Rod-like ruthenium(II) coordination polymers: synthesis and properties in solution

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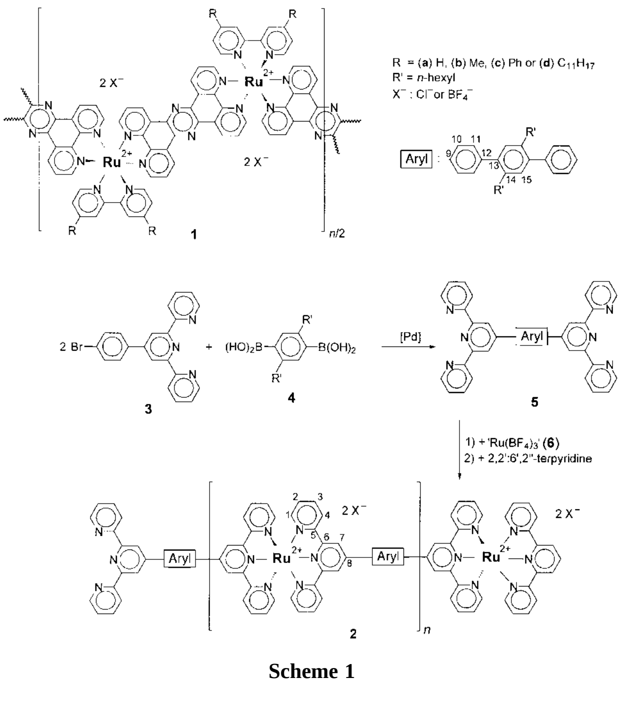
Well defined coordination polymers obtained *via* the conversion of 4,4″-bis(2,2′:6′,2″-terpyridine)-2′,5′-dihexyl-*p*-terphenyl and activated ruthenium(III) show intrinsic viscosities of up to [*η*] ≈ 300 mL g^{-1} and a tremendous polyelectrolyte effect in salt-free DMA solution proving both their high molecular weights and considerable chain stiffness.

Soluble ruthenium(II) coordination polymers of well defined constitution are of actual interest because of their electronic, photooptical, magnetic and catalytic properties.[1–8] Moreover, they represent important reference systems for the profound analysis of polyelectrolyte behaviour in solution which is a field of research that urgently needs appropriate model polymers. Recently, we described the first high-molecular-weight ruthenium(II) coordination polyelectrolytes **1**.[9–11] These polymers have a rigid, randomly coiled backbone and display characteristic polyelectrolyte behaviour in salt-free solutions. To further deepen the understanding of the structure–property relationship of these rather unusual coordination polyelectrolytes it is worthwhile to also make available ruthenium(II) coordination polymers which have rod-like backbones. We therefore decided to prepare polymers **2** *via* the conversion of 4,4″-bis(2,2′:6′,2″-terpyridine)-2′,5′-dihexyl-*p*-terphenyl **5** and an activated ruthenium(III) species such as **6**,[12] and thus *via* a procedure which has only been used so far for the preparation of mono- and oligonuclear ruthenium complexes (Scheme 1).

Polyelectrolytes **2** were expected to be readily soluble because of their flexible *n*-hexyl side chains[13] and to have a rod-like shape because of (i) the constitution of the bis-tridentate ligand monomers and (ii) the octahedral coordination sphere around the transition-metal atoms. The required ligand monomer **5** was prepared in almost quantitative yields and high purity *via* the Pd-catalysed condensation of 4′-(*p*-bromophenyl)-2,2′:6′,2″-terpyridine **3**[14] and 2,5-dihexylbenzene-1,4-diboronic acid **4**[15] in a heterogeneous mixture of toluene and 1 M aqueous Na_2CO_3, and its constitution was verified using ^{1}H [Fig. 1(a)] and ^{13}C NMR spectroscopy.

