Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

POLYMERS WITH METAL BINDING UNITS: BIPYRIDINE AND TERPYRIDINE CONTAINING POLYOXAZOLINES

Ulrich S. Schubert[a]; Oskar Nuyken[a]; Georg Hochwimmer[a]
[a] Technische Universität München, Garching, Germany

To cite this Article Schubert, Ulrich S. , Nuyken, Oskar and Hochwimmer, Georg(2000) 'POLYMERS WITH METAL BINDING UNITS: BIPYRIDINE AND TERPYRIDINE CONTAINING POLYOXAZOLINES', Journal of Macromolecular Science, Part A, 37: 6, 645 — 658

To link to this Article: DOI: 10.1081/MA-100101115

URL: http://dx.doi.org/10.1081/MA-100101115

J.M.S.—PURE APPL. CHEM., A37(6), pp. 645–658 (2000)

NOTE

POLYMERS WITH METAL BINDING UNITS: BIPYRIDINE AND TERPYRIDINE CONTAINING POLYOXAZOLINES

Ulrich S. Schubert,* Oskar Nuyken, and Georg Hochwimmer

Lehrstuhl für Makromolekulare Stoffe
Technische Universität München
Lichtenbergstr. 4, 85747 Garching, Germany

Key Words: Supramolecular Chemistry, Polyoxazolines, Living Polymerization, Metal Binding Units, Telechelics, Bipyridines

ABSTRACT

2,2’-Bipyridines functionalized with one bromomethyl group in the 5-position were used as metallo-supramolecular initiators for the living cationic polymerization of 2-oxazolines utilizing cobalt(II), iron(II) and ruthenium(II) transition metal ions. The central metal ions could be removed using basic conditions resulting in uncomplexed polymers with a free metal binding side. The obtained polymers were characterized using NMR, UV/Vis spectroscopy, GPC and MALDI-TOF mass spectrometry. The termination of the living end groups with an amino-functionalized terpyridine during the polymerization process opens the possibility for the construction of polymers with different metal binding sides. Due to the exact control of molecular

---

*Author to whom correspondence should be addressed.

weight, defined end groups and the variability of the oxazoline monomers new supramolecular polymers can be obtained.

INTRODUCTION

The design of polymer architectures with metal binding sides is a major goal in today's polymer chemistry due to the expected potential properties of the corresponding metal containing polymers [1-4]. However, the controlled incorporation of such units is the main synthetic problem. We described recently a new approach towards bipyridine and terpyridine containing polymers utilizing metallo-supramolecular initiators for the living cationic polymerization of 2-oxazolines [5-7] (see also results by Fraser *et al*. [8-10]). This method offers a suitable way to incorporate one metal binding side into each polymer chain. To include bipyridine ligands, different initiator systems based on 4,4'-*bis*functionalized-2,2'-bipyridines [8, 9] and 6,6'-*bis*functionalized-2,2'-bipyri-dines [5, 6] were used in previous work by us and others. To extend this approach to other interesting metal binding units and telechelics, we chose 5-mono-functionalized-2,2'-bipyridine ligands (for the first synthesis of the initiator see [11]).

EXPERIMENTAL

Preparation of the Ligand

5-Bromomethyl-5'-methyl-2,2'-bipyridine was synthesized starting from 5,5'-dimethyl-2,2'-bipyridine using LDA (lithium diisopropylamide) and TMSCl (trimethylsilylchloride) followed by a reaction with $(CBrF_2)_2$ and CsF in DMF (dimethylformamide). Experimental details are published elsewhere [11, 12].

