Asymmetrical supramolecular interactions as basis for complex responsive macromolecular architectures

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Intrigued by natural responsive systems based on a combination of macromolecules and non-covalent interactions, polymer scientists have mimicked such systems by the formation of supramolecular polymers based on ionic interaction, hydrogen bonding and metal coordination. In recent years, the focus has shifted from rather simple non-directional and self-complementary interactions to the use of asymmetrical directional supramolecular interactions that allow the formation of complex responsive macromolecular architectures such as block copolymers, star-shaped polymers and graft copolymers. This feature article covers these recent developments on the use of asymmetrical supramolecular interactions in polymer science. Special attention is given to the formation of complex macromolecular architectures using directional supramolecular interactions. In addition, the responsiveness of the resulting macromolecular systems is discussed based on the assembly and/or disassembly that can be triggered by changes in external conditions.

1 Introduction

The synthesis of well-defined macromolecular architectures is one of the main research topics in current polymer science. Driven by the major developments in living and controlled polymerization techniques, more and more complex architectures have been prepared including (multi) block copolymers, star-shaped (co)polymers as well as graft and comb-like (co)polymers.[1–3] Despite this excellent control over macromolecular architecture, these systems are far less advanced than natural macromolecular systems that can often spontaneously assemble and disassemble driven by the surrounding environmental needs. These natural responsive systems are based on a combination of macromolecules and non-covalent interactions including solvophobic and ionic interactions as well as hydrogen bonding and metal coordination. Driven by

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David Fournier was born in 1978 in Le Mans (France). In 2002, he received his Master degree in Chemistry and Physicochemistry of Polymers at the Université du Maine (Le Mans, France). In 2005, he obtained his PhD under the direction of Professor Laurent Fontaine and the supervision of Dr Sagrario Pascual as well as Dr Véronique Montembault (Unité de Chimie Organique Moléculaire et Macromoléculaire, Le Mans, France). The research topics were focused on the synthesis and the design of functionalized (co)polymers by controlled radical polymerizations in solution and onto polymeric support and their applications in fields of scavenging and supported catalyst. He moved to the Laboratory of Macromolecular Chemistry and Nanoscience in Eindhoven as a postdoctoral fellow where he is working on the synthesis of well-defined thermosensitive copolymers via controlled radical polymerizations and living cationic ring-opening polymerization using high-throughput experimentation.

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these natural systems, polymer scientists have explored the use of non-covalent interactions for the construction of supramolecular polymers resulting in responsive materials with properties that can be changed by varying the environmental conditions.[4–7] The main advantage of supramolecular interactions is the reversible character of the used supramolecular interactions. In other words, the self-assembled (polymer) systems can be switched between the assembled and the disassembled states by changing (external) environmental parameters, such as temperature, pH, redox state or concentration.[8] This reversible switching of the supramolecular interactions will be accompanied by changes in the macroscopic polymer properties allowing their application in property changing materials. In addition, multiple reversible orthogonal interactions can be used simultaneously that might be switched by different parameters.[9–11] However, the majority of these systems are based on self-complementary interactions and, thus, do not allow the formation of complex supramolecular macromolecular architectures such as, *e.g.*, block copolymers and graft copolymers.

The formation of more complex macromolecular architectures, like block copolymers and star-shaped polymers, requires the use of asymmetrical (directional) supramolecular interactions (Fig. 1). The resulting asymmetrical architectures will retain the reversible character of the supramolecular interactions: In the dissembled state a mixture of components will be present while in the assembled state asymmetrical macromolecular architectures are formed. As such, the polymer properties in the assembled and disassembled will be very different allowing the development of smart switchable materials. In addition, the possible disassembly might result in easily processable materials and it provides the possibility for selective removal of one of the components. Finally, this asymmetrical supramolecular approach can provide a simple access to complex architectures of building blocks that are difficult to combine in a covalent manner. This latter advantage of self-assembling different modules might be compared to the recently introduced concept of 'click' chemistry[12–14] and, thus, could be referred to as supramolecular 'click' chemistry.[15–17]

