Terpyridine Based Metallo-Supramolecular Initiators: Towards Novel Self-Organizing Materials

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Abstract. [Fe(II){5,5″-*bis*(bromomethyl)-terpyridine}$_2$](PF$_6$)$_2$ complexes were used as metallo-supramolecular initiators for the living polymerization of 2-ethyl-2-oxazolines yielding defined hydrophilic polymers with a central supramolecular building unit and star-like architectures. The living character of the polymerization allows an exact control of the molecular weight as well as the incorporation of additional (complexing) units at the polymer chain ends.

Key words: terpyridine, supramolecular chemistry, polyoxazoline, self-organization.

1. Introduction

The construction of novel functional materials with useful self-assembly features is one major goal in supramolecular, polymer and material science due to the potential applications of these systems as advanced materials [1]. One promising approach uses the incorporation of special supramolecular building units into well-defined polymer architectures. Systems containing metal ions are of particular interest due to their potential electrochemical, photochemical and magnetic properties. Recent approaches have taken advantage of the well-known terpyridine, bipyridine and *oligo*(bipyridine) building blocks for the preparation of new supramolecular polymers [2, 3].

It has been demonstrated that some of these polymers display new material properties due to their ability to form well-defined complexes and supramolecular structures via metal ion based self-organization and self-recognition processes [2, 3]. However, the preparation of the corresponding functionalized heterocyclic ligands, as well as their incorporation into the polymer, has always been the main drawback in this approach to such supramolecular structures. Here we report a different approach to the incorporation of terpyridine building units into polymer main chains as an extension of our recent metallo-supramolecular initiator route [4] (see also [5]). We have used *bis*functionalized 5,5″-dimethyl-2,2′:6′,2″-terpyridine

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metal complexes as initiators for the living polymerization of 2-ethyl-2-oxazoline, obtaining functional metallo-supramolecular star-like polymers.

2. Experimental

2.1. MATERIALS

The solvent acetonitrile was purified by distillation over calcium hydride. 2-Ethyl-2-oxazoline and 2-phenyl-2-oxazoline were refluxed and distilled over CaH_2. $FeSO_4 \cdot 7 H_2O$ (Aldrich) was used as received. Piperidine (Bayer) was purified by distillation. The reactants for the synthesis of the ligands were used as received from Aldrich.

2.2. SYNTHESIS

5,5″-Dimethyl-2,2′:6′,2″-terpyridine (2,6-di(5′-methylpyrid-2′-yl)pyridine) (**6**)
Terpyridine **6** was synthesized according to published procedures (for unfunctionalized terpyridine, see e.g., [6]) and using a new synthetic strategy with organotin intermediates and Stille type coupling procedures [7]. M.p.: 174–175 °C decomposition temperature 245 °C (95%). ^{1}H-NMR (CDCl$_3$, 300 MHz): δ 2.39 (s, 6 H, H-7,-7″), 7.63 (dd, 2 H, H-4,-4″, $J_1 = 8.01$ Hz, $J_2 = 2.28$ Hz), 7.91 (t, 1 H, H-4′, $J = 7.82$ Hz), 8.38 (d, 2 H, H-3′,-5′, $J = 7.62$ Hz), 8.49 (d, 2 H, H-3,-3″, $J = 8.40$ Hz), 8.50 (s, 2 H, H-6,-6″). ^{13}C-NMR (CDCl$_3$, 75 MHz): δ 18.34 (C-7,-7″), 120.32 (C-3,-3″), 120.64 (C-3′,-5′), 133.32 (C-5,-5″), 137.32 (C-4,-4″), 137.70 (C-4′), 149.46 (C-6,-6″), 153.75 (C-2,-2″), 155.33 (C-2′,-6′). EI MS, m/z 261 (100%, M + 1). *Elemental Analysis: Calc.* for C$_{17}$H$_{15}$N$_3$: C. 78.13, H. 5.79, N. 16.08. *Found:* C. 77.92, H. 5.73, N. 16.07. UV/VIS (CH$_3$CN): λ_{max}/nm ($\epsilon/10^4$ cm^2 mol^{-1}) = 245 (1.89), 286 (2.17). IR (KBr): 2916, 1591, 1557, 1484, 1443, 1375, 1257, 1132, 1024, 812, 754.