Preparation of the Metallo-Supramolecular Initiators

[Ru(II)((5-bromomethyl-5'-methyl)-2,2'-bipyridine) (2,2'-bipyridine)$_2$] $(PF_6)_2$ (**1**): *Cis*-Ru(2,2'-bipyridine)$_2$Cl$_2$ • 2 H_2O (108 mg, 0.206 mmol) and $AgSO_3CF_3$ (108 mg, 0.420 mmol) were dissolved in dry acetone (9 mL). The reaction mixture was stirred for 18 hours at room temperature and the precipitated AgCl was removed by filtration. 5-Bromomethyl-5'-methyl-2,2'-bipyridine (54.0 mg, 0.205 mmol) was added to the eluent and the reaction mixture was stirred for 2 hours. After the addition of a saturated solution of NH_4PF_6 (0.7 g, 4.3 mmol) in methanol, a red precipitate appears. The remaining solid was filtered off, dissolved in a small amount of acetone, and precipitated in diethylether. The red solid was further purified by column chromatography using Alumina (CH_3CN/toluene (1:1)) resulting in 198 mg (40%) of the desired [Ru(II)((5-bromomethyl-5'-methyl)-2,2'-bipyridine)(2,2'-bipyridine)$_2$](PF_6)$_2$. $C_{32}H_{27}N_6Br_2RuP_2F_{12}$ • 0.5 acetone (995.6): Calcd.: C 40.42, N 8.44, H 3.04. Found: C 40.83, N 9.08, H 3.40.

[Co(II)((5-bromomethyl-5'-methyl)-2,2'-bipyridine)$_3$](PF_6)$_2$ (**2**): 5-Bromomethyl-5'-methyl-2,2'-bipyridine (154 mg, 0.584 mmol) was dissolved in methanol (8 mL) and treated with $Co(CH_3COO)_2$ • 4 H_2O (48.4, 0.194 mmol) in methanol (3 mL). The yellow mixture was stirred for 4 hours at room temperature and a solution of NH_4PF_6 (0.60 g, 3.7 mmol) in methanol was added. The reaction mixture was cooled to –40°C resulting in a yellow precipitate. The solid was filtered off, washed with cold methanol, H_2O and diethylether and finally dissolved in acetone. The solution was dropped into diethylether and the solid was filtered off again and dissolved in a small amount of acetone. Diffusion of diethylether into the solution gave a yellow precipitate of [Co(II)((5-bromomethyl-5'-methyl)-2,2'-bipyridine)$_3$] (PF_6)$_2$ (108 mg, 49%). $C_{36}H_{33}N_6Br_3CoP_2F_{12}$ • acetone (1196.35): Calcd.: C 39.15, N 7.02, H 3.28. Found: C 39.72, N 7.42, H 3.19. UV/VIS (CH_3CN): λ_{max}/nm ε/(L · mol^{-1} · cm^{-1})) = 257 (45 560), 303 (52 510). ESI-MS: 1138.8 [M^+]. MALDI-TOF-MS: 993 [M^+ - PF_6].

[Fe(II)((5-bromomethyl-5'-methyl)-2,2'-bipyridine)$_3$](PF_6)$_2$ (**3**): 5-Bromomethyl-5'-methyl-2,2'-bipyridine (156 mg, 0.591 mmol) was dissolved in methanol (8 mL) and reacted with $FeSO_4$ • 7 H_2O (54.6 mg, 0.196 mmol) in methanol (3 mL). The red mixture was stirred for 4 hours at room temperature. A solution of NH_4PF_6 (0.60 g, 3.7 mmol) in methanol was added and the mixture was stirred for another 2 days. The reaction volume was reduced to 6 mL *in vacuo* resulting in a red solid. The solid was filtered off, washed with cold methanol, H_2O and diethylether, and dissolved in acetone. The solution was dropped into diethylether and the solid was filtered off and dissolved in a small amount of acetone. Diffusion of diethylether into this solution yielded a red precipitate of [Fe(II)((5-bromomethyl-5'-methyl)-2,2'-bipyridine)$_3$](PF_6)$_2$ (70 mg, 31%). $C_{36}H_{33}N_6Br_3FeP_2F_{12}$ • acetone (1193.27): Calcd.: C 39.26, N 7.04, H 3.29. Found: C 39.27, N 7.41, H 3.12. UV/VIS (CH_3CN): λ_{max}/nm (ε/(L · mol^- cm^{-1})) = 257 (31 770), 304 (68 290), 525 (3 780). MALDI-TOF-MS: 1006 [M^+ - PF_6 + H_2O].

Preparation of the Polymers

A typical procedure for the polymerization of 2-oxazolines was as follows: The initiator (**1**-**3**) was dissolved in dry acetonitrile (7.5 mg initator/1 mL acetonitrile), dry monomer was added and the mixture was stirred at 80°C for 24 hours. Piperidine or amino functionalized terpyridine was added and the mixture was stirred for 4 hours. The solvent was evaporated *in vacuo*, the polymer was dissolved in CH_2Cl_2 and precipitated in diethylether. This procedure was repeated two times. Terpyridine terminated polymers were obtained by adding amino functionalized terpyridine units.

