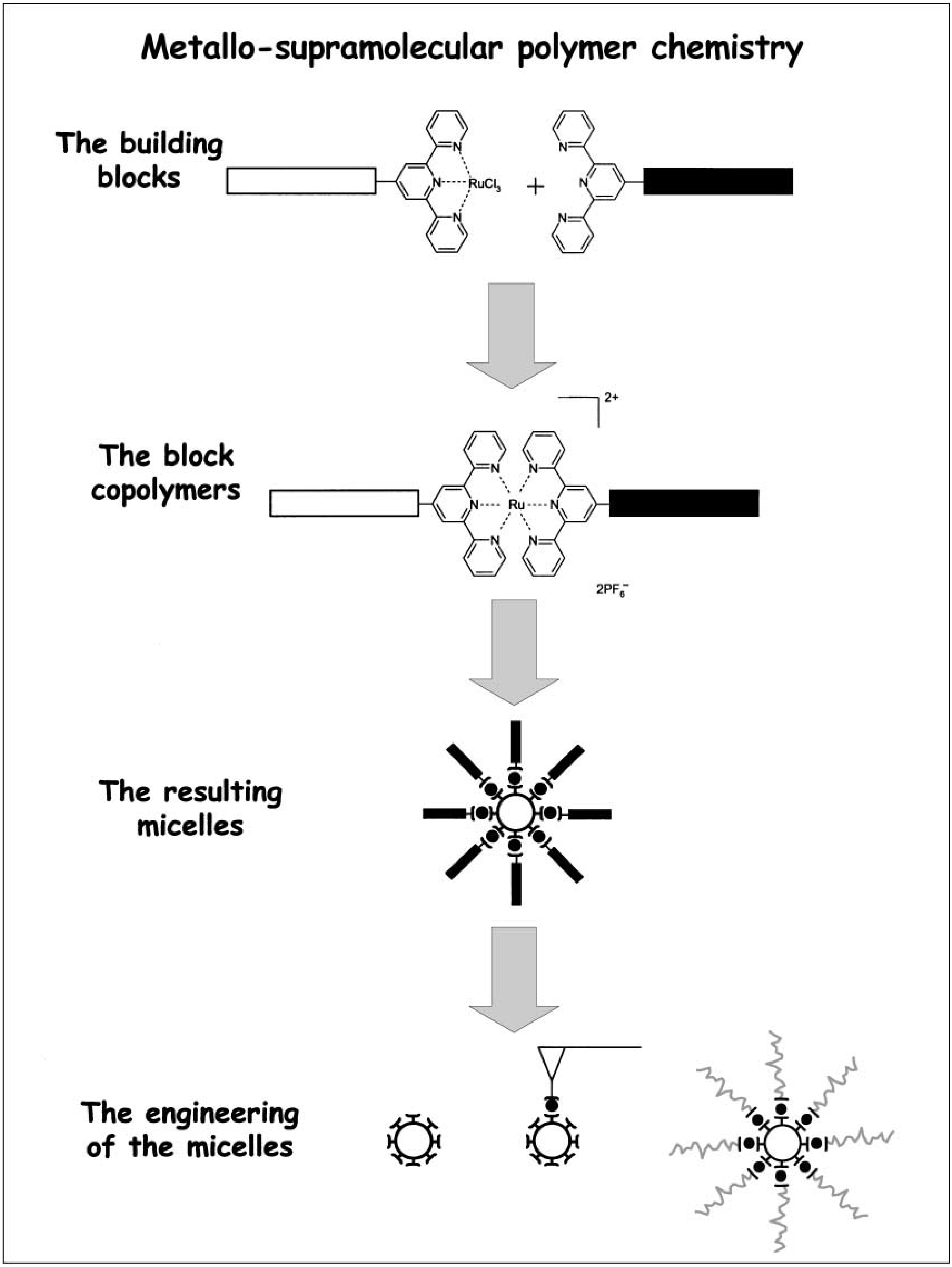

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From Supramolecular Block Copolymers to Advanced Nano-Objects

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Abstract: The formation of asymmetric bis-complexes, based on terpyridine ligands and ruthenium ions, is described as a powerful tool for the self-assembly of polymer blocks end-functionalized with terpyridine units. This is illustrated in this contribution for the synthesis of amphiphilic metallo-supramolecular block copolymers, which are further used to produce aqueous micelles. Finally, the reversibility of the supramolecular bond opens new avenues for the preparation and manipulation of these nano-objects.

