# Synthesis and Properties in Solution of Rodlike, 2,2′:6′,2″-Terpyridine-Based Ruthenium(II) Coordination Polymers

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ABSTRACT: Rodlike ruthenium(II) coordination polymers have been prepared via the conversion of 4,4″-bis(2,2′:6′,2″-terpyridine)-2′,5′-dihexyl-*p*-terphenyl and an appropriately reactive ruthenium(III) species in 1-butanol/DMA. The diamagnetic polymers readily dissolve in polar organic solvents, and their homogeneous constitution could thus be proven and their degrees of polycondensation could be estimated to be $P_n \geq 30$, using $^1H$ and $^{13}C$ NMR spectroscopy. The Pd-catalyzed polycondensation of bis[4′-(*p*-bromophenyl)-2,2′:6′,2″-terpyridine]ruthenium(II) tetrafluoroborate and 2,5-dihexylbenzene-1,4-diboronic acid, on the other hand, which should lead to a constitutionally identical polymer, only resulted in oligomers under all tested conditions. The intrinsic viscosity [$\eta$] of the high-molecular-weight polymers (determined in 0.02 M $NH_4PF_6$/DMA) is of the order of 300 mL $g^{-1}$. In salt-free DMA solution and thus at low ionic strengths, the polymers display the characteristic polyelectrolyte behavior in viscosity experiments which becomes more and more pronounced with increasing $P_n$. The UV−vis absorption spectra recorded in DMA solution do not show any evidence of intramolecular electronic interactions of the metal centers along the polymer chains: on the contrary, the coordination polymers behave like sequences of electronically independent ruthenium(II) complexes.

## Introduction

Soluble, constitutionally well-defined transition-metal coordination polymers, that is, polymers whose main chains are held together by transition-metal complexes and thus by coordinative bonds, are of considerable current interest because of their unusual electronic, photooptical, magnetic, and catalytic properties.[1−11] Moreover, such self-assembled multinuclear complexes are key compounds of modern supramolecular chemistry and have been shown, for example, to serve as useful building blocks for well-defined multilayer systems.[12,13] Last but not least, if coordination polymers became available that (i) are sufficiently stable in solution, (ii) have a conformationally rigid backbone, and (iii) contain charged metal complexes, these polymers could develop into important model systems for the exploration of polyelectrolyte behavior: the quantitative understanding of the properties in a solution of common flexible-chain polyelectrolytes is a difficult task since both the chain conformation and the strength of the intermolecular Coulomb interactions are functions of the ionic strength and since the actual contribution of the respective parameter to the observed properties is hard to determine. Rigid-chain polyelectrolytes, on the other hand, will retain their chain conformation regardless of the respective ionic strength. Hence, only the intermolecular Coulomb interactions are variables here, and this kind of polymeric electrolyte thus allows a more reliable comparison of experimental data with theoretical predictions.[14−21] For this reason, several naturally occurring as well as synthetic organic polyelectrolytes of rigid-chain conformation have been studied during recent decades.[22−25] The potential of transition-metal coordination polymers in this field, on the other hand, has been widely ignored up to now because of the lack of appropriate systems. Only in 1994, Chen and Archer reported for the first time on the synthesis and the properties in solution of some charged Schiff-base coordination polymers.[26] Two years later, the first soluble, high-molecular-weight ruthenium(II) coordination polyelectrolytes **1a**−**d** were developed in our group.[27] All these polymers have randomly coiled main chains and display the typical polyelectrolyte behavior in salt-free solution—despite the fact that the former Schiff-base systems still have a certain chain flexibility while the latter polymers **1a**−**d** have a ribbonlike and thus quite rigid backbone. To further deepen the knowledge of the structure−property relationship of such rather unusual coordination polyelectrolytes and to make available more experimental information needed for the development of a powerful theoretical model that can also quantitatively describe their properties in solution, we are interested in the synthesis of further stiff-chain ruthenium(II) coordination polymers which, however, have a rigid-rod-like backbone instead of a coiled one.

Taking into account the (pseudo)octahedral coordination geometry of ruthenium−polyimine complexes, rodlike coordination polyelectrolytes should result when appropriately designed bis-tridentate chelating monomers are catenated by ruthenium(II) centers.[5,12,28−31] Thus, polyelectrolytes of the general structure **2** were our target structures provided that bridging units Y can be found which ensure (i) rigidity, (ii) rodlike shape, and (iii) a solubility of the polymers that is high enough for the analysis of their constitution, their degrees of polymerization, and their properties in solution.

In the present paper, we discuss the specific advantages of using 2′,5′-dihexyl-*p*-terphenylene as the bridging unit Y. Moreover, we present the results of two competitive synthetic pathways developed for the preparation of the thus chosen target polymer **2a** and provide a first insight into its properties in solution.

## Strategy

For the selection of an appropriate bridging unit Y and thus for establishing the constitution of the desired

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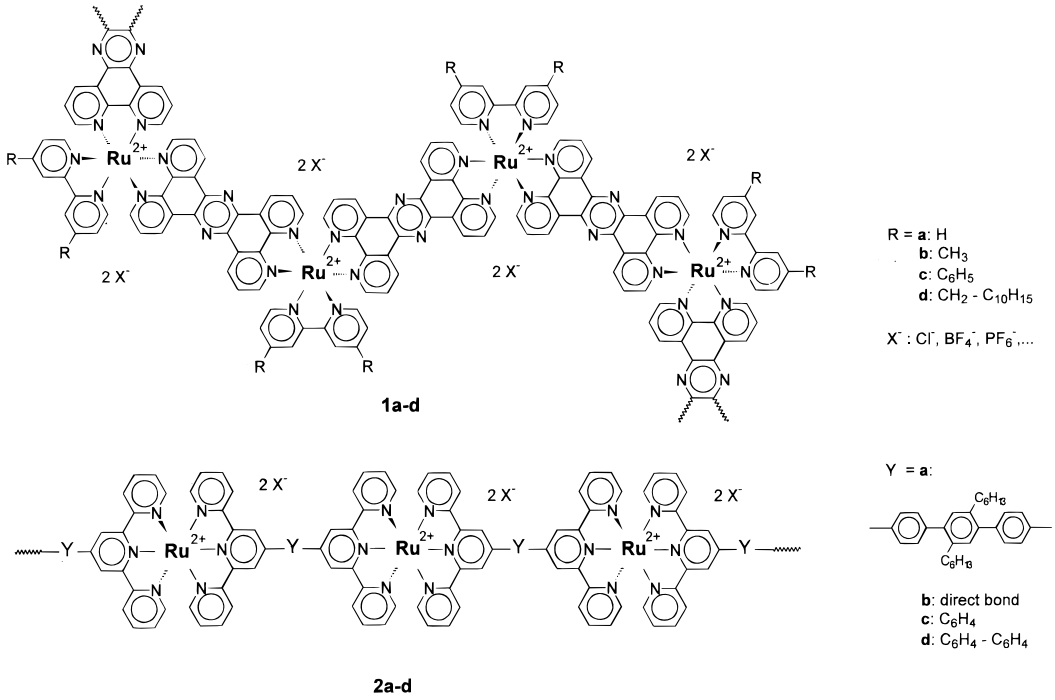
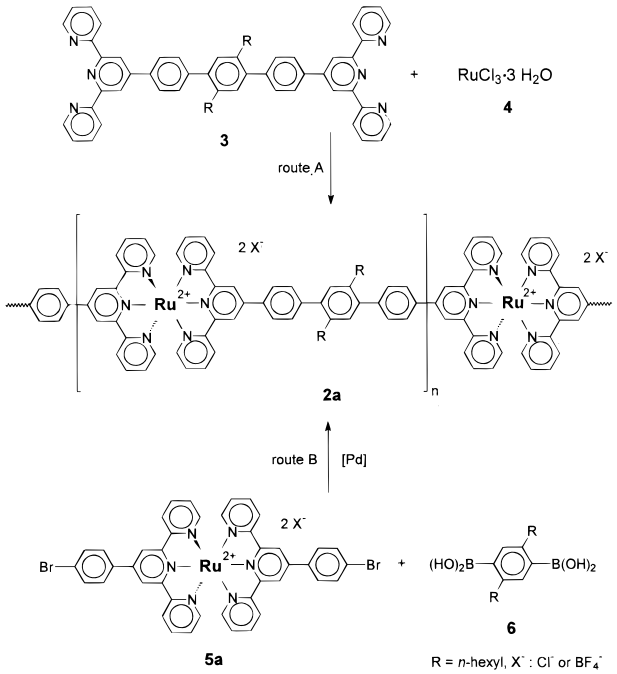



