

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/227985922>

Metallo-Supramolecular Block Copolymers

ARTICLE *in* ADVANCED MATERIALS · JUNE 2007

Impact Factor: 17.49 · DOI: 10.1002/adma.200602170

CITATIONS

106

READS

15

4 AUTHORS, INCLUDING:



Pierre Guillet

Université d'Avignon et des Pays du Vaucluse

27 PUBLICATIONS 671 CITATIONS

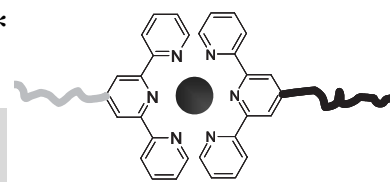
SEE PROFILE

DOI: 10.1002/adma.200602170

Metallo-Supramolecular Block Copolymers**

By Charles-André Fustin, Pierre Guillet,
Ulrich S. Schubert,* and Jean-François Gohy*

Supramolecular copolymers have become of increasing interest in recent years for the search of new materials with tunable properties. In particular, metallo-supramolecular block copolymers—copolymers in which the blocks are linked together by a metal–ligand complex—have seen important progresses, allowing better control over the synthetic strategies for various architectures, and providing a better understanding of the parameters governing their self-assembly. We review here recent developments on the synthesis and self-assembly of such materials achieved in this field.



1. Introduction

In the past twenty years, since the Nobel prize of Lehn, Pedersen, and Cram, supramolecular chemistry has become increasingly important and is now a major field in chemical research. Self-recognition and self-assembly are the two pillars on which supramolecular chemistry is based, involving mainly interactions of noncovalent nature (e.g., van der Waals, hydrogen bonding, and coordinative interactions). The large range of interaction strengths, directionality, and reversibility offered by these interactions allows unprecedented control over the structure and properties of materials, enabling the synthesis of large and complex structures with diverse functions that are interesting for many different fields.

In recent years, supramolecular polymer chemistry, applying the principles of supramolecular chemistry to the synthesis of macromolecules, has gained special interest. Various approaches towards supramolecular polymers have been consid-

ered so far. They can be classified according to the nature of the noncovalent interaction (i.e., hydrogen bonding, coordinative interactions, and others) and to the structure of the supramolecular polymer (i.e., polycondensation-type supramolecular polymers versus supramolecular block copolymers).

In polycondensation-type polymers, each monomer or macromonomer is linked by noncovalent interactions. This approach requires the use of monomers or macromonomers bearing at least two binding sites that can be further condensed through supramolecular interactions (Fig. 1). This approach leads to polymers that contain many supramolecular linkers along the main chain, and has been successfully applied to the synthesis of supramolecular polymers by using hydrogen bonds^[1] and metal–ligand coordination.^[2–4] Many reports have been devoted to this approach, which represents by far the main route to supramolecular polymers. This route will not be considered in the present Report.

In the second approach, supramolecular linkers are introduced at specific locations in block copolymer architectures,

[*] Prof. U. S. Schubert
Laboratory of Macromolecular Chemistry and Nanoscience
Eindhoven University of Technology
PO Box 513, 5600 MB Eindhoven (The Netherlands)
E-mail: u.s.schubert@tue.nl

Prof. J.-F. Gohy, Dr. C.-A. Fustin, P. Guillet
Unité de Chimie des Matériaux Inorganiques et Organiques
(CMAT) & Research Center in Micro- and Nano-Materials and
Electronic Devices (CeRMiN)
Université catholique de Louvain (UCL)
Place Pasteur 1, 1348 Louvain-la-Neuve (Belgium)
E-mail: gohy@chim.ucl.ac.be

[**] C.-A.F. is Chargé de Recherches FNRS. P.G. and J.F.G. thank the Communauté française de Belgique for ARC NANOMOL 03/08-300. U.S.S. thanks NWO (VICI award) and the Fonds der Chemischen Industrie for financial support.

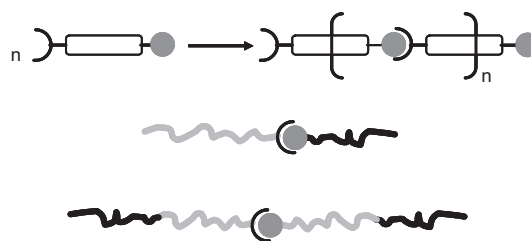


Figure 1. Schematic representation of a) a polycondensation-type supramolecular polymer; b) a supramolecular block copolymer where the linker is located at the junction of the two blocks, and c) a supramolecular block copolymer where the linker holds two copolymer chains together.

leading to supramolecular block copolymers. This should lead to systems that combine the characteristic features of block copolymers (e.g., microphase separation between immiscible constituent blocks) with the ones of supramolecular polymers (e.g., reversibility and tunability of the strength of the supramolecular bonds). The supramolecular linkers can be used to either bridge together different homopolymer blocks, or to link together different block copolymers. The first approach leads to diblock copolymers containing a supramolecular linker between the constituent blocks (Fig. 1b). The integrity of the block copolymer is, in this case, directly related to the supramolecular linker. In this respect, microphase separation between the polymer blocks is expected when the supramolecular interactions are operative, while macrophase separation between free polymer blocks should occur if the supramolecular interactions are turned off. The second strategy is based on the use of block copolymers containing a linking group specifically introduced at a defined locus of the copolymer chain (generally at the chain end or the block junction). These linking groups can further promote the formation of a supramolecular structure by bridging two or more copolymer chains together (Fig. 1c). In this case, microphase separation still occurs upon disruption of the supramolecular interactions.

Metal–ligand coordination is particularly interesting for the synthesis of both types of supramolecular block copolymers because the coordination bond is highly directional, a wide range of easily functionalized ligands is available, and the interaction strength can be fine-tuned by choosing appropriate metal ions. Such supramolecular copolymers, coined metallo-supramolecular block copolymers, offer several advantages compared to their covalent counterparts. The reversibility of the supramolecular bond allows an improved control over the material properties and the construction of “smart” materials. Moreover, the presence of a metal complex in the copolymer structure introduces additional electrochemical, photophysical, catalytic, and magnetic properties, and potentially allows the use of these copolymers as precursors for the generation of inorganic or hybrid structures. These novel copolymers represent therefore highly promising candidates for the formation of functional nanostructured materials.