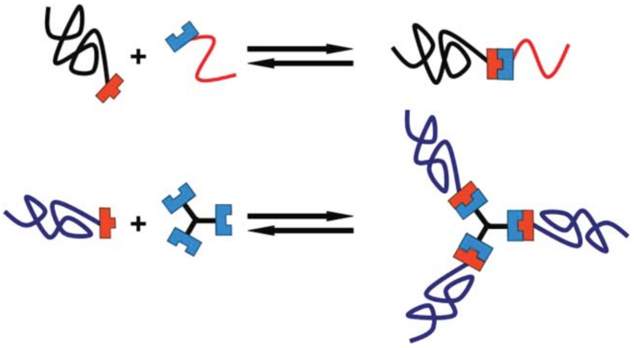

Fig. 1 Schematic representation of the reversible formation of diblock copolymers and star-shaped polymers based on asymmetrical supramolecular interactions.

Ulrich S. Schubert

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 PhD work was performed under the supervision of Professor Eisenbach (Bayreuth, Germany) and Professor Newkome (Florida, USA). In 1995 he obtained his doctorate with Prof. 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). From June 2000 to March 2007 he was Full Professor at the Eindhoven University of Technology, combined with several scientific and management functions at the Dutch Polymer Institute. Since April 2007 he is Full Professor for Organic and Macromolecular Chemistry (Chair) at the Friedrich-Schiller-Universität Jena (Germany). In addition he is Part-time Professor at the Eindhoven University of Technology. 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 the research interest of his relates to organic heterocyclic chemistry, supramolecular materials, combinatorial material research, nanoscience, inkjet printing functional materials and tailor-made macromolecules.

In this feature article, we will evaluate recent literature on the use of asymmetrical supramolecular interactions in polymer science including ionic (or coulomb) interactions,[4] hydrogen bonding[5] and metal coordination.[6,7] The self-assembly into complex macromolecular architectures as well as the reversible character of these macromolecular assemblies will be discussed in detail.

2 Ionic interactions

The use of ionic supramolecular interactions for the self-assembly of polymers is based on the attraction between positively and negatively charged species and, thus, always involves asymmetrical self-assembly. However, ionic interactions are non-directional and the scope of ionic self-assembly is limited due to relatively weak binding strengths in solution. Nevertheless, self-assembly based on ionic interactions exhibit reversible binding that can be addressed by the solvent since the ionic groups are well solvated in polar media leading to lower binding strengths and/or dissociation.

The most studied use of ionic interactions in polymer science is the self-assembly of ionic side-chains to a polymer backbone, which leads to what is often referred to as polyelectrolyte–surfactant complexes.[4,18] Poly(4-vinylpyridine)[19] and other pyridine containing polymer structures[20] are often used as the cationic polymer structure, whereby a variety of sulfonic

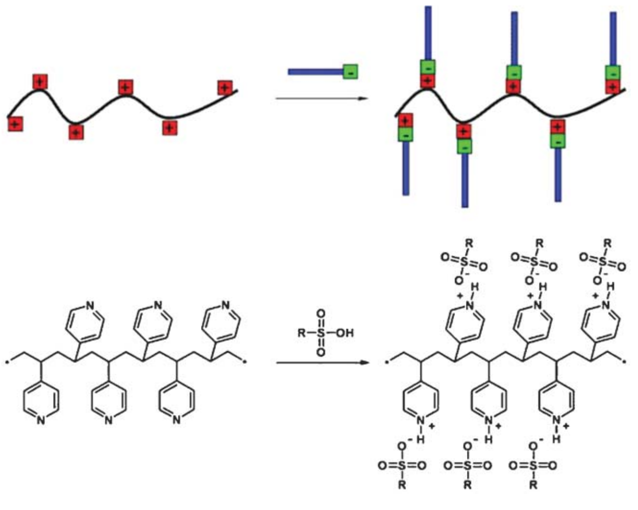

Fig. 2 Schematic (top) and structural (bottom) representation of the self-assembly of poly(4-vinylpyridine) and sulfonic acids based on ionic interactions.[19]

acid side chains can be introduced based on the ionic interactions as depicted in Fig. 2.