*5,5″-Bis(bromomethyl)-2,2′:6′,2″-terpyridine (2,6-di(5′-bromomethyl-2′-yl)-pyridine (**7**)*
To 2.27 g (8.69 mmol) 5,5″-dimethyl-2,2′:6′,2″-terpyridine **6** was added 7.75 g (43.5 mmol) NBS, 221 mg (1.35 mmol) AIBN and tetrachloromethane (120 mL). The mixture was refluxed under nitrogen for 32 min and the unreacted solid NBS was removed immediately from the hot mixture by filtration. The precipitate was washed with CCl$_4$, the combined CCl$_4$ phases were reduced to 50 mL *in vacuo* and the precipitate was removed by filtration. The solid was dissolved in CH$_2$Cl$_2$ (100 mL) and shaken out twice with 0.5 M Na$_2$S$_2$O$_3$ solution (150 mL). The combined Na$_2$S$_2$O$_3$ fractions were extracted with CH$_2$Cl$_2$ and the combined CH$_2$Cl$_2$ layers were dried over Na$_2$SO$_4$ yielding 870 mg (23.9%) of 5,5″-*bis*(bromomethyl)-2,2′:6′,2″-terpyridine **7**. Further purification by recrystallisation in CHCl$_3$ yielded 545 mg of a very pure product. M.p. 195–196 °C (188 °C [8]). ^{1}H-NMR (CDCl$_3$, 300 MHz): δ 4.56 (s, 4 H, H-7,-7″), 7.92 (dd, 2 H, H-4,-4″, J_1

= 8.39 Hz, J_2 = 2.29 Hz), 7.97 (t, 1 H, H-4″, J = 8.01 Hz), 8.47 (d, 2 H, H-3′,-5′, J = 8.02 Hz), 8.61 (d, 2 H, H-3,-3″, J = 8.01 Hz), 8.72 (d, 2 H, H-6,-6″, J = 2.29 Hz). ^{13}C-NMR (CDCl$_3$, 75 MHz): δ 29.54 (C-7,-7″), 121.24 (C-3,-3″), 121.55 (C-3′,-5′), 133.87 (C-5,-5″), 137.79 (C-4,-4″), 138.08 (C-4′), 149.06 (C-6,-6″), 154.61 (C-2,-2″), 155.78 (C-2′,-6′). EI MS, m/z 419 (20%, M + 1). *Elemental Analysis: Calc.* for C$_{17}$H$_{13}$N$_3$Br$_2$: C. 48.72, H. 3.13, N. 10.03. *Found:* C. 48.63, H. 2.68, N. 10.05.

*Bis(5,5″-bis(bromomethyl)-2,2′:6′,2″-terpyridine) iron(II) hexafluorophosphate (**8**)*
To a solution of 246.7 mg (0.589 mmol) 5,5″-*bis*(bromomethyl)-2,2′:6′,2″-terpyridine **7** in methanol (80 mL) was added 81.9 mg (0.295 mmol) FeSO$_4$·7 H$_2$O suspended in methanol (15 mL). The reaction mixture turned immediately to a red color. After stirring at room temperature under nitrogen for 8 h, excess NH$_4$PF$_6$ (2.5 g, 15 mmol) was added (solution in methanol) leading to an immediate precipitation of a red solid and the mixture was further stirred for 5 min. After 24 h the solid was filtered off and washed with cold methanol (5 mL), water (20 mL) and diethylether (10 mL) followed by a recrystallization from acetonitrile/diethylether yielding 282 mg (80.1%) of {[Fe(**7**)$_2$](PF$_6$)$_2$} **8** as a red crystalline solid. M.p. 225–226 °C. ^{1}H-NMR (CD$_3$CN, 300 MHz): δ 4.23 (s, 8 H, H-7,-7″), 7.00 (s, 4 H, H-6,-6″), 7.97 (d, 4 H, H-4,-4″, J = 8.40 Hz), 8.48 (d, 4 H, H-3,-3″, J = 8.39 Hz), 8.75 (t, 2 H, H-4′, J = 8.01 Hz), 8.96 (d, 4 H, H-3′,-5′, J = 8.01 Hz). ^{13}C-NMR (CD$_3$CN, 75 MHz): δ 28.24 (C-7), 124.05, 124.68, 138.69, 138.83, 139.98, 153.08, 157.85, 160.40, 177.44. *Elemental Analysis: Calc.* for C$_{34}$H$_{26}$Br$_4$N$_6$FeF$_{12}$P$_2$: C. 34.49, H. 2.21, N. 7.10. *Found:* C. 34.77, H. 2.52, N. 7.06. UV/VIS (CH$_3$CN): λ_{max}/nm (ϵ/10^4 cm^2 mol^{-1}) = 561 (0.64), 328 (6.20), 280 (4.89).