This Progress Report will deal only with metallo-supramolecular block copolymers. In the following, linear architectures based on 2,2':6',2''-terpyridine ligands will be distinguished from starlike architectures based mainly on 2,2'-bipyridine ligands. Both parts of the Report are devoted to selected recent examples of linear and starlike architectures, respectively.



Ulrich S. Schubert was born in Tübingen in 1969. He studied chemistry at the Universities of Frankfurt and Bayreuth (both Germany) and the Virginia Commonwealth University, Richmond (USA). His Ph.D. work was performed under the supervision of Professor Eisenbach (Bayreuth, Germany) and Professor Newkome (Florida, USA). In 1995, he obtained his doctorate with Professor Eisenbach. After a postdoctoral training with Professor Lehn at the Université Strasbourg (France) he moved to the Technische Universität München (Germany) to obtain his habilitation in 1999 (with Professor Nuyken). From 1999 to Spring 2000 he held a temporal position as a professor at the Center for NanoScience at the Universität München (Germany). Since Summer 2000 he has been Full Professor at the Eindhoven University of Technology (Chair for Macromolecular Chemistry and Nanoscience). His awards include the Bayerischen Habilitations-Förderpreis, the Habilitandenpreis of the GDCh (Makromolekulare Chemie), the Heisenberg-Stipendium of the DFG, the Dozenten-Stipendium of the Fonds der Chemischen Industrie, and a VICI award of NWO. The major focus of his research interests relates to organic heterocyclic chemistry, supramolecular materials, combinatorial material research, nanoscience, and tailor-made macromolecules.



Jean-François Gohy was born in 1971 in Verviers (Belgium). He received his Ph.D. from Prof. Robert Jérôme's group (University of Liège, Belgium) in 1999, working on liquid crystalline ionomers and block copolymers. He then got a “Chargé de Recherches” position from the Belgian National Foundation for Scientific Research and started to work on stimuli-responsive block copolymer micelles in the same group. In 2001–2002, he was post-doc in the group of Prof. Ulrich S. Schubert at the Eindhoven University of Technology (The Netherlands) and worked on the so-called “metallo-supramolecular block copolymers”. In 2003, he was appointed as an Assistant Professor at the catholic University of Louvain (Belgium) where he is at the head of the polymer chemistry laboratory within the Chemistry Unit of Inorganic and Organic Materials. He was appointed in 2006 as an Associate Professor at the same place. He is coordinator from the STIPOMAT (Stimuli-Responsive Polymeric Materials) network from the ESF and author or co-author of more than 90 scientific papers, most of them in the field of block copolymer micelles.

2. Metallo-Supramolecular Block Copolymer Architectures

2.1. Linear Metallo-Supramolecular Block Copolymers

Linear metallo-supramolecular copolymers can be obtained from three different combinations of supramolecular interactions, depending on the structure of the building blocks used and on the position of the ligand. Combining A-[and B-[blocks yields A-[M]-B diblock copolymers,]-A-[and B-[blocks yield B-[M]-A-[M]-B triblock copolymers, and two A-B-[copolymers yield A-B-[M]-B-A diblock copolymers (A and B represent two different polymer blocks, -[the ligand attached to these blocks, and M the metal ion used in the complex). For A-[M]-B and B-[M]-A-[M]-B copolymers, the supramolecular linker -[M]- is located at the junction between the A and B polymer blocks. If these two blocks are immiscible and phase separate, an effect of the metal-ligand complex on the phase separation process might be expected. Because microphase separation in AB block copolymers is known to lead to well-defined nanostructured materials, the characteristic features (e.g., morphology and size) of the resulting self-assembled structures might be strongly influenced by the supramolecular linkers. Some preliminary results on this issue will be discussed here. In the case of A-B-[M]-B-A copolymers, the metallo-supramolecular complexes are located in a single polymer phase (in this case, B) and, thus, should have less influence on the microphase separation process.

The first step toward the synthesis of such metallo-supramolecular architectures is of course the attachment of the ligand to a polymer chain end. The only ligand that has been used to date is 2,2':6',2''-terpyridine. Two main strategies towards reaching this goal have been reported so far. The first involves the grafting of a terpyridine functionalized at the 4'-position onto the reactive chain end of a polymer.^[5] In this regard, the commercially available 4'-chloro-2,2':6',2''-terpyridine is a very useful compound for reaction with α - or ω -hydroxyl-functionalized polymers. A variation on this approach

has been recently reported, where the authors terminated the anionic polymerization of styrene with the chloro-terpyridine, thus avoiding the post-functionalization step.^[6] The second synthesis strategy consists of using a terpyridine-functionalized initiator (a so-called "supramolecular initiator") for the polymerization of the desired polymer. This method has the advantage of producing polymer chains with a theoretical functionalization degree of 1. Two examples of such initiators have been reported; one developed for nitroxide-mediated radical polymerization (NMRP)^[7] and another for reversible addition-fragmentation chain transfer polymerization (RAFT).^[8]

The synthesis of A-[M]-B and B-[M]-A-[M]-B metallo-supramolecular block copolymers requires the formation of heteroleptic complexes. In case of the A-[M]-B system, this means that the reaction between A-[, B-[, and M should only selectively lead to A-[M]-B complexes and that the formation of homoleptic A-[M]-A and B-[M]-B complexes should be avoided. Very few metals (Ru, Os, Ir, and Co) are suitable for this approach, among which only Ru has been used for the synthesis of metallo-supramolecular block copolymers. Such a selective complexation process requires a two-step complexation procedure. Indeed, ruthenium(III) ions are known for forming a stable mono-complex with terpyridine, while ruthenium(II) ions do form a stable bis-complex with the same ligand.^[9] Therefore, the synthesis of A-[Ru^{II}]-B metallo-supramolecular block copolymers can be selectively achieved by first making the A-[Ru^{III}] (or B-[Ru^{III}]) mono-complex, which is then further reacted under appropriate reducing conditions with B-[(or A-[) to form the desired A-[Ru^{II}]-B bis-complex (Fig. 2). The high selectivity of this two-step process was demonstrated by using several analytical and spectrometric methods, such as ¹H NMR, UV-vis spectroscopy, matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS), and size-exclusion chromatography.^[10] The high stability of the bis-2,2':6',2''-terpyridine-ruthenium(II) complexes allows to retain the integrity of the formed block copolymers in various environments, such as organic

