Synthesis and Thermal Properties of Diblock Copolymers Utilizing Non-Covalent Interactions

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Summary: Diblock copolymers of poly(styrene) and poly(ethylene oxide) were prepared utilizing a *bis*terpyridine ruthenium complex as non-covalent interaction for the connection of the two blocks. Apart from the synthesis and characterization of four metallo-supramolecular block copolymers, first studies on the thermal properties of the block copolymers have been performed. A complex crystallization behavior was observed and is described in a qualitative fashion. The influence of the metal complex on the thermal stability of the metallo-supramolecular block copolymers remains a question for further investigation.

Keywords: block copolymers; differential scanning calorimetry; supramolecular chemistry; synthesis; terpyridine

Introduction

The merging of supramolecular chemistry and polymer chemistry has become an area of increasing interest in the past decade.[1-3] In supramolecular chemistry, non-covalent interactions are employed to selectively build-up well-defined architectures. The implementation of supramolecular binding sites into polymer chains gives rise to materials that reveal additional features due to the generally weaker nature of the non-covalent interaction: external stimuli can have a great influence on the material properties by switching the non-covalent interactions reversibly and simultaneously from on to off (in the case of highly dynamic supramolecular systems). Important examples of non-covalent interactions are hydrogen bonding and metal-ligand interactions.[2-4] Supramolecular binding sites may be introduced at the chain ends of

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polymers or along the polymer backbone, allowing the formation of 'classical' polymer architectures such as high molecular weight chain extended polymers, block copolymers, graft copolymers or cross-linked/gel-forming systems, among others.[5]

Our interest lies in supramolecular block copolymers that eventually enable manipulation of the morphologies formed by such block copolymers. This requires a strong non-covalent interaction that is able to withstand the opposing van-der-Waals forces described by the Flory-Huggins interaction parameter upon microphase separation of block copolymers. Moreover, it should not be highly dynamic in order to prevent the formation of a macrophase separated system or compatibalized blends. Metal-ligand complexes that are by nature inert are therefore the most suitable candidates. In particular, the possibility of selectively constructing heteroleptic complexes utilizing the same type of ligands is a major advantage to design and prepare a wide variety of block copolymer architectures. In our experience *bis*terpyridine ruthenium complexes fulfill all these requirements.[6-8] In this contribution we describe in detail the synthetic aspects of metallo-supramolecular block copolymers bearing a *bis*terpyridine ruthenium complex at the junction point between the two constituting polymer blocks (Figure 1). Last but not least, we will briefly reflect upon the thermal behavior of this new class of block copolymers.

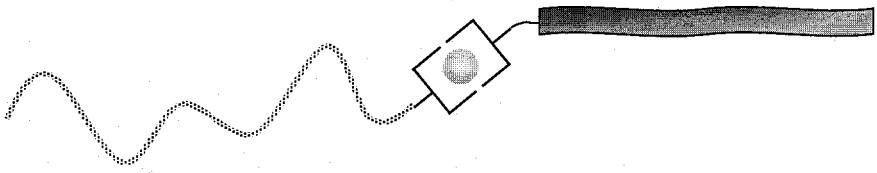


Figure 1. Schematic representation of an AB diblock copolymer bearing a metal complex at the junction between the two constituting blocks.

Experimental Part

Synthesis of terpyridine end-functionalized poly(ethylene oxide): see ref. 6.