Keywords: block copolymers · micelles · nanotechnology · supramolecular chemistry · terpyridines

Introduction

The rapidly growing research in the area of nanoscience has created an increasing demand for complex block copolymer architectures, that should be easily synthesized in a highly reproducible way and with a perfect control of the molecular architecture. For polymer chemists, sequential "controlled" and "living" copolymerisation techniques are the tools in order to obtain block copolymers with such requirements. In this respect, anionic,[1] cationic,[2] controlled radical,[3] group transfer[4] and metathesis[5] polymerisation techniques as well as their combination[6] have been widely used as synthetic routes to block copolymers. However, all these techniques, relying on the use of covalent bonds between all the substructural units, do show limitations concerning the choice of monomers that could be polymerised or the sequential order of the different blocks as well as the accessible lengths.

A different synthetic strategy towards block copolymer architectures relies on a combination of polymer and supramolecular chemistry. Supramolecular chemistry is generally defined as the "chemistry beyond the molecule" and relies on the use of non-covalent interactions as tools to assemble several individual molecules into a perfectly defined supramolecular structure.[7] As far as macromolecules are concerned, the polymer chains can be end-functionalized with specific moieties which are able to further self-assemble and give rise to a supramolecular organization of macromolecules. In this respect, hydrogen bonding,[8] ionic interactions[9] and metal–ligand complexes[10] have been used as non-covalent interactions for the engineering of supramolecular polymers.

In order to construct supramolecular AB block copolymers, the supramolecular interaction between the starting A and B end-functionalized polymers must exclusively lead to an AB "hetero-assembly" and not to AA and BB "homo-assemblies". In principle, all known non-covalent interactions can be utilized for this purpose; this is depicted in Figure 1 for

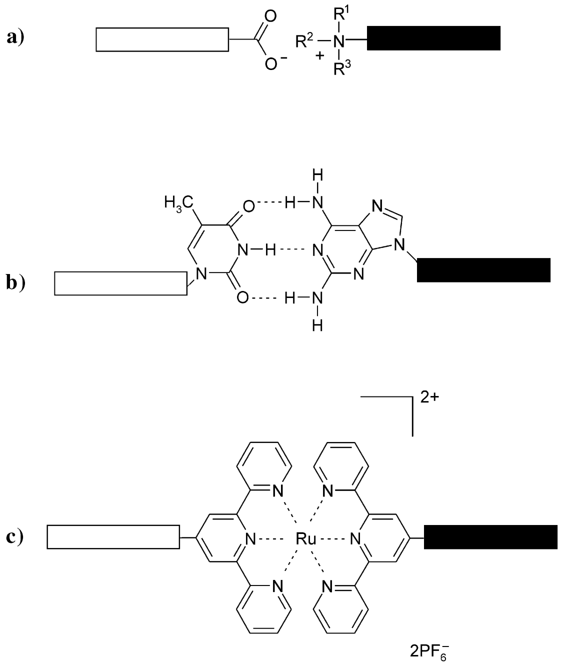

Figure 1. Different strategies to supramolecular AB diblock copolymers. a) Ionic interactions between blocks bearing oppositely charged end-groups. b) Complementary hydrogen bonding between purine- and thymine-functionalized blocks. c) Metal–ligand interaction in asymmetrical bis-2,2′:6′,2″-terpyridine–ruthenium(II) complex.

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hydrogen bonding, ionic and metal–ligand based systems. The use of ionic interactions to form supramolecular AB block copolymers (see Figure 1 a) is exemplified by the work of Jérôme et al.[9, 11] This strategy was aimed at compatibilization of immiscible polymer blends, for example polystyrene and polyisoprene. Indeed, the mixing of carboxylic acid end-functionalized polystyrene with tertiary amine end-functionalized poly(isoprene) resulted in materials that resemble to the covalently-bonded poly(styrene)–*block*-poly(isoprene) analogue. The magnitude of the ionic interactions could be rather high and easily modulated through the dielectric constant. However, such ionic interactions are not directional and not selective.

