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First GPC results of terpyridine based chain extended supramolecular polymers: comparison with viscosity and analytical ultracentrifugation

*Michael A. R. Meier,[1] Harald Hofmeier,[1] Caroline H. Abeln,[1] Christos Tziatzios,[2] Mircea Rasa,[1] Dieter Schubert[2] and Ulrich S. Schubert[1]**

1) Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology and Dutch Polymer Institute, PO Box 513, 5600 MB Eindhoven, The Netherlands. E-Mail: u.s.schubert@tue.nl, http://www.schubert-group.com.

2) Johann Wolfgang Goethe Universität, Institut für Biophysik, 60590 Frankfurt am Main, Germany.

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Abstract: The molecular weight of an extended metallo-supramolecular polymer, based on a α,ω-*bis*-terpyridine-poly(ethylene glycol) polymer linked via ruthenium(II) ions, was determined by gel permeation chromatography, viscosimetry as well as analytical ultracentrifugation. An optimized GPC method was applied for the first time to this kind of chain extended supramolecular polymers and the obtained results showed a good agreement with viscosimetry and analytical ultracentrifugation. A chain extended polymer with an average molecular weight of around 140 000 was found. These results clearly demonstrate that well-soluble high-molecular-weight metal-containing coordination polymers that are based on well-defined telechelics can be synthesized and fully characterized.

Introduction

Supramolecular polymers [1, 2] have evolved from an exotic side-subject of macromolecular chemistry into the focus of modern polymer science [3]. Mostly hydrogen-bonding interactions and metal coordination have been applied for the construction of linear (see e.g. refs. [4, 5] for hydrogen-bonded systems and refs. [6-8] for metal coordination), cross-linked [9-11] or grafted polymers [12,13]. Moreover, a large variety of supramolecular polymers and macromolecules based on terpyridine chemistry have been described and evaluated in the literature (see, e.g., [14-16] for recent examples). These polymers are widely studied due to their possible applications as smart, tunable materials. Several examples in that direction were already described in the literature including for instance thermoreversible rubbers based on hydrogen bonding interactions [10], supramolecular polyelectrolyte gel-like materials that show thixotropic behavior [17], or fluorescent transition metal sensors based on terpyridine moieties [18].

As for classical polymers, the material properties of such systems are highly dependent on their molecular mass. However, the determination of the molecular weight of such polymers represents a special challenge: gel permeation chromatography (GPC), one of the most frequently applied methods, turned out to be difficult or even impossible in the case of reversible systems such as hydrogen-bonds

or weak metal-ligand interactions (e.g. zinc(II) or cobalt(II) *bis*-terpyridine complexes) since i) column interactions could lead to a breaking of the above discussed non-covalent interactions and/or ii) high molecular weight species of these dynamic systems might re-equilibrate in the course of the measurement due to dilution. However, for the case of the stable *bis*-terpyridine-ruthenium(II) complexes, a GPC method was developed and proven to be suitable for the evaluation of low molecular weight metal containing supramolecular AB block copolymers [19]. In addition, viscosity investigations turned out to be a suitable tool for determining molecular weights of supramolecular polymers [20]. Through suppressing the polyelectrolyte effect by the addition of salt, the molecular weight of metallopolymers based on terpyridine ruthenium(II) complexes could be determined by this method [20]. Viscosimetry was even shown to be applicable for the evaluation of dynamic systems, such as hydrogen-bonded polymers, where the molecular weight is highly dependant on the concentration of the monomers [4]. Finally, analytical ultracentrifugation is a very versatile tool that allows the determination of molecular masses of supramolecular systems. A small drawback of this method is that it is rather time-consuming and therefore not suitable for fast standard analytics. However, it allows the determination of absolute molecular weight distributions, whereas the other mentioned methods are relative methods that require calibration. In the case of supramolecular polymers calibration materials are usually not available and assumptions need to be made. Within this contribution, the molecular weight of a chain extended supramolecular polymer based on a *bis*-terpyridine-Ru(II) type of connectivity is evaluated. Therefore, GPC, viscosimetry, and analytical ultracentrifugation measurements are described and carefully compared.

Results and discussion

The synthesis and characterization of the metallo-supramolecular polymer **P2** was described in the literature [20]. A *bis*-terpyridine-functionalized poly(ethylene glycol) (**P1**) was reacted with hexaacetone ruthenium(III) tetrafluoroborate in chloroform with 5 mol% ethanol for 72 h, leading to the coordination polymer **P2** through formation of *bis*-terpyridine ruthenium(II) complexes (reduction from Ru(III) to Ru(II)) (compare Figure 1).

