Synthesis and Properties in Solution of Ruthenium(II) Coordination Polymers

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Summary: Synthetic strategies are presented for the preparation of readily soluble ruthenium(II) coordination polymers of high molecular weight. The constitutional homogeneity of the polymers is proved using high-resolution NMR spectroscopy, and their molar masses are estimated from ^{1}H NMR spectra, viscosity data and SAXS investigations. The polymers are shown to be conformationally rigid, and to form either densely packed coils or rods. It is mainly this difference in shape which causes the very specific properties of the respective polyelectrolytes in the solid state as well as in dilute solution. Finally, the UV-vis absorption spectra of some of these materials are presented.

Keywords: coordination polymers; polyelectrolytes; rodlike polymers; ruthenium complexes; supramolecular chemistry

Introduction

When our research program on transition-metal containing polymers started in the mid 1990th, nearly all known macromolecules had backbones held together only by covalent bonds. Examples of such "classic" macromolecules are technical thermoplasts like PE, PP or PS as well as the naturally occurring polymers like polysaccharides, polypeptides or DNA, but also most of the organometallic and inorganic polymers like polymeric sulfur, polysiloxanes or polyphosphazanes. The situation was slightly different only in inorganic solid-state chemistry where some non-covalently linked chains were known. However, these species are stable only as crystals and decompose immediately into small fragments when brought in contact with appropriate solvents. Hence, from the polymer scientist's point of view, these materials are no real polymers because there is no way of determining their molar masses and molar mass distributions. All in all, there was a nearly complete lack of non-covalently linked but nevertheless readily soluble "non-classic" chain architectures that time. This situation motivated research groups to develop synthetic routes to novel supramolecular structures like polyrotaxanes and polycatenanes.[1,2]

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Also, soluble chain architectures were built up where the repeating units are connected by hydrogen bonds. Finally, we decided – among others[3-5] – to join together small molecular entities in a non-covalent fashion using transition-metal complexes and thus via coordinative bonds. This way of connecting small molecular entities creates the so-called "coordination polymers". In addition to fundamental aspects like answering the question to what extent transition-metal complexes can be used as connecting units in soluble macromolecules it was our aim to combine – in one single material – the advantageous mechanical properties of conventional polymers with specific electronic, optic or magnetic properties of transition-metal complexes. Moreover, most coordination polymers are polyelectrolytes and thus very interesting model compounds for this very actual field of research.

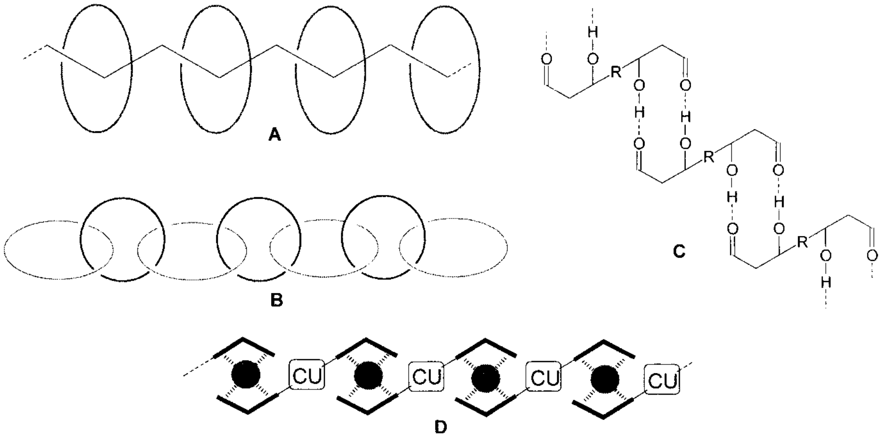
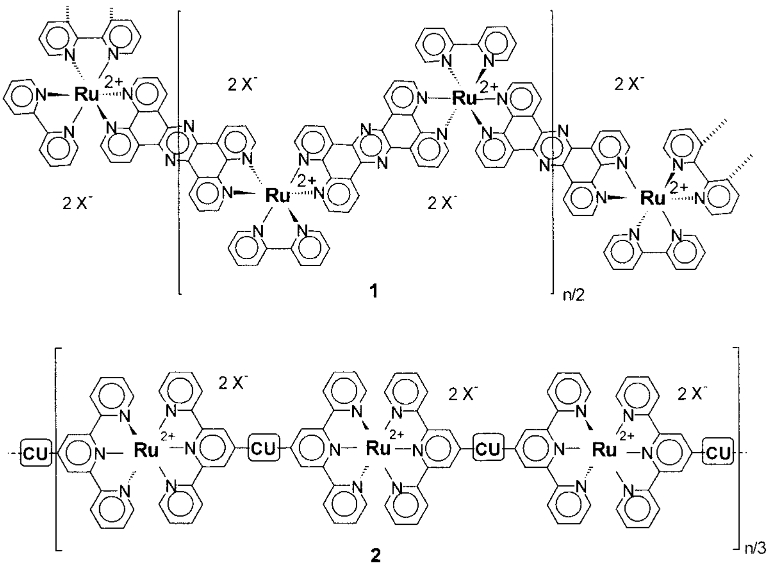


Figure 1: Schematic drawings of non-classic polymers: polyrotaxanes (A), polycatenanes (B), hydrogen-bonded polymers (C) and transition-metal coordination polymers (D); CU: conneting unit.