**Figure 1.** Formulas of the coiled coordination polymers **1a**−**d** and their rodlike counterparts **2a**−**d**.

coordination polyelectrolyte **2**, we had to take into consideration geometric, synthetic, and solubility aspects. First, to ensure the rodlike shape of **2**, the two 2,2′:6′,2″-terpyridine (tpy) moieties of the ligand monomers required for its synthesis must be connected via their 4′-positions. The unit Y serving as the bridge might be either a direct bond (leading to polymer **2b**) or a subunit which itself has a conformationally rigid-rodlike shape such as a *p*-(oligo)phenylene. The latter would lead to polymers such as **2c** or **2d** (Figure 1). For synthetic as well as for solubility reasons, we decided to use a 4,4″-*p*-terphenylene bearing two solubilizing *n*-hexyl side chains attached to the central phenylene moiety as the bridging unit. The synthesis of the thus chosen target polymer **2a** was expected to be possible, on one hand, via a "complex-formation strategy" using 4,4″-bis(2,2′:6′,2″-terpyridine)-2′,5′-dihexyl-*p*-terphenyl (**3**) and $RuCl_3 \cdot 3H_2O$ (**4**) as the monomers (Scheme 1, route A). On the other hand, a constitutionally identical polymer **2a** should be available via Pd-catalyzed polycondensation of bis[4′-(*p*-bromophenyl)-2,2′:6′,2″-terpyridine]ruthenium(II) tetrafluoroborate (**5a**) and 2,5-dihexylbenzene-1,4-diboronic acid (**6**) and hence via a "ligand-formation strategy" (Scheme 1, route B).

**Scheme 1**

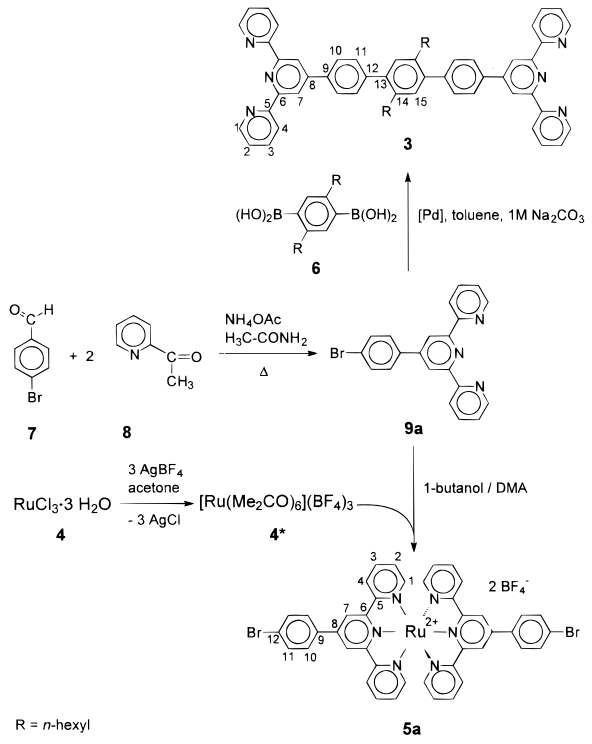



## Results and Discussion

**Monomer Synthesis**. The key monomer required for the planned polymer synthesis according to route A, 4,4″-bis(2,2′:6′,2″-terpyridine)-2′,5′-dihexyl-*p*-terphenyl (**3**), was prepared in a two-step procedure according to Scheme 2. In the first step, *p*-bromobenzaldehyde (**7**) and *o*-acetylpyridine (**8**) were heated in a mixture of acetamide and ammonium acetate.[32] The intermediate, 4′-(*p*-bromophenyl)-2,2′:6′,2″-terpyridine (**9a**), was obtained in about 20% yield from this process and subsequently treated with 2,5-dihexylbenzene-1,4-diboronic acid (**6**)[33] using a palladium complex as catalyst. Monomer **3** was obtained from this latter conversion in almost quantitative yields when the reaction was performed in a heterogeneous mixture of toluene and 1 M aqueous $Na_2CO_3$, using 1 mol % of $[Pd(PPh_3)_4]$ as the precursor complex of the catalytically active Pd species.[33−35]

Bis[4′-(*p*-bromophenyl)-2,2′:6′,2″-terpyridine]ruthenium(II) tetrafluoroborate (**5a**), on the other hand, was the required starting material for the synthesis of polymers **2a** according to route B. It was obtained as a deep red solid in nearly quantitative yields via conversion of **9a** with the appropriately reactive ruthenium(III) complex **4*** which was prepared by refluxing $RuCl_3 \cdot 3H_2O$ (**4**) and a 3-fold molar excess of $AgBF_4$ in acetone.[36] The constitution of monomers **3**, **5a**, and **6** as well as of intermediate **9a** was verified using $^1H$ and $^{13}C$ NMR spectroscopy. The purity of monomers **3**, **5a**, and **6** was estimated to be >98% ($^1H$ NMR).

**Scheme 2**




**Model Investigations.** Model studies were carried out on low-molecular-weight reference compounds to develop optimized reaction conditions for the planned polymer syntheses via routes A and B. For route A, conditions must be found which (i) ensure the nearly quantitative formation of the $[Ru(tpy)_2]^{2+}$ motif and (ii) reliably prevent the formation of defect structures such as **A** or **B** (Figure 2) in which the terpyridine ligands act as *bi*dentate ligands only and thus will bend the polymer main chains and destroy the rodlike shape of **2a**. For route B, on the other hand, a coupling medium had to be found which ensures (i) the solubility of both monomers as well as of the formed products, (ii) practically quantitative aryl−aryl bond formation, and (iii) inertness of the ruthenium(II) complexes.

To find out the optimized conditions for the formation of the $[Ru(tpy)_2]^{2+}$ motif, first, 2,2′:6′,2″-terpyridine (**9b**, Z = H) was converted with $RuCl_3 \cdot 3H_2O$ (**4**) under various conditions which were known from the literature to give $[Ru(tpy)_2]X_2$ derivatives in good yields (Scheme 3). A nearly quantitative formation of model complex **5b** was achieved when the conversion of **9b** and **4** was carried out in a mixture of DMF and water. In this case, neither the $^1H$ nor the $^{13}C$ NMR spectra showed any evidence of remaining starting materials or of side products in which, for example, the 2,2′:6′,2″-terpyridine ligands act as bidentate ligands only. Unfortunately, this very convenient procedure proved to

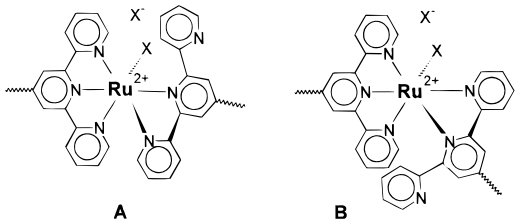
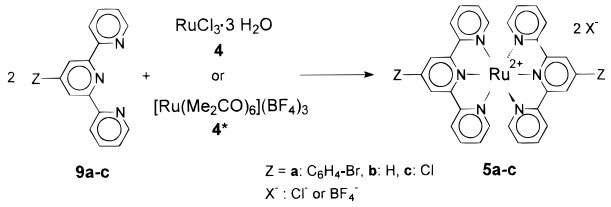



**Figure 2.** Possible defect structures that may lower the persistence length of polymers **2**.

**Scheme 3**




be unappropriate for the homogeneous formation of other model complexes such as **5c** (Z = Cl) or **5a** (Z = $C_6H_4Br$). Just after the transformation of $RuCl_3 \cdot 3H_2O$ (**4**) into the activated complex **4***, all absorptions observed in the $^1H$ and $^{13}C$ NMR spectra of representative product mixtures obtained via conversion of **4*** and **9c**/**9a** in 1-butanol/DMA-solution could be assigned to the desired complexes **5c**/**5a**. As an example, Figure 3A displays the aromatic region of a typical $^1H$ NMR spectrum of complex **5a** obtained in this manner. On the basis of this result, ruthenium(III) derivative **4*** and 1-butanol/DMA were chosen as the metal monomer and solvent system, respectively, for the following polymer syntheses according to route A.

