

Supramolecular Engineering with Macromolecules: Preparation of Block Copolymers and Nanomaterials

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A comprehensive overview of part of the work of the authors on metallo-supramolecular block copolymers is provided. Special focus is on the potential these new compounds have in the field of nanotechnology. Therefore some design principles as well as synthetic strategies are presented and characterization of these charged compounds is briefly discussed.

Key words: block copolymers, metal-containing polymers, supramolecular chemistry, synthesis, terpyridine

1. INTRODUCTION

The introduction of supramolecular moieties into polymer backbones represents an elegant way to create materials that have reversible or switchable properties.^[1] Applications for such materials can be found in 'smart' coatings, 'intelligent' glues and functional nanomaterials. Here we will present a route towards functional nanomaterials based on metallo-supramolecular block copolymers. Among the types of supramolecular interactions,^[2] metal-ligand bonding is one of the most versatile methods. Labile as well as inert metal complexes can be prepared by using the same ligands and only changing the metal ion.^[3] Labile metal complexes are fully reversible systems, like hydrogen bonded systems, whereas inert metal complexes are of special interest as a kind of dormant switch present in the resulting material. This means that first such a material can be (self-)assembled into a certain morphology, frozen into that morphology by e.g. cross-linking and then the dormant 'switch' can be addressed to lead to functional nanomaterials.^[4] Block copolymers are well recognized for their self-assembly into a variety of well-defined microphase-separated structures depending on the volume fraction of the different blocks and the molecular weights.^[5] In selective solvents block copolymers can form micelles, rods and/or vesicles.^[6] It is this self-assembly process we will use for the preparation of functional nano-materials. Metallo-supramolecular block copolymers are the starting materials for this advanced supramolecular engineering process. An inert metal complex serves as the supramolecular linker between two different polymer blocks. This paper will deal mainly with the synthesis of this class of compounds.

2. PRINCIPLE

The synthesis of a metallo-supramolecular block copolymer is based on a two step self-assembly process of terpyridine ligands around ruthenium metal ions: one polymer containing a terpyridine ligand at one chain end is reacted with RuCl_3 and a mono complex is being formed. This mono complex is subsequently reacted with a second polymer containing a terpyridine ligand

under reducing conditions: Ru(III) is reduced to Ru(II) and hence a metallo-supramolecular block copolymer containing an inert metal complex at the block junction is formed (Figure 1).^[7]

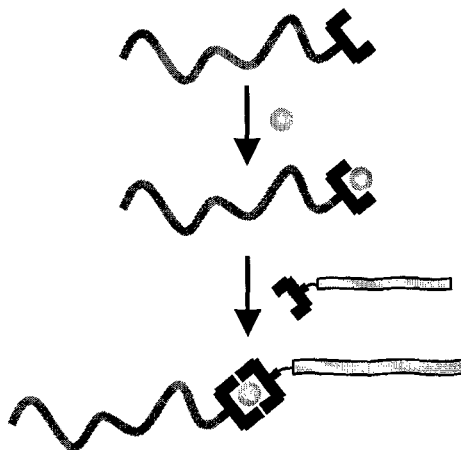


Figure 1: Schematic representation of the synthesis of a metallo-supramolecular block copolymer.

The possibility of isolating and purifying the mono complex is a very powerful way to create any kind of block copolymer by adding any kind of polymer having a terpyridine end group to this mono complex. The important steps are the introduction of a single terpyridine ligand at one polymer chain end, the preparation of the mono complex and the final synthesis of the metallo-supramolecular diblock copolymer. In the following sessions these three steps will be addressed.

3. POLYMERS WITH TERPYRIDINE END GROUPS

One of the prerequisites for a well-defined phase behavior of the resulting metallo-supramolecular block copolymers is a low polydispersity in each of the constituting blocks. Several polymerization procedures fulfill this requirement, such as anionic^[5] and nitroxide mediated controlled radical polymerization techniques.^[8]

3.1 End group modification

A straightforward method for the introduction of a single terpyridine as end group of a polymer is by modification of an existing end group. Typically hydroxy end groups can be produced by anionic polymerization techniques. A subsequent chemical modification by a Williamson type etherification reaction with 4'-chloroterpyridine gives the terpyridine end group. Several conditions were tried and applied due to solubility reasons of the polymers of interest. An isocyanate reaction was conducted in cases where the reaction conditions gave rise to side reactions. In this way, poly(ethylene oxides), poly(propylene oxides), poly(tetramethylene oxides) polystyrenes, polybutadienes, poly(ethylene-co-butylene) and polyisoprene have been prepared (Figure 2).^[7,9]