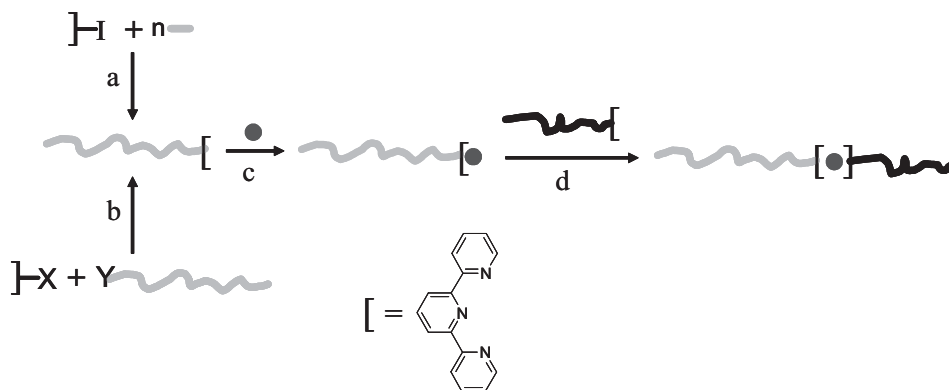


Figure 2. Schematic representation of the synthetic strategy to prepare linear metallo-supramolecular block copolymers. The first step is the synthesis of the macroligands by using either a functionalized (supramolecular) initiator (a), or grafting a terpyridine onto a reactive chain end (b). The second step is the preparation of a mono-complex with Ru^{III} (c). Finally, the second block, bearing a free terpyridine unit, is added to form a terpyridine-ruthenium(II) bis-complex (d).

solvents or water, even under extreme pH and salt concentration.^[11]

The synthesis of A-[Ru^{II}]-B copolymers from the respective macroligands has the drawback of requiring rather long reaction times (several days) to reach reasonable yields, most probably because of solvent and conformational effects on the polymer chains that limit access to the coordination sites. One way to circumvent this limitation would be to grow the two polymer blocks from a heteroleptic complex, acting as a dual initiator. In this manner the complexation will be more efficient because it will occur between small molecules.

In the following, the metallo-supramolecular block copolymers will be 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.

The most studied system is poly(styrene)-[Ru]-poly(ethylene oxide) (PS-[Ru]-PEO) block copolymer, and in particular the PS₂₀-[Ru]-PEO₇₀ composition. For this copolymer, the macroligands were prepared by reacting chloro-terpyridine with the hydroxy chain ends of PEO and PS (which was end-capped with one unit of ethylene oxide at the end of the anionic polymerization).^[10] The formation of micelles from this amphiphilic copolymer was studied by different techniques. Dynamic light scattering (DLS) revealed the presence of two populations, one with a hydrodynamic diameter of ca. 65 nm, and one with a diameter of ca. 200 nm.^[12] A cryo-transmission electron microscopy (TEM) investigation enabled the identification of these two populations.^[13] The first population did not only comprise individual micelles but a mixture of micelles and small aggregates, while the second population, with a larger size, resulted from the clustering of a large number of micelles. The characteristic features of the micelles formed by the PS₂₀-[Ru]-PEO₇₀ copolymer were also compared to the ones formed by a classical covalent block copolymer: PS₂₂-*b*-PEO₇₀.^[11] The diameter of the PS core was found to be the same for the covalent and metallo-supramolecular samples, but in the case of the covalent counterpart only individual micelles were formed, showing that micelles formed by metallo-supramolecular PS-[Ru]-PEO copolymers have a strong tendency to aggregate. In a more recent paper, it was shown that the formation of micellar aggregates could almost be totally suppressed by modifying the method of preparation of the micelles.^[14] Indeed, a slow and regular addition of water, with the help of a syringe pump, to an initial dimethyl formamide (DMF) solution of the PS₂₀-[Ru]-PEO₇₀ copolymer resulted in a well-defined micellar solution with almost no further aggregation of micelles. The micelles thus formed were analyzed by analytical ultracentrifugation, revealing a unimodal size distribution with an average molar mass of 318 000 g mol⁻¹, corresponding to an aggregation number of 53 copolymer chains per micelle.

The PS₂₀-[Ru]-PEO₇₀ copolymer was not only studied in solution but also in the melt. A small-angle X-ray scattering (SAXS) investigation revealed that, in contrast to its covalent

counterpart PS₂₂-*b*-PEO₇₀, a microphase separation occurred for the metallo-supramolecular copolymer. When hexafluorophosphate (PF₆⁻) was used as counter ion the morphology observed was spherical, and not the expected lamellar morphology considering the composition of the copolymer.^[15] This is due to aggregation of the terpyridine-ruthenium(II) complexes and of the counter ions, forming spherical aggregates with a radius of ca. 1.5 nm surrounded by a polymer shell with an outer radius of ca. 2.4 nm. When the more bulky tetraphenylborate (BPh₄⁻) was used as counterion, a highly ordered lamellar melt with a period of 11.9 nm was obtained after annealing at 55 °C for 40 h.^[16] It was inferred from the SAXS curves that the lamellar structure is composed of segregated domains of PS and PEO blocks, with the metal ions and their associated counter ions confined to the lamellar interfaces. In fact, the system behaves as an ABC triblock copolymer, where the metal-ligand complex and the associated counter ions act as a middle block strongly incompatible with the other blocks. The order-disorder temperature of this system was found to be around 70 °C, in agreement with Leibler's random phase approximation theory. This transition is reversible upon cooling, but more and more time is needed to achieve the lamellar morphology when increasing the annealing temperature. Schematic drawings of the morphologies obtained for both types of counterion are shown in Figure 3.