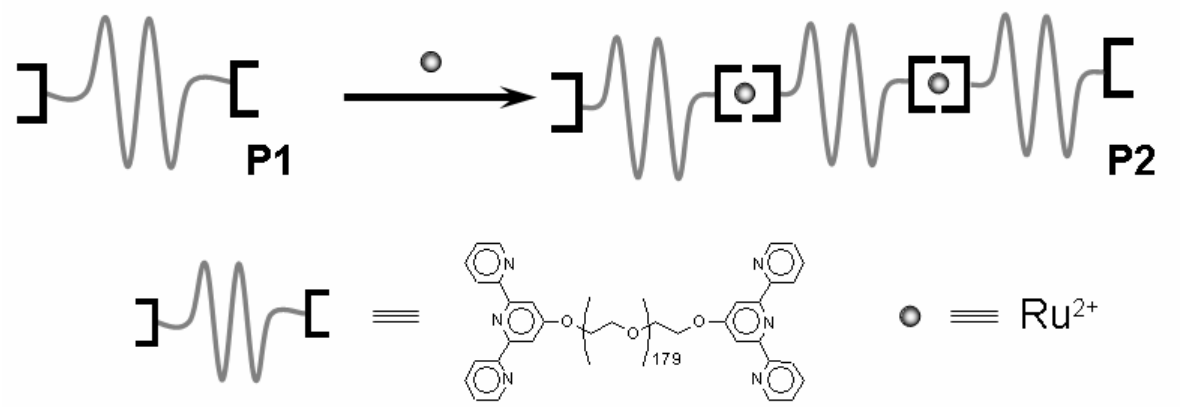

Fig. 1. Schematic representation of the formation of the metallo-supramolecular **P2**. (counter ions are omitted for clarity).

The reaction was monitored by UV/Vis spectroscopy revealing the increase of the metal to ligand charge transfer band at 485 nm, typical for the Ru(II)-*bis*-terpyridine complex, in time. Solution viscosimetry (in methanol as solvent and addition of salt to suppress the polyelectrolyte effect) provided a first evidence for the formation of polymeric species of high molecular weight. Moreover, an improved thermal stability (compared to **P1**) was found by TGA and the mechanical properties were studied by temperature-dependent rheometry [21]. GPC investigations of this metal coordination polymer applying special conditions (DMF containing 5 mmol/L of NH_4PF_6 as eluent at 50 °C) in order to minimize the interactions of the coordination polymer with the column material [19] revealed high molecular mass polymers.

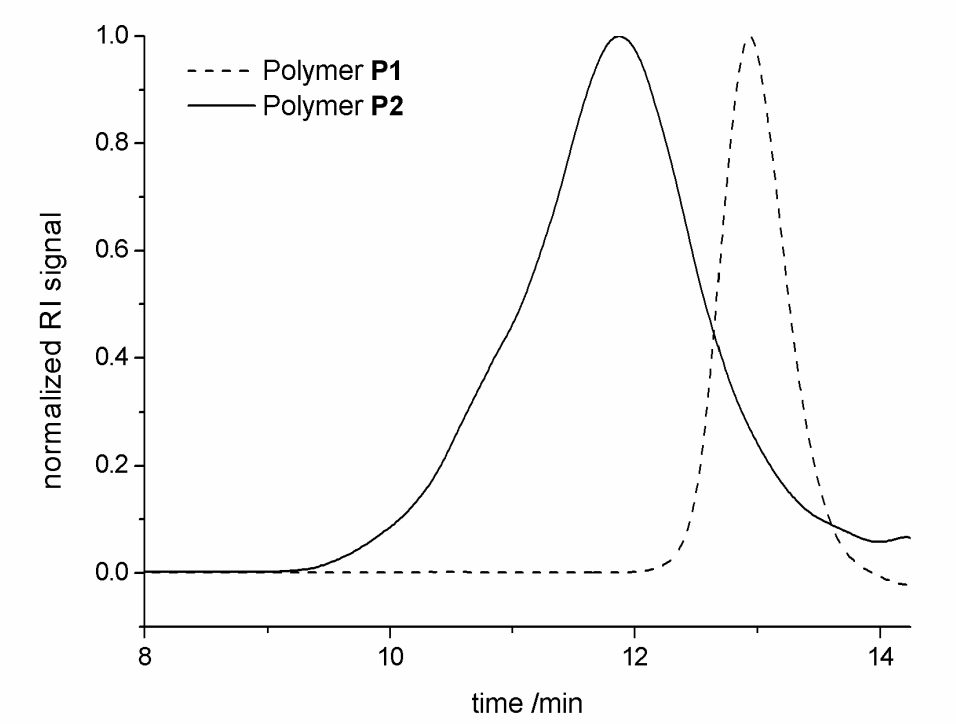

Fig. 2. Refractive index gel permeation chromatography traces of polymers **P1** and **P2**.