In order to select promising target structures, we specified some essentials that ligand moieties and metal complexes should fulfill when applied as building blocks in soluble coordination polymers. The ligand monomers – *i.e.* the covalent molecular entities between two transition-metal complexes in a polymer like D – must be difunctional, *i.e.* have precisely two independent coordination sites. Moreover, the ligand monomer's constitution and geometry should prevent intramolecular ring closure upon complexation as efficiently as possible. Otherwise, entropy will prevent the formation of high-molecular-weight chains. This requirement can be fulfilled by using ligand monomers in which two independent coordinating sites are fixed in opposite direction by a rigid connecting unit (CU in Figure 1). We here use aromatic units because they are rigid and moreover might allow a certain metal-metal communication via their conjugated π-electron system. Finally, there must be available efficient synthetic accesses to the ligand monomers. The transition-metals, on the other hand, must form 2:1 complexes with the ligand monomer's coordinating sites. Otherwise, branched or crosslinked products result. Moreover, the complexes must be thermodynamically very stable, as can be rationalized by the Carother's equation. Therefore, complexes formed by multidentate ligands are favored. Also, the complexes should be diamagnetic to allow proving the constitution of the chain molecules using NMR spectroscopy. Finally, the question was whether the complexes must be kinetically inert or could be kinetically labile as well. In the meantime, some soluble, constitutionally well-defined but kinetically labile copper(I) and silver(I) coordination polymers could be prepared.[4,6,7] Hence, kinetic inertness is not a necessary pre-requirement for soluble coordination polymers but simplifies preparation tremendously: one is much more free in selecting conditions for synthesis, analysis and processing. Therefore, coordination polymers based on kinetically inert complexes play the key role in this paper. Specifically, coordination polymers held together by octahedrally coordinated ruthenium(II) centers will be discussed. When linear chain molecules have to be prepared from bis-chelating ligand monomers and octahedrally coordinated metal ions, there are two general ways of realization (Figure 2).

On the one hand, bis-bidentate chelating ligands can be used for the preparation of chains like **1**. In this case, two coordination sites of the ruthenium ion have to be saturated by an additional mono-bidenate ligand such as 2,2'-bipyridine in order to prevent crosslinking. On the other hand, use of bis-tridentate ligands is possible as well to form chain-like structures such as **2**. Here, all available coordination sites of the metal ions are saturated by the ligand monomers, and no additional monofunctional ligand is needed.

Let us start with the first concept.[8-10] In polymer **1**, the chains assume an angle of approx. 120° at every ruthenium center. Thus, a coiled conformation is expected for these polymers which should guarantee solubility despite of the rigid ladder-like constitution. Therefore, no additional solubilizing side groups were attached to these materials at first.[8]



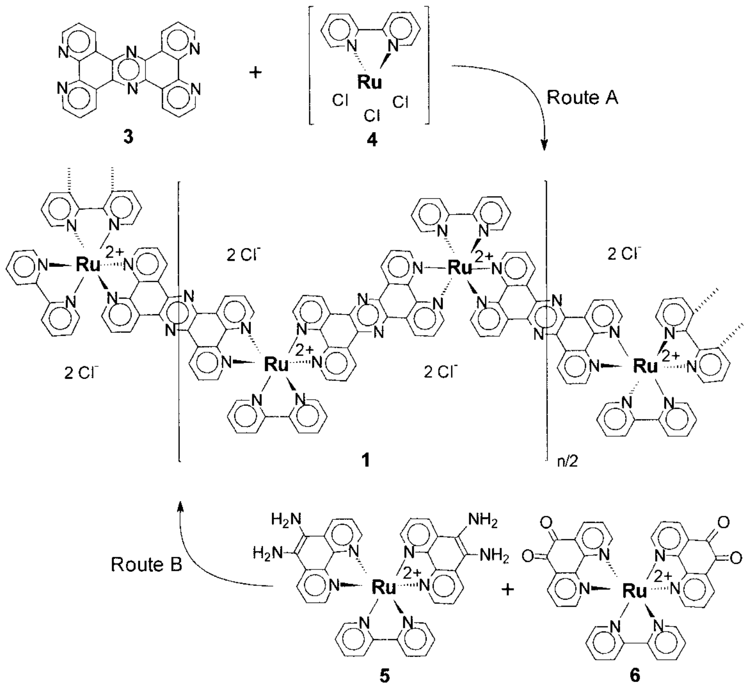
1

2

Figure 2: Coordination polymers from octahedrally coordinated ruthenium(II) and bis-bidentate (**1**) and bis-tridentate (**2**) ligand monomers, respectively.

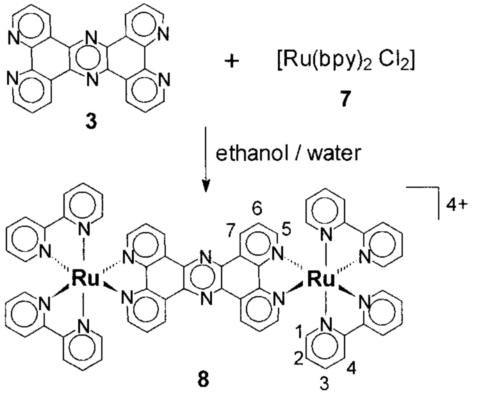
There are two different synthetic strategies leading to such materials. On the one hand, one can prepare a ligand monomer like **3** and a metal monomer like **4** and subsequently generate the polymer via complex formation (route A in Scheme 1). Alternatively, one can preform the desired metal complexes in monomers like **5** and **6** and then allow the polymers to grow via a ligand formation reaction (route B in Scheme 1). We decided to use the so-called "complex formation strategy" (route A) because complex formation was expected to be much more efficient and complete in comparison to competitive ligand syntheses. Hence, tetrapyridophenazine **3** had to be prepared as ligand monomer, and a ruthenium compound like **4** as the metal counterpart which already contains one mono-bidentate ligand like 2,2'-bipyridine at every ruthenium center.

Tetrapyridophenazine **3** was obtained from 1,10-phenanthroline via oxidation in 5,6-position followed by melt-condensation in ammonium acetate.[8] $[Ru(bpy)_1Cl_3]$ **4**, on the other hand, was prepared as a brownish-black, insoluble solid from 2,2'-bipyridine and $RuCl_3 \cdot 6H_2O$.



Scheme 1: Synthetic pathways for the preparation of ruthenium(II) coordination polymers **1**.

Prior to polymerization experiments, we tested the monomers **3** and **4** in some model experiments. The tetrapyridophenazine ligand monomer **3** was converted with two equivalents of $[Ru(bpy)_2Cl_2]$ **7**. Formation of the dinuclear species **8** was easily achieved by heating the mixture in aqueous ethanol (Scheme 2): a dark-red solution resulted after heating for several hours. The formed ruthenium complexes were precipitated quantitatively by adding an excess of aqueous NH_4PF_6. Redissolution of the representative product mixture in acetonitrile allowed recording NMR spectra. A full signal assignment could be done as is shown in Figure 3 for the ^1H NMR spectrum. One can see that only absorptions were detected which correspond to the pure dinuclear complex. Hence, **3** seemed to be a well-appropriate ligand monomer, and just heating the starting materials in ethanol/water was sufficient to achieve complete and homogeneous complex formation.