These initial investigations on the nanometer-scale organization of the PS₂₀-[Ru]-PEO₇₀ metallo-supramolecular copolymer in both a selective solvent and in the bulk revealed a deep influence of the bis-terpyridine ruthenium complexes on the microphase separation between the PS and PEO blocks. Therefore, other compositions than the PS₂₀-[Ru]-PEO₇₀ were also synthesized and characterized. Because the method for preparing metallo-supramolecular block copolymers relies

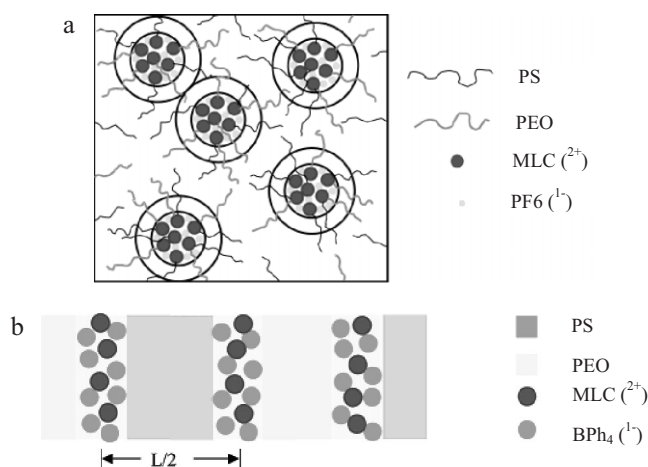


Figure 3. Schematic drawing of models of the melt morphology of PS₂₀-[Ru]-PEO₇₀ with either a) PF₆⁻ counter ions or b) BPh₄⁻ counter ions. The 2+ and 1- indicate the charges on each metal-ligand complex and counterion, respectively. a) Reproduced with permission from [15]. Copyright 2003 American Chemical Society. b) Reproduced with permission from [16]. Copyright 2005 American Chemical Society.

on the coupling of two macroligands via a simple two-step synthesis, it is rather straightforward to prepare a library of block copolymers. A 4×4 library of $\text{PS}_x\text{--}[\text{Ru}]\text{--PEO}_y$ block copolymers was thus prepared, and the morphology of thin films obtained from these copolymers was investigated by scanning force microscopy (SFM).^[17] The different PS blocks were synthesized by NMRP using an initiator bearing a terpyridine moiety. The SFM images obtained from those thin films are shown in Figure 4. These results illustrate that a wide variety of morphologies with tunable domain size can be obtained from a limited number of terpyridine-functionalized polymer blocks. This combinatorial approach is certainly an advantage of metallo-supramolecular block copolymers compared with classical covalent ones. Although not discussed in the original work, this study also shows that the PEO microdomains are always oriented perpendicularly to the film surface. This effect, also observed in another study (creation of nanopores, see below), is again most probably linked to interactions between metal–ligand complexes, and is currently under investigation. Another 13-member library was also very recently synthesized and the micellization behavior in water was studied.^[18] SFM and TEM characterization of the micelles revealed that the core size did not scale linearly with the degree of polymerization (DP) of the PS block, as expected from the theory of classical covalent copolymers. Only two core sizes

were observed, one of ca. 10 nm for DP values of 70 and below, and one of ca. 20 nm for DP values of 200 and above. For copolymers having a DP in the transition region between 70 and 200, two populations were observed. This unusual behavior has been attributed to electrostatic repulsions between the charged terpyridine-ruthenium bis-complexes present at the junction of the two blocks, which strongly affect the self-assembly behavior. This has been demonstrated by preparing micelles in the presence of salt to screen out the repulsions. In this case, the metallo-supramolecular block copolymers behaved as their covalent counterpart; the core diameter scaling linearly with $\text{DP}^{3/5}$. The evolution of the core diameter for micelles prepared with and without salt is shown in Figure 5.

The two studies reported above dealt with libraries in which the composition of the copolymer was varied. Considering the results obtained on the effect of the counterion on the melts of the $\text{PS}_{20}\text{--}[\text{Ru}]\text{--PEO}_{70}$ copolymer (Fig. 3), it would be interesting to build a library by using only a few different compositions of the copolymer, and varying the nature of the counterion. In this manner, the relative influence of the bulkiness and solubility of the counterion with respect to the block length would be established.

Beside the formation of libraries of copolymers, another advantage of metallo-supramolecular block copolymers lies in the reversibility of the bis-terpyridine complexes. Indeed, an

oxidation of Ru^{II} ions to Ru^{III} should be accompanied by a transformation of the initial bis-complexes into mono-complexes. Such a reversibility could be used advantageously to create well-defined nanoporous structures. In this respect, nanoporous thin films were obtained from a $\text{PS}_{375}\text{--}[\text{Ru}]\text{--PEO}_{225}$ copolymer.^[19] In a first step, cylindrical microdomains oriented normally to the substrate were easily obtained by spin-coating a solution of the copolymer in a non-selective solvent without the need for further treatment. In a second step, the metal–ligand complexes were opened by oxidizing the Ru^{II} to Ru^{III} , which can only form mono-complexes. This releases the minor block and creates the nanopores. The removal of the PEO was evidenced by SFM, X-ray photoelectron spectroscopy, and X-ray reflectivity. However, the conditions used to open the complex were rather harsh (a strong oxidizing agent, Ce^{IV} , at pH 1), limiting the possible applications. To increase the versatility of the method it would be interesting to develop a system based on a less stable complex (e.g., by using another metal), which would allow the use of milder conditions to create the nanopores.