Figure 2 displays GPC traces of **P1** and **P2**. It is obvious that the molecular weight of **P2** shifted to a shorter retention time and therefore a higher molecular weight if compared to **P1**. Moreover, a broadening of the molecular weight distribution was observed. This behavior is explainable since a polydispersity index of 2 is expected for a classical polycondensation and 100% functional group conversion if the theory developed by Flory is taken into account [22, 23]. Furthermore, the presence of the small shoulder on the high molecular weight side of the molecular weight distribution of **P2** might be explained by the presence of different macromolecular species, namely linear chain extended polymers as well as macromolecular rings. Once more, this behavior is typical for polycondensation like polymerization reactions. Using a RI-detector and a linear PMMA calibration revealed a number averaged molecular weight (M_n) of 138 000 and a polydispersity index (PDI) of 1.55. These results represent the first successful evaluation of a high molecular weight chain extended supramolecular polymer based on a Ru(II)-*bis*-terpyridine connectivity by an optimized GPC method. The calculated molecular weight of **P2** corresponds to 15

repeat units of the α,ω-*bis*-terpyridine-poly(ethylene glycol) polymer **P1** clearly demonstrating the chain extension of a linear terpyridine functionalized polymer is feasible. In addition to the RI-detector, a photodiode array (PDA) detector was used to study **P2** with GPC techniques. Figure 3 shows a three dimensional elution profile of **P2**. An extracted UV/Vis spectrum at an elution time of 11.5 minutes is displayed in the inset of Figure 3 revealing the typical metal to ligand charge transfer (MLCT) band of the *bis*-tpy-Ru(II) complex at ~490 nm. Furthermore, the three dimensional plot clearly shows that this characteristic MLCT band can be found over the whole polymer distribution indicating that the *bis*-tpy-Ru(II) type connectivity is present in all observed macromolecular species of **P2**.

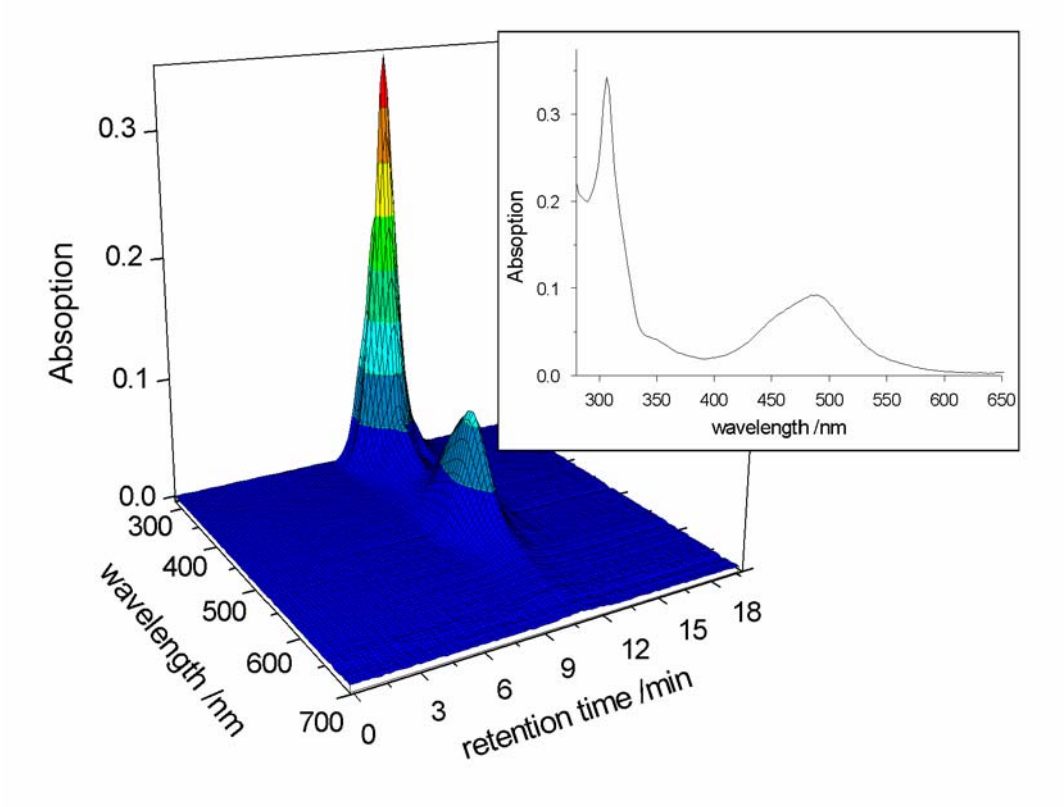

Fig. 3. Photo diode array gel permeation chromatogram results of polymer **P2**. The inset shows an extracted UV/Vis spectrum (in DMF with 5 mM NH_4PH_6) at a retention time of 11.5 minutes.