General procedure for polymerization

The complex **8** was dissolved in dry acetonitrile (4 mg of **8** per 1 mL of acetonitrile) under nitrogen and the dry monomer (2-ethyl-2-oxazoline) was added. The reactor was closed and stirred at 80 °C for 44 h. After taking a small sample, an excess of dry piperidine (3 equivalents per initiating CH$_2$Br group) was added to terminate the polymerization and the mixture was stirred for another day at 80 °C. The mixture was then allowed to cool to room temperature and the solvent was evaporated. The remaining polymer was dissolved in CH$_2$Cl$_2$ and precipitated in diethylether. After stirring for 2 h the resulting polymer was isolated by filtration and dried *in vacuo*. The polymers were characterized by NMR, GPC and UV/VIS. Analytical data (ethyl homopolymer, [M]/[I] = 40): ^{1}H-NMR (CDCl$_3$, 300 MHz): δ = 1 0–1.2 (m; CH$_3$), 2.1–2.5 (m; COCH$_2$), 3.2–3.6 (m; NCH$_2$CH$_2$). Intensity ratio: 3 : 2 : 4.
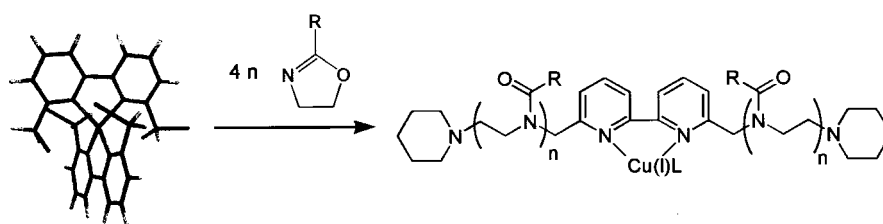
Figure 1. General polymerization procedure towards polyoxazolines containing 6,6′-*bis*functionalized 2,2′-bipyridine units [4].
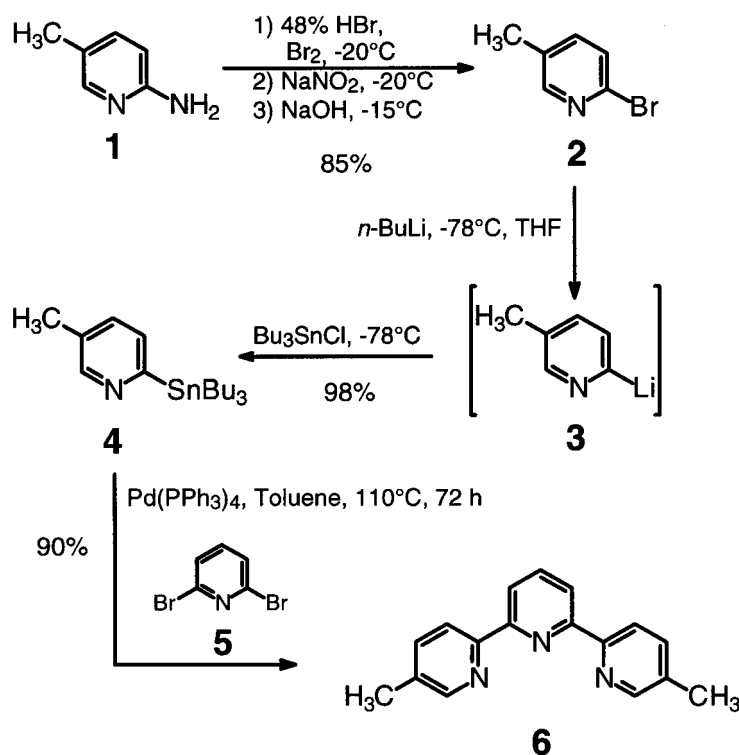

Figure 2. Synthetic route to 5,5″-dimethyl-2,2′:6′,2″-terpyridine (**6**).