Scheme 2: Model conversion leading to the dinuclear ruthenium(II) complex **8**.

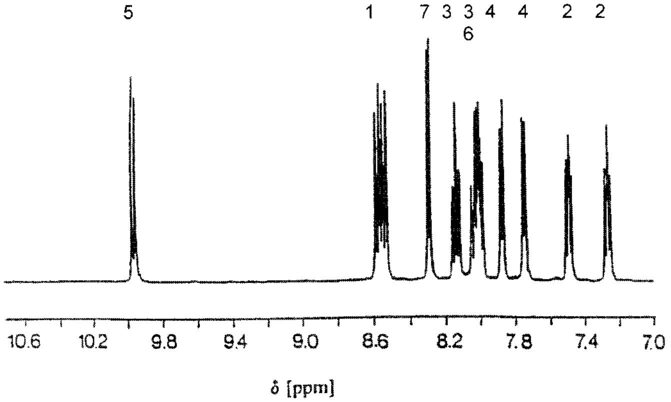
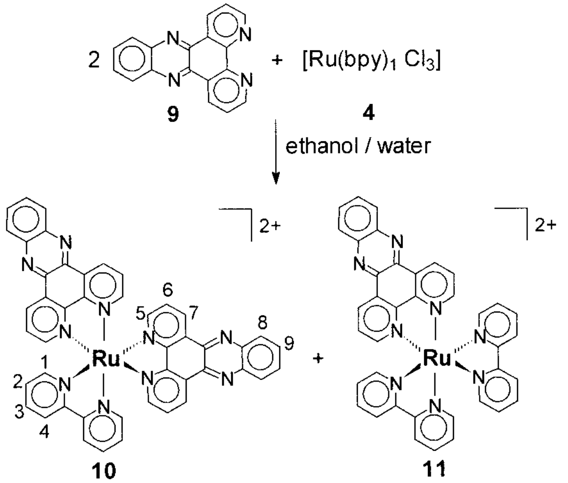


Figure 3: ^1H NMR analysis of the product mixture obtained according to Scheme 2.

The next question was whether $[Ru(bpy)_1Cl_3]$ **4** is an efficient metal counterpart. Both, purity and reactivity of **4** were checked via reaction with two equivalents of dipyridophenazine **9** in boiling ethanol / water (Scheme 3). After complete conversion, quantitative precipitation of the formed ruthenium complexes was achieved by counterion exchange. The representative product mixture gave NMR spectra like that shown in Figure 4. From the given signal assignment it is evident that all intense absorptions correspond to the desired complex $[Ru(bpy)_1(dppz)_2]Cl_2$ **10**. However, there are some additional absorptions of minor intensity in the spectrum.



Scheme 3: Model conversion leading to the mononuclear ruthenium(II) complex **10**.

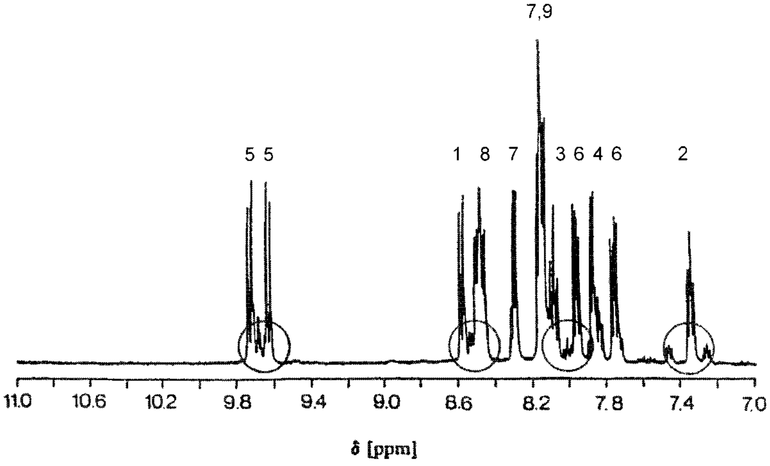


Figure 4: ^1H NMR analysis of the product mixture obtained according to Scheme 3.

These small signals could be assigned to approx. 5 - 10 % of $[Ru(bpy)_2(dppz)_1]Cl_2$ **11** in product **10**. Formation of **11** is possible either due to ligand exchange during the conversion according to

Scheme 3, or due to impurities already present in the [Ru(bpy)$_1$Cl$_3$] starting material **4**. As we did not observe any evidence for a ligand exchange during the synthesis of the dinuclear complex **8**, we concluded that **11** is the result of impurities in metal monomer **4**: here, some ruthenium centers seem to bear two 2,2'-bipyridine ligands instead of only one. Unfortunately, no way was found to remove this impurity from **4**. Therefore, and because [Ru(bpy)$_2$Cl$_2$]-centers should not lead to constitutional irregularities but only to end-groups in polymer **1**, we used the impure metal monomer **4** for first polymerization experiments according to Scheme 1.[8] Tetrapyridophenazine **3** was treated with equimolar amounts of [Ru(bpy)$_1$Cl$_3$] **4** in boiling ethanol/water. The formed complexes were precipitated via counterion exchange. The dried material could be redissolved completely in acetonitrile, and NMR spectra were recorded. A representative spectrum is shown in Figure 5A.