Moreover, analytical ultracentrifugation was performed to determine the average molecular mass of the metallopolymer **P2**. Sedimentation equilibrium measurements were carried out and the obtained equilibrium profile was fitted with the exponential describing the ideal sedimentation behavior [24]. In this way, an average molar mass of the metallopolymer (which is, in general, different from the known average values M_n and M_w) was obtained. The experiments were carried out in DMF as solvent using NH_4PF_6 as buffer salt to screen out electrostatic interactions. As a result, a molecular weight of 143 000 was determined. This corresponds to 16 repeat units of the α,ω-*bis*-terpyridine-poly(ethylene glycol) **P1** in the supramolecular polymer P2 and is in good agreement with the above described results obtained by GPC measurements. In addition, the molecular weight of **P2** was evaluated by viscosity measurements [20]. The intrinsic viscosity of **P2** was shown to be 120 mL/g and this value was used to calculate a viscosity average molecular weight of 123 000 (based on Mark-

Houwink constants for completely covalent poly(ethylene glycol)) [20]. This value would correspond to approximately 14 repeat units of **P1** in the supramolecular polymer **P2**.

Table 1 summarized the different molecular weight values obtained from the different described techniques. In general, the obtained results accordingly show the formation of high molecular weight chain extended supramolecular polymers with approximately 15 repeat units of **P1**. Analytical ultracentrifugation (AUC), as an absolute analytical technique in terms of molecular weight, should provide very accurate results if compared to the relative techniques, GPC and viscosimetry. However, the high experimental effort of AUC in combination with a difficult interpretation of the resulting molecular weight values (see also above) make AUC anything but straightforward. Therefore, especially the new and interesting GPC results clearly demonstrate the advantages of this easier and faster technique. GPC can quickly provide accurate and conclusive results for the difficult to analyze investigated supramolecular polymers, especially if hyphenated techniques are applied (as demonstrated with the PDA detector) are applied. In the future, this GPC technique will be very valuable for the evaluation of different polymerization parameters for a variety of supramolecular *bis*-terpyridine type of monomers in terms of their molecular weight, reaction speed and conversion.

Tab. 1. Comparison of the molecular weights obtained for **P2** by gel permeation chromatography (GPC), analytical ultracentrifugation (AUC) and viscosimetry.

	Molecular weight	**repeat unit number of P1**
GPC (M_n)	136 700	15
AUC (M_{AUC})	143 000	16
Viscosimetry (M_v)	123 000	14

In conclusion, the determination of the molecular weight of a supramolecular polymer based on *bis*-terpyridine ruthenium(II) complexes by GPC, viscosimetry as well as analytical ultracentrifugation was described. Especially, the novel insights obtained from the optimized GPC system in combination with the results from analytical ultracentrifugation experiments show that GPC can be a very versatile and straightforward tool for the investigation of these metal containing polymers. All obtained results were in good accordance. Therefore, the results obtained by different analytical techniques undoubtfully confirm the formation of high-molecular metallopolymers through complexation of polymeric telechelics with ruthenium(II) ions. An average of 15 polymeric repeat units was found for the supramolecular polymer **P2** corresponding to a molecular weight of approximately 140 000.

Experimental part

Materials

All reagents were used without further purification unless stated otherwise. Solvents were purchased from Biosolve Ltd. (Valkenswaard, The Netherlands).

The synthesis and standard characterization of the investigated metallo-supramolecular polymer are described in the literature [20].

Instrumentation

Gel permeation chromatograms were measured on a Waters GPC system consisting of an isocratic pump, solvent degasser, column oven, 2996 photo diode array (PDA) detector, 2414 refractive index detector, 717plus autosampler and a Styragel HT 6E GPC column with precolumn installed. The eluent was *N,N*-dimethyl formamide (DMF) with 5 mM NH_4PF_6 at a flow of 0.3 mL/min. The column temperature was set to 50 °C. PMMA standards were utilized for calibration.

Analytical ultracentrifugation was carried out with a Beckmann Optima XL-A ultracentrifuge. Sedimentation equilibrium measurements were performed at 20 °C and a rotor speed of 5000 rpm. The absorption was measured at 488 nm (metal-to-ligand charge transfer band of the terpyridine ruthenium(II) complex). Ammonium hexafluorophosphate or tetrabutyl ammonium hexafluorophosphate (20 mmol) were added to screen out the electrostatic interactions in the solution.

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