg/mL) on silicon. The height images showed a uniform flat surface for both materials. However, the phase images of **1** (Figure 7a) and of the linear coordination polymer (Figure 7b) clearly revealed a lamellar structure. The dimensions did not significantly vary between both materials. The sizes of the lamella were about 14−18 nm for **1** and 13−18 nm for the coordination polymer. Subsequently, the samples were annealed at 70 °C for 30 min (utilizing the heating stage of the AFM) and measured again at room temperature. The morphology of the coordination polymer revealed a double-lamella structure (Figure 7d). For annealed compound **1**, no double-lamella structure could be obtained. Double-lamella structures have already been reported in the literature for unfunctionalized, low-molecular-weight poly(ethylene oxide)s.[32] They are based on crystalline, folded chains. Uneven folds result in a double-lamella structure. The folding is believed to result from hydrogen bonding of the free hydroxy end groups of the polymer. Consequently, the absence of hydrogen bonding units due to end-of-chain functionalization hinders chain folding and a multiple-lamella structure. This has already been reported for α,ω-bismethoxy functionalized poly(ethylene oxide)s.[33] In contrast, the metal-induced polymerization of the telechelic provides these secondary interactions in the form of the iron(II)-bis(2,2′:6′,2″-terpyrid-4′-yl) complexes and leads to the build-up of double-lamella structures (Figure 8). The model of a once-folded chain for [bis(2,2′:6′,2″-terpyrid-4′-yl)-FeCl$_2$-poly(ethylene oxide)$_{179}$]$_n$ is furthermore 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 are about the same size. Because of the strong dependence on the crystallization conditions (e.g., temperature), a comparison of the lamella domain size with literature data is critical. However, the lamellae dimensions of the telechelic bis(2,2′:6′,2″-terpyrid-4′-yl)-poly(ethylene oxide)$_{179}$ seem to be very small; possibly the terpyridine unit is acting as a defect that inhibits larger crystalline domains.

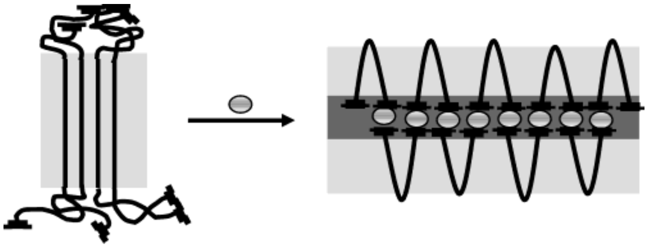


Figure 8. Model for extended chains of free telechelic bis-(2,2′:6′,2″-terpyrid-4′-yl)-poly(ethylene oxide)$_{179}$ and the once-folded double-lamella structure of coordination polymer [bis-(2,2′:6′,2″-terpyrid-4′-yl)-FeCl$_2$-poly(ethylene oxide)$_{179}$]$_n$.

Finally, DSC measurements were undertaken for **1** and the coordination polymer (prepared by procedure C). At a heating rate of 40 °C/min, the crystallization temperature (T_c) and the melting temperature (T_m) were determined: $T_c = 32.5$ °C ($\Delta H_c = -148.7$ J/g) and $T_m = 60.8$ °C ($\Delta H_m = 155.5$ J/g) for **1** and $T_c = 22.5$ °C ($\Delta H_c = -99.2$ J/g) and $T_m = 54.5$ °C ($\Delta H_m = 102.0$ J/g) for the coordination polymer. The coordination polymer reveals considerably lower crystallization temperatures and melting points. Having similar lamella domain dimensions, a different size for the crystalline regions cannot be the reason for the lower T_c and T_m values of the coordination polymer in comparison with those of free telechelic **1**. The reason is rather the more demanding build-up of crystals from the elongated chains as well as the need for chain folding. The glass-transition temperature (T_g) of [bis(2,2′:6′,2″-terpyrid-4′-yl)-FeCl$_2$-poly(ethylene oxide)$_{179}$]$_n$ was determined to be −47.6 °C (determined at a heating rate of 10 °C/min), whereas telechelic **1** did not show a glass transition.

Conclusions

In this contribution, we presented the synthesis and full characterization of the coordination polymer [bis-(2,2′:6′,2″-terpyrid-4′-yl)-FeCl$_2$-poly(ethylene oxide)$_{179}$]$_n$. By applying suitable reaction conditions, high-molecular-weight coordination polymers could be instantly prepared on the basis of self-assembly at ambient temperatures. A quantitative complexation of the (2,2′:6′,2″-terpyrid-4′-yl) moieties could be proven by ^{1}H NMR and UV/vis spectroscopy. MALDI-TOF-MS revealed masses corresponding to oligomers of up to seven repeating units. In addition, the material revealed film-forming properties and swelling characteristics that indicate the polymeric character of the material. Furthermore, the molecular weight has been estimated on the basis of concentration-dependent viscosity measurements. The calculated M_n of 80 000 g/mol represents one of the highest reported molecular weights for iron(II) coordination polymers. AFM investigations revealed a lamellar morphology for **1** as well as for the coordination polymer. A substructure was obtained for the latter one, which might be attributed to an ordering of the metal complex units. In the future, the “switching” properties of the coordination polymer will be investigated.

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