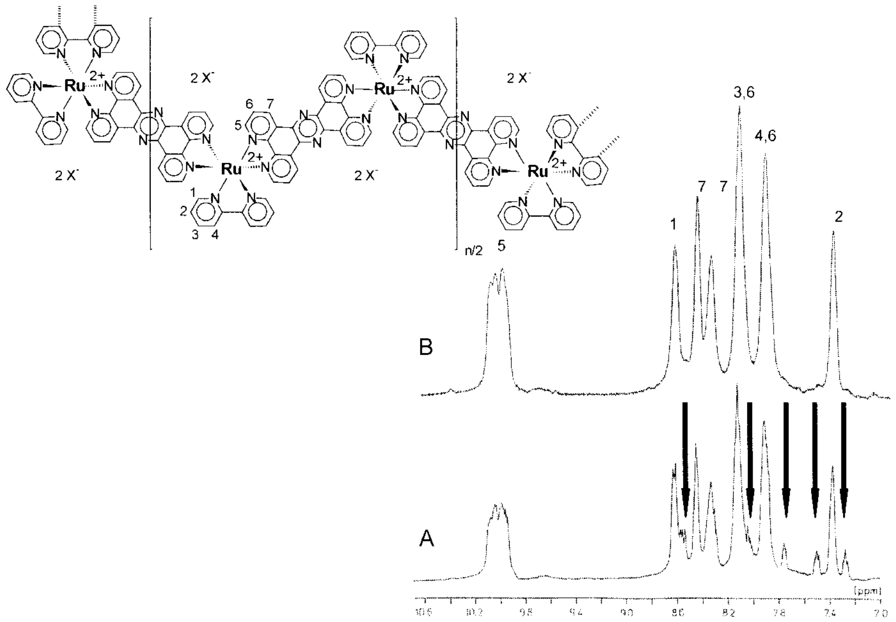
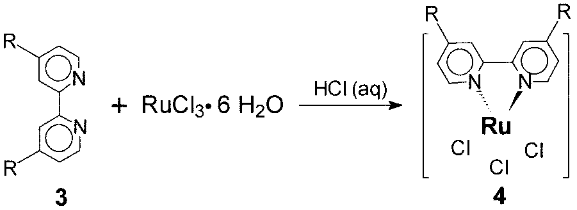


Figure 5: ^{1}H NMR spectra of polymers **1** prepared from impure (A) and pure (B) metal monomer, respectively, recorded in DMAc-d_8 at room temperature.

All intensive absorptions can be assigned to the inner-chain repeating units of a constitutionally homogeneous polymer **1**. But there are also the expected small absorptions caused by the

$[Ru(bpy)_2Cl_2]$ chain termini which were generated by the impurity in metal monomer **4**. Nevertheless, the formation of readily soluble, non-crosslinked materials **1** was considered as the desired proof of the whole synthetic concept. Therefore, we spent some more effort in optimizing the still imperfect metal monomer **4**. Its final purification proved to be impossible because **4** itself is a polymer which contains the $[Ru(bpy)_2]$ centers as defects or end groups. Hence, we must modify the reaction conditions applied for the synthesis of **4** (Scheme 4) systematically.



Scheme 4: Synthesis of metal monomer **4**; R = (**a**) H, (**b**) methyl, (**c**) phenyl and (**d**) adamantylmethylene.

Finally, a metal monomer **4** was obtained which gave readily soluble ruthenium(II) coordination polymers **1** whose NMR spectra did not show any evidence of $[Ru(bpy)_2]^{2+}$ end groups any more (Figure 5B).[9] Encouraged by this success, we broadened the scope of this synthesis to derivatives of **4** and **1** bearing (**b**) methyl, (**c**) phenyl or (**d**) adamantylmethylene substituents R attached to the 5,5'-positions of the 2,2'-bipyridine ligands. In all these cases, we succeeded in preparing high-molecular-weight polymers – provided optimized conditions were applied for the synthesis of metal-monomers **4**, and provided that a precise 1:1 molar ratio of the ligand- and the metal monomer was used in polymer synthesis.[10] As an example, Figure 6 shows ^1H NMR spectra of phenyl-substituted coordination polymers **1c**, once prepared from impure (A) and once prepared from a very pure metal monomer **4c** (B). While in the former case there are absorptions of end-groups, these signals are absent in the latter spectrum. Due to the lack of end-group absorptions, NMR spectroscopy indicates polymers **1** of very high molar masses. However, NMR spectroscopy cannot provide any quantitative information about the average chain lengths when endgroup absorptions are absent. Therefore, viscosity- and scattering experiments were performed.

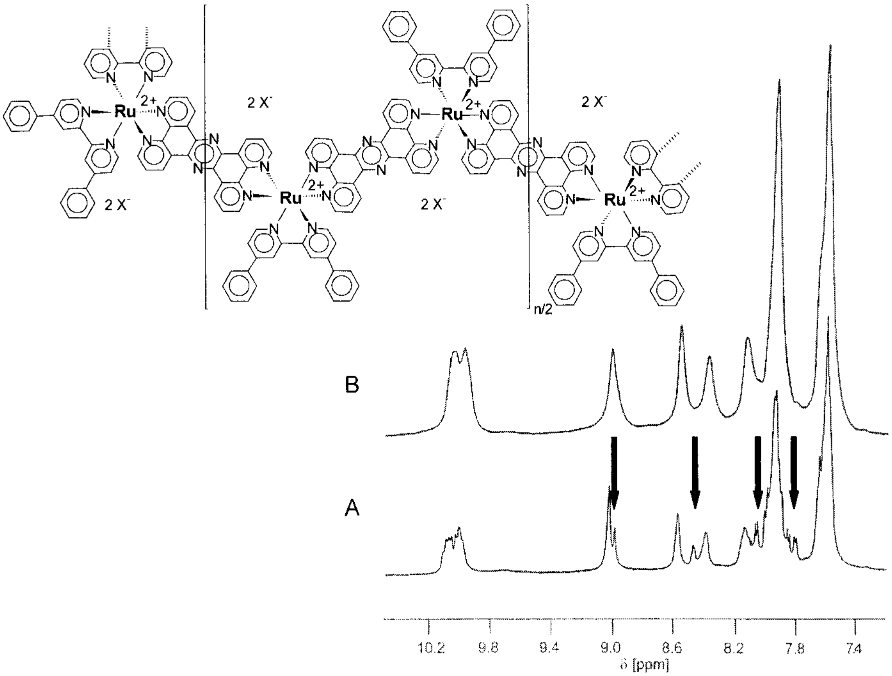


Figure 6: ^{1}H NMR spectra of polymers **1c** prepared from impure (A) and pure (B) metal monomer **4c**. The spectra were recorded in DMAc-d_8 at room temperature.