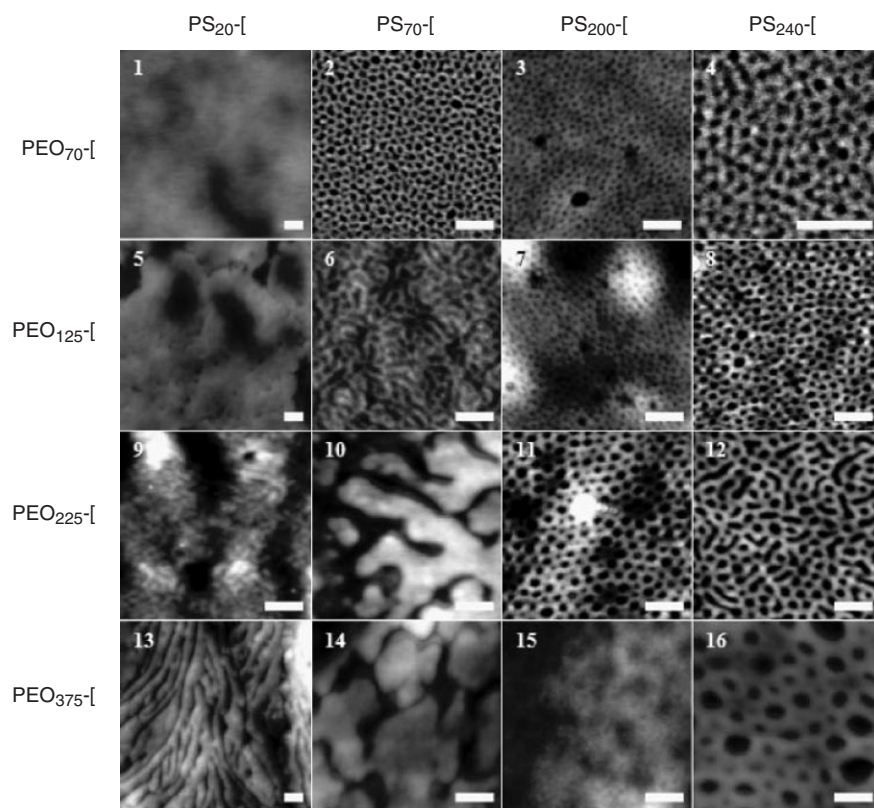


Figure 4. SFM phase images of thin films prepared by spin-coating 2% solutions (w/v) of all the $\text{PS}_x\text{--}[\text{Ru}]\text{--PEO}_y$ block copolymers in the library in toluene. The scale bars represent 100 nm. Reproduced with permission from [17]. Copyright 2004 The Royal Society of Chemistry.

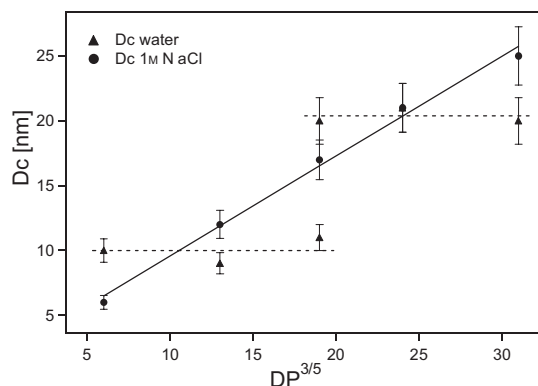


Figure 5. Relationship between the measured (SFM) core size of PS_x–[Ru]–PEO_y micelles (Dc) and the 3/5th power of the PS block DP, for micelles prepared in pure water (▲) and in 1 M NaCl (●). The solid line represents the linear regression obtained from the data in 1 M NaCl. The dashed lines, evidencing the presence of only two sizes, are only a guide for the eyes. Reproduced with permission from [18]. Copyright 2006 American Chemical Society.

PS_x–[Ru]–PEO_y are not the only metallo-supramolecular copolymers that have been synthesized. An amphiphilic poly(ethylene-*co*-butylene)–[Ru]–PEO (PEB–[Ru]–PEO) copolymer was prepared, and its micellization in water was studied.^[20] As with the PS–[Ru]–PEO, DLS and SFM characterizations revealed a strong tendency to aggregate, but in the case of the PEB–[Ru]–PEO a quasi-equilibrium state between micelles and clusters was found, presumably resulting from the softness of the micellar core. The addition of a large excess of a water-soluble competitive ligand resulted in the breaking of the bis-terpyridine complexes, and led to water-dispersed PEB nanoparticles decorated with charged metal complexes at their surface.^[20,21] Rodlike micelles were obtained from a poly(ferrocenylsilane)–[Ru]–PEO (PSF–[Ru]–PEO) copolymer in water as evidenced by DLS, TEM, and SFM.^[22] The micelles had a constant diameter but were rather polydisperse in length, and DLS measurements indicated that they were rather flexible. Crystallization of the PFS in these micelles was observed by differential scanning calorimetry (DSC), and is thought to be responsible for the formation of these rodlike structures. Zhou and Harruna reported the synthesis of an amphiphilic PS–[Ru]–poly(*N*-isopropylacrylamide) using RAFT polymerization with a terpyridine-functionalized chain transfer agent.^[8] An ABC triblock copolymer was prepared by complexing a terpyridine-functionalized polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP) with a terpyridine-functionalized PEO.^[23] This copolymer was used to prepare stimuli-responsive core/shell-corona micelles, consisting of a PS core, a P2VP shell, and a PEO corona. These micelles can indeed respond to pH via the protonation/deprotonation of the P2VP shell, increasing or decreasing their size. Triblock copolymers of this kind are very interesting systems from a morphological and stimulus-responsiveness point of view, but little synthetic efforts have been done in this direction. With the ever-progressing development of controlled

radical polymerization methods, tolerating the use of functional initiators and allowing the preparation of well-defined diblock copolymers, scientists now have all the tools needed for the synthesis of various metallo-supramolecular ABC, or even ABCD, copolymers. By these methods, new combinations of multiblock copolymers could be prepared that were not accessible, or have been very difficult to access, to date by the classical covalent approach.

2.2. Starlike Metallo-Supramolecular Block Copolymers

The most frequently used ligand to prepare star-shaped block copolymers is 2,2′-bipyridine. This ligand forms tris-complexes with a large variety of metal ions, and is an ideal candidate for the preparation of multiarm stars because bipyridines functionalized at the 4- and/or 4′-position can be rather easily prepared. Thus, stars with 3, 4, 5, or 6 arms can in principle be synthesized according to the functionality of the bipyridines used. Two approaches towards starlike metallo-supramolecular block copolymers can be distinguished: i) the coordination of different kinds of polymeric ligands around the metal center, yielding hetero-arm star copolymers (heteroleptic complexes); and ii) the coordination of identical ligands (homoleptic complexes), each ligand being a block copolymer (Fig. 6). After self-assembly, the metal–ligand complexes will be positioned at the domain interface in the case of hetero-arm star copolymers, while they will be positioned in the core of the domain formed by the block directly attached to the ligand in the other case (Fig. 7). The prepara-

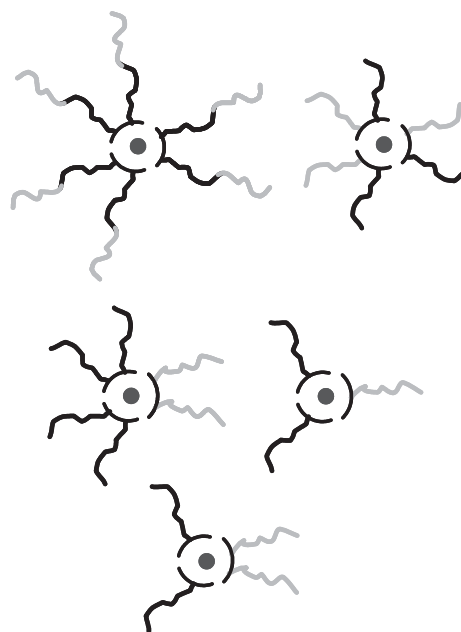


Figure 6. Schematic representation of the different architectures based on bipyridine complexes reported in the literature. The two examples at the top are obtained by the homoleptic-complex approach, the other three by the heteroleptic-complex approach.