Hydrogen bonding in macromolecular architectures has recently received significant attention due to the thermoreversible and molecular recognition features of the resulting self-assemblies.[12a,b, 13–15] Complementary multiple hydrogen bonding units are good candidates to synthesize supramolecular hydrogen-bonded AB copolymers. Heterocyclic base pairing between adenine, guanine, thymine, uracil and tyrosine in DNA and RNA are well-known as tailored complementary hydrogen-bonded units in biological systems. Indeed, these typical moieties can be incorporated in synthetic polymers, as illustrated in Figure 1b for the purine–thymine pair and in the work recently published by Long et al.[16] However, the strength of the hydrogen bonds is rather weak compared with ionic or metal–ligand interactions. Initial systems based on complementary hydrogen-bonding motives were reported by Lehn,[17] Fréchet[18] and Whitesides[19] and focused on the formation of supermolecules from low molecular weight complementary receptor–substrate pairs. Complementary hydrogen bonding was also used to promote noncovalent interaction between functional polymers, as exemplified by Stadler,[12c] Jiang[20] and Hogen-Esch.[21]

Finally, metal–ligand complexes can be used as supramolecular linkers, as illustrated in Figure 1 c for an asymmetrical bis-2,2′:6′,2″-terpyridine–ruthenium(II) complex. This strategy has been previously successfully used to produce asymmetrical bis-2,2′:6′,2″-terpyridine–ruthenium complexes from various organic molecules. Indeed, Newkome et al. have utilized this principle to connect two independently prepared dendrons in a process that mimicked a key and lock system.[22] Following the same principle, stepwise self-assembly was used by Mohler and co-workers to synthesize rigid rods containing up to seven metal centers.[23] Other related examples based on asymmetrical bis-2,2′:6′,2″-terpyridine–ruthenium(II) complexes have been reported by Rehahn et al.,[24] Ziessel et al.[25] and are summarized in a recent review by Schubert and Eschbaumer.[26]

Synthetic Strategy to Metallo-Supramolecular Block Copolymers

Terpyridine ligands are known to form mono- and bis-complexes with a wide variety of transition metal ions.[27] The stability constants and the kinetics of formation of these different complexes strongly depends on the nature of the used metal ions.[28] In this respect, Ru^{III} is known to form a very stable mono-complex with one terpyridine ligand, while Ru^{II} only forms a stable bis-complex with two terpyridine ligands.[29] This peculiar character of ruthenium ions and the possibility to easily functionalize the terpyridine ligand in the 4′-position[30] can be used for the synthesis of asymmetrical bis-2,2′:6′,2″-terpyridine–ruthenium(II) complexes containing two terpyridine ligands bearing different polymeric substituents in the 4′-position.

Different synthetic strategies have been implemented to introduce the terpyridine ligand into macromolecular architectures, that will be further self-assembled with the aid of the process described above. Earlier work focused on the incorporation of terpyridine in the side-chain. In this respect, 4-vinyl- and 4′-vinylterpyridine were homopolymerized and copolymerized with styrene by free-radical (co)polymerization.[31, 32] Hanabusa et al. prepared 4′-[4-(2-acryl-oyloxy-ethoxy)phenyl]terpyridine and copolymerized this compound with styrene and methylmethacrylate.[33] Homopolymerization of 4′-(4-styrene)-terpyridine and its copolymerization with styrene, vinyl acetate and acrylic acid was reported by the same group[33] (for a recent example see ref. [34]). Recently, Hofmeier and Schubert as well as Tew et al. reported the free-radical copolymerization of methylmethacrylate with a terpyridine-functionalized methacrylate.[35]

Terpyridine moieties have also been introduced as terminal units of macromolecules. In that respect two different strategies can be implemented, as illustrated in Figure 2.

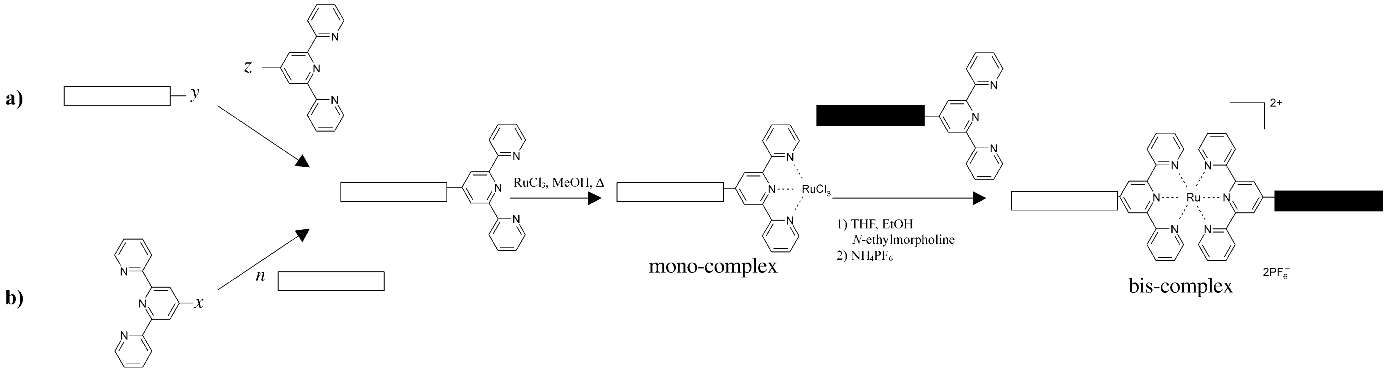

Figure 2. Synthetic strategies towards metallo-supramolecular AB diblock copolymers. a) End-capping of ω-functional polymer by a terpyridine ligand. b) Polymerization initiated by a terpyridine-functionalized initiator.