3. Results and Discussion

We have recently demonstrated that 6,6′-bisfunctionalized 2,2′-bipyridine cop-per(I) complexes can be used as metallo-supramolecular initiators for the living cationic polymerization of 2-oxazolines resulting in star-like polymers. (See also experiments performed by Fraser et al. with 4,4′-*bis*functionalized 2,2′-bipyridine metal complexes [5].) This method opens a new avenue for the preparation of supramolecular polymers (Figure 1). The bipyridine units used are of great interest in supramolecular chemistry due to their ability to form well-defined architec-tures, like double helices, as well as to their selective complexation behavior
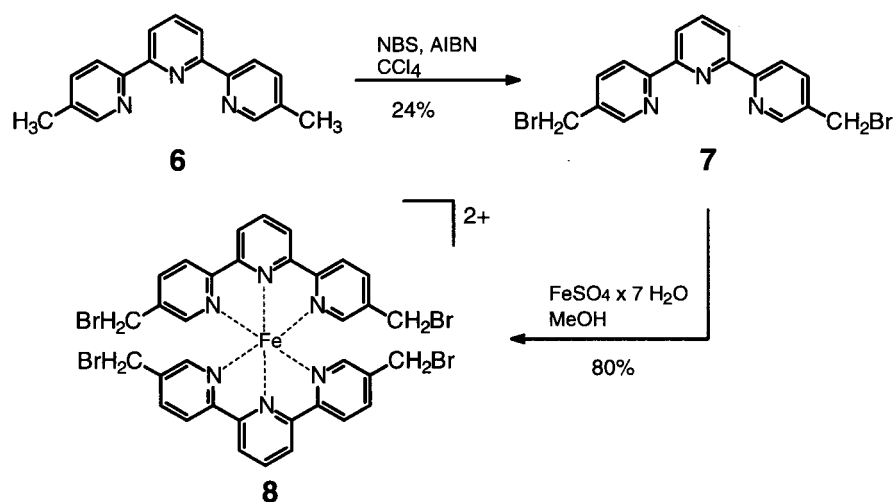
Figure 3. Synthetic route to di(5,5″-*bis*(bromomethyl)-2,2′:6′,2″-terpyridine) iron(II) hexa-fluorophosphate (**8**).
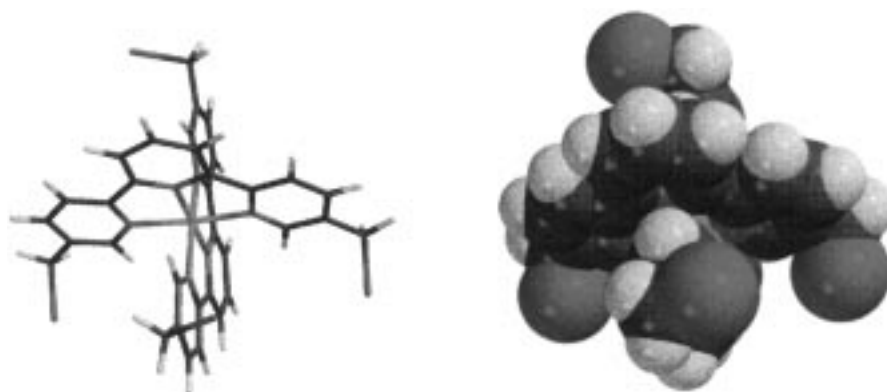

Figure 4. Molecular modeling (MAC Spartan Plus, Level MM2) of the initiator complex (**8**). *Left:* wireframe model. *Right:* space filling representation.