The second series of model reactions was performed to assess whether the Pd-catalyzed polycondensation reaction of the bis(*p*-bromophenyl)-substituted ruthenium(II) complex **5a** and benzenediboronic acid derivative **6** (Scheme 1, route B) is an alternative to the synthesis of polymer **2a** via route A. In analogy to recent studies on the Pd-catalyzed polycondensation of ferrocene-containing monomers,[37] monomer **5a** was treated with 2 equiv of benzeneboronic acid **10** in the presence of various Pd catalysts, solvents, and bases (Scheme 4). Again, the success of the respective experiment was

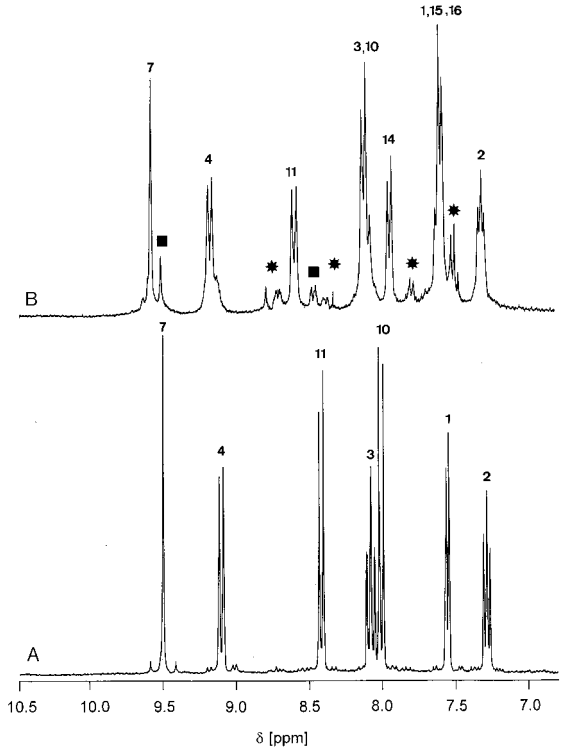
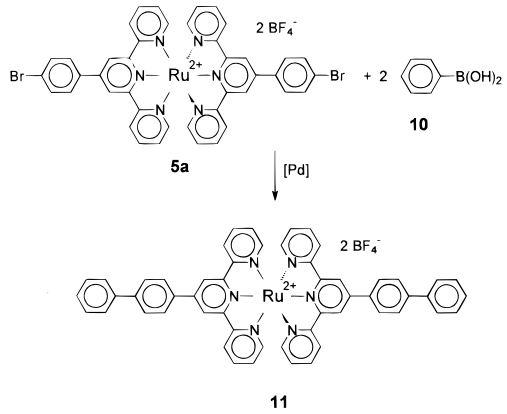



**Figure 3.** Aromatic regions of the $^1H$ NMR spectra of (A) the bis(*p*-bromophenyl)-substituted monomer **5a** and (B) a representative product mixture obtained via Pd-catalyzed condensation according to Scheme 4, recorded in DMSO-$d_6$ at room temperature. The signal assignment is according to the numbering specified in Scheme 2. See text for details.

**Scheme 4**

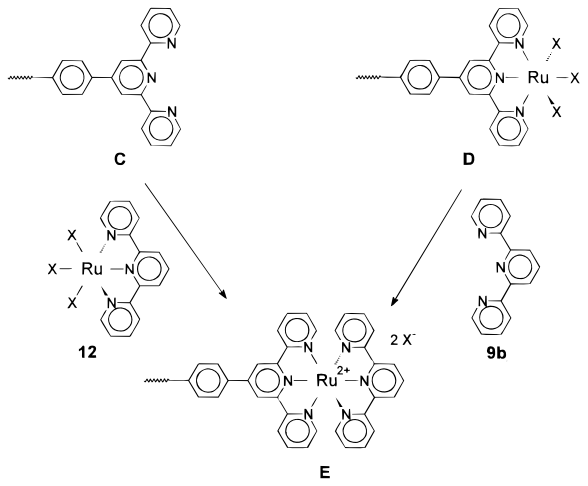



determined by analyzing the NMR spectra of representative product mixtures. It soon became evident that the low solubility of the charged ruthenium complex **5a** in toluene or THF and thus in solvents that are well-known to give top results elsewhere (≥98% conversion)[33−35] prevented their use for the present condensation reaction. Therefore, further reaction media were tested which give somewhat lower yields in general (<95%) but readily dissolve starting materials and products. Finally, the mixture of DMA, triethylamine, and [Pd(dppf)$Cl_2$] {dppf = 1,1′-bis(diphenylphosphino)-ferrocene} was found to be the most promising system for the model conversion shown in Scheme 4. Under these conditions, complex **11** was formed in approximately 90% yield. Figure 3B displays the aromatic region of a representative $^1$H NMR spectrum of the product mixture obtained under these conditions. All intensive absorptions observed in this spectrum correspond to the desired model complex **11**. However, there are also clearly detectable further small absorptions which presumably originate from unreacted starting materials [absorptions (■) at $\delta$ = 8.4 and 9.5 ppm in Figure 3B, for example] and from side products [absorptions (★) at $\delta$ = 7.5, 7.8, and 8.35−8.90 ppm in Figure 3B, for example]. Most of these side products are presumably formed by dehalogenation of **5a**, by hydrolysis of **10**, and by the decomposition of the Pd catalyst, but also side reactions of the $[Ru(tpy)_2]^{2+}$ motif cannot be excluded definitively. Since a coupling reaction with an approximately 90% conversion will result in coordination polymers **2a** having degrees of polycondensation of only $P_n \approx 10$, it was tried to further optimize the coupling conditions for the Pd-catalyzed condensation reaction. Unfortunately, we have not succeeded in finding such improved conditions yet.

Finally, some reference compounds were prepared which were needed for the characterization of polymers **2a** using NMR spectroscopy.[38] In particular, the reliable assignment of absorptions of potential chain termini like **C** and **D** (Scheme 5) was essential because it allows an estimate of the achieved values of $P_n$ via $^1$H NMR end-group analysis. This method was of importance here because most conventional methods usually applied for the determination of the molar masses such as osmometry, size-exclusion chromatography, or light scattering can hardly be used in the case of the intensely colored polyelectrolytes **2a**.

For chain-terminus **C**, ligand monomer **3** is the appropriate model compound. Its $^1$H and $^{13}$C NMR spectra are shown in Figures 4A and 5A, respectively, together with the full signal assignment. A somewhat

**Scheme 5**




more problematical end group is structure **D** in which a ruthenium species of unknown constitution forms the chain terminus. Here, characteristic absorptions cannot be expected in the polymer spectra, and thus their quantitative evaluation will be impossible. Therefore, prior to the end-group analysis, potential chain termini **D** had to be converted into end groups **E** via reaction of chain termini **D** with 2,2′:6′,2″-terpyridine (**9b**) (Scheme 5). Accordingly, the dinuclear complex **13** was the necessary model compound for metal-containing end groups **E**. For its synthesis according to Scheme 6, first [Ru(tpy)$Cl_3$] (**12**)[39] was prepared by refluxing a 1:1 mixture of $RuCl_3 \cdot 3H_2O$ (**4**) and 2,2′:6′-2″-terpyridine (**9b**) in dry ethanol. Subsequently, **12** was transformed into the reactive complex **12***, and finally, the reaction of 2 equiv of **12*** and 1 equiv of ligand monomer **3** in

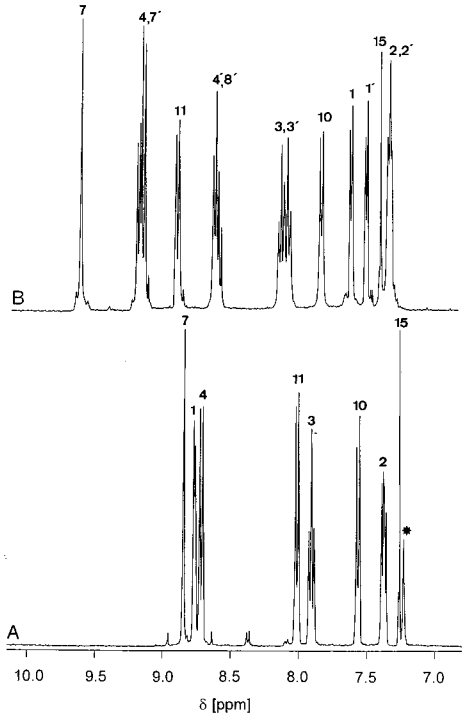
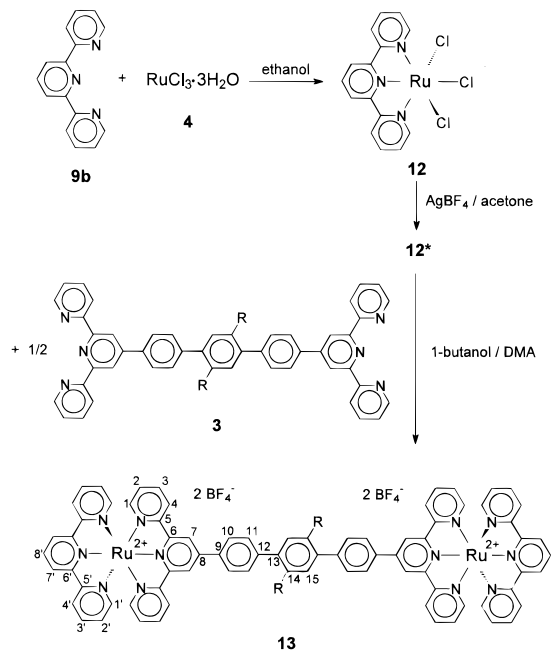



**Figure 4.** Aromatic regions of the $^1$H NMR spectra of (A) ligand monomer **3** and (B) of a representative sample of the dinuclear complex **13** obtained via the conversion according to Scheme 6, recorded in $CDCl_3$ (A, ★) and DMSO-$d_6$ (B), respectively, at room temperature. The signal assignment is according to the numbering specified in Scheme 6.