Extraction of the Central Metal Ion

The polymer (200 mg) was dissolved in 80 mL CH_3CN/H_2O (1:1) and K_2CO_3 (8 g) was added. The mixture was refluxed for 12 hours and the layers were separated. The CH_3CN phase was evaporated *in vacuo* and the remaining polymer was dissolved in CH_2Cl_2 and precipitated in diethylether.

Measurements

^{1}H NMR spectra were recorded at 300 K on a Bruker AM 300 spectrometer in $CDCl_3$ with tetramethylsilane as internal standard. Gel permeation chromatography (GPC) analysis was performed on a Waters Liquid Chromatograph system using Shodex GPC K-802S column and Waters Differential Refractometer 410 in chloroform. Calibration was conducted with polystyrene standards. UV/VIS measurements were recorded using a Varian Cary 3. MALDI-TOF-MS measurements were performed on a Bruker Biflex 3 with dithranol as matrix, acetone as solvent and by addition of potassium trifluoroacetate.

RESULTS AND DISCUSSION

Recently we demonstrated, that 6,6'-*bis*functionalized 2,2'-bipyridine copper(I) complexes were able to initiate the living cationic polymerization of 2-oxazolines [5, 6]. The resulting star-like polymers showed a narrow molecular weight distribution and a predetermined molecular weight. In this paper we describe an extension of this strategy towards other supramolecular building blocks. 5,5'-Dimethyl-2,2'-bipyridines are of special interest in supramolecular

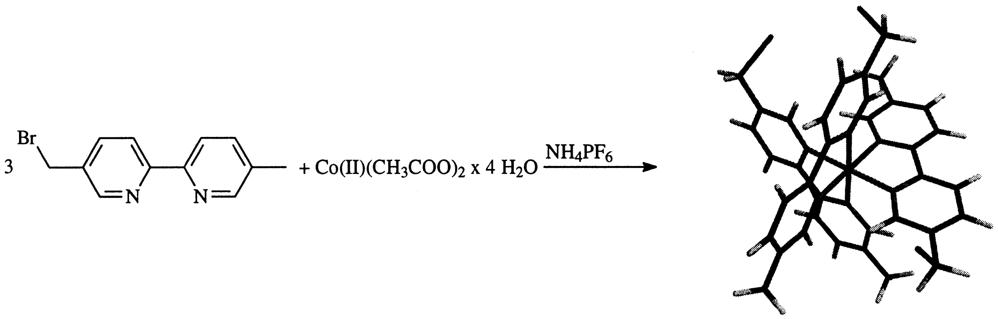

Figure 1. Schematic representation of the complex formation. Right: Molecular modeling (MAC Spartan Plus, Level MM2) of the initiator complex based on Co(II) (wireframe representation).

chemistry due of their ability to form well-defined metal complexes with a broad range of different metal ions (e.g. see [13, 14]. However, the lack of an efficient directed synthesis to functionalized units has always been the major drawback in the incorporation of this building blocks into polymer architectures. To overcome this problem we applied a novel high yield synthesis utilizing organo-tin chemistry and Stille-type carbon-carbon bond forming reactions for the synthesis of 5-bromomethyl-5'-methyl-2,2'-bipyridine functionalized ligands [11, 12]. Furthermore, we synthesized the corresponding metallo-supramolecular complexes by reaction with suitable transition metal ions like Ru(II), Fe(II) or Co(II) in 30% to 50% yield. Figure 1 shows a schematic representation of the typical complexation reaction.

This metallo-supramolecular complexes were then used as initiatior for the living polymerization of 2-ethyl-2-oxazoline. In general, this type of monomers can be polymerized by a living cationic mechanism using electrophiles such as bromomethyl endgroups [15]. The metallo-supramolecular complexes described above contain such initiating groups. Obviously, the functionalized ligands alone without the metal ions are also able to initiate the polymerization. However, in our previous research [4] we have demonstrated that the uncomplexed bipyridine unit can act as a termination agent resulting in branched polymers as well as in some crosslinked polymer chains. The function of the metal ion in the metallo-supramolecular complexes during the polymerization process is therefore similar to a classical protecting group which prevents the growing polymer chains from termination processes.