Similarly, combinations of poly(ethylene imine) with sulfonic acids,[21] poly(styrenesulfonate) with quaternary ammonium salts[22] and poly(acrylic acid) with quaternary ammonium salts have been reported as polyelectrolyte surfactant complexes.[23] Ikkala, Ten Brinke and co-workers[24] used such ionic interactions between poly(4-vinylpyridine) and oligo(ethylene oxide) sulfonic acid for the formation of coil–comb block copolymers starting from poly(styrene)-*block*-poly(4-vinylpyridine). These supramolecular copolymers exhibited phase-separation into lamellar structures and addition of $LiClO_4$ resulted in conductive materials. The decoration of poly(4-vinylpyridine) with sulfonic acid functionalized dendritic wedges was demonstrated by Beginn, Möller and co-workers.[25] The ratio of dendritic wedge to pyridine was found to strongly effect the bulk organization of the material going from lamellar to a hexagonal columnar phase with increasing wedge density. Furthermore, it was demonstrated that the dendritic wedges can move over the chain and from chain to chain. Besides the formation of such graft and comb-shaped copolymers, the use of disulfonic acids will lead to the formation of supramolecular networks as has been demonstrated by Shibata *et al.*[26] The supramolecular crosslinking of the material allowed tuning the glass transition and melting temperature while maintaining high thermal stability.

To overcome the low directionality and the low binding strength of single ionic interactions, Shellnut and co-workers[27] combined multiple ionic interactions with directional π–π stacking interactions resulting in the ionic self-assembly of oppositely charged porphyrins into nanotubes in aqueous solution. The self-assembled nanotubes were stable in the dark and could be addressed by light illumination resulting in smaller rodlike structures that reassembled into nanotubes in the dark. This observed reversible switching behavior is thought to be caused by a softening of the tube walls by disruption of the charge balance that is caused by photo-initiated intermolecular electron transfer processes. Faul and co-workers[28] have reported the self-assembly of a perylene dye with two positive charges and a copper phthalocyanine derivative with four negative charges. The aqueous self-assembly of these dyes resulted in the formation of one-dimensional chains that was proposed to be a helical twisted triple stack structure stabilized by a combination of ionic interactions and π–π stacking as depicted in Fig. 3. Even though the used ionic interactions on there own are not directional, the combination of multiple ionic interactions and π–π stacking results in directional asymmetric self-assembly.

Stoddart and co-workers[29] reported another strong and directional ion–dipole interaction, namely the self-assembly of dialkylammonium ions with crown ethers. This crown ether–ammonium salt self-assembly has been applied for the preparation of main-chain self-assembled polymeric structures by Gibson and co-workers.[30,31] A heteroditopic molecule that consists of both a crown ether and a quaternary ammonium salt was prepared and its self-assembly into a supramolecular polymer with a maximum degree of polymerization of 50 (analyzed by both ^{1}H NMR spectroscopy and viscosimetry), which was strongly dependent on the concentration.[30] Besides these heteroditopic compounds, the homoditopic analogues, bis(crown ether) and bis(ammonium salt) with flexible spacers, were prepared as well.[31] At low concentration the stoichiometric mixture of these homoditopic compounds resulted in the formation of cyclic dimers, whereas increasing the concentration led to the formation of supramolecular