In a first study, we tried to determine the intrinsic viscosities of polymers **1** as a measure of their hydrodynamic volumina. In DMAc solution, however, an intense polyelectrolyte effect was observed, *i.e.* a maximum of η_{sp}/c_P at low polymer concentration, c_P (Figure 7). This maximum is due to the increasing intermolecular Coulomb repulsion of the polyelectrolyte molecules **1** when ionic strength decreases upon dilution. To suppress this undesired effect, NH_4PF_6 was added to the solutions until linear Huggins plots resulted (Figure 7C). The thus determined values of the intrinsic viscosity of $[\eta] = 10 - 25$ mL·g^{-1} were rather low and pointed towards short oligomers rather than towards long polymer chains. However, there was a second explanation possible for such low values of $[\eta]$. This is a very compact shape of the coiled macromolecules **1**. Here as well, the materials would show very small hydrodynamic volumina. In order to make clear this point, small-angle X-ray scattering (SAXS) was carried out in salt-containing DMA solution (Figure 8).

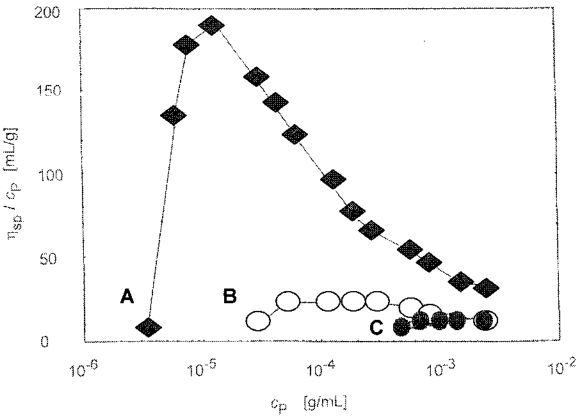


Figure 7: Huggins plots of ruthenium(II) coordination polymers, obtained in salt-free (A,B) and NH_4PF_6-containing DMAc solution at room temperature.

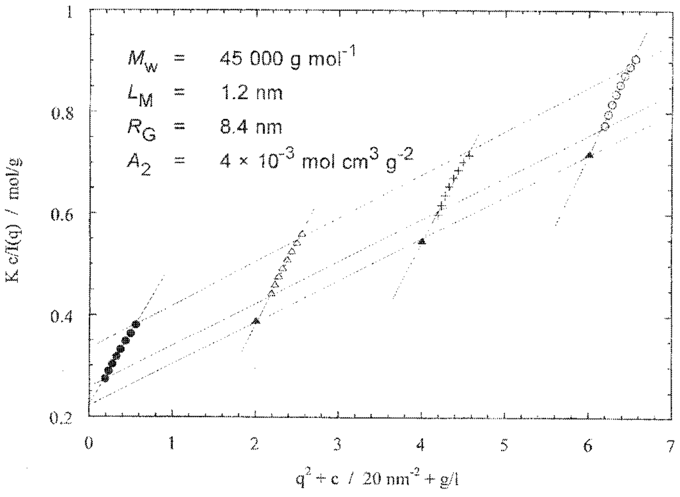
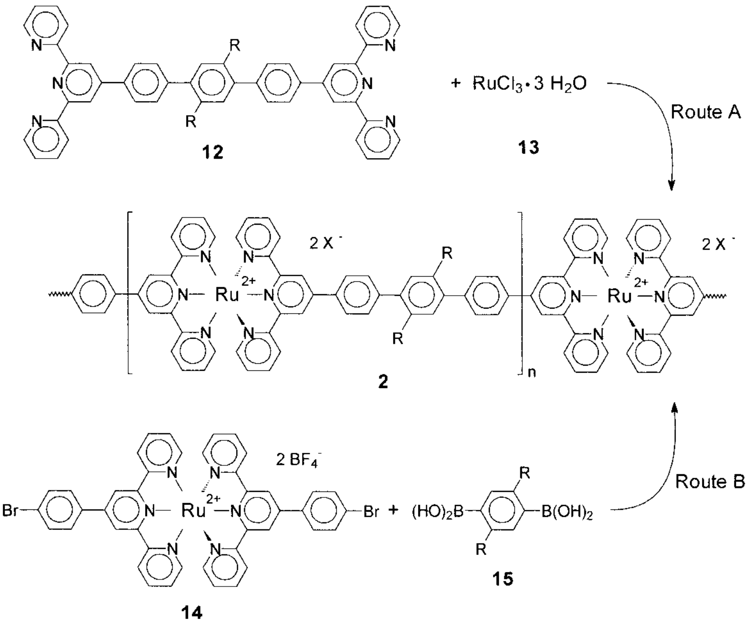


Figure 8: SAXS investigation of a ruthenium(II) coordination polymer **1c** in DMAc solution.

Evaluation of the scattering data according to the Zimm procedure gave a weight-average molar mass of $M_w \approx 45.000$ for high-molecular-weight materials **1c**. This corresponds to approx. 50

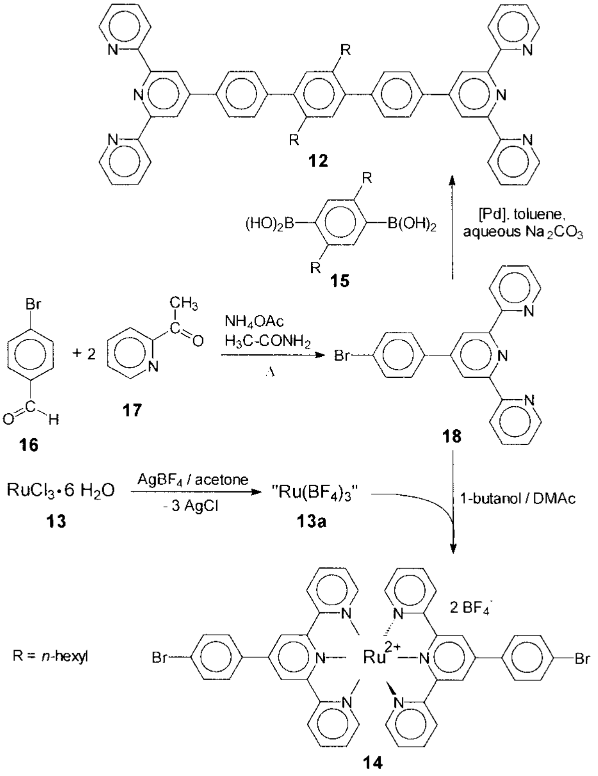
repeating units per chain. On the other hand, the radius of gyration of this material, R_G = 8.4 nm, proved to be very low. This observation supports our assumption that polymers **1** form very compact coils.