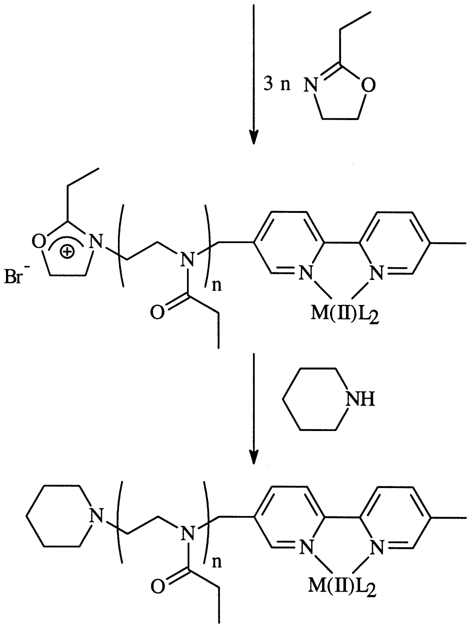

Figure 2. Schematic representation of the polymerization.

Figure 2 shows the general polymerization procedure. The living nature of the polymerization was demonstrated by a linear relationship between [monomer]/[initiator] and the average molecular weight (Figure 3), the narrow molecular weight distribution of the polymers as well as by the preparation of block copolymers (Figure 4). Table 1 gives an overview of the different polyethyloxazoline homopolymers synthesized. Figure 4 shows typical GPC plots of polyethyloxazolines inititated with [Co(II)((5-bromomethyl-5'-methyl)-2,2'-bipyridine)$_3$](PF$_6$)$_2$.

The supramolecular building block in the center of the polymers is rather fragile. Under distinct circumstances this architecture can be destroyed removing the central metal ion. For example, polyethyloxazolines initiated with [Cu(I)(6,6'-*bis*(bromomethyl)-2,2'-bipyrdine)$_2$](PF$_6$) showed a partially destruction of the star-shaped architecture on the GPC column due to shear forces resulting in two peaks in the GPC plot [5, 6]. In contrast to this behavior, polyethyloxazolines inititated with [Co(II)((5-bromomethyl-5'-methyl)-2,2'-bipyridine)$_3$](PF$_6$)$_2$ completely fragmented on the GPC column. Extracting the central metal ion (in the present example Co(II)) under basic conditions revealed an

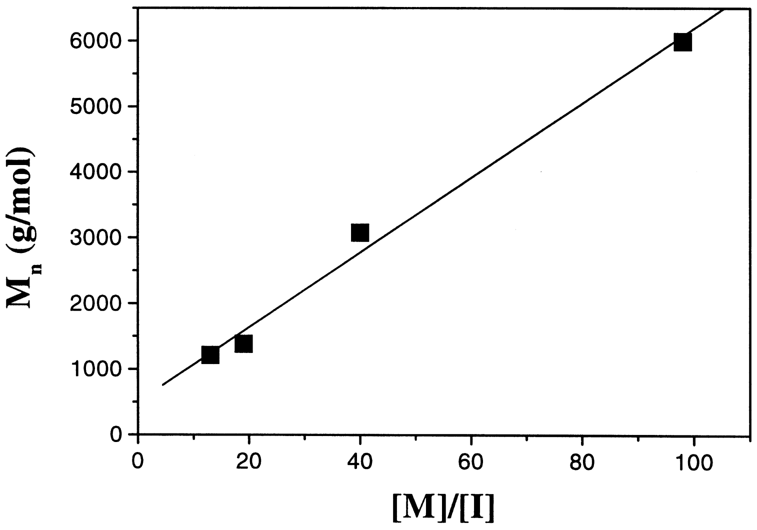

Figure 3. Average Molecular weight M_n versus [M]/[I] for polyethyloxazoline initiated with (**2**).