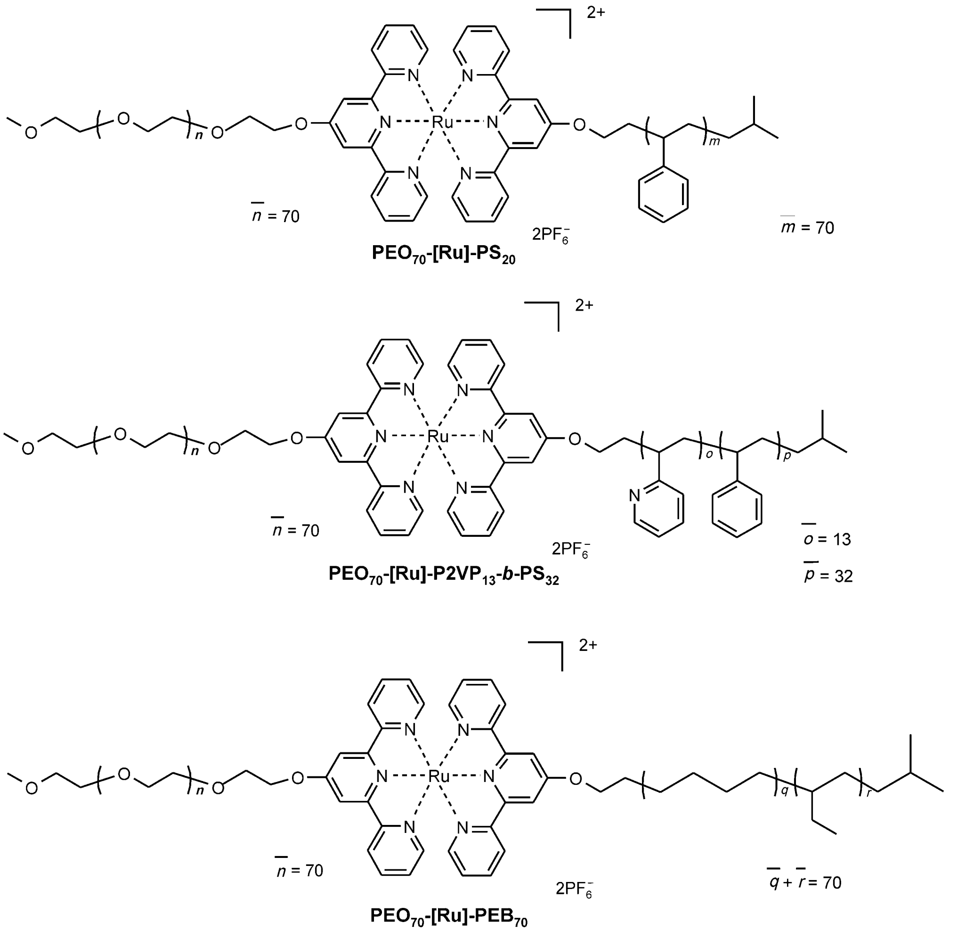

Figure 3. Structure of the isolated metallo-supramolecular block copolymers.

The terpyridine group can either be reacted with a) a suitable polymer end-group or b) a terpyridine-functionalized iniator can be used for the polymerization of the desired polymers. Strategy b) has recently been reviewed elsewhere[36] and will not be further discussed herein. However, this method has the advantage to produce polymer chains with a theoretical functionalization degree of 1. The reaction of 4′-chloro-2,2′:6′,2″-terpyridine with polymer chains bearing hydroxy end-groups has recently proven to be a very effective route regarding strategy a).[37] This was successfully applied to a variety of hydroxy-functionalized polymers.[38–42] In a following procedure the two-step self-assembly process based on Ru^{III}/Ru^{II} chemistry was then used for polymers end-capped with the 2,2′:6′,2″-terpyridine ligand. More precisely, the terpyridine-functionalized polymers have been complexed with $RuCl_3$ to selectively form a mono-complex (see Figure 2). In a further step, this mono-complex was reacted under reducing conditions (methanol, *N*-ethylmorpholine) with other uncomplexed 2,2′:6′,2″-terpyridine-terminated polymer blocks in order to form an asymmetrical AB ruthenium(II) bis-complex (see Figure 2).