**Scheme 6**




1-butanol/DMA gave the dinuclear complex **13**. Figure 4B shows the aromatic region of the $^1$H NMR spectrum of the raw product isolated by pouring the whole reaction mixture into water. Figure 5B shows the corresponding $^{13}$C NMR spectrum, recorded in DMSO-$d_6$. These spectra make clear that a nearly quantitative conversion was reached under the chosen conditions: no evidence is found of remaining starting materials or the formation of side products. Moreover, the given signal

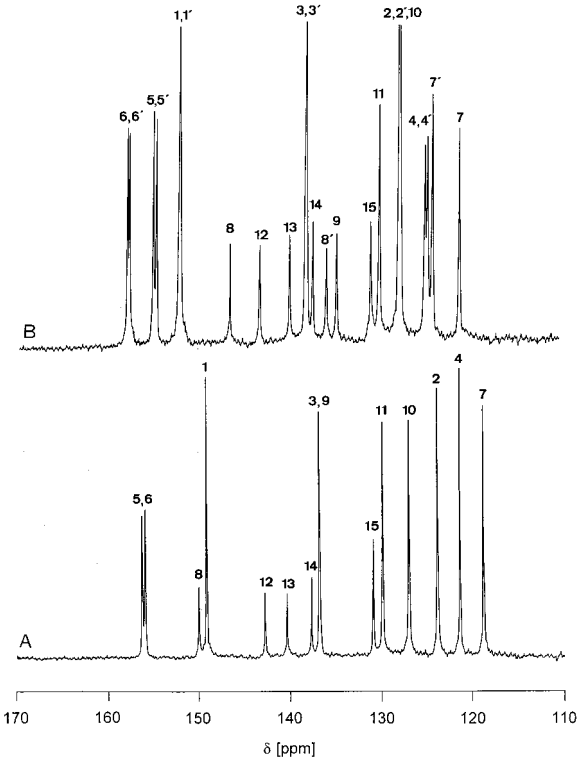



**Figure 5.** Aromatic regions of the $^{13}$C NMR spectra of (A) ligand monomer **3** and (B) of a representative sample of the dinuclear complex **13** obtained via the conversion according to Scheme 6, recorded in DMSO-$d_6$ at room temperature. The signal assignment is according to the numbering specified in Scheme 6.

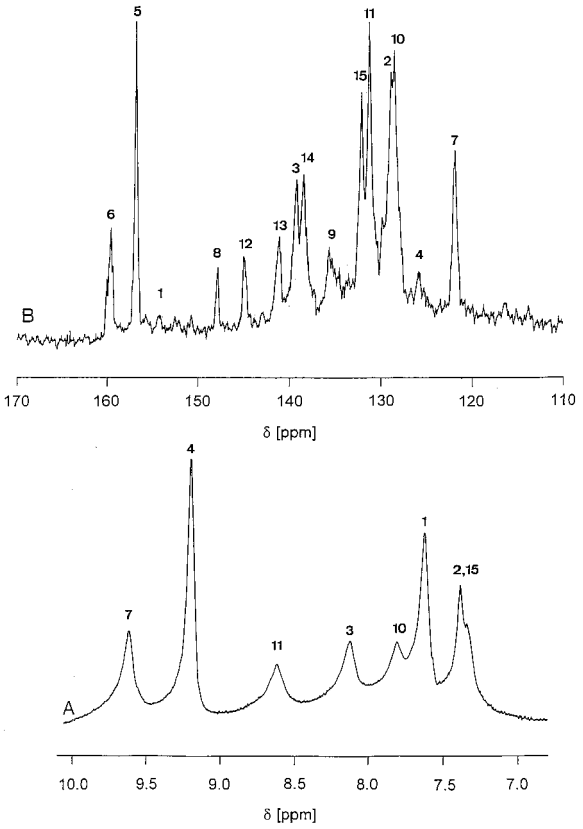


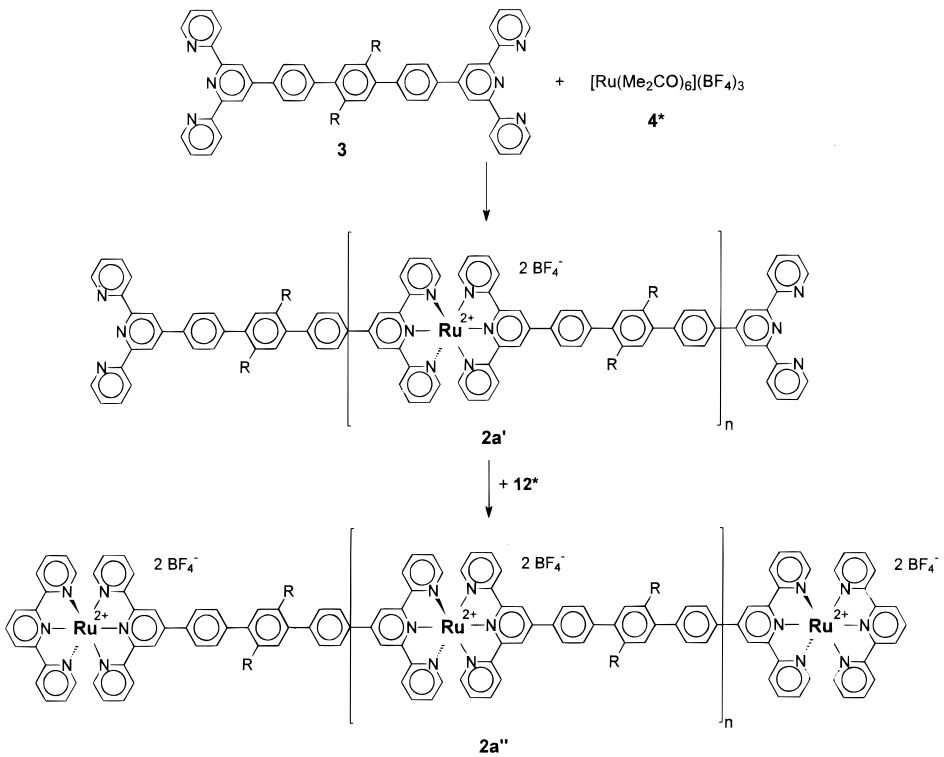

**Figure 6.** Aromatic regions of (A) a representative $^1$H NMR spectrum and (B) a representative $^{13}$C NMR spectrum of a high-molecular-weight polymer **2a**, recorded in DMSO-$d_6$ at room temperature. The signal assignment is according to the numbering specified in Scheme 2.

assignment provided the required chemical shifts of potential polymer end groups **E**.

To conclude, the model experiments clearly showed route A to be the method of choice for the preparation of polymers **2a** since conditions could be found for the synthesis of the $[Ru(tpy)_2]^{2+}$ motif that guarantee practically quantitative yields—an essential prerequisite for the successful synthesis of polymer **2a**. In contrast to this, the model complex **11** prepared via the Pd-catalyzed condensation was obtained in only 90% yield. This result allows prediction of the formation of only oligomeric **2a** from route B at best.

**Polymer Synthesis.** The coordination polymers **2a** were prepared according to Scheme 1 using the optimized reaction conditions discussed above. In a typical polymerization experiment via route A, an appropriate quantity of $RuCl_3 \cdot 3H_2O$ (**4**) was first activated using the system $AgBF_4$/acetone. The metal monomer **4*** thus obtained was subsequently heated with exactly 1 equiv of ligand monomer **3** in 1-butanol/DMA for 5 days. Simultaneously with the chain growth process, the ruthenium(III) centers turn to ruthenium(II) using the solvent 1-butanol as the reducing agent. The product was precipitated in practically quantitative yields as a dark red, fibrous material by pouring the whole reaction mixture into water. After filtration, the material formed a brittle film which readily and completely redissolved in DMA or DMSO. Its constitution was analyzed using $^1$H and $^{13}$C NMR spectroscopy. Figure 6A displays a representative $^1$H NMR spectrum of the obtained material; Figure 6B shows the corresponding $^{13}$C NMR spectrum. All absorptions observed in these spectra can

**Scheme 7**




be assigned to the inner-chain repeating units of polymer **2a**, and no signals were found in these spectra which might correspond to chain termini or defect structures. Thus, these spectra pointed toward the formation of constitutionally homogeneous and high-molecular-weight polymers **2a**. To prove this assessment, it must be ensured (i) that there were no end groups **D** (Scheme 5) in the polymer which are hard to detect by NMR and (ii) that at least some of the characteristic absorptions of potential chain termini **C** absorb baseline-separated from the absorptions of the inner-chain repeating units of **2a**. To clarify the first point, solutions of the raw polymers **2a** were treated in 1-butanol/DMA with 2,2′:6′,2″-terpyridine (**9b**) to convert potential end groups **D** into readily detectable end groups **E**. However, even after this treatment, no additional absorptions were found in the NMR spectra of polymers **2a**. Moreover, this experiment showed additionally the polymers **2a** to be kinetically inert. Otherwise, the treatment with **9b**—which might act as a monofunctional comonomer—would have caused a significant chain degradation.