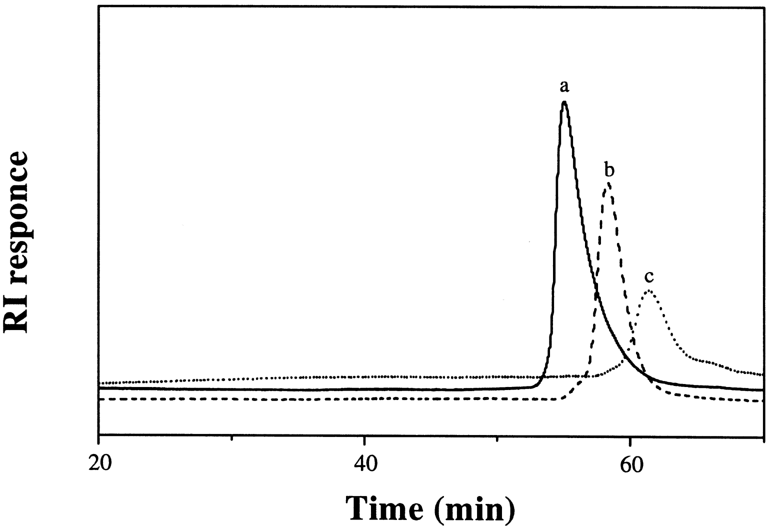

Figure 4. Typical GPC plots ($CHCl_3$ as eluent, RI-detection) of polyethyloxazoline initiated with (**2**); a) refers to [M]/[I] = 98, b) refers to [M]/[I] = 40; c) refers to [M]/[I] = 19. [I] refers to the initiating CH_2Br-group.

TABLE 1. GPC Data ($CHCl_3$ Versus PS-Standards) of Different Polyethyoxazoline Homo Polymers Initiated with Metallo-Supramolecular Complexes. [I] Refers to the Initiating CH_2Br Group.

Initiator	[M]/[I]	$\overline{M_n}$ / g mol^{-1}	$\overline{M_w}$ / g mol^{-1}	$\overline{M_w}$ / $\overline{M_n}$
[Ru(II)(5'-CH_2Br-5'-CH_3)(byp)$_2$](PF$_6$)$_2$ (1)	60	1330	1390	1.05
[Co(II)(5'-CH_2Br-5'-CH_3)(byp)$_2$](PF$_6$)$_2$ (2)	19	1230	1480	1.21
[Co(II)(5'-CH_2Br-5'-CH_3)(byp)$_2$](PF$_6$)$_2$ (2)	40	3080	3550	1.15
[Co(II)(5'-CH_2Br-5'-CH_3)(byp)$_2$](PF$_6$)$_2$ (2)	98	5990	7260	1.21
[Fe(II)(5'-CH_2Br-5'-CH_3)(byp)$_2$](PF$_6$)$_2$ (3)	16	1540	2030	1.32

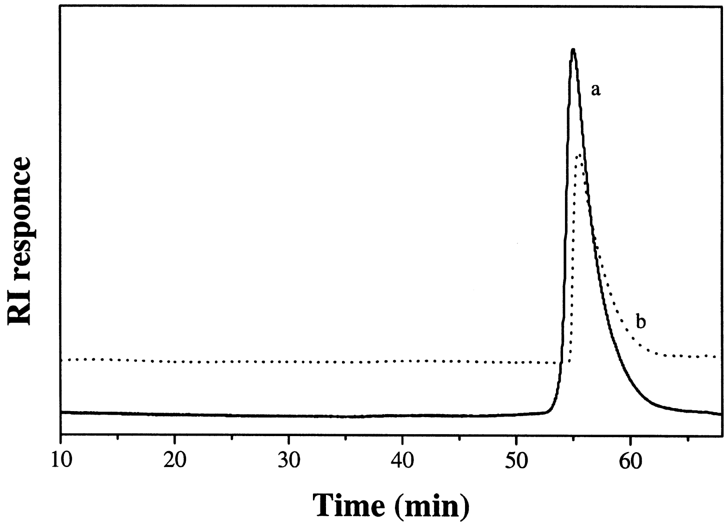

Figure 5. GPC plot before a) and after b) extraction of the central metal ion; [M]/[I] = 98.

identical GPC plot (Figure 5). Therefore, we conclude that the shear forces on the GPC column are sufficient for a loss of the supramolecular architecture.