The high selectively of the self-assembly process was demonstrated by using several analytical and spectrometric methods such as ^{1}H NMR, UV/Vis spectroscopy, MALDI-TOF-MS, size-exclusion chromatography.[40, 41] Various linear AB block copolymers were obtained utilizing this strategy (Figure 3). A complete description of the synthetic methodology and the characterization of the accordingly obtained metallo-supramolecular block copolymer is reported in a very recent paper.[40] These compounds will be referred as "metallo-supramolecular block copolymers" and designated by the acronym **A_x-[Ru]-B_y**, where A and B are the two different polymer blocks, -[Ru]- stands for the bis-2,2′:6′,2″-terpyridine–ruthenium(II) linkage between the A and B blocks and *x* and *y* represent the average degree of polymerization of the A and B blocks, respectively. Compared with "classical" covalent block copolymers, metallo-supramolecular block copolymers offer several advantages. A wide variety of polymeric blocks can be combined, regardless of the chemical structure and reactivity ratios of the constituting comonomers. Thus, new and original block copolymers, that could not be prepared by classical polymerization techniques, can be easily obtained by using this strategy. The high stability of the bis-2,2′:6′,2″-terpyridine–ruthenium(II) complexes[43] allows the integrity of accordingly formed block copolymers to be kept in various environments, such as organic solvents or water, even under extreme pH (the complex is stable for pH values ranging from 0 to 14) and salt concentration.[44] Nevertheless, the reversibility of the supramolecular bond allows in principle the construction of "smart materials" with tunable properties. Moreover, the electrochemical and photochemical properties of the utilized complexes can be engineered by choosing the appropriate metal ion.[45]

Metallo-Supramolecular Micelles

Amphiphilic AB block copolymers are known to aggregate into block copolymer micelles in aqueous media. Aqueous polymeric micelles consist of a core formed by the insoluble blocks, surrounded by a corona formed by the water-soluble segments.[46] In a very recent set of papers, the synthesis and characterization of metallo-supramolecular amphiphilic block copolymers containing a hydrophilic poly(ethylene oxide) (PEO) block linked to a hydrophobic poly(styrene) (PS) or poly(ethylene-*co*-butylene) (PEB) block through a bis-2,2′:6′,2″-terpyridine–ruthenium(II) complex, have been described.[40, 44, 47–50] These copolymers form the so-called "metallo-supramolecular micelles" with a hydrophobic core and a

PEO corona. The bis-2,2′:6′,2″-terpyridine – ruthenium(II) complexes are assumed to be located at the core – corona interface, as schematically depicted in Figure 4. The high stability of the bis-2,2′:6′,2″-terpyridine – ruthenium(II) complex in various environments allows the integrity of the amphiphilic copolymers to be kept intact. No exchange was observed so far between the macromolecular ligand at a timescale of more than one year.

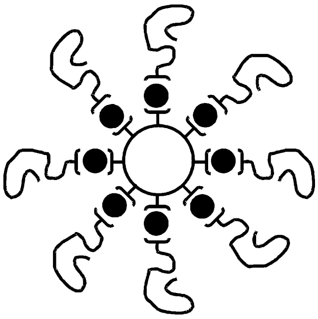
Figure 4. Structure of a metallo-supramolecular micelle. The central hydrophobic core is surrounded by terpyridine (brackets) – ruthenium (●) bis-complexes; PEO chains are forming the corona.

Dynamic light scattering (DLS) studies on metallo-supramolecular micelles systematically revealed the presence of two populations of aggregates/micelles. The population with the smaller size (hydrodynamic diameters ranging from 30 to 70 nm, depending on the investigated copolymer) was attributed to individual micelles or small clusters of micelles while the population with larger size was thought to result from the clustering of a large numbers of micelles. The relative proportion of clusters was increasing with time. This was attributed to a lack of colloidal stability of the individual micelles, most likely due to too short PEO blocks. A quasi-equilibrium state between micelles and clusters was, however, found for micelles containing a low glass transition PEB core. Moreover, the hydrodynamic diameter of micelles containing a PEB core (30 nm) was in the range of the value expected for usual block copolymer micelles.[46]