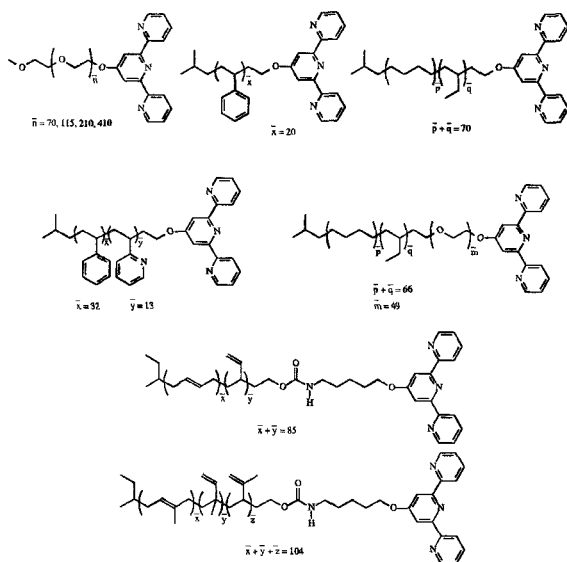
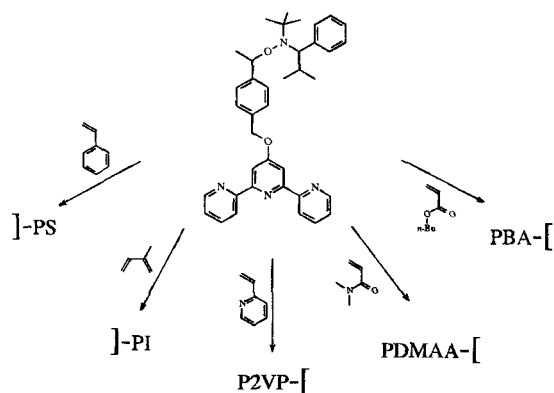


Figure 2: Terpyridine end functionalized polymers obtained by end group modification.

3.2 Functional initiator

We have designed a terpyridine functionalized initiator that is capable of controlling the nitroxide



mediated radical polymerization of a large variety of vinylic monomers (Figure 3).^[10]

Figure 3: Polymers obtained by nitroxide mediated controlled radical polymerization using a terpyridine functionalized initiator, where $[-]$ denotes the terpyridine.

The key advantage of radical polymerization is its tolerance to functional groups and small impurities in monomer and solvent. Using a unimolecular initiator it is possible to selectively introduce a single terpyridine end group into polymers as polystyrene, poly(butyl acrylate), poly(vinyl pyridine), polyisoprene, poly(dimethyl acrylamide) and others.

Using these methods a whole range of block copolymers of different composition and different block lengths can easily be accessed.

4. MONO COMPLEXES

The second step in the preparation of metallo-supramolecular block copolymers is the formation of a mono complex. The metal ion must be selectively introduced into one single terpyridine ligand. Additionally, this mono complex has to be inert, since any exchange of the terpyridine ligand during the subsequent block copolymer synthesis will lead to A-A, A-B and B-B polymer combinations. Ru(III)Cl₃ can fulfill all these requirements, although some care has to be taken: enough excess (at least 1.5 with respect to the ligand), dry solvents and an inert atmosphere are needed [11]. Polystyrene as well as poly(ethylene oxide) RuCl₃ mono complexes of different molecular weights have been prepared. The process of mono complex formation can be followed by UV/vis, where a metal-to-ligand charge transfer band (MLCT) can be observed at 400 nm (Figure 4).^[7]

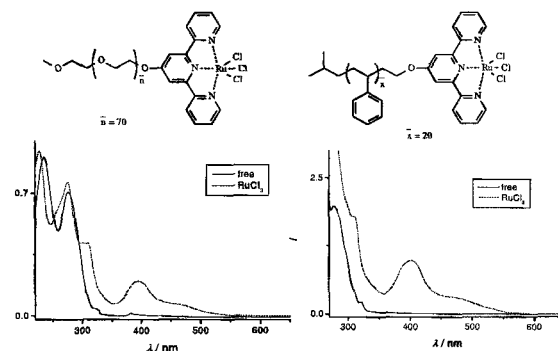


Figure 4: UV-spectra of RuCl₃ mono complexes of poly(ethylene oxide) and polystyrene showing the characteristic MLCT-band at 400 nm.