[9]. The oxazoline monomers are perfectly suited for these applications, due to their variability in structure and due to the living nature of the polymerization of many 2-oxazoline derivatives [10]. Besides the synthesis and characterization of the star-like polymers obtained, we could also show that the central metal ion could be removed using basic or acid conditions as well as shear forces (e.g., on a GPC column) [4]. However, the 6,6′-*bis*functionalized 2,2′-bipyridine ligands used are only able to complex metal ions like copper(I) or silver(I). With a view to extending to more interesting metal ions we chose the terpyridine ligand as the new basic heterocyclic unit for the construction of a different metallo-supramolecular initiator. The terpyridine molecule has for a long time been known as an excellent complexing unit for transition metal ions, providing complexes with
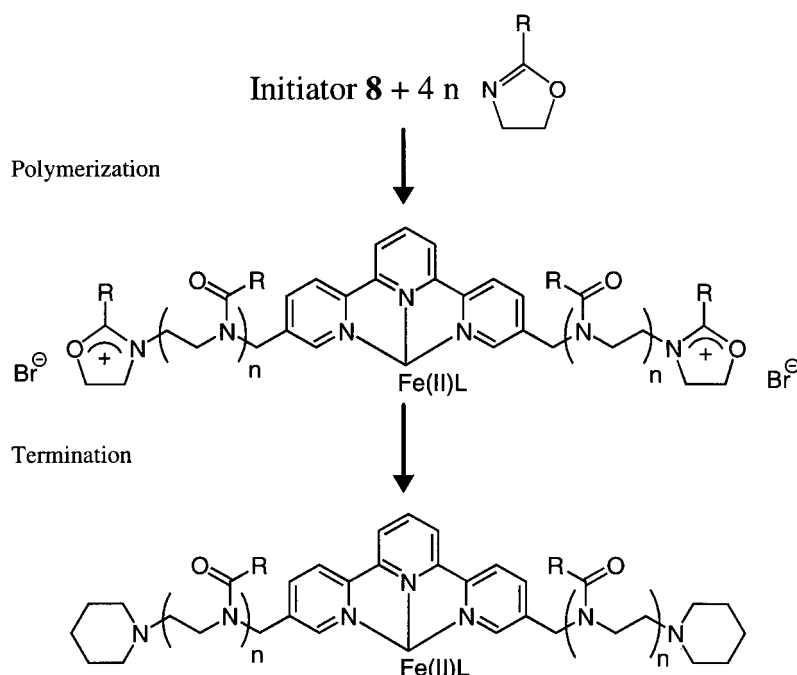
Figure 5. General polymerization procedure leading to polyoxazolines containing 5,5″-*bis*functionalized 2,2′: 6′,2″-terpyridines.

interesting physical properties as well as high stabilities [11]. We decided to use the 5,5″-position of the terpyridine for functionalization due to the relatively simple synthetic availability. Due to the fact that 5,5″-dimethyl-2,2′:6′,2″-terpyridine **6** as well as bromo-functionalized derivatives are not commercially available and the published synthetic strategies are not suitable for the synthesis of larger quantities [6, 12], we developed a new synthetic strategy for this interesting building block (Figure 2). Starting from the commercially available 2-amino-5-picoline **1** the well-described 2-bromo-5-methyl-pyridine **2** could be synthesized at a 140 g scale with 85% yield using a modified literature procedure [13] in a special glass reactor. The bromo compound **2** was then treated with butyllithium at −78 °C to obtain the corresponding lithio compound **3** and then reacted directly with tributyltin chloride to yield 98% of the 2-tributyltin-5-methyl-pyridine **4** at a 70 g scale using Kugelrohr distillation for purification (for earlier preparations of **4** using the same strategy see [7, 14]). Stille-type coupling of **4** with 2,6-dibromopyridine **5** yielded 90% of the 5,5″-dimethyl-2,2′:6′,2″-terpyridine **6** (the synthetic details will be published elsewhere [15]).

Subsequent radical bromination via the NBS route resulted in the pure 5,5″-*bis*(bromomethyl)-2,2′:6′,2″-terpyridine **7** (see also [8]) without critical purification procedures (Figure 3). The corresponding octahedral iron complex **8** was obtained by a simple complexation reaction and isolated as PF_6 salt (Figure 3).