General procedure for the synthesis of terpyridine end-functionalized poly(styrene): Hydroxy end-functionalized poly(styrene) and *t*-BuOK (3 eq.) were refluxed for 15 min in dry THF under argon. Via an addition funnel a 2-fold excess of 4'-chloro-2,2':6',2''-terpyridine was added to the solution and was refluxed for additional 4 hours. Hereafter the solution was directly precipitated in methanol (1:10 v/v). The white precipitate was re-precipitated from THF into methanol and washed with hexane. Yields varied from 76% to 85%. Selected analytical data of poly(styrene) with DP = 100: ^{1}H-NMR: 400 MHz, $CDCl_3$, 25°C): signals are broadened δ = 8.67 (bm, 2H, H6;H6''), 8.60 (bm, 2H, H3;H3''), 7.91 (s, 2H, H3';H5'), 7.83 (bm, 2H, H4; H4''), 7.31-6.39 (C_6H_5 PS backbone; H5;H5''), 4.11-3.96 (bm, 2H, tpyOCH_2), 2.66, 2.18-1.10, 0.78 (PS backbone). UV/Vis (CH_2Cl_2): λ_{max} (nm) = 278, 243. MALDI-TOF MS: M_n = 9487 g/mol. GPC (RI): M_n = 9800, PDI = 1.13.

General procedure for the synthesis of $RuCl_3$ *mono*complexes of poly(styrene) and poly(ethylene oxide): A suspension of anhydrous $RuCl_3$ in dry degassed DMF was heated under argon at 130°C. Not until the color of the suspension had turned dark brown, a 1/3-fold equivalent of the polymer in dry degassed DMF was added slowly. The reaction mixture was stirred overnight at 130°C, after which it was allowed to cool to room temperature and partitioned between water and CH_2Cl_2. The organic layer was quickly separated and dried over Na_2SO_4 and removed *in vacuo*. The resulting solid was precipitated from CH_2Cl_2 in a non-solvent, methanol and diethyl ether for poly(styrene) and poly(ethylene oxide) respectively. Yields varied from 89% to 98%. Selected analytical data: PS_{20}:UV/vis (CH_2Cl_2): λ_{max} (nm): 400, 312, 277, 270, 259. PEO_{375}: UV/vis (CH_2Cl_2): λ_{max} (nm): 395, 309, 276. In ^{1}H-NMR the terpyridine signals have completely vanished due to the paramagnetic nature of the compound. Only the polymer backbones were visible.

General procedure for the synthesis of A_x-[Ru]-B_y block copolymers: see ref. 6-8. The following block copolymers have been prepared: PS_{20}-[Ru]-PEO_{70} (**1**), PS_{20}-[Ru]-PEO_{375} (**2**),

PS_{100}-[Ru]-PEO_{70} (**3**) and PS_{100}-[Ru]-PEO_{375} (**4**). Selected analytical data: ^{1}H-NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.36 (td, 2H, H3;H3'', PEO), 8.26 (s, 2H, H3';H5', PS), 8.17 (bm, 2H, H3;H3'', PS), 7.88-7.73 (bm, 6H), 7.33-6.32 (bm, x = 110 H for **1** and **2**, x = 520 H for **3** and **4** C_6H_5 PS backbone and terpyridine signals), 4.74 (t, 2H, tpyOCH_2, PEO), 4.28-4.04 (m, 4H, tpyOCH_2CH_2 (PEO), tpyOCH_2 (PS)), 3.92-3.42 (m, x = 290 H for **1** and **3**, 1550 H for **2** and **4**, PEO backbone), 3.38 (s, 3H, OCH_3), 1.72-0.60 (m, x = 50 H for 1 and 2, x = 204 H for **3** and **4**, CH_2, CH PS backbone). UV/vis (CH_2Cl_2): λ_{max} (nm): 487, 305, 269, 262 (in case of **3** and **4**, styrene), 244.

Results and Discussion

Terpyridine is a well-known tridentate chelating ligand that forms stable octahedral complexes with a wide variety of transition metal ions.[9] In order to create diblock copolymers this ligand needs to be introduced at one chain end of two different polymers using a 'blocking onto'-procedure. We have selected poly(ethylene oxide) and poly(styrene) as constituting polymer blocks. The important difference is the solubility of these polymers and this requires a different approach for the introduction of the terpyridine ligand. In both cases the starting polymers have been prepared by living anionic polymerization techniques. Intrinsically, polymerization of ethylene oxide renders a hydroxyl group at the chain end of poly(ethylene oxide), whereas for poly(styrene) this same end group was introduced by addition of the living polymer reaction mixture to a solution of ethylene oxide in THF. This hydroxy end group was subjected in both cases to an addition-elimination reaction using a base to deprotonate the polymer and 4'-chloro-2,2':6',2''-terpyridine as the other reactant (Figure 2).