5. SYNTHESIS OF METALLO-SUPRAMOLECULAR BLOCK COPOLYMERS

The addition of a second polymer having a terpyridine end group under reducing conditions to a polymer mono complex gives rise to a metallo-supramolecular block copolymer (see Figure 5 for an example). Ru(III) is reduced to Ru(II), after which the chlorides are easily displaced by the second terpyridine ligand. This process can again be followed by UV/vis spectroscopy, where the MLCT shifts from 400 nm for the mono complex to 490 nm for the bis-complex and a color change from brown to red can be observed. Afterwards a counter-ion exchange is performed and chlorides are replaced by hexafluorophosphates. This renders the block copolymer readily soluble in organic solvents. Purification of the diblocks copolymer from the starting materials is carried out by preparative size exclusion chromatography and if

necessary, in combination with column chromatography. The charged compounds tend to stick to the stationary phase and the non-charged material can be washed down easily using the right solvent combinations (note that the Ru(III)Cl₃ mono complex is also uncharged). The charged compound can be removed from the column material by adding some salt (typically NH₄PF₆) to the eluent. Finally, the metallo-supramolecular block copolymer is precipitated into a non-solvent.^[7]

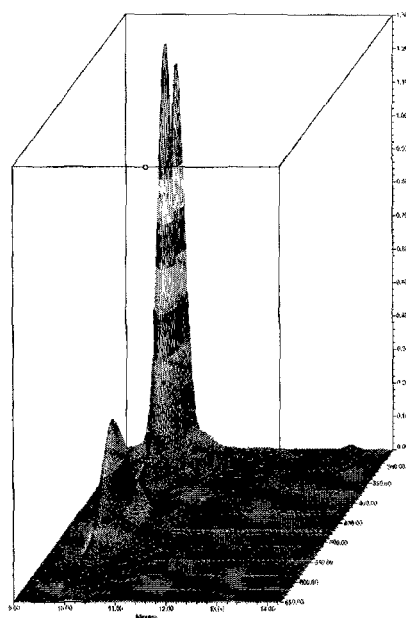
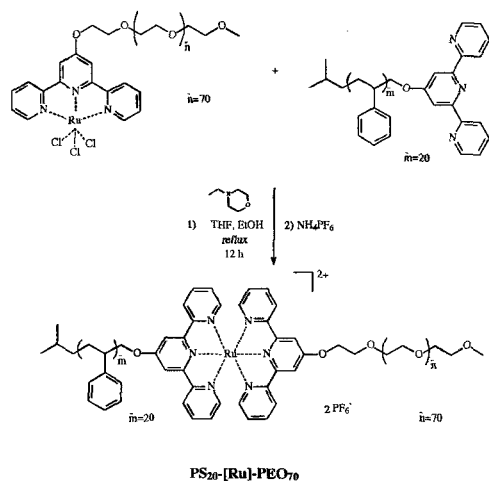


Figure 5: Synthetic scheme for the preparation of a metallo-supramolecular block copolymer, PS₂₀-[Ru]-PEO₇₀ (left) and the corresponding GPC-chromatogram as measured with a photo-diode-array detector and showing the shift of the MLCT-band from 400 nm to 490 nm.

Characterization of these compounds proved to be a challenge, however, we succeeded to analyze the compound successfully by GPC using DMF with 5 mM of NH₄PF₆ as the eluent (Figure 5).^[12] The presence of the different blocks can be determined by MALDI-TOF MS or FT-IR, but ¹H-NMR reveals the ratio of the constituting blocks and provides the molecular weight

through integration of the polymer backbone peaks with respect to the metal complex that has typical absorptions in the region between 7.2 and 8.6 ppm. Other tools that we have used for molecular weight determination are analytical ultracentrifugation^[13] and capillary electrophoresis.^[14] Block copolymers that have been prepared up to now, although the list is by no means complete, include PS-[Ru]-PEO, PEB-[Ru]-PEO, PS-*b*-P2VP-[Ru]-PEO, PS-[Ru]-PI, PI-[Ru]-PEO, and PS-[Ru]-PBA of varying molecular weights.

6. CONCLUDING REMARKS AND OUTLOOK

Understanding the morphological features of such block copolymers will be of key importance for their final application as precursors for nanomaterials. We have successfully prepared micelles from several of the amphiphilic block copolymers.^[15-18] Moreover, in the solid state these compounds differ from their covalent analogues through aggregation of the metal complexes, especially in the melt.^[19] Nevertheless, phase separation can still take place and typical morphologies such as hexagonally packed cylinders of PS-[Ru]-PEO block copolymers have been observed. Current efforts are devoted to understand the role of the counter-ion, to develop a reliable method for the opening of the ruthenium complex that allows manipulation of the morphology on the nanoscale, to the engineering of new block copolymer architectures (such as ABC-[Ru]-DE pentablock copolymers) and to prepare libraries of block copolymers. In all of the area's mentioned above, there is already some important progress and we are confident metallo-supramolecular block copolymers will play an important role for patterned surfaces with added functionality, nano-catalysis and completely new block copolymer architectures.

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