Application of other solvents for viscosity and SAXS studies did not lead to an increase of the hydrodynamic radii or of the radii of gyration. This proves the rigidity of the chains: once formed within a specific chain conformation, the macromolecule's shape is maintained due to the ladder-like constitution independently of the quality of the solvent. Unfortunately, this dense coiling of the individual chains leads to a very inefficient intramolecular entanglement which results in rather poor mechanical properties: The polymers form brittle films only. Good film-forming ability, however, is a pre-requirement for many potential applications of such materials. In order to improve the mechanical properties of coordination polymers, more elongated chains must be realized. Therefore, further coordination polymers were designed (Scheme 5).[11,12]



Scheme 5: Synthetic strategies for the preparation of rodlike coordination polymers **2**.

Here, really rodlike macromolecules should result. An extended shape of ruthenium(II) coordination polymers can be achieved by using bis-tridentate ligand monomers whose chelating moieties are connected in a 180° fashion by rigid bridges. We decided to use terphenyl moieties as bridging units which were additionally decorated by flexible *n*-hexyl side chains to ensure solubility of the resulting polymers **2** despite of their rodlike shape. For the synthesis of these polymers, again, two competitive strategies exist. On the one hand, complex formation can lead to the desired polymers (route A in Scheme 5). Alternatively, polymer preparation is possible via ligand formation (route B in Scheme 5). In this specific case, it was open which route might be the best. Therefore we decided to test both possibilities. All required monomers **12** – **15** are easily available according to Scheme 6.



Scheme 6: Synthesis of monomers for rodlike coordination polymers **2**.

Using *p*-bromobenzaldehyde **16** and 2-acetylpyridine **17**, terpyridine derivative **18** was obtained in good yields. Compound **18** can be converted, in a Pd-catalyzed Suzuki condensation, with benzene-1,4-diboronic acid **15** into ligand monomer **12**. Alternatively, conversion of **18** with activated ruthenium(III) **13a** leads to monomer **14** which contains the preformed $[Ru(tpy)_2]^{2+}$ complex. Then, we tried to synthesize polymers **2** first via complex formation (route A): heating equimolar amounts of pure bis-terpyridine ligand monomer **12** and activated ruthenium(III) **13a** in DMAc followed by precipitation of the formed material via counterion exchange resulted in a dark red, fibrous material which could be redissolved easily and completely in, for example, DMAc or DMSO. Its ^1H NMR spectrum shows the expected strong absorptions of the inner-chain repeating units of **2** as is evident from the signal assignment given in Figure 9A. No endgroup absorptions were found in these spectra.

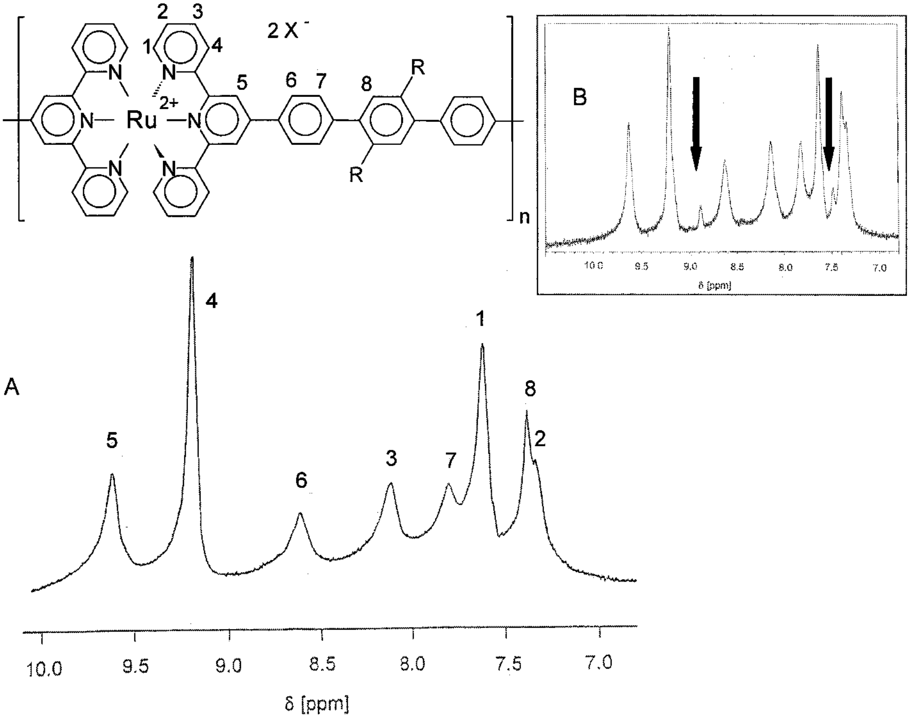


Figure 9: ^1H NMR spectra of polymers **2** (prepared according to Scheme 5, route A), recorded in DMAc-d_8 at room temperature.

If the 1:1 ratio of the two comonomers **12** and **13a** was not adjusted properly, on the other hand, additional small absorptions appear in the spectrum (Figure 9B) which correspond to chain termini. This observation allows to conclude that in Figure 9A the end-group absorptions are not covered by strong absorptions of the inner-chain repeating units but are really absent. Hence we were sure that – under optimum reaction conditions – really high-molecular materials **2** are available via the complex-formation route A. The competitive ligand-formation route B, on the other hand, proved to be inappropriate. This is because we could not find a solvent which both, readily dissolves the growing polymer species and does not affect the Pd-catalyzed Suzuki coupling. Therefore, either side reactions or precipitation of the growing chains prevented the formation of long chains **2** by this latter strategy.