TEM studies revealed that individual micelles and clusters of micelles were coexisting in the aqueous solution. Because clustering of micelles could be an artifact due to TEM sample preparation (during the drying process), several TEM techniques were combined. TEM observations of dried non-contrasted metallo-supramolecular micelles on Formvar-coated TEM grid revealed spherical micelles and aggregates of micelles with a poor electronic contrast, as a result of the presence of ruthenium ions.[47–50] However, these results did not show the internal structure of the micelles and aggregates. Cryo-TEM observations could successfully demonstrate that the large aggregates were a result from clustering of individual micelles and visualize the core – corona internal organization of the metallo-supramolecular micelles.[51] The characteristic features of micelles formed by metallo-supramolecular copolymers have been compared to the ones of "classical" covalent block copolymers. This is illustrated by the PS_{20}-[Ru]-PEO_{70} and PS_{22}-*b*-PEO_{70} copolymers. DLS revealed hydrodynamic radii of 20 nm for the PS_{22}-*b*-PEO_{70} and 65 nm for the PS_{20}-[Ru]-PEO_{70} sample.[44] Moreover, no aggregates were observed for the covalent micelles. These findings were confirmed by cryo-TEM and showed that covalent and individual metallo-supramolecular micelles have PS cores of the same size.[51] However, metallo-supramolecular micelles do form small clusters resulting from the merging of a limited number (4 – 6) of individual micelles, coexisting with individual micelles and large clusters.

Metallo-supramolecular micelles were found to be strongly sensitive to the ionic strength. This behavior was attributed to the charged bis-2,2′:6′,2″-terpyridine – ruthenium(II) complexes, their associated counter-anions (PF_6^-) and to residual salts interacting with PEO segments. The most striking features observed upon salt addition was the sharp decrease in the hydrodynamic diameter of the metallo-supramolecular micelles (decrease from 65 to 25 nm). This was attributed to reduce electrostatic repulsions among coronal chains that initially resulted in the breaking of the small clusters into individual micelles, in agreement with the hydrodynamic diameter of 25 nm. At high salt concentration, aggregation started again as a result of a decreased steric stabilization of the micelles (PEO is no longer effective as stabilizing block at high salt concentration).

Finally, "covalent" and "metallo-supramolecular" block copolymers have been combined in a single macromolecular structure. In this respect a terpyridine-functionalized polystyrene – *block*-poly(2-vinylpyridine) has been complexed with a terpyridine-functionalized PEO to lead to a PS_{32}-*b*-$P2VP_{13}$-[Ru]-PEO_{70} ABC triblock copolymer (see structure in Figure 3). This copolymer was further used to prepare core – shell – corona micelles consisting of a PS core, a P2VP shell and a PEO corona. This kind of micelle has the capability to respond to pH via the protonation/deprotonation of the P2VP shell, as illustrated in Figure 5.[42] The pH response of these micelles can be advantageously used for the encapsulation or

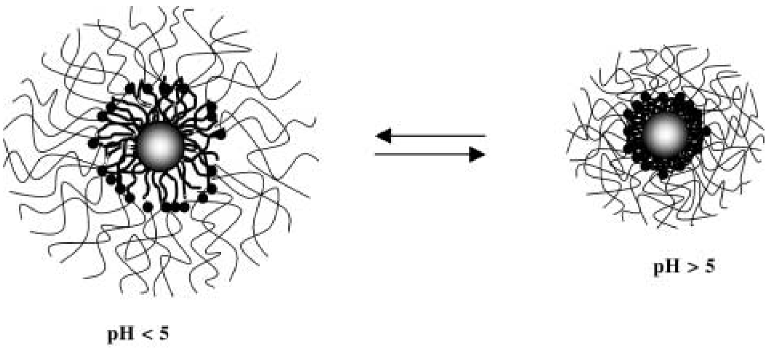

Figure 5. Structure of PEO_{70}-[Ru]-$P2VP_{13}$-*b*-PS_{32} core-shell-corona aqueous micelles as a function of pH (central PS core surrounded by a P2VP shell in black, bis-2,2′:6′,2″-terpyridine – ruthenium(II) complexes as black dots, outer PEO corona). Depending on pH, the P2VP shell is protonated and hydrophilic (pH < 5) or hydrophobic and collapsed on the PS core (pH > 5).

release of active species reversibly trapped in the P2VP shell. Moreover, the P2VP shell can serve as a nanoreactor for the production of metal nanocapsules.[52]