Prior to the polymer synthesis itself, several model studies were performed to find out the optimum reaction conditions for the conversion **5** + **6** → **2** which guarantee selective and practically quantitative formation of the $[Ru(tpy)_2]^{2+}$ motif (tpy = 2,2′:6′,2″-terpytidine). These conditions should further prevent formation of defect structures within the chains of **2** which could destroy its rod-like shape. In the course of these experiments, DMA–butan-1-ol was found to be the solvent mixture of choice for our purpose. The conversion of $RuCl_3 \cdot 3H_2O$ with $AgBF_4$–acetone, on the other hand, provided us the appropriately reactive metal monomer **6**.[12] Finally, knowledge of the chemical shifts of all absorptions of both possible chain termini of **2** is imperative for NMR end-group analysis which is a convenient method for the estimation of the



Scheme 1

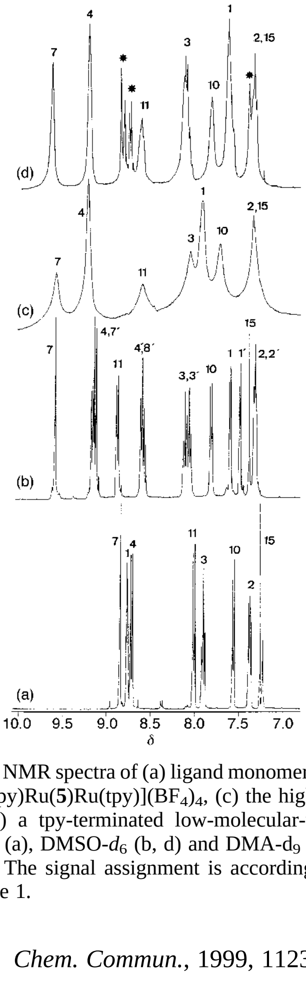


Fig. 1 400 MHz ^{1}H NMR spectra of (a) ligand monomer **5**, (b) the dinuclear model complex $[(tpy)Ru(\mathbf{5})Ru(tpy)](BF_4)_4$, (c) the high-molecular-weight polymer **2** and (d) a tpy-terminated low-molecular-weight polymer **2**, recorded in $CDCl_3$ (a), DMSO-d_6 (b, d) and DMA-d_9 (c), respectively, at room temperature. The signal assignment is according to the numbering specified in Scheme 1.

achieved degree of polymerisation (P_n). Therefore, the dinuclear complex [(tpy)Ru(**5**)Ru(tpy)]$(BF_4)_4$ was prepared *via* the conversion of **5** with 2 equiv. of an activated ruthenium(III)–terpyridine complex which was obtained *via* the treatment of [Ru(tpy)Cl_3][16] with $AgBF_4$–acetone. The resulting dinuclear complex subsequently allowed the identification of all NMR absorptions that are caused by $[Ru(tpy)_2]^{2+}$ end-groups of **2** (right-hand side terminus of **2** in Scheme 1; [see Fig. 1(b) for its ^{1}H NMR spectrum]. For the tpy-termini of **2** (left-hand side terminus of **2** in Scheme 1), on the other hand, monomer **5** itself is the appropriate model compound [Fig. 1(a)]. Coordination polymers **2** were prepared under the optimised reaction conditions. For this purpose, an appropriate quantity of $RuCl_3 \cdot 3H_2O$ was first converted into the activated metal monomer **6** and subsequently heated with exactly 1 equiv. of ligand monomer **5** in butan-1-ol–DMA for 5 d. The product was precipitated in practically quantitative yields as a dark red, fibrous material which readily and completely redissolved in DMA or DMSO. Its constitution was analysed using ^{1}H and ^{13}C NMR spectroscopy. Fig. 1(c) displays a representative ^{1}H NMR spectrum of the product.

All intense absorptions clearly correspond to the inner-chain repeating units of **2**. No signals were found, on the other hand, of defect structures or of end-groups. In order to prove that such absorptions are not only covered by the broad signals of the repeating units, further polymerisations were carried out where a slight excess of either ligand monomer **5** or metal monomer **6** was used. In the latter case, 5% of tpy was added to the reaction mixture prior to work-up to produce well defined $[Ru(tpy)_2]^{2+}$ chain termini (Scheme 1). As expected, additional signals that correspond to the respective end-groups were observed in the NMR spectra of all these latter polymers. As an example, Fig. 1(d) displays the ^{1}H NMR spectrum of a polymer **2** prepared by using an excess of **5**.

We conclude that end-groups are reliably detectable by NMR despite the broad and intense absorptions of the polymer backbone but obviously have intensities below the limits of accuracy of the NMR method for polymers **2** prepared from an exact 1 : 1 equivalence of comonomers **5** and **6**. Moreover, formation of cyclic oligomers can be excluded because of the rod-like shape of **2**. It is evident, therefore, that very high-molecular-weight polymers were produced: considering the limits of the NMR method, we estimate average degrees of polymerisation of $P_{n(NMR)} \geqslant 30$ ($M_n \geqslant 36\,000$ g mol^{-1}) for the best products synthesized so far.