To reliably also prove that the respective absorptions of ligand termini **C** are not just covered by those of the repeating units of **2a**, further polymerization experiments were carried out where a slight excess of ligand monomer **3** was used (Scheme 7, step 1). After isolation and redissolution of the obtained oligomers **2a′** in DMSO-$d_6$, NMR spectra were recorded which showed clearly detectable absorptions of free terminal 2,2′:6′,6″-terpyridine moieties at, for example, $\delta = 8.72$ and 8.80 ppm and hence baseline-separated from the absorptions of the inner-chain repeating units. Finally, to also prove that at least some signals of the protons or carbon atoms of chain termini **E** appear baseline-separated from the absorptions of the repeating units of **2a**, a terpyridine-terminated oligomer **2a′** was treated with **12*** (Scheme 7, step 2). NMR analysis of the isolated product **2a″** proved the success of this conversion **C** → **E**: the characteristic absorptions of end groups **C** at $\delta = 8.72$ and 8.80 ppm disappeared while new absorptions could be observed at $\delta \approx 7.48$ and 8.88 ppm. This finding permits the conclusion that at least two protons of end groups **E** absorb baseline-separated from the signals of the inner-chain repeat units. All together, these experiments clearly indicated that the amount of chain termini present in the initial polymers **2a** is in fact below the limits of accuracy of the $^1$H and $^{13}$C NMR method. Moreover, formation of cyclic oligomers which could also explain the lack of end-group absorptions can be excluded here because of the rodlike shape of the target polymers. Therefore, it was concluded that really high-molecular-weight polymers **2a** are formed via route A when exactly equimolar amounts of the comonomers **3** and **4*** are used. Considering the limits of accuracy of the NMR method, the average degrees of polymerization achieved were estimated to be $P_{n,NMR} \geq 30$ ($M_n \geq 36\,000$ g mol$^{-1}$). This assessment is in full agreement with the results reported previously for the coiled coordination polymers **1** for which similar values of $P_n$ were found.[27]

A completely different situation arose when route B was used for the synthesis of polymers **2a**. Here, exactly equimolar amounts of monomer **5a** and benzenediboronic acid derivative **6** were treated for 7 days in a mixture of DMA and triethylamine (2:1) in the presence of 5 mol % [Pd(dppf)Cl$_2$]. A reddish-brown, powdery precipitate was isolated in typically 75% yield by pouring the whole reaction mixture into a large excess of an aqueous $NH_4BF_4$ solution. It readily redissolved in DMSO or DMA and was analyzed using $^1$H and $^{13}$C NMR spectroscopy. These spectra showed that hardly no coupling reaction had occurred, despite the fact that exactly the same reaction conditions were applied which had been shown before to give model complex **11** in about 90% yield. Instead, the main constituents of the isolated material were side products formed by most probably dehalogenation of **5a** and hydrolysis of **6**. It

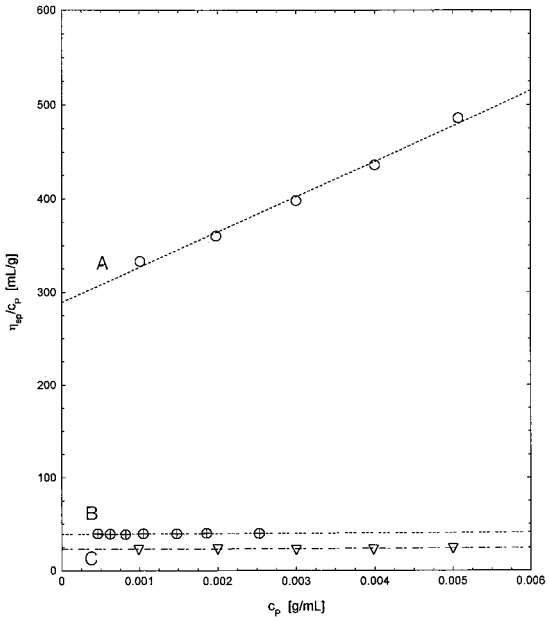
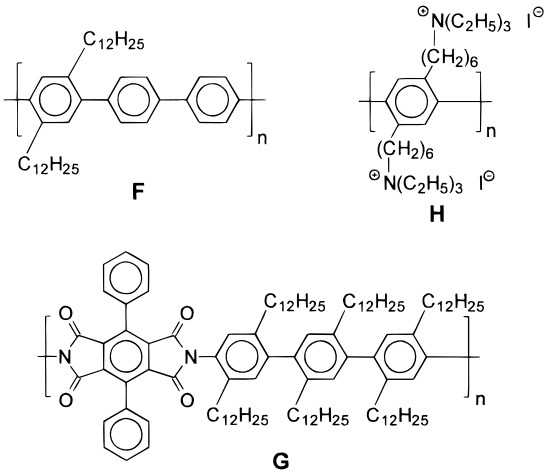



**Figure 7.** Huggins plots of (A) a high-molecular-weight sample of **2a** (○; $P_{n,NMR} \geq 30$), (B) a low-molecular-weight sample of **2a** (⊕; $P_{n,NMR} < 10$), and (C) a high-molecular-weight sample of the coiled polymer **1d** (▽; $P_{n,NMR} \geq 30$), recorded in DMA/0.02 M $NH_4PF_6$ at room temperature.

was assumed that this failure is the result of the very low solubility of the oligomers **2a** in the mixture of DMA and triethylamine: in the course of the polymerization the growing species precipitate, and their further chain growth is thus slowed down. In addition to this, side reactions destroy the reactive functionalities more efficiently than during the model studies.

To increase the solubility of the growing species in the reaction medium and hence to suppress the above side reactions, tributylamine was used as the base instead of triethylamine in further experiments. However, the chain lengths of **2a** could not be increased significantly by this modification. To conclude, the loss of the bromo functionalities of **5a**, the hydrolysis of the boronic acid functionalities of **6**, unidentified side reactions, and in particular the very low solubility of **2a** in all tested coupling media prevented the formation of constitutionally regular and high-molecular-weight polymers **2a** via Pd-catalyzed polycondensation up to now. Route A is therefore the method of choice for the preparation of ruthenium(II) coordination polymers **2a**.

**Viscosimetric Investigations.** The hydrodynamic behavior of the rodlike ruthenium(II) coordination polymers **2a** prepared via route A has been analyzed by viscosimetry both in salt-free and in salt-containing solutions. In a first series of experiments, polyelectrolytes **2a** were studied in 0.02 M $NH_4PF_6$ in DMA and thus at high ionic strength. Under these conditions, the intermolecular Coulomb interactions between the charged macromolecules are screened out completely, and the evaluation of the experimental data is possible according to the procedures usually applied for uncharged polymers. By means of these experiments we expected to reconfirm at least qualitatively the high degrees of polymerization ($P_{n,NMR}$) estimated by NMR end-group analysis as well as the rodlike shape and the considerable chain stiffness of **2a** anticipated because of its constitution. Figure 7 displays the Huggins plots (A) of a high-molecular-weight sample of **2a** ($P_{n,NMR} \geq 30$), (B) of a low-molecular-weight sample of **2a** ($P_{n,NMR} < 10$), and, for comparison purposes, (C) of a high-molecular-weight sample of the coiled ruthenium(II) coordination polymer **1d** ($P_{n,NMR} \geq 30$) bearing adamantylmethylene side groups. In all three cases, linear extrapolation of the values of $\eta_{sp}/c_P$ is possible to $c_P = 0$ g mL$^{-1}$. By this procedure, an intrinsic viscosity of $[\eta] \approx 300$ mL g$^{-1}$ is determined for the high-molecular-weight sample of polymer **2a**. This value is approximately 1 order of magnitude higher than the values of $[\eta]$ determined for the rodlike oligomer **2a** ($[\eta] \approx 40$ mL g$^{-1}$) and for the high-molecular-weight but randomly coiled ruthenium(II) coordination polymer **1d** ($[\eta] \approx 25$ mL g$^{-1}$). Moreover, a value of $[\eta] \approx 300$ mL g$^{-1}$ is not only the highest value ever observed for a ruthenium(II) coordination polymer but also higher than those found for many other monodispersely soluble, rodlike macromolecules. Poly(*p*-phenylenes) (PPPs) **F**, for example, have a value of $[\eta] = 207$ mL g$^{-1}$ when $P_n$ is 37 (osmometry).[33,40] For rodlike polyimides **G**, a value of $[\eta] = 268$ mL g$^{-1}$ is found for samples of $P_n = 46$ (osmometry) and $P_w = 111$ (static light scattering).[41] Finally, $[\eta] = 15$ mL g$^{-1}$ has been determined for a rodlike PPP polyelectrolyte **H** ($P_n = 27$) in an aqueous KI solution.[19,42] These additional reference compounds clearly support the anticipated high molecular weights of coordination polymers **2a**. The