Hydrophilic poly(ethylene oxide) of various molecular weights was easily converted to the terpyridine functionalized polymer using a suspension of KOH in DMSO. The synthesis and characterization have been described elsewhere.[6,10] For poly(styrene) this approach did not work for solubility reasons. We have already used an approach in which we applied 18-crown-6 as a phase transfer catalyst for KOH in toluene-solution and this was rather successful, although the reaction times were quite long (typically 48 hours).[6]

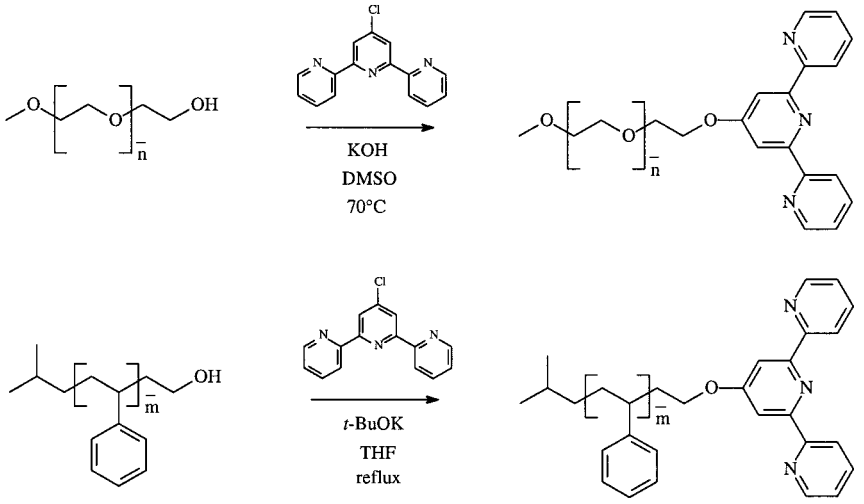


Figure 2. Synthetic scheme for the preparation of terpyridine end-functionalized poly(ethylene oxide) with n = 70 or n = 375 and poly(styrene) with m = 20 or m = 100.

We therefore applied a different method using *t*-BuOK in dry THF for the deprotonation of the polymer and then added the 4'-chloroterpyridine in excess. The reaction has gone to completion within 4 hours, requires less starting materials and represents therefore an important improvement to the route developed before. We have used poly(styrene) of two different molecular weights (~2 and 10 kDa) and the obtained results were comparable. The excess 4'-chloroterpyridine was removed by a double precipitation in methanol and subsequent washing with hexanes. Alternatively, a preparative size exclusion chromatography could be carried out. However, this was not necessary in the present case. The terpyridine functionalized poly(styrene) was analyzed by ^{1}H-NMR, size exclusion chromatography (GPC), FT-IR and MALDI-TOF MS. In IR, characteristic vibrations at 1600, 1582 and 1563 cm^{-1} of the terpyridine ligand can be observed. In ^{1}H-NMR the corresponding signals for the terpyridine unit arise and can be integrated to the backbone. This was in excellent agreement with results obtained from GPC using poly(styrene) standards and MALDI-TOF MS measurements. Figure 3 shows the MALDI-TOF MS spectra of the hydroxy end-functionalized poly(styrene) (10 kDa) and the resulting terpyridine functionalized polymer having a mass difference of 232 Da corresponding to the mass of a

terpyridine ligand.