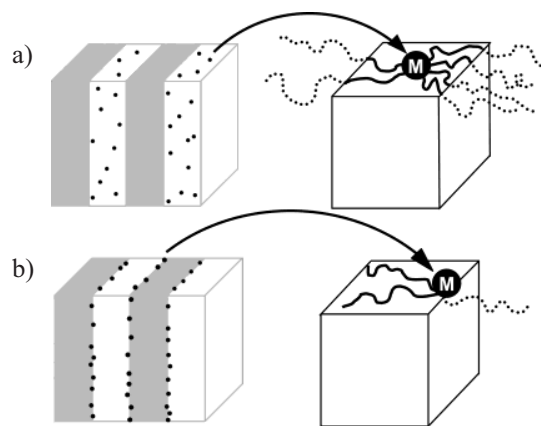


Figure 7. Schematic representation of the metal placement predicted for a) a metal-centered star block copolymer and b) a metal-centered hetero-arm star in microphase-separated films. Reproduced with permission from [31]. Copyright 2003 American Chemical Society.

tion of star block copolymers based on homoleptic complexes can be achieved by two strategies. The first one employs a bipyridine-metal tris-complex as initiator for the polymerization of the arms; each bipyridine bearing the proper functional group. The second strategy consists of growing the polymer arms not from a tris(bipyridine) complex, but from the free bipyridine ligand. The macroligands thus created are complexed around the metal center in a subsequent step (Fig. 8). The synthesis of hetero-arm star copolymers relies on the same principle as the terpyridine-based linear AB copolymers. A bis-bipyridine-metal complex is first prepared by using two identical macroligands. The third, differently functionalized, bipyridine-based macroligand is then added in a subsequent step to yield the tris-complex (Fig. 9). As for the linear architectures, the same two strategies, that is, the grafting of the ligand onto a polymer chain end or the use of a functionalized initiator to grow the polymer chain from the ligand, can be applied to obtain a polymeric ligand. In this context, modified bipyridines have been used as initiators in atom-transfer radical polymerization (ATRP) and in ring opening polymerization (ROP). In the following paragraphs, we will describe some examples of these two classes of compounds: homoleptic and heteroleptic complexes.

The first reported example of a homoleptic complex was the preparation of six-arm star block copolymers by

using $[\text{Fe}\{\text{bpy}(\text{CH}_2\text{Cl})_2\}_3](\text{PF}_6)_2$ (bpy: 2,2'-bipyridine) as hexafunctional initiator for the polymerization of oxazolines.^[24] The first block was made of the hydrophilic 2-ethyl-2-oxazoline (EtOx), and the second, hydrophobic, block of either 2-phenyl-2-oxazoline (PhOx) or 2-undecyl-2-oxazoline (UnOx). The morphology of thin and thick films of the poly(EtOx)-*b*-poly(UnOx) six-arm star copolymer was later investigated by X-ray scattering (SAXS and wide-angle X-ray scattering (WAXS)), TEM, and SFM.^[25] It was found that the pEtOx block forms cylindrical microdomains in a matrix of pUnOx. Upon annealing at 160 °C, iron nanoclusters are formed on top of the pEtOx domains for thin films, and micrometer-size iron-rich clusters form on the surface of bulk samples. Another example of a six-arm star copolymer was synthesized by a combination of ROP and ATRP.^[26] The first step of the synthesis was the polymerization of D,L-lactide by ROP using $[\text{Ru}\{\text{bpy}(\text{CH}_2\text{OH})_2\}_3](\text{PF}_6)_2$ as hexafunctional initiator. The hydroxyl end groups were then converted to bromoesters, and *tert*-butyl acrylate was polymerized by ATRP. In a final step, PtBA was hydrolyzed into poly(acrylic acid). Six-arm star block copolymers have also been obtained by the macroligand strategy.^[27] D,L-lactide (DLPLA) and ϵ -caprolactone (CL) were sequentially polymerized by ROP, using bis(hydroxymethyl)-2,2'-bipyridine as initiator, to yield $\text{bpy}(\text{PCL-DLPLA})_2$ and $\text{bpy}(\text{DLPLA-PCL})_2$ copolymers. The macroli-

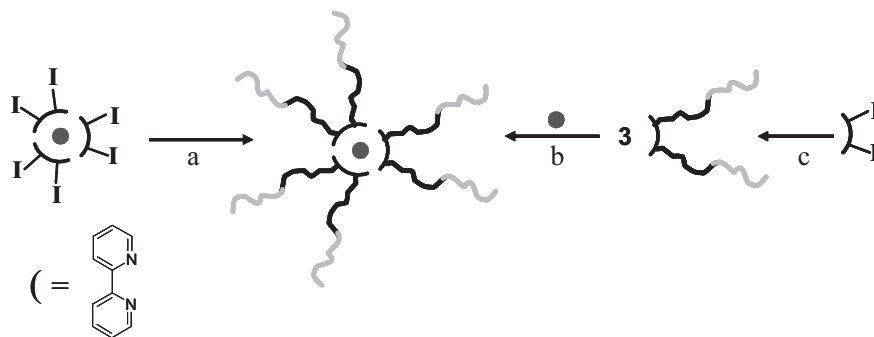


Figure 8. Schematic representation of the synthetic strategies for preparing metallo-supramolecular star copolymers. The first strategy (a) consists of growing the polymeric arms by using a bipyridine-metal tris-complex as initiator. The second strategy involves first the synthesis of the macroligands (c), followed by the complexation with the metal (b).