above polyimide **G**, for example, has an average of 46 repeating units per chain and hence an average chain length of $l_n = 96$ nm (the length of the monomeric unit is $l_u = 2.09$ nm).[41] As its intrinsic viscosity ($[\eta] = 268$ mL g$^{-1}$) is still somewhat lower than that of **2a**, it is reasonable to assume that the average chain length of the novel ruthenium(II) coordination polymers **2a** is at least similar. That means if polymer **2a** has an average chain length of $l_n \approx 100$ nm as well, its $P_n$ is approximately 43 ($l_u = 2.32$ nm). Even if this procedure does not give the exact values of $P_n$, it nevertheless strongly supports the results from NMR spectroscopy. Moreover, the above results corroborate not only the high chain length of coordination polymers **2a** but also their rodlike shape: if **2a** had a substantially flexible or even coiled backbone, neither the high values of the intrinsic viscosity nor the tremendeous influence of the chain length on the intrinsic viscosity would be observed. The latter aspect is supported in particular by comparison of the data of polymers **2a** with those of the coiled reference polymers **1** where the influence of the $P_n$ on the intrinsic viscosity is quite low under the same conditions.

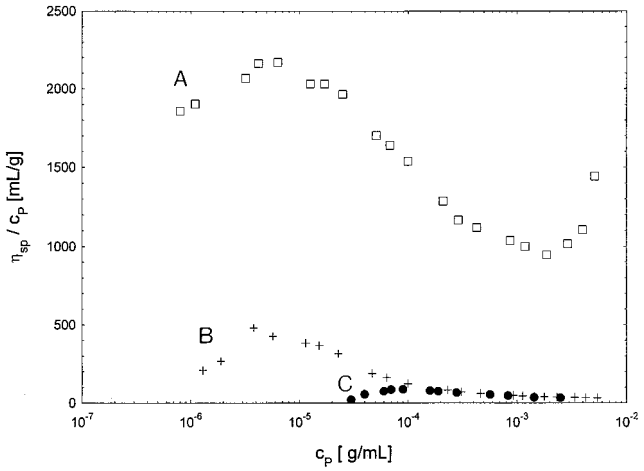



**Figure 8.** Huggins plots of (A) a high-molecular-weight sample of **2a** (□; $P_{n,NMR} \geq 30$), (B) a low-molecular-weight sample of **2a** (+; $P_{n,NMR} < 10$), and (C) a high-molecular-weight sample of the coiled polymer **1a** (●; $P_{n,NMR} \geq 30$), recorded in salt-free DMA at room temperature.

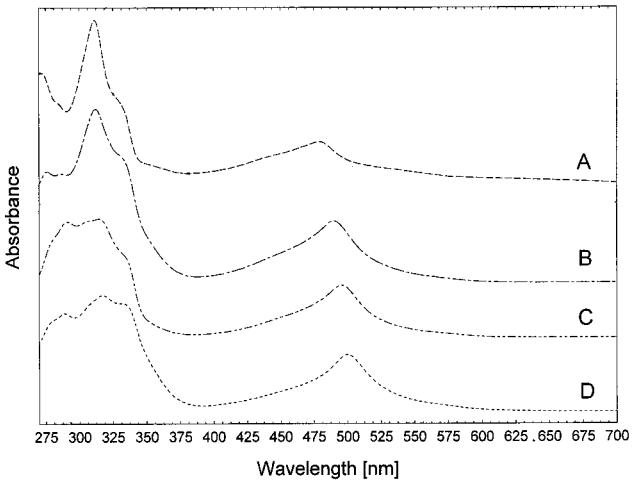



**Figure 9.** UV−vis absorption spectra of (A) the mononuclear model complex **5b**, (B) the dinuclear model complex **13**, (C) the mononuclear complex **5a**, and (D) a high-molecular-weight sample of coordination polymer **2a**, recorded in DMA at room temperature.

In a second series of experiments, the hydrodynamic behavior of coordination polyelectrolytes **2a** was studied in pure DMA and thus at low ionic strength. Under these conditions, the intermolecular Coulomb interactions between the charged macromolecules are in operation. Figure 8 displays the Huggins plot of (A) a high-molecular-weight sample of **2a** ($P_{n,NMR} \geq 30$), (B) a low-molecular-weight sample of **2a** ($P_{n,NMR} < 10$), and (C) a high-molecular-weight sample of the coiled polymer **1a** ($P_{n,NMR} \geq 30$). Under salt-free conditions as well, the high-molecular-weight polymer **2a** stands out from the other samples: it displays by far the most pronounced polyelectrolyte effect. A maximum of $(\eta_{sp}/c_P)_{max} \approx 2000$ mL g$^{-1}$ is found for this sample in the Huggins plot at a polymer concentration of $c_P \approx 5 \times 10^{-6}$ g mL$^{-1}$. However, the corresponding maximum is also clearly detectable for the low-molecular-weight rodlike system **2a** where a value of $(\eta_{sp}/c_P)_{max} \approx 500$ mL g$^{-1}$ is reached at approximately the same polymer concentration of $c_P \approx 5 \times 10^{-6}$ g mL$^{-1}$. Finally, as expected, the maximum of the reduced specific viscosity of the high-molecular-weight but randomly coiled reference polymer **1a** is again less pronounced $\{(\eta_{sp}/c_P)_{max} \approx 100$ mL g$^{-1}\}$. It appears at a polymer concentration of $c_P \approx 9 \times 10^{-5}$ g mL$^{-1}$, which is more than 1 order of magnitude higher than the concentration where the maximum is found for polymers **2a**. These results highlight the tremendeous influence of the chain length and in particular of the shape of the macromolecules on their hydrodynamic behavior also in solutions of low ionic strength: extended chains give rise to much more pronounced polyelectrolyte effects than chains of similar length but coiled conformation. Moreover, while the $P_n$ influences the values of $(\eta_{sp}/c_P)_{max}$ considerably in the case of the rodlike polyelectrolytes **2a**, this effect is nearly negligible in the case of the coiled systems **1**.

Finally, comparison of the hydrodynamic behavior of the low-molecular-weight polymer **2a** with that of the recently investigated rodlike PPP polyelectrolyte **H** might be instructive.[19,42] In the latter case, a value of $(\eta_{sp}/c_P)_{max} \approx 350$ mL g$^{-1}$ is again found in salt-free aqueous solution at $c_P \approx 5 \times 10^{-6}$ g mL$^{-1}$ in the Huggins plot of a sample **H** having a $P_n$ of 40 (osmometry). This value of $P_n$ corresponds to an average chain length of $l_n \approx 17.6$ nm ($l_u = 0.44$ nm). The low-molecular-weight polymer **2a**, on the other hand, which has a $P_{n,NMR} < 10$ and thus an average length of $l_n \approx 23.2$ nm, shows a maximum in the Huggins plot of $(\eta_{sp}/c_P)_{max} \approx 500$ mL g$^{-1}$ (curve B). At first glance, these two results fit fairly well. However, prior to a final assessment and more extensive conclusions, the influence of the solvent and of the shear gradient on the observed quantities must be investigated in more detail.