Table I. Molecular weight data for the investigated homo polymers (monomer: 2-ethyl-2-oxazoline, solvent: acetonitrile, polymerization temperature: 80 °C, polymerization time: 44 h, [I] refers to the initiating CH_2Br groups)

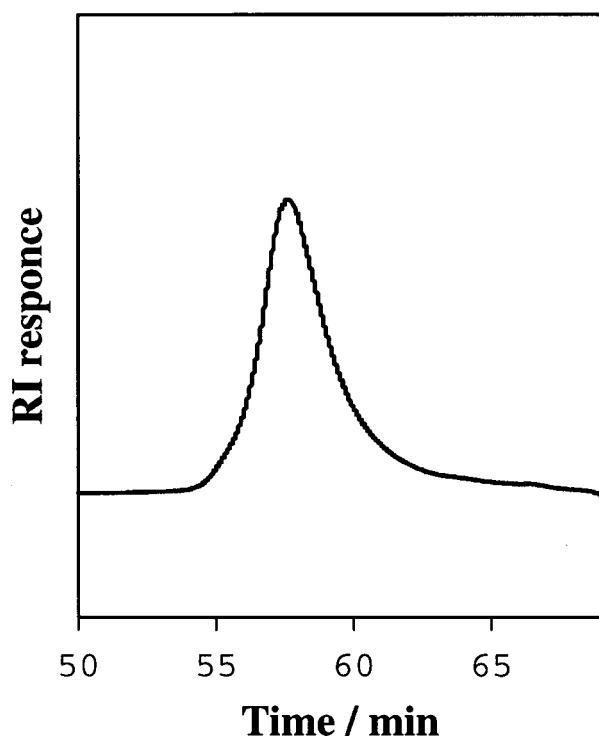| Initiator	M_n (g mol^{-1}) (GPC)	M_w (g mol^{-1}) (GPC)	M_w/M_n (GPC)	[M]/[I]
[Fe(II)(5,5″-*bis*(bromomethyl)-2,2′:6′,2″-terpyridine)$_2$](PF$_6$)$_2$	1050	1240	1.18	10
[Fe(II)(5,5″-*bis*(bromomethyl)-2,2′:6′,2″-terpyridine)$_2$](PF$_6$)$_2$	1500	2130	1.33	20
[Fe(II)(5,5″-*bis*(bromomethyl)-2,2′:6′,2″-terpyridine)$_2$](PF$_6$)$_2$	2500	3160	1.26	30
[Fe(II)(5,5″-*bis*(bromomethyl)-2,2′:6′,2″-terpyridine)$_2$](PF$_6$)$_2$	3280	4140	1.26	40

Figure 6. GPC plot (CHCl$_3$ as eluent, RI-detection) of a typical poly-2-ethyloxazoline containing 5,5″-*bis*functionalized 2,2′:6′,2″-terpyridine; [M]/[I] = 40, terminated with piperidine.

Molecular modeling results reveal the four initiating groups on the surface of the supramolecular complex (Figure 4).

The complex **8** was then treated with 2-ethyl-2-oxazoline in dry acetonitrile at 80 °C for 2 days. The resulting polymer was isolated after or without termination with piperidine (Figure 5). GPC investigation demonstrated the narrow, monomodal molar mass distributions of the polymers obtained (Figure 6). As shown in our earlier papers, the unfunctionalized metal complex as well as the free metal salt (FeSO$_4$·7 H$_2$O) did not operate as initiator [4]. However, reaction of the uncomplexed 5,5″-*bis*(bromomethyl)-2,2′:6′,2″-terpyridine **7** with 2-oxazolines also initiated the polymerization – but in this case, the nitrogen atoms of the bipyridines can act as termination reagents and therefore branch and finally cross-link the living polymer chains, resulting in higher molecular weight or insoluble material [4]. The UV/VIS spectra of the iron-containing red polymers clearly show the incorporation of the terpyridine iron complexes into the polymer (Figure 7).