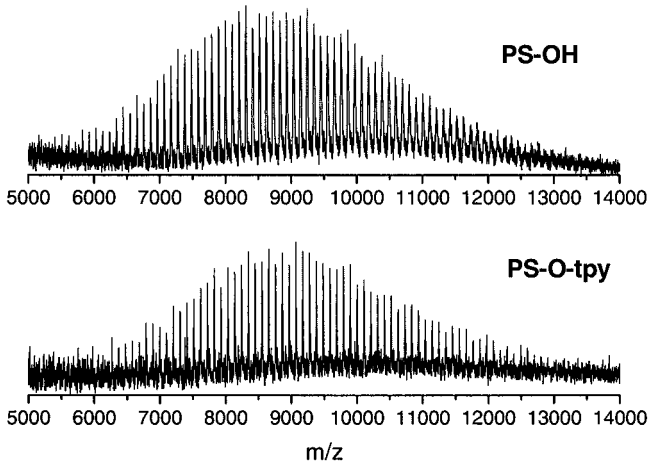


Figure 3. MALDI-TOF mass spectra of poly(styrene) of DP = 100 bearing a hydroxyl end group (top) and having a terpyridine end group (bottom).

To construct heteroleptic *bis*terpyridine metal complexes, ruthenium was employed as transition metal ion. Ruthenium(III)chloride forms a stable *mono*complex with a terpyridine ligand, which can be isolated. When using the right conditions the chlorides block the three other coordination sites, preventing the formation of *bis*complexes. This *mono*complex is paramagnetic from the d^5 configuration and therefore in ^{1}H-NMR the terpyridine signals disappear upon complexation. UV/Vis-spectroscopy revealed a typical metal-to-ligand-charge-transfer band (MLCT) at ~400 nm, corresponding to the *mono*-complex (Figure 4). The versatility of the $RuCl_3$ *mono*complex formation is demonstrated through the general applicability to both poly(styrene)s and poly(ethylene oxide)s. This means that either the *mono*complex of poly(styrene) or of poly(ethylene oxide) may be used for further reaction. This enhances the applicability of preparative size exclusion chromatography for purification in later steps: the lower molecular weight polymer with a free terpyridine ligand can be applied in excess and later easily removed.

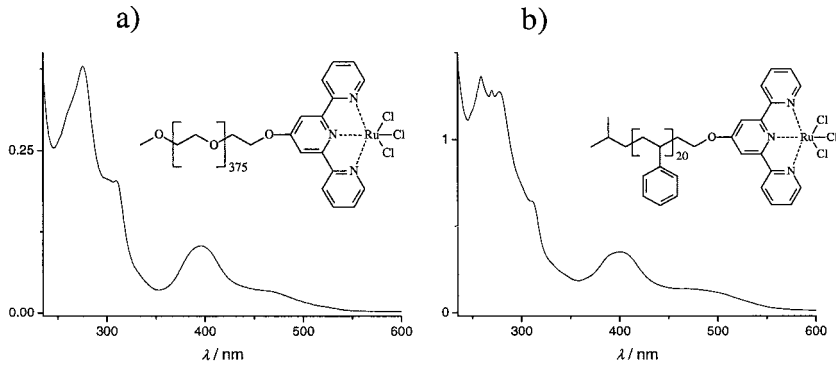
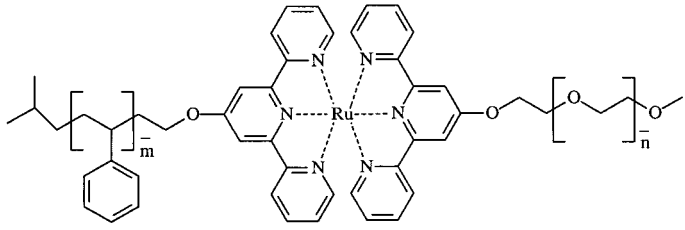


Figure 4. UV/Vis-spectra showing the MLCT band at ~ 400 nm for the $RuCl_3$ *mono*-complexes of a) poly(ethylene oxide) of 17 kDa and b) poly(styrene) of 2 kDa (both measured in CH_2Cl_2).