In the next step, some viscosity studies were performed in DMAc solution in order to get more detailed information about the chain lengths achieved in polymers **2**. Without added salt, again, we observed a very pronounced polyelectrolyte effect, especially for high-molecular-weight materials **2** (Figure 10A).

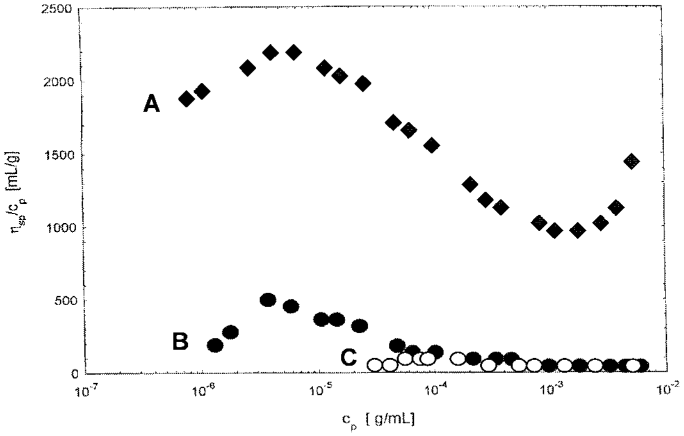


Figure 10: Huggins plots of ruthenium(II) coordination polymers **2** of high (A) and low (B) molecular weight, respectively, and of a high-molecular-weight coiled polymer **1** (C), obtained in salt-free DMAc solution at room temperature.

But even low-molecular-weight rods **2** (Figure 10B) show a much more pronounced polyelectrolyte effect as compared to the high-molecular-weight but coiled polymers **1** (Figure

10C). These studies prove that the well-known polyelectrolyte effect is not the result of coil expansion upon dilution – as discussed in many papers – but is due to intermolecular Coulomb interactions of the charged chains and hence electrostatic in nature. To support the rodlike shape and the considerable chain length of coordination polymers **2**, viscosity measurements were carried out in salt-containing DMAc. Here, the long-range electrostatic interactions are screened, and the real hydrodynamic volume of the rodlike chains can be estimated (Figure 11).

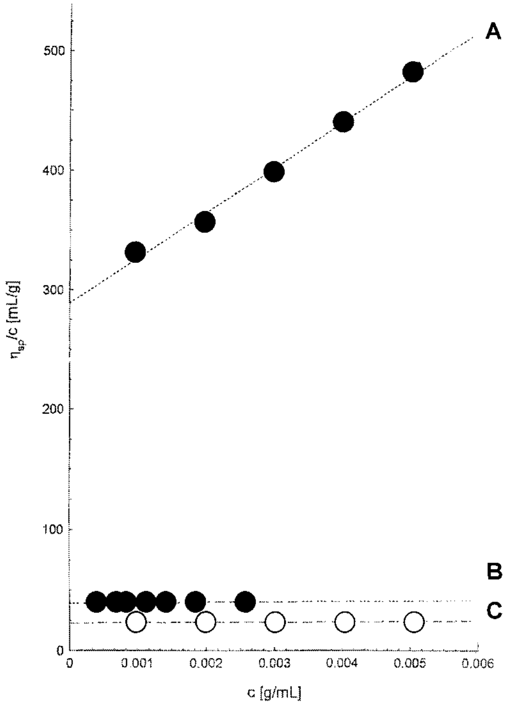
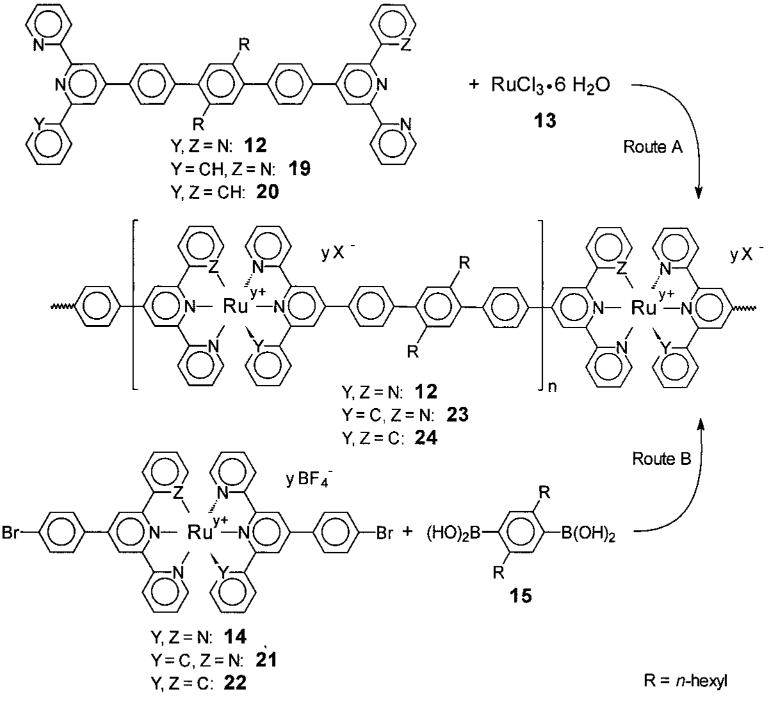


Figure 11: Huggins plots of ruthenium(II) coordination polymers **2** of high (A) and low (B) molecular weight, respectively, and of a high-molecular-weight coiled polymer **1** (C), obtained in NH_4PF_6-containing DMAc solution at room temperature.

These experiments reconfirmed the very high molar masses of the rods **2**: an intrinsic viscosity of $[\eta] \approx 300$ mL·g^{-1} allows estimating the average degree of polymerization to be of the order of $P_n \approx 30 - 50$. For shorter rods **2**, $[\eta]$ is considerably lower but still higher than for high-molecular-weight but coiled systems **1**. This shows the tremendous consequences of a rod-like shape not only for the properties in bulk but also for those in solution. To conclude, the dark-red polymer **2** was the desired coordination compound with excellent film-forming and mechanical properties.