Reversibility of the Metallo-Supramolecular Bond

Although bis-2,2′:6′,2″-terpyridine–ruthenium(II) complexes have proven to be extremely stable in various environments, some recent experiments have shown that the addition of a large excess of a competing ligand (hydroxyethyl ethylenediaminetriacetic acid, trisodic salt) did allow the opening of the initial bis-2,2′:6′,2″-terpyridine–ruthenium(II) complex. However, a very large excess of the competing ligand (10^5 molar excess) was required and the sample needed to be heated at 60 °C for a few hours. This experiment was conducted directly on the aqueous micelles and resulted in the formation of original nano-objects decorated at their surfaces with terpyridine ligands (Figure 6). The opening of the complex was directly seen macroscopically by the disappearance of the characteristic orange color of the bis-2,2′:6′,2″-terpyridine–ruthenium(II) complex (Figure 6). A sharp decrease in micelle diameter was also observed by AFM and DLS, as a proof of the breaking of the metal–ligand complexes, the release of the coronal chains and accordingly the formation of nano-objects (see AFM pictures in Figure 6).[47] The excess of competing ligand and the released coronal chains were then eliminated by dialysis against pure water. That terpyridine ligands were still present at the surface of these nano-objects was proven by observation of the characteristic violet color of iron-terpyridine complexes after addition of iron(II) acetate (see Figure 6). Current investigations focus on the opening of the complexes via redox chemistry.

Conclusion and Outlook

The new approach described here represents a valuable route to the synthesis of novel block copolymers that can hardly be obtained by classical sequential block copolymerisation. Morevover, a great variety of block copolymers architectures (linear, comblike, star-shaped etc.) can be obtained depending on the location of the terpyridine ligand in the polymer chain. Metallo-supramolecular block copolymers are therefore the precursors of new smart nanomaterials.

In this concept paper, we focused on the use of low molecular weight amphiphilic “metallo-supramolecular block

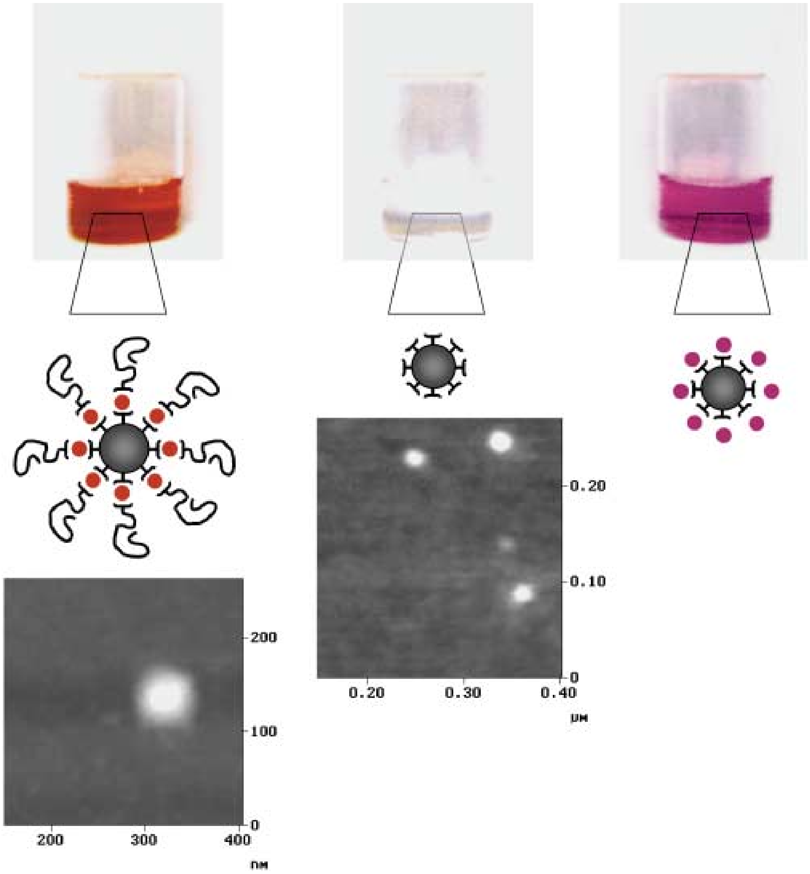

Figure 6. Release of the coronal chains in metallo-supramolecular micelles. Left: Initial metallo-supramolecular micelles with bis-terpyridine ruthenium (orange dots) complexes, orange-colored micellar solution on top, schematic structure of the micelles and AFM height image of the micelles (bottom). Middle: Hydrophobic cores decorated with terpyridine ligands, after addition of a strong competing ligand, as evidenced macroscopically by the formation of a colorless micellar solution (top), schematic structure of the core and AFM height image of the core (bottom). Right: Micellar cores have been isolated and Fe^{II} ions have been added, resulting in a violet solution (top) in agreement with the formation of a mixture of mono- and bis-terpyridine-iron(II) complexes, schematic picture of micellar core with mono-terpyridine iron(II) (violet) at their surface.