The hydrodynamic behaviour of **2** was analysed by viscosimetry to further support its high P_n and its rod-like shape. In DMA–0.02 M NH_4PF_6 solution—where intermolecular Coulomb interactions between the charged macromolecules are screened out—the high-molecular-weight samples of **2** show intrinsic viscosities of up to $[\eta] \approx 300$ mL g^{-1}. These values are *ca.* one order of magnitude higher than those reported for the randomly coiled reference polymers **1** ($[\eta] \leqslant 25$ mL g^{-1}). Moreover, a value of $[\eta] \approx 300$ mL g^{-1} is not only the highest intrinsic viscosity ever observed for a ruthenium(II) coordination polymer but also of the same order of magnitude as the intrinsic viscosities observed for purely covalent rod-like macromolecules such as poly(*p*-phenylenes)[16,17] or polyimides.[18] These results thus strongly support the high values of P_n and the rod-like shape of **2**.

In a second series of experiments, the hydrodynamic behaviour of a high- ($P_n \geqslant 30$) and a low-molecular-weight ($P_n \leqslant 10$) sample of **2** was studied in pure DMA where the intermolecular Coulomb interactions between the macromolecules are in operation. Under these conditions, the high-molecular-weight sample displays a very pronounced polyelectrolyte effect, *i.e.* a maximum in the Huggins plot of $(\eta_{sp}/c_p)_{max} \approx 2000$ mL g^{-1} at a polymer concentration of $c_P \approx 5 \times 10^{-6}$ g mL^{-1}. Nevertheless, the maximum is also clearly detectable for the low-molecular weight polymer **2** where a value of (η_{sp}/c_P)max ≈ 500 mL g^{-1} is reached at a polymer concentration of $c_P \approx 5 \times 10^{-6}$ g mL^{-1}. Finally, the maximum is again less pronounced $\{(\eta_{sp}/c_P)$max ≈ 100 mL g$^{-1}\}$ for the high-molecular-weight but randomly coiled reference polymer **1a** and appear at a polymer concentration of $c_P \approx 7 \times 10^{-6}$ g mL^{-1}. These results highlight the tremendous influence of the chain length and in particular the shape of the macromolecules on their hydrodynamic behaviour also in solutions of low ionic strength. Comparably high-molecular-weight ($P_n \geqslant 30$) but randomly coiled reference polymers **1** reach maxima of $(\eta_{sp}/c_p)_{max} \approx 100$ mL g^{-1} at the best.

Finally, UV–VIS spectra were recorded in DMA solution of the mononuclear complex $[Ru(tpy)_2](PF_6)_2$, the dinuclear complex [(tpy)Ru(**5**)Ru(tpy)]$(BF_4)_4$ and the high-molecular-weight polymer **2** to analyse the absorption behaviour of the $[Ru(tpy)_2]^{2+}$ motif as a function of the number of complexes present in one molecule. In all cases, intense absorptions are observed at wavelengths below $\lambda = 380$ nm (ligand-centered $\pi^* \longleftarrow \pi$ transitions) and at wavelengths above $\lambda = 400$ nm (metal-to-ligand charge-transfer transitions). No evidence is found in these spectra that might be interpreted as the result of intramolecular electronic interaction between the metal centers in the dimeric and polymeric species. This conclusion is further supported by cyclic voltammetry performed in DMF–NBu_4BF_4 solution: half-wave potentials of $E_{1/2}{}^{ox} = 1.20$, 1.24 and 1.25 V are found for the metal-localized first oxidation in the case of the mononuclear complex $[Ru(tpy)_2](PF_6)_2$, the dinuclear complex [(tpy)Ru(**5**)Ru(tpy)]$(BF_4)_4$, and the high-molecular-weight polymer **2**, respectively.

Therefore, in full agreement with previous studies on related oligomeric complexes,[19] polymer **2** can be considered as a sequence of electonically nearly independent ruthenium(II) complexes. Presently, we are analysing the spectroscopic and electrochemical behaviour of polymers **2** in more detail.

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