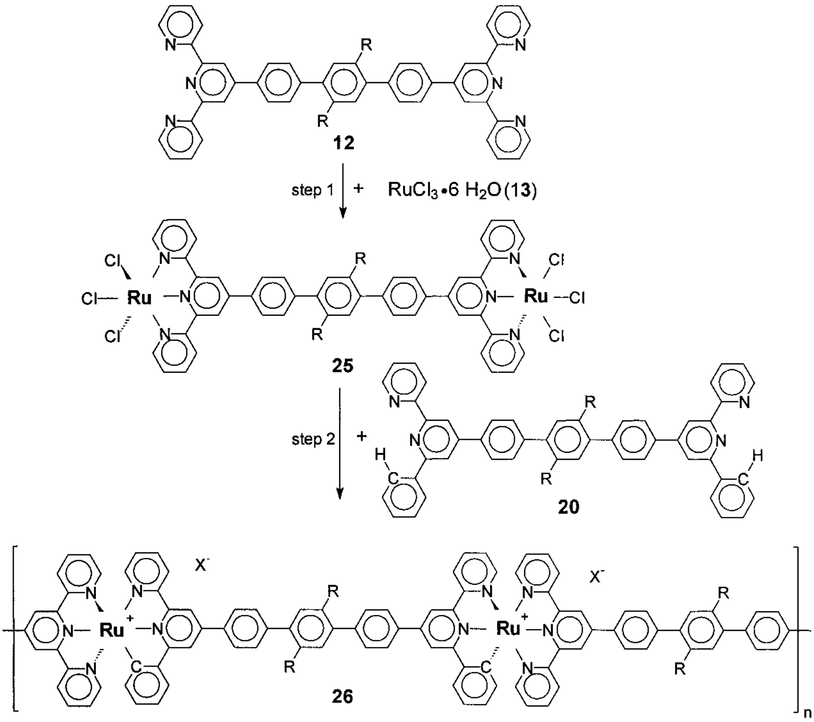
In contrast to our expectations, however, the UV-vis absorption behavior of the ruthenium(II) coordination polymers presented so far is nearly unchanged with respect to that of mononuclear reference complexes. For applications as, for example, light-harvesting materials the polymers should have a broad absorption range in order to take advantage of an as large part of the sunlight spectrum as possible. Therefore, we looked for possibilities to shift λ_{max} to longer wavelengths – but without loosing the just realized mechanical properties simultaneously.

It was known that the MLCT band of octahedrally coordinated ruthenium(II) polyimine complexes shifts towards longer wavelengths when one or even two Ru-N bonds are replaced by Ru-C bonds. Thus we decided to prepare polymers like **23** and **24** (Scheme 7).



Scheme 7: Synthetic strategies leading to ruthenium(II) coordination polymers **2**, **23** and **24**.

Their synthesis should be quite similar to that of polymers **2**, *i.e.*, either via a ligand-formation- or a complex-formation strategy (routes A and B, respectively, in Scheme 7). Because of the good results of the complex-formation strategies in all above studies, we focused our efforts on syntheses according to route A. As the most simple target polymer, copolymer **26** was selected. It contains two different ligand monomers in an alternating fashion, *i.e.*, **14** and **20** (Scheme 8). These monomers are available in analogy to the synthesis of **12** shown in Scheme 6, however, using acetophenone instead of 2-acetylpyridine. For the subsequent synthesis of polymer **26**, a two-step strategy was applied (Scheme 8).



Scheme 8: Synthesis of coordination polymer **26**

First, the bis-terpyridine ligand monomer **12** was treated with $RuCl_3 \cdot 6\ H_2O$ **13**, leading to the new dimetallic metal monomer **25**, which can be activated in the known manner subsequently. Then, the activated **25** is treated with the new ligand monomer **20** to give the desired alternating copolymer **26**. After careful optimization of the reaction conditions we obtained **26** as a violet fibrous, readily film-forming material. It gives a quite complicate NMR spectrum due to the loss of symmetry. Using reference spectra from low-molecular-weight and oligomeric model compounds, however, we were able to assign all observed absorptions to the inner-chain repeating units.[13] Hence we conclude that a constitutionally homogeneous polymer **26** is formed. Due to the lack of endgroup absorptions and the high viscosity of its solutions we conclude, moreover, that very long chains were obtained. Finally, we studied the optical and electronic properties of polymers **2** and **26**. The UV-vis spectra, for example, show that **26** absorbs at clearly longer wavelengths as compared to the polymers **2** which do not have Ru-C bonds (Figure 12).

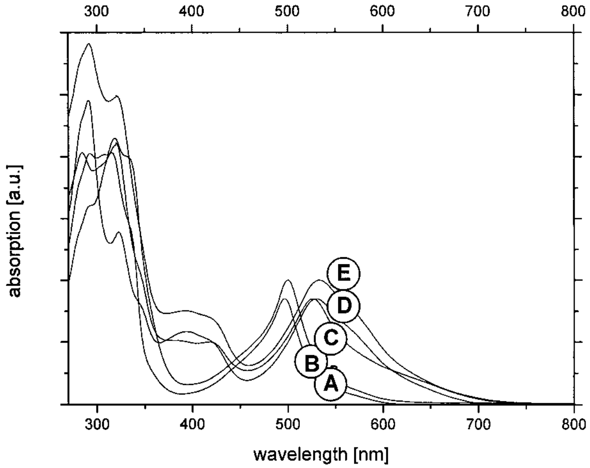


Figure 12: UV-vis spectra of ruthenium(II) complexes: dimeric complex 2 (A), high-molecular weight polymer **2** (B), monomeric (C), dimeric (D) and polymeric (E) complexes **26**, recoded in DMSO solution at room temperature.

Conclusions and Outlook

Highly efficient routes have been presented for the synthesis of soluble, constitutionally well-defined ruthenium(II) coordination polymers of high molar masses. The polymers show the classic polyelectrolyte effect when studied in salt-free solution. When salt is added, determination of the intrinsic viscosities is possible, and also SAXS studies can be carried out. The collected data point towards densely coiled chains in the case of polymers **1** which are not sufficiently entangled for good mechanical properties. Much better performance was achieved in the case of their rodlike counterparts such as **2** and **26**.

Acknowledgement

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