The living character of the polymerization was demonstrated by experiments with various monomer-to-initiator concentrations. These experiments illustrated the linear relationship between the average molecular weight M_n and the [monomer]/[**8**] ([M]/[I]) ratio for the polymers (Figure 8) and the low polydis-
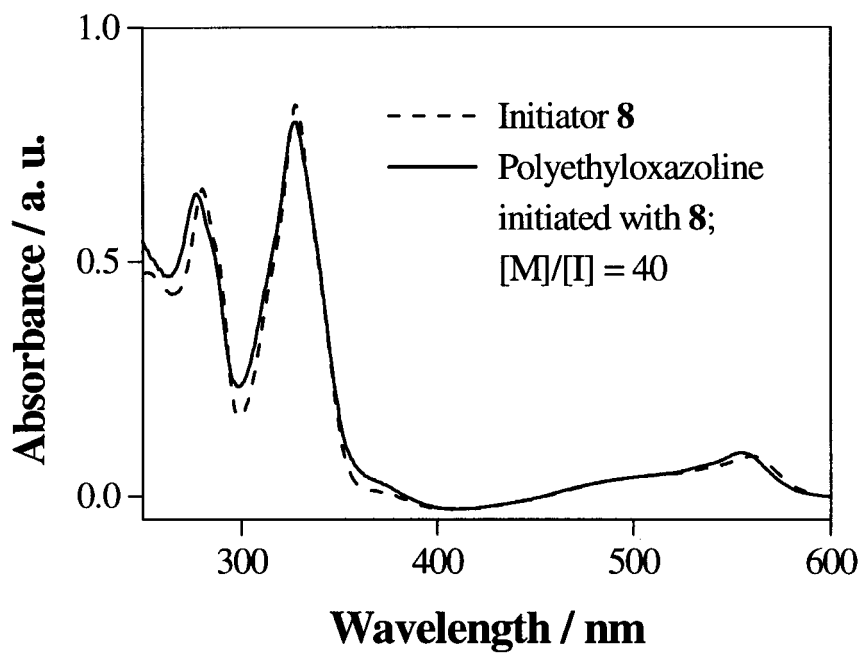
Figure 7. UV/VIS spectrum of a typical poly-2-ethyloxazoline containing 5,5″-*bis* functionalized 2′,2′:6′,2″-terpyridine (solid line). [M]/[I] = 40, terminated with piperidine.
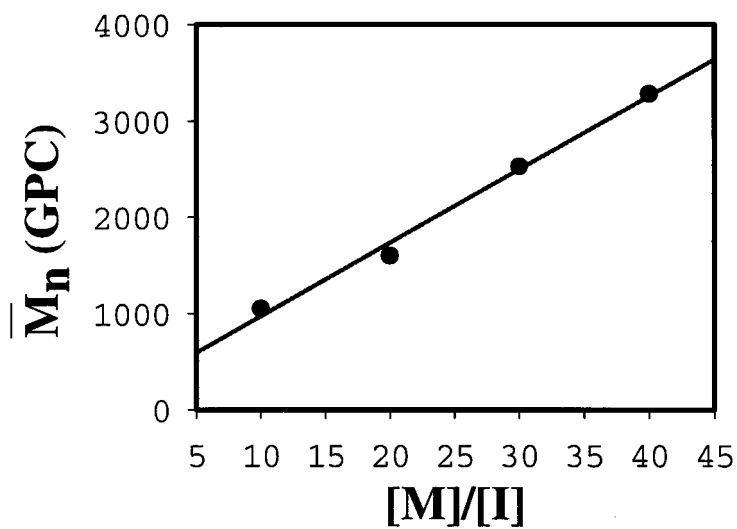