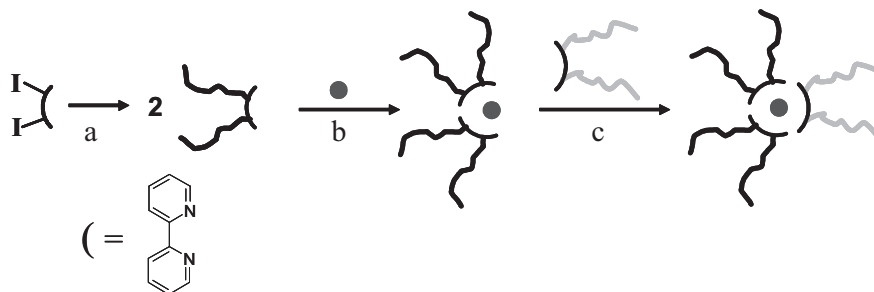


Figure 9. Schematic representation of the synthetic strategy for preparing metallo-supramolecular hetero-arm star copolymers. The first step is the synthesis of the macroligands (a). The second step is the preparation of a bis-complex with the metal (b). Finally, the second type of macroligand is added, forming a bipyridine tris-complex (c).

gands were then complexed with iron(II) ions to yield biocompatible copolymers with a labile metal center, or to ruthenium(II) to generate luminescent copolymers with an inert metal core. This ruthenium tris(bipyridine) core could be useful as a luminescent tag for drug-delivery model studies. It was observed that the iron-centered star copolymers decolorize in response to some stimuli (heat, acid, bases, peroxides, ammonia), suggesting interesting possibilities for their use in qualitative and quantitative assays. Other examples of this alternative strategy include the synthesis of macroligands by a combination of ROP (for PCL or DLPLA) and ATRP (for PtBA or poly(methyl methacrylate) (PMMA)), or sequential ATRP to produce bpy(PMMA-PS)₂ and bpy(PS-PMMA)₂.^[28] Those macroligands were then complexed with iron(II) to yield six-arm star copolymers. However, for bpy(PCL-PtBA)₂ and bpy(PLA-PtBA)₂ macroligands, only bis(bpy) complexes resulted. The reasons for these differences between several polymers may originate from variations in chain conformation in the solvent mixture used, inducing steric hindrance around the metal binding site. Hetero-arm star copolymers can also be produced by the homoleptic complex approach. This requires the orthogonal synthesis of unsymmetrical macroligands from a dual initiator. 4-Chloromethyl-4'-hydroxymethyl-2,2'-bipyridine (bpy-(CH₂Cl)(CH₂OH)) was used as dual initiator for the sequential polymerization of ϵ -caprolactone by ROP, and of styrene by ATRP.^[29] The bpy(PS)(PCL) macroligand was best prepared by growing the PS block first from the more reactive halide, followed by the generation of the PCL block from the hydroxyl site. In a final step, the macroligands were complexed with iron(II).

Several examples of hetero-arm star copolymers based on heteroleptic complexes have been reported. Macroligands bearing one or two PS chains were first synthesized by ATRP using 4-(chloromethyl)-2,2'-bipyridine and 4,4'-bis-(chloromethyl)-2,2'-bipyridine as initiator, respectively.^[30] Bis-bipyridine ruthenium complexes were then prepared with those macroligands. In a final step, a second type of macroligand, bearing one or two PMMA chains also grown by ATRP, was attached to the bis-complexes, yielding hetero-arm star copolymers with 3 or 6 arms. It was demonstrated that solvent polarity, influencing the conformation of the polymer chains, is an important tuning parameter to achieve control over the assembly of hetero-arm star copolymers. In another example, the synthesis of hetero-arm star copolymers with 4 or 6 arms was reported.^[31] Six-arm stars were obtained by first forming a ruthenium bis-complex with bipyridines bearing two PCL chains, grown by ROP, as macroligands, followed by complexation with a bipyridine bearing either two PS chains (grown by ATRP) or two poly(ethylene glycol) (PEG) chains prepared by grafting PEG onto 4,4'-bis-(chloromethyl)-2,2'-bipyridine by the Williamson reaction. Four-arm stars were prepared by complexing to a ruthenium-bipyridine bis-complex bearing one PS chain on each bipyridine, a bipyridine bearing either two PLA chains (grown by ATRP), or two PEG chains.

The synthesis of a hetero-arm star copolymer with ligands other than bipyridines has also been reported. Ligands of the β -diketonate family, in conjunction with a bipyridine, were chosen to build a heteroleptic complex with a lanthanide ion.^[32] The macroligands were obtained by polymerizing D,L-lactide by ROP with dibenzoylmethane functionalized with a hydroxyl site as initiator. Three macroligands were then chelated to europium(III) to yield a three-arm star. A bipyridine bearing two PCL chains was finally complexed to this tris-complex to obtain a five-arm star block copolymer.

3. Conclusions

As shown by the results already available in the literature, important progress has been made in the development of synthetic strategies towards metallo-supramolecular block copolymers. From these preliminary reports, it is clear that the presence of metal-ligand complexes in block copolymers has a deep impact at several levels, ranging from the synthetic aspects to the final structure and functionality of the accordingly obtained materials. Indeed, the sequential self-assembly process used for the synthesis of metallo-supramolecular block copolymers is compatible with a combinatorial approach towards libraries of copolymers. In such an approach, various parameters, including the length of the block precursors, the nature of the metal-ion in the complex, and the architecture of the copolymer, can be easily screened. As the final properties of the accordingly obtained materials critically depend on these parameters, metallo-supramolecular copolymers will certainly play an important role in polymer-based materials with tunable properties in the next few years. Furthermore, the studies reported to date have clearly evidenced that the metal-ligand complexes, and the nature of the counter ions used, are strongly affecting the self-assembly of such copolymers. Indeed, slight variations in, for example, the nature of the counter ion are able to induce morphological changes in the copolymer nanostructure. The combination of a highly modular synthetic approach, enabling the preparation of various architectures, with the presence of a metal center having particular properties makes metallo-supramolecular block copolymers ideal candidates for the assembly of new, stimuli-responsive, functional materials. The possibility to fine-tune material properties by changing the metal center as well as the associated counter ions is a real advantage compared to classical block copolymers, in which only the block chemical nature, order, and architecture can be changed. Moreover, the supramolecular strategy could be used to go beyond the synthesis of block copolymers and to generate a superior level of ordering in nanostructures. The metallo-supramolecular interactions could indeed be considered as mortar to bind previously self-assembled structures (e.g., micelles), giving rise to hierarchically organized superstructures, or as molecular grips for nano-object manipulation. For such applications, now actively sought after in nanotechnology, the intrinsic properties

of the complexes (special photo- or electric properties, complex reversibility, and stimuli-responsiveness) offer major advantages compared with other approaches.