**UV−vis Spectroscopy**. UV−vis spectra of a series of ruthenium(II) complexes described above were recorded to analyze the absorption behavior of the $[Ru(tpy)_2]^{2+}$ motif as a function of the substitution pattern of the ligands and the number of complexes present in the respective molecules. The main aspect was to find out whether the spectra of the monomeric, dimeric, and polymeric complexes are basically different from each other, i.e., whether there is observable evidence for a potential electronic interaction between the individual metal complexes along the chains of polymers **2a**. Figure 9 displays the UV−vis absorption spectra of $[Ru(tpy)_2](PF_6)_2$ **5b** (A), of the dinuclear model complex **13** (B), of the monomeric complex **5a** (C), and of a high-molecular-weight sample of polymer **2a** (D) in DMA solution. In all these spectra, intense absorptions are observed at wavelengths below $\lambda = 380$ nm, which can be assigned to ligand-centered (LC) $\pi^* \leftarrow \pi$ transitions within the pyridine moieties as well as to $\pi^* \leftarrow \pi$ transitions within the phenylene moieties in spectra B−D. Differences in this region between the spectra of the monomeric, dimeric, and polymeric complexes are rather negligible and can be explained on the basis of the different constitution of the respective ligand moieties themselves. Thus, no systematic shift of these absorptions is observed as a function of the length of the species under consideration. This statement is tantamount to the lack of $\pi$-electron conjugation along the chains and in particular across the transition-metal complexes. The situation is seemingly different for all those transitions that are excited by light of wavelengths above $\lambda = 400$ nm. In this region absorptions are observed which correspond to the metal-to-ligand charge-transfer (MLCT) transitions. A bathochromic shift becomes clearly evident when, for example, spectrum A of the monomeric complex $[Ru(tpy)_2](PF_6)_2$ (**5b**) is compared with spectrum D of coordination polymer **2a**. In the former case,

the absorption maximum is found at $\lambda_{max} = 475$ nm while it appears at $\lambda_{max} = 500$ nm in the multinuclear system. Moreover, the value of $\lambda_{max} = 490$ nm of the dinuclear model complex **13** is observed just in between these two values. This systematic shift of $\lambda_{max}$ to longer wavelengths with an increasing number of complexes per molecule might be interpreted as a result of intramolecular electronic interactions of the metal centers in the dimeric and polymeric species. However, this is not the case as becomes evident, for example, from the comparison of spectra A, B, and D with spectrum C that results from monomer **5a**, $[Ru\{(p\text{-}BrC_6H_4\text{-}tpy)_2\](BF_4)_2$. This mononuclear complex exhibits an absorption maximum at $\lambda_{max} = 495$ nm and hence at nearly the same wavelength as the high-molecular-weight polymer **2a**. This clearly shows that the observed shift of the MLCT bands is a consequence of the substitution pattern of the respective terpyridine ligand rather than of the intramolecular electronic interaction of the ruthenium centers: the more electron-withdrawing substituents a terpyridine ligand bears, the more is the value of $\lambda_{max}$ shifted toward longer wavelengths. This interpretation is in agreement with theoretical arguments as well as with results of measurements on related complexes. We therefore conclude that there is no intramolecular electronic interaction observable by UV−vis spectroscopy between the ruthenium(II) centers of the polynuclear complexes under investigation here. The polymers **2a** can therefore be considered as sequences of electronically nearly independent ruthenium(II) complexes.

## Conclusions and Outlook

Rodlike ruthenium(II) coordination polymers **2a** have been prepared via conversion of 4,4″-bis(2,2′:6′,2″-terpyridine)-2′,5′-dihexyl-*p*-terphenyl **3** and **4*** in 1-butanol/DMA. The Pd-catalyzed polycondensation also used for the preparation of **2a** gave oligomers at best. The homogeneous constitution of the high-molecular-weight polymers **2a** ($P_{n,NMR} \geq 30$) could be proven using $^1$H and $^{13}$C NMR spectroscopy. The considerable length of the rods **2a** is further supported by viscosimetry experiments which resulted in intrinsic viscosities of $[\eta] \approx 300$ mL g$^{-1}$ (0.02 M $NH_4PF_6$/DMA). In salt-free DMA solution, polymers **2a** display a pronounced polyelectrolyte effect which is strongly dependent on $P_n$. Finally, the UV−vis investigations show that the polymers **2a** behave like sequences of electronically nearly independent ruthenium(II) complexes. Presently, we are analyzing the molar masses of **2a** quantitatively and attempting to determine the persistent length to assess the extent by which the octahedral metal complexes lower the rigidity of the chains. Moreover, the spectroscopic and electrochemical behavior of polymers **2a** is under further investigation.

## Experimental Section

All chemicals and solvents were purchased from Aldrich, Fluka, Strem, and Lancaster Chemical Co. and used without further purification. Complex **12** was prepared according to the literature.[39] All reactions were carried out under an atmosphere of nitrogen. NMR spectra were recorded using a Bruker AM 400 NMR spectrometer working at 400 MHz ($^1$H NMR) and 100 MHz ($^{13}$C NMR). The signal assignment in the $^1$H and $^{13}$C NMR spectra is done according to the numbering given for the protons and carbons, respectively, of selected compounds shown in Schemes 2 and 6. Viscosity measurements were carried out at 30 ± 0.1 °C using Ubbelohde viscosimeters (type 0c, Schott). Flow times of the order of 200 s were measured with an accuracy of ±0.1 s. UV−vis measurements were carried out using a Perkin-Elmer Lambda S2 photospectrometer. Other methods and techniques were carried out as described elsewhere.[27]

**4′-(*p*-Bromophenyl)-2,2′:6′,2″-terpyridine (9a).**[32] A mixture of acetamide (35.50 g, 0.60 mol), ammonium acetate (23.00 g, 0.3 mol), 4-bromobenzaldehyde (**7**) (3.70 g, 0.02 mol), and 2-acetylpyridine (**8**) (4.85 g, 0.04 mol) is heated within 30 min up to 180 °C and then stirred and refluxed for a further 2.5 h. The reaction mixture is cooled to 120 °C, a solution of NaOH (17.5 g) in water (40 mL) is added, and refluxing is continued for a further 2 h. The aqueous layer is removed at room temperature, the black, rubberlike residue is washed with water and dissolved in acetic acid (20 mL, 50 °C), and aqueous HBr (30 mL, 48%) is added. Instantaneously, golden crystals precipitate. The mixture is allowed to stay overnight at room temperature to complete the crystallization; the formed solid is filtered off and washed with aqueous HBr (100 mL, 48%). Water is added to the crystals, the resulting slurry is neutralized (pH 7) using 4 M aqueous NaOH, and the suspension is extracted with $CH_2Cl_2$ (3 × 100 mL). The combined organic layers are dried ($Na_2SO_4$), the solvent is removed, and the thus obtained raw material is recrystallized from ethanol (50 mL) and dried in vacuo ($P_4O_{10}$). Yield: 1.17 g (19%).

$^1$H NMR ($CDCl_3$): $\delta = 7.36$ (m; 2 H, H$^2$), 7.64 (m; 4 H, H$^{10}$), 7.78 (m; 2 H, H$^{11}$), 7.88 (m; 2 H, H$^3$), 8.67 (m; 2 H, H$^4$), 8.70 (s; 2 H, H$^7$), 8.73 (m; 2 H, H$^1$). $^{13}$C NMR ($CDCl_3$): $\delta = 118.53$ (d; C$^7$), 121.36 (d; C$^4$), 123.40 (s; C$^{12}$), 123.92 (d; C$^2$), 128.87 (d; C$^{10}$), 132.08 (d; C$^{11}$), 136.90 (s; C$^3$), 137.50 (s; C$^9$), 149.12 (d; C$^{1,8}$), 156.03 (s; C$^{5,6}$).

**Bis[4′-(*p*-bromophenyl)-2,2′:6′,2″-terpyridine]ruthenium-(II) Tetrafluoroborate (5a).** *Activation of **4***. A mixture of $RuCl_3 \cdot 3H_2O$ (**4**) (0.047 g, 0.18 mmol) and $AgBF_4$ (0.116 g, 0.59 mmol) is refluxed for 2 h in acetone (15 mL). After cooling to room temperature, the precipitated AgCl is filtered off, and the obtained solution is rotavaporated to dryness. The remaining solid **4*** is redissolved in 1-butanol (15 mL).

*Complex Formation.* 4′-(*p*-Bromophenyl)-2,2′:6′,2″-terpyridine (**9a**) (0.140 g, 0.36 mmol) is added to the above solution of **4***, and the mixture is refluxed for 12 h. Another portion of **9a** (0.10 g, 0.026 mmol) is added, and refluxing is continued for a further 12 h. At room temperature, the formed solid is filtered off, washed with 1-butanol (100 mL), and dried in vacuo at room temperature ($P_4O_{10}$). If NMR analysis shows the presence of $[Ru(\mathbf{9a})_1X_3]$ species in the product mixture, the whole material is refluxed again with a slight excess of the free ligand **9a** for 24 h in a mixture of 1-butanol and water (2:1, v/v). Yield: 0.198 g (99%).

$^1$H NMR (DMSO-$d_6$): $\delta = 7.29$ (m; 4 H, H$^2$), 7.55 (d; 4 H, H$^1$), 8.01 (d; 4 H, H$^{10}$), 8.08 (m; 4 H, H$^3$), 8.42 (d; 4 H, H$^{11}$), 9.10 (d; 4 H, H$^4$), 9.50 (s; 4 H, H$^7$). $^{13}$C NMR (DMSO-$d_6$): $\delta = 120.94$ (d; C$^7$), 124.09 (s; C$^{12}$), 124.81 (d; C$^4$), 127.72 (d; C$^2$), 129.62 (d; C$^{10}$), 132.31 (d; C$^{11}$), 135.25 (s; C$^9$), 137.99 (d; C$^3$), 145.59 (s; C$^8$), 152.19 (d; C$^1$), 155.09 (s; C$^5$), 157.88 (s; C$^6$). Anal. Calcd for $C_{42}H_{26}N_6Br_2B_2F_8Ru \cdot 3H_2O$: C, 45.64; H, 3.10; N, 7.60. Found: C, 45.98; H, 3.11; N, 7.54.