Molecular weights measured using GPC in general do not give the true molecular weights due to the utilized PS standard calibration and the possible interactions between the amphiphilic polymers and the GPC column. Therefore, we applied MALDI-TOF mass spectrometry to obtain the absolute molecular weights (details will be published elsewhere [16]). Figure 6 shows a typical MALDI-TOF-MS spectra of a polyethyloxazoline initiated with [Co(II)((5-bromomethyl-5’-methyl)-2,2’-bipyridine)$_3$](PF$_6$)$_2$ (we used the non-terminated polyoxazoline sample before termination with the terpyridine unit for this comparison). Calculating the peak at 1 643 g/mol gives a degree of polymerization of 16 which is close to the adjusted value by the [M]/[I] ratio (in this case 19). In contrast, GPC measurements yielded 1 230 g/mol for M_n (utilizing PS calibration). For higher molecular weights the difference is sometimes much larger.

The incorporation of the metallo-supramolecular complex into the polymer was prooven by UV/VIS spectroscopy. Figure 7 shows the identical absorption band at 320 nm for both the initiator complex **2** (curve a) and the resulting polymer (curve b). Removing the central metal ion under basic conditions revealed a clear shift of the π–π* transition band (Figure 7, curve c). The remaining shoulder at around 300 nm results from a small amount of Co(II) remaining

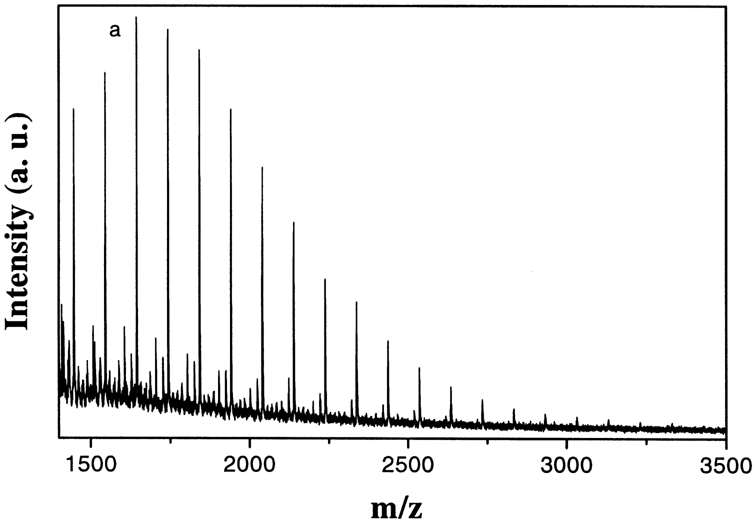

Figure 6. MALDI-TOF-MS spectra of polyethyloxazoline initiated with (**2**) without termination; [M]/[I] = 19.

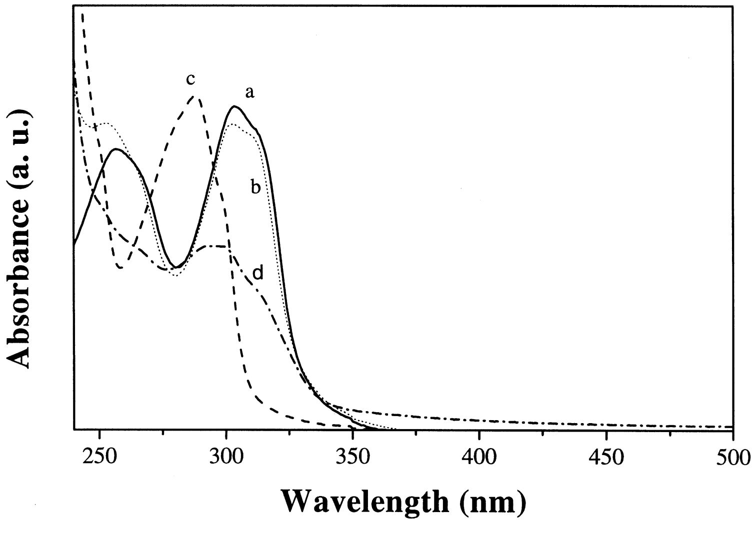

Figure 7. UV/VIS spectra: a) Initiator (**2**); b) polyethyloxazoline initiated with (**2**); c) polyethyloxazoline after removal of the cobalt (II) ions; d) after addition of a Co(II)-salt solution to the metal free polymer in (c).

in the polymer after one extraction procedure. Analysis of this polymer with AAS revealed a remaining cobalt content of 72 ppm (content in the uncomplexed polymer: 1900 ppm). Addition of a solution of Co(II) to the solution of the uncomplexed polymer rebuild the supramolecular architecture and resulted in a "redshift" of the π–π* transition band to the original absorption region (Figure 7, curve d). However, the same absorption behavior of the original complexed polymer cannot exactly be reached indicating that the complex formation is not complete. We assume that this is an effect of both a steric hindrance and a kinetic phenomena of the bipyridine containing polymer.