Metallo-supramolecular block copolymers were prepared upon addition of a slight excess of free terpyridine end-functionalized polymer to the *mono*complex of poly(styrene) or poly(ethylene oxide) respectively. The metallo-supramolecular polymers that have been prepared are described by the following acronyms: PS_{20}-[Ru]-PEO_{70} (**1**), PS_{20}-[Ru]-PEO_{375} (**2**), PS_{100}-[Ru]-PEO_{70} (**3**) and PS_{100}-[Ru]-PEO_{375} (**4**) (see Figure 5).



PS_m-[Ru]-PEO_n

1 : m = 20 n = 70
2 : m = 20 n = 375
3 : m = 100 n = 70
4 : m = 100 n = 375

Figure 5. Metallo-supramolecular block copolymers based on poly(styrene) and poly(ethylene oxide).

The block copolymer formation was carried out in a mixture of chloroform and methanol: the reduction of Ru(III) to Ru(II) is accompanied by an oxidation of methanol and is catalyzed by *N*-ethylmorpholine. The reactions were followed by UV/Vis spectroscopy, where a shift of the MLCT band had occurred from 400 nm for the Ru(III) *mono*complex to 490 nm for the Ru(II)

*bis*complex (Figure 6). Purification was carried out by preparative size exclusion chromatography. Figure 6 also shows a photograph of such a size exclusion of the PS_{20}-[Ru]-PEO_{375} on a column packed with BioBeads SX-1. Three bands are visible: the lower (red) band represents the product, the top band can be assigned to the starting material and in between an intense purple band can be observed, which is not understood yet due to analytical difficulties. Nevertheless, the isolated amount of this fraction was very little (~5%).

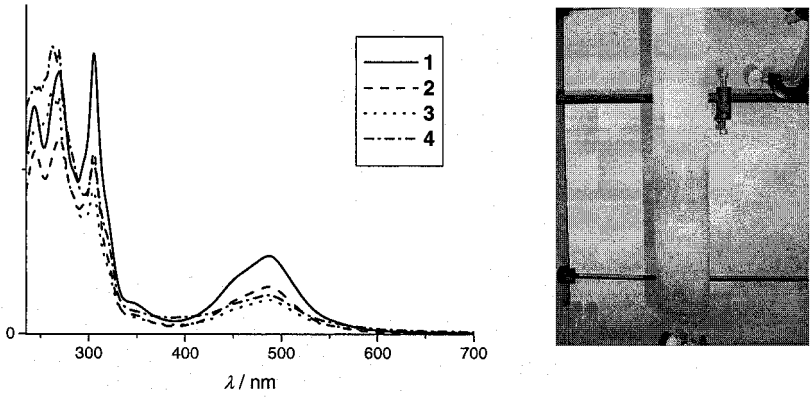


Figure 6 (left): UV/vis spectra of the four block copolymers, clearly showing the MLCT band at 490 nm for all compounds. Right: Photograph of preparative BioBeads size exclusion chromatography column applied on PS_{20}-[Ru]-PEO_{375}.

All the metallo-supramolecular block copolymers were purified using preparative size exclusion chromatography. Characterization was carried out by UV/Vis (Figure 6), FT-IR, ^{1}H-NMR and where possible GPC and MALDI-TOF MS. In the latter technique a breakage of metal-ligand interaction could be observed depending on the laser intensity applied. GPC showed severe problems owing to column interactions and shear forces on the column. We are currently trying to find a reliable set-up. From ^{1}H-NMR we could obtain an idea of the molecular weight of the block copolymers by integrating the terpyridine-signals to the polymer backbones. Figure 7 shows a ^{1}H-NMR-spectrum of PS_{20}-[Ru]-PEO_{70}, where the peaks have been assigned.