Figure 8. Plot of the number average molecular weight M_n versus [M]/[I] ratio for the polymers ([I] refers to the initiating CH_2Br groups).
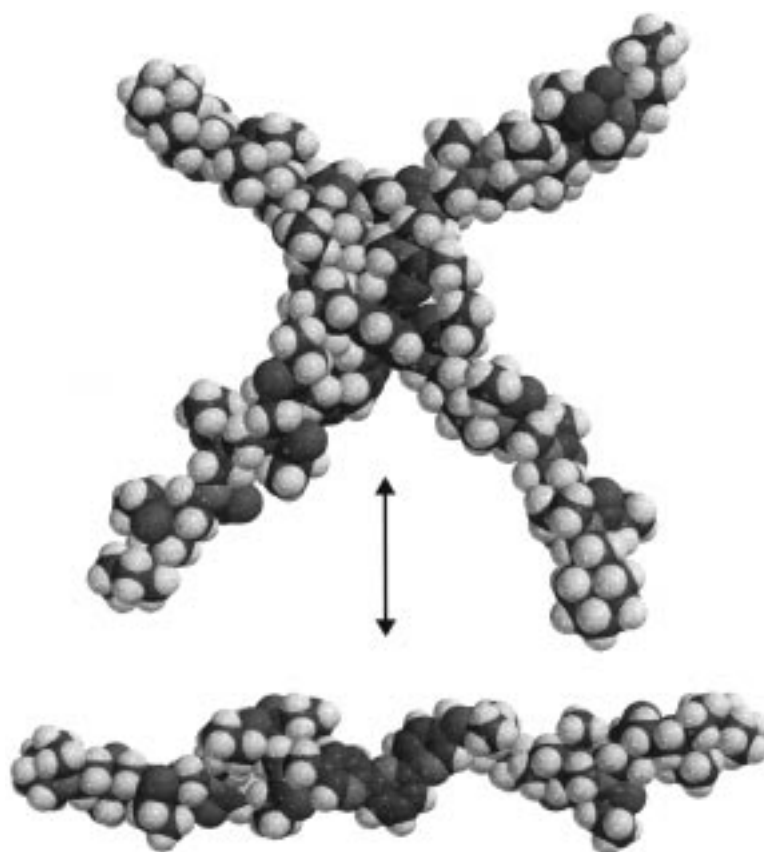
Figure 9. Molecular modeling (MAC Spartan Plus, Level MM2) of the poly-2-ethyloxazoline. *Top:* star-shaped structure of a polymer with a metallo-supramolecular core. *Bottom:* linear polymer with free metal binding unit.
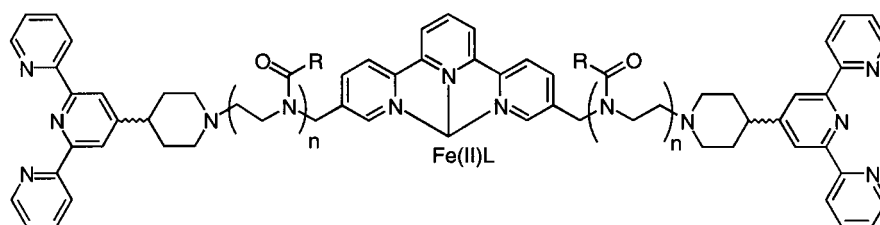

Figure 10. Schematic representation of a terpyridine terminated polyoxazoline.

persity of the polymers investigated (Table I). In addition, we synthesized block copolymers using different types of oxazoline monomers. Polymerization of 2-ethyl-2-oxazoline was initiated by **8** using the conditions described above. After the 2-ethyl-2-oxazoline monomer was consumed at 80 °C, 2-phenyl-oxazoline was

added and the temperature was adjusted to 110 °C. The formation of the block copolymers was confirmed by NMR and GPC.

The molecular modeling in Figure 9 shows the star-like architecture of the obtained polymer with a metallo-supramolecular core unit. Removing the metal ions using basic or acidic conditions lead to a linear polymer, with a free metal binding unit (Figure 9). This 'switching' of the 3-dimensional architecture of the polymer can also be obtained using electrochemical manipulations as well as shear forces. Furthermore, other supramolecular units can be introduced to the outside of the star-like polymer using suitable termination agents (Figure 10).

4. Conclusion

The results reported above demonstrate a novel route to terpyridine-containing functional polymers. The obtained star-like polymers with a metallo-supramolecular core can be manipulated and therefore the three-dimensional structure can be controlled, providing new supramolecular materials with interesting potential application. Due to the exact control of molecular weight, defined (functionalized) end groups and the variability of the polymer main chain itself, an interesting combination between supramolecular chemistry and classical polymer chemistry has been introduced. Further experiments in this direction are currently in progress.

Acknowledgements

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