In order to further extend this approach to systems multi-metal binding sides, we terminated the living polymer chain end with a modified nucleophile. It is well known, that piperidine is able to terminate a living polyoxazoline chain nearly quantitatively [17]. We chose this concept and connected a supramolecular building unit based on 4'-functionalized-2,2':6',2"-terpyridine to a piperidine. This unit was then used to terminate a living polyethyloxazoline polymerization initiated by [Fe(II)((5-bromomethyl-5'-methyl)-2,2'-bipyr-idine)$_3$](PF$_6$)$_2$ resulting in a system containing two different types of metal binding sites (Figure 8). The incorporation of the terpyridine unit could be demonstrated by various techniques, e.g. by NMR spectroscopy (Figure 9). The typical signals for the terpyridine ligand in the aromatic region could be observed for the final polymer: π = 8.69 (2 H, 6, 6", d), 8.65 (2 H, 3, 3", d), 8.00 (2 H, 3', 5', s), 7.85 (2 H, 4, 4", t), 7.32 (2 H, 5, 5", t). They correspond exactly with the signals for the termination agent alone (Figure 9, inset a and b). The signals of the initiator core could not be observed due to the influence of the central metal ion. Studies of the complexation behavior and the use of different metal ions are currently in progress.

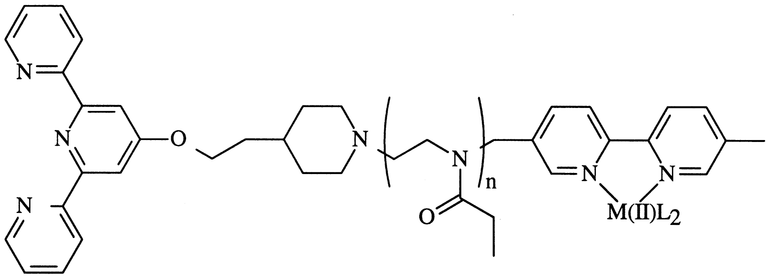

Figure 8. Schematic representation of a polyoxazoline containing a bipyridine and a terpyridine unit.