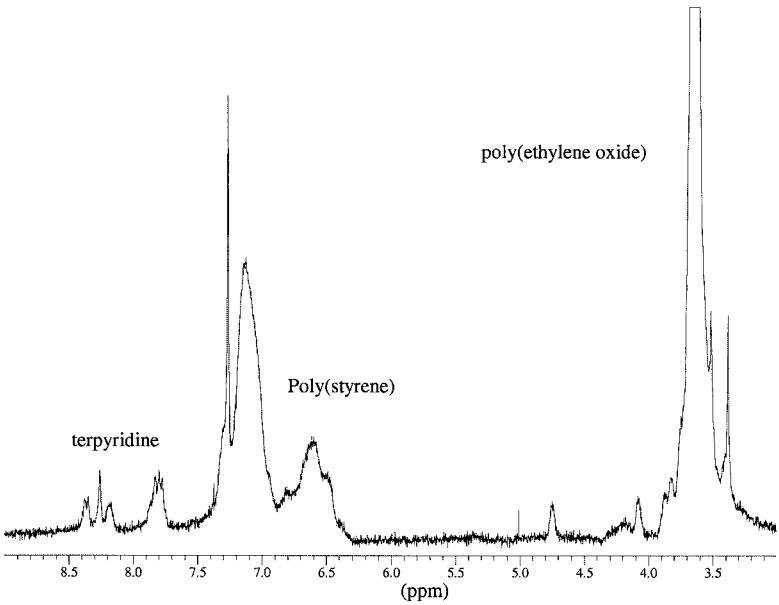


Figure 7. ^{1}H-NMR spectrum of PS_{20}-[Ru]-PEO_{70} in $CDCl_3$. Indicated are the signals coming from the metal complex, poly(styrene) and poly(ethylene oxide). The sharp signals at 4.7 and 4.1 ppm originate from the methylene protons next to the terpyridine ligand on the PEO-backbone, whereas the broad peak at 4.2 ppm is caused by the methylene protons next to the terpyridine on the PS-backbone.

As a first step towards the understanding of the thermal properties of the metallo-supramolecular block copolymers, DSC-measurements have been performed on all samples. Figure 8 shows the respective heating and cooling runs for the four block copolymers. Compounds 2 and 4 show clear melting and crystallization temperatures. They contain a high volume fraction of the long PEO-block. It is worth noting that in both cases the same T_m of 59°C was found for the corresponding uncomplexed poly(ethylene oxide). Interestingly, in the cooling runs 2 and 4 show different crystallization temperatures of 19°C and 34°C, respectively. This may be attributed to compatibilization of the short PS-block in 2, leading to retarded crystallization effects in the PEO-block.

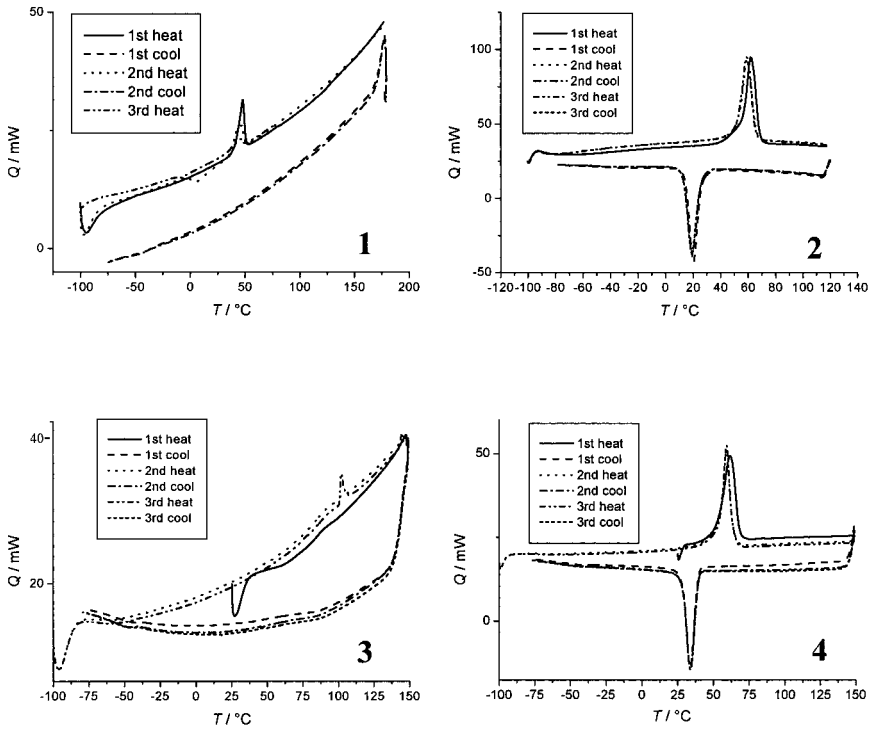


Figure 8. DSC-traces of 1 (top left), 2 (top right), 3 (bottom left) and 4 (bottom right) at a heating rate of 40°C/min.