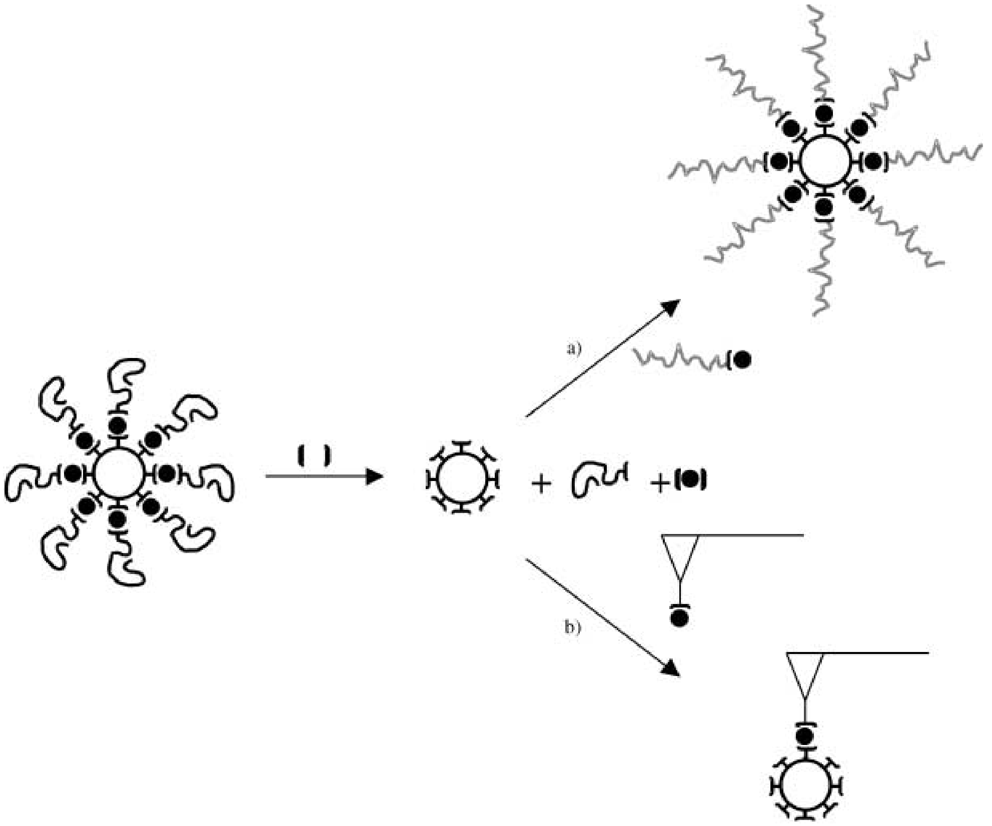

Figure 7. The reversibility of the bis-2,2′:6′,2″-terpyridine–ruthenium(II) complexes allow a) post-modification and b) nano-manipulation of the metallo-supramolecular nano-objects. This is illustrated by a) the exchange of the coronal chains of metallo-supramolecular micelles and b) their potential manipulation by a modified AFM tip. The micellar hydrophobic core (○) is surrounded by terpyridine (brackets)–ruthenium (●) bis-complexes; addition of a strong competing ligand (bold brackets) allows the release of the coronal chains and the micellar core can be isolated. Different coronal chains end-capped with a terpyridine–ruthenium mono-complex can be attached to the micellar core (a) or an AFM tip functionalized with a terpyridine–ruthenium mono-complex can be used for manipulation of the micellar core (b).

copolymers" for the preparation of "metallo-supramolecular micelles". The characteristic features of these micelles have thoroughly been characterized and compared to the covalent counterparts. The most appealing feature of metallo-supramolecular micelles certainly lies in the reversibility of the bis-2,2′:6′,2″-terpyridine–ruthenium(II) complexes under certain external stimuli. It allows not only an easy chemical modification of these nano-objects by for example exchanging coronal chains, but also their potential manipulation by for example a terpyridine-functionalized AFM tip as depicted in Figure 7.

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