However, metallo-supramolecular block copolymers are still an emerging field, and a lot of work still needs to be done to get a clear structure–property correlation and gain better understanding and control over the parameters governing the self-assembly and nanostructure formation.

Received: September 22, 2006

Revised: January 16, 2007

Published online: June 6, 2007

- [1] L. Brunsveld, B. J. B. Folmer, E. W. Meijer, R. P. Sijbesma, *Chem. Rev.* **2001**, *101*, 4071.
- [2] U. S. Schubert, C. Eschbaumer, *Angew. Chem. Int. Ed.* **2002**, *41*, 2893.
- [3] R. Dobrawa, F. Würthner, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4981.
- [4] P. R. Andres, U. S. Schubert, *Adv. Mater.* **2004**, *16*, 1043.
- [5] a) U. S. Schubert, C. Eschbaumer, *Macromol. Symp.* **2001**, *163*, 177. b) U. S. Schubert, C. Eschbaumer, O. Hien, *Macromol. Rapid Commun.* **2000**, *21*, 1156.
- [6] C. Guerrero-Sanchez, B. G. G. Lohmeijer, M. A. R. Meier, U. S. Schubert, *Macromolecules* **2005**, *38*, 10388.
- [7] a) B. G. G. Lohmeijer, U. S. Schubert, *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 1413. b) B. G. G. Lohmeijer, U. S. Schubert, *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4016. c) B. G. G. Lohmeijer, U. S. Schubert, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 6331.
- [8] G. Zhou, I. I. Harruna, *Macromolecules* **2005**, *38*, 4114.
- [9] B. P. Sullivan, J. M. Calvert, T. J. Meyer, *Inorg. Chem.* **1980**, *19*, 1404.
- [10] B. G. G. Lohmeijer, U. S. Schubert, *Angew. Chem. Int. Ed.* **2002**, *41*, 3825.
- [11] J. F. Gohy, B. G. G. Lohmeijer, S. K. Varshney, U. S. Schubert, *Macromolecules* **2002**, *35*, 7427.
- [12] J. F. Gohy, B. G. G. Lohmeijer, U. S. Schubert, *Macromolecules* **2002**, *35*, 4560.
- [13] O. Regev, J. F. Gohy, B. G. G. Lohmeijer, S. K. Varshney, D. H. W. Hubert, P. M. Frederik, U. S. Schubert, *Colloid Polym. Sci.* **2004**, *282*, 407.
- [14] G. Mayer, V. Vogel, B. G. G. Lohmeijer, J. F. Gohy, G. A. van den Broek, W. Haase, U. S. Schubert, D. Schubert, *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4458.
- [15] M. Al-Hussein, B. G. G. Lohmeijer, U. S. Schubert, W. H. De Jeu, *Macromolecules* **2003**, *36*, 9281.
- [16] M. Al-Hussein, W. H. De Jeu, B. G. G. Lohmeijer, U. S. Schubert, *Macromolecules* **2005**, *38*, 2832.
- [17] B. G. G. Lohmeijer, D. Wouters, Z. Yin, U. S. Schubert, *Chem. Commun.* **2004**, 2886.
- [18] P. Guillet, C. A. Fustin, B. G. G. Lohmeijer, U. S. Schubert, J. F. Gohy, *Macromolecules* **2006**, *39*, 5484.
- [19] C. A. Fustin, B. G. G. Lohmeijer, A. S. Duwez, A. M. Jonas, U. S. Schubert, J. F. Gohy, *Adv. Mater.* **2005**, *17*, 1162.
- [20] J. F. Gohy, B. G. G. Lohmeijer, U. S. Schubert, *Macromol. Rapid Commun.* **2002**, *23*, 555.
- [21] J. F. Gohy, B. G. G. Lohmeijer, U. S. Schubert, *Chem. Eur. J.* **2003**, *9*, 3472.
- [22] J. F. Gohy, B. G. G. Lohmeijer, A. Alexeev, X. S. Wang, I. Manners, M. A. Winnik, U. S. Schubert, *Chem. Eur. J.* **2004**, *10*, 4315.
- [23] J. F. Gohy, B. G. G. Lohmeijer, S. K. Varshney, B. Décamps, E. Leroy, S. Boileau, U. S. Schubert, *Macromolecules* **2002**, *35*, 9748.
- [24] J. E. McAlvin, C. L. Fraser, *Macromolecules* **1999**, *32*, 1341.
- [25] C. Park, J. E. McAlvin, C. L. Fraser, E. L. Thomas, *Chem. Mater.* **2002**, *14*, 1225.
- [26] R. M. Johnson, C. L. Fraser, *Biomacromolecules* **2004**, *5*, 580.
- [27] P. S. Corbin, M. P. Webb, J. E. McAlvin, C. L. Fraser, *Biomacromolecules* **2001**, *2*, 223.
- [28] R. M. Johnson, C. L. Fraser, *Macromolecules* **2004**, *37*, 2718.
- [29] A. P. Smith, C. L. Fraser, *Macromolecules* **2002**, *35*, 594.
- [30] C. L. Fraser, A. P. Smith, X. Wu, *J. Am. Chem. Soc.* **2000**, *122*, 9026.
- [31] A. P. Smith, C. L. Fraser, *Macromolecules* **2003**, *36*, 5520.
- [32] J. L. Bender, P. S. Corbin, C. L. Fraser, D. H. Metcalf, F. S. Richardson, E. L. Thomas, A. M. Urbas, *J. Am. Chem. Soc.* **2002**, *124*, 8526.