In 1 and 3 a crystallization peak is absent and the heat required for melting 1 is much smaller compared to the corresponding uncomplexed poly(ethylene oxide). Therefore, the poly(styrene)-block must prevent the crystallization of the poly(ethylene oxide) block. The complete absence of a melting peak for compound 3, (with the highest PS-content) also supports this hypothesis. Moreover, at 102°C the T_g of the PS can be observed. Similar effects have been reported for covalent PS-*b*-PEO analogues.[11-13]

Conclusions and Outlook

Block copolymers in which the constituting blocks of poly(styrene) and poly(ethylene oxide) are held together via a metal complex have been prepared and characterized. Efficient and high-yield

strategies have been developed for the various steps. The thermal behavior of the new block copolymers was studied by DSC. It is difficult to draw conclusions about the influence of the metal complex on the thermal properties of the block copolymers. The block copolymers in itself show, in analogy with their covalent counterparts, interesting behavior regarding crystallization retardation and compatibilization effects. In the near future, WAXS and SAXS experiments will be carried out in order to elucidate the crystallization phenomena as well as the role of the metal complex. More block copolymers having different PS and PEO contents will be prepared for this purpose, leading to a library of PS_x-[Ru]-PEO_y block copolymers. Morphological studies will be undertaken as well. Finally, the opening of the metal complex and the manipulation of defined nano-structures on surfaces will be addressed.

Acknowledgements

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[1] J.-M. Lehn, *Makromol. Chem. Macromol. Symp.* **1993**, *69*, 1.
[2] L. Brunsveld, B. J. B. Folmer, R. P. Sijbesma, E. W. Meijer, *Chem. Rev.* **2001**, *101*, 4071.
[3] U. S. Schubert, C. Eschbaumer, *Angew. Chem. Int. Ed.* **2002**, *41*, 2892.
[4] J.-M. Lehn, "*Supramolecular Chemistry - concepts and perspectives*", VCH, Weinheim, Germany, **1995**.
[5] B. G. G. Lohmeijer, U. S. Schubert, *J. Polym. Sci.: Part A: Polym. Chem.* **2003**, in press.
[6] B. G. G. Lohmeijer, U. S. Schubert, *Angew. Chem. Int. Ed.* **2002**, *41*, 3825.
[7] J.-F. Gohy, B. G. G. Lohmeijer, U. S. Schubert, *Macromolecules* **2002**, *35*, 4560.
[8] J.-F. Gohy, B. G. G. Lohmeijer, S. K. Varshney, B. Decamps, E. Leroy, S. Boileau, U. S. Schubert, *Macromolecules* **2002**, *35*, 9748.
[9] E. C. Constable, *Adv. Inorg. Chem. Radiochem.* **1986**, 69.
[10] U. S. Schubert, C. Eschbaumer, *Macromol. Symp.* **2001**, *163*, 177.
[11] Y. Shimura, T. Hatakeyama, *J. Polym. Sci.: Part B: Polym. Phys.* **1975**, 13, 653.
[12] L. Zhu, Y. Chen, A. Zhang, B. H. Calhoun, M. Chun, R. P. Quirk, S. Z. D. Cheng, B. S. Hsiao, F. Yeh, T. Hashimoto, *Phys. Rev. B* **1999**, *60*, 10022.
[13] C. Tsitsilianis, G. Staikos, P. Lutz, P. Rempp, *Polymer* **1992**, *33*, 3369.