**4,4″-Bis(2,2′:6′,2″-terpyridine)-2′,5′-dihexyl-*p*-terphenyl (3).** 4′-(*p*-Bromophenyl)-2,2′:6′,2″-terpyridine (**9a**) (1.000 g, 2.58 mmol), 2,5-dihexylbenzene-1,4-diboronic acid (**6**) (0.431 g, 1.28 mmol), and $[Pd(PPh_3)_4]$ (0.015 g, 0.013 mmol, 1 mol %) were refluxed and vigorously stirred for 24 h in the heterogeneous system of toluene (25.0 mL) and aqueous $Na_2CO_3$ (25 mL, 1 M). At room temperature, water (100 mL) is added, and the resulting mixture is extracted with $CHCl_3$ (3 × 100 mL). The combined organic layers are dried ($Na_2SO_4$), the solvent is removed, and the obtained solid is recrystallized from a mixture of ethanol and chloroform (9:1; v/v). Yield (after recrystallization): 0.906 g (82%).

$^1$H NMR ($CDCl_3$): $\delta = 0.83$ (t; 6 H, $CH_3$), 1.25 (m; 12 H, $CH_2$), 1.54 (dd; 4 H, $\beta$-$CH_2$), 2.66 (t; 4 H, $\alpha$-$CH_2$), 7.23 (s; 2 H, H$^{15}$), 7.36 (m; 4 H, H$^2$), 7.55 (d; 4 H, H$^{10}$), 7.88 (m; 4 H, H$^3$), 8.00 (d; 4 H, H$^{11}$), 8.70 (d; 4 H, H$^4$), 8.75 (d; 4 H, H$^1$), 8.84 (s; 4 H, H$^7$). $^{13}$C NMR ($CDCl_3$): $\delta = 14.05$ (q; $CH_3$), 22.51, 29.26, 31.52, 32.75 (4t; $CH_2$), 118.78 (d; C$^7$), 121.32 (d; C$^4$), 123.80 (d;

$C^{2}$), 127.00 (d; $C^{10}$), 129.87 (d; $C^{11}$), 130.89 (d; $C^{15}$), 136.83 (m; $C^{3,9}$), 137.68 (s; $C^{14}$), 140.34 (s; $C^{13}$), 142.77 (s; $C^{12}$), 149.11 (d; $C^{1}$), 149.98 (s; $C^{8}$), 155.91 (s; $C^{5}$), 156.24 (s; $C^{6}$). Anal. Calcd for $C_{60}H_{56}N_6$: C, 83.69; H, 6.55; N, 9.76. Found: C, 83.13; H, 6.56; N, 9.68.

**4,4″-Bis(2,2′:6′,2″-terpyridine)-2′,5′-dihexyl-*p*-terphenyl-bis[2,2′:6′,2″-terpyridineruthenium(II)] Tetrafluoroborate (13).** *Activation of* ***12***. A mixture of [Ru(2,2′:6′,2″-terpyridine)$Cl_3$] (**12**) (0.100 g, 0.2 mmol), $AgBF_4$ (0.120 g, 0.62 mmol), and acetone (30.0 mL) is refluxed for 2 h. At room temperature, the formed AgCl is filtered off, the resulting solution is rotavaporated to dryness, and the residue of **12*** is redissolved in 1-butanol (25 mL).

*Complex Formation.* 4,4″-Bis(2,2′:6′,2″-terpyridine)-2′,5′-dihexyl-*p*-terphenyl (**3**) (0.082 g, 0.095 mmol) is added to the above solution of **12***, and the mixture is refluxed for 48 h. During this time, three portions of DMA are added to the reaction mixture in order to ensure the solubility of the formed product: 6 mL after 1 h, 4 mL after 2 h, and 2 mL after 24 h. Finally, the product is precipitated by pouring the whole reaction mixture into an aqueous $NH_4BF_4$ solution (200 mL). The solid is filtered off, washed successively with 1-butanol and water, and dried in vacuo ($P_4O_{10}$). Yield: 0.185 g (98%).

$^1$H NMR (DMSO-$d_6$): $\delta = 0.86$ (t; 6 H, $CH_3$), 1.26 (m; 12 H, $CH_2$), 1.58 (m; 4 H, $\beta$-$CH_2$), 2,79 (m; 4 H, α-$CH_2$), 7.32 (m; 8 H, $H^{2,2'}$), 7.38 (s; 2 H, $H^{15}$), 7.49 (d; 4 H, $H^{1'}$), 7.60 (d; 4 H, $H^{1}$), 7.81 (d; 4 H, $H^{10}$), 8.09 (m; 8 H, $H^{3,3'}$), 8.59 (m; 8 H, $H^{4',8'}$), 8.88 (d; 4 H, $H^{11}$), 9.16 (2d; 8 H, $H^{4,7'}$), 9.60 (s; 4 H, $H^{7}$). $^{13}$C NMR (DMSO-$d_6$): $\delta = 13.94$ (q; $CH_3$), 22.03, 28.65, 30.88 (3t; $CH_2$), 121.06 (d; $C^{7}$), 124.03 (d; $C^{7'}$), 124.57, 124.86 (2d; $C^{4,4'}$), 127.77 (m; $C^{2,2',10}$), 129.98 (d; $C^{11}$), 130.94 (d; $C^{15}$), 134.70 (s; $C^{9}$), 135.87 (d; $C^{8'}$), 137.38 (d; $C^{14}$), 138.12 (d; $C^{3,3'}$), 139.98 (s; $C^{13}$), 143.27 (s; $C^{12}$), 146.60 (s; $C^{8}$), 152.18 (2d; $C^{1,1'}$), 154.80, 155.13 (2d; $C^{5,5'}$), 157.81, 158.04 (2d; $C^{6,6'}$). Anal. Calcd for $C_{90}H_{78}N_{12}B_4F_{16}Ru_2 \cdot 6H_2O$: C, 54.45; H, 4.57; N, 8.47. Found: C, 54.99, H, 4.94; N, 8.40.

**Polymer 2a** *(Synthesis via Route A).* $RuCl_3 \cdot 3H_2O$ (**4**) (0.052 g, 0.20 mmol) is activated according to the procedure described for **5a** and then dissolved in 1-butanol (10 mL). To this solution, ligand monomer **3** (0.164 g, 0.19 mmol) is added, and the resulting solution is refluxed for 5 days. As soon as precipitation of the formed polymer is observed, small portions of DMA are added to the mixture ($\Sigma \approx 14$ mL) to redissolve the product. Finally, DMA (20 mL) is added to the hot reaction mixture to redissolve the product completely, and the resulting solution is dropwise poured into water (1000 mL). The precipitated product is filtered off, washed with methanol (200 mL), and dried in vacuo ($P_4O_{10}$). Yield: 0.218 g (96%).

$^1$H NMR (DMSO-$d_6$): $\delta = 0.85$ (m; 6 H, $CH_3$), 1.27 (m; 12 H, $CH_2$), 1.58 (m; 4 H, $\beta$-$CH_2$), 2.51 (m; 4 H, α-$CH_2$), 7.39 (m; 6 H, $H^{2,15}$), 7.63 (m; 4 H, $H^{1}$), 7.82 (m; 4 H, $H^{10}$), 8.14 (m; 4 H, $H^{3}$), 8.63 (m; 4 H, $H^{11}$), 9.21 (m; 4 H, $H^{4}$), 9.63 (m; 4 H, $H^{7}$). $^{13}$C NMR (DMSO-$d_6$): $\delta = 13.98$ (q; $CH_3$), 22.06, 28.68, 30.99 (3t; $CH_2$), 121.07 (d; $C^{7}$), 124.88 (d; $C^{4}$), 127.69 (2d; $C^{2,10}$), 130.00 (d; $C^{11}$), 130.96 (d; $C^{15}$), 134.69 (s; $C^{9}$), 137.37 (s; $C^{14}$), 138.11 (d; $C^{3}$), 139.97 (s; $C^{13}$), 143.30 (s; $C^{12}$), 146.54 (s; $C^{8}$), 152.28 (d; $C^{1}$), 155.15 (s; $C^{5}$), 158.10 (s; $C^{6}$). Anal. Calcd for $[(C_{60}H_{56}N_6B_2F_8Ru \cdot 3H_2O)_n]$: C, 60.57; H, 5.25; N, 7.06. Found: C, 60.29; H, 5.42; N, 6.71.

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