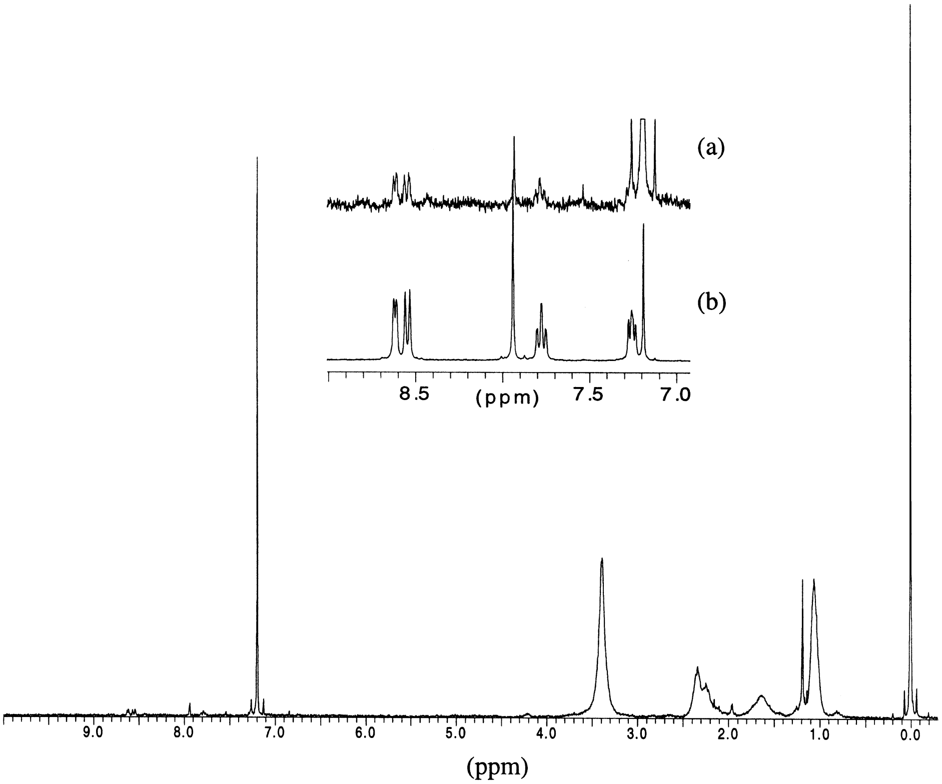

Figure 9. NMR spectra of a polymer containing a bipyridine and a terpyridine unit. The signals of the terpyridine unit were enlarged in the inset (a) and compared with the signals of the original terpyridine termination agent (b).

CONCLUSION

The described results demonstrate a new approach towards monofunctionalized polymers with terminal metal binding units. Due to the exact control of molecular weight, defined (functionalized) endgroups and the variability of the polymer main chain itself interesting combinations between supramolecular chemistry and classical polymer chemistry can be obtained. Further research will focus on the incorporation of other supramolecular structures as well as the extension of this concept to different monomers and polymerization techniques.

ACKNOWLEDGEMENTS

The research was supported in parts by the Bayerisches Staatsministerium für Wissenschaft, Forschung und Kunst and the Fonds der Chemischen Industrie. We thank C. Eschbaumer and C. H. Weidl for mass spectrometry measurements.

REFERENCES

[1] Y. Chujo, K. Sada, and T. Saegusa, *Macromolecules, 26*, 6315 (1993).
[2] C. D. Eisenbach and U.S. Schubert, *Macromolecules*, *26*, 7372 (1993).
[3] P. K. Ng, X. Gong, W. T. Wong, W. K. Chan, *Macromol. Rapid Commun., 18*, 1009 (1997).
[4] U. Velten and M. Rehahn, *Macromol. Chem. Phys., 199*, 127 (1998).
[5] G. Hochwimmer, O. Nuyken, and U. S. Schubert, *Macromol. Rapid Commun., 19*, 309 (1998).
[6] U. S. Schubert, O. Nuyken, and G. Hochwimmer, *Division of Polymeric Materials: Science and Engineering, Preprints*, *79*, 11 (1998).
[7] U. S. Schubert, C. Eschbaumer, O. Nuyken, and G. Hochwimmer, *J. Incl. Phenom. 35*, 23 (1999).
[8] J. J. S. Lamba and C. L. Fraser, *J. Am. Chem. Soc., 119*, 1801 (1997).
[9] J. J. S. Lamba, J. E. McAlvin, B. P. Peters, C. L. Fraser, *Div. Polym. Chem., Polymer Preprints, 38(1)*, 193 (1997).
[10] J. E. Collins and C. L. Fraser, *Macromolecules*, *31*, 6715 (1998).
[11] U. S. Schubert, C. Eschbaumer, and G. Hochwimmer, *Tetrahedron Lett.*, *39*, 8543 (1998).
[12] U. S. Schubert, C. Eschbaumer, and G. Hochwimmer, *Synthesis*, 779 (1999).
[13] B. Hasenknopf, J.-M. Lehn, B. O. Kneisel, G. Baum, and D. Fenske, *Angew. Chem., 108*, 1987 (1996); *Angew. Chem., Int. Ed. Engl., 35*, 1838 (1996).
[14] R. Krämer, J.-M. Lehn, B. O. Kreisel, G. Baum, and D. Fenske, *Angew. Chem.*, *108*, 1987 (1996*); Angew. Chem., Int. Ed. Engl.*, *35*, 1838 (1996).
[15] S. Kobayashi, *Progr. Polym. Sci*., *15*, 751(1990).
[16] U.S. Schubert, G. Hochwimmer, C. Eschbaumer, in preparation.

[17] O. Nuyken, G. Maier, A. Groß, and H. Fischer, *Macromol. Chem. Phys.*, *197*, 83 (1996).

Received June 4, 1999
Revision received February 1, 2000