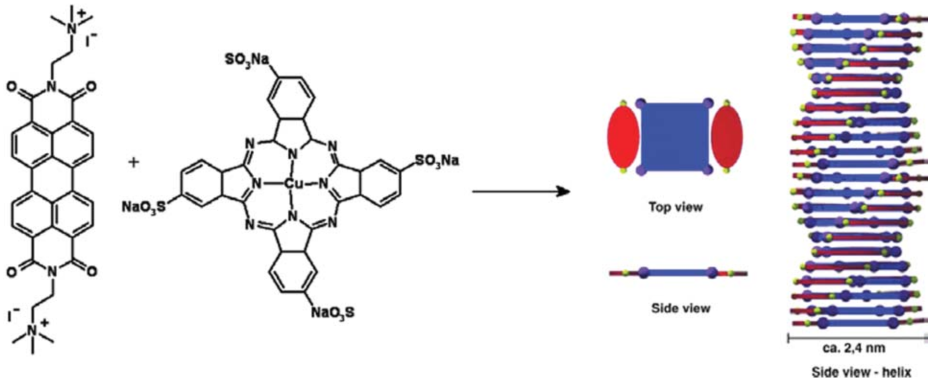

Fig. 3 Structure and proposed self-assembly of oppositely charged perylene and copper phthalocyanine dyes. The proposed self-assembly into a helical stack is reprinted with permission from ref. 28. Copyright 2005, Wiley Interscience.

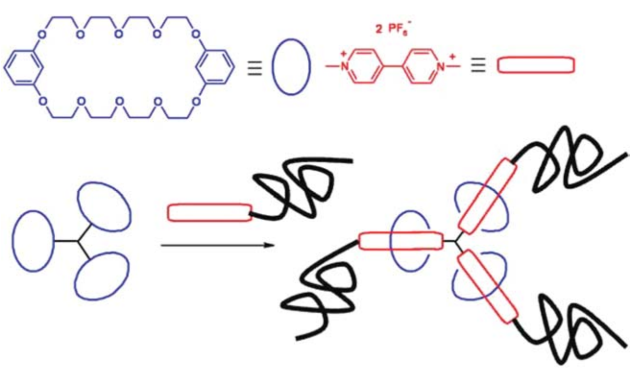

Fig. 4 Schematic representation of the formation of a supramolecular tri-arm star-shaped polymer based on ion–dipole interactions.[33]

polymers. In contrast, the self-assembly of a rigid cylindrical homoditopic bis(crown ether) with a rigid bis(ammonium salt) results solely in the formation of linear chain-extended polymers.[32] The higher binding strength of this system led to higher degrees of aggregation at lower concentration at the cost of increased complexity. More recently, the same group reported that these strong directional ion–dipole interactions can be used for the self-assembly of star-shaped (Fig. 4)[33] and hyperbranched[34] polymers as well.

Stoddart and co-workers[35] synthesized polyacetylene and polystyrene with crown ether moieties in the side chains. Additionally, dendritic dialkyl ammonium salts were prepared and it was demonstrated that the supramolecular self-assembly led to the formation of dendronized polymers. The attachment of dendritic wedges to the polymers resulted in generation dependent stretching of the polymer backbone. Moreover, the advantages of the supramolecular polymer were displayed by reversible acid–base switching from free polymer chains and ammonium salts to dendronized polymers.

3 Hydrogen bonding

Hydrogen bonding supramolecular interactions are weaker than ionic interactions. As a result, the use of single- or double-hydrogen bonding motifs does not result in strong association making them unsuitable for the preparation of complex macromolecular architectures (a recent review addressed the use of monovalent, divalent, and larger hydrogen bonding arrays in supramolecular polymers).[36] Therefore the focus of this part will be on asymmetrical triple, quadruple and larger hydrogen bonding motifs with the focus on work from the last several years. The older literature on trivalent and larger hydrogen bonding arrays in supramolecular polymers has been extensively covered in a review by Meijer and co-workers.[5] The origin of current research on multiple hydrogen bonding motifs can be found in Nature with the nucleobase pairs of DNA[37] (for the use of nucleobases as supramolecular motifs in synthetic systems, see ref. 38). The widespread occurrence of these base pairs in natural systems makes them readily available starting materials.

The use of single nucleobase pairs for the formation of supramolecular polymers has been used to improve the bulk properties of polymeric materials. Rowan and co-workers demonstrated that the end-functionalization of poly(tetrahydrofuran) with nucleobases changed the bulk material from a waxy soft material into a film-forming elastic material.[39] The relatively weak binding between the base pairs resulted in a strong thermosensitive material that softened to a large extend with increasing temperature. Long and co-workers[40] end-functionalized polystyrene (PS) with adenine, purine and thymine and subsequently demonstrated the solution dimerization of thymine-PS with adenine-PS or purine-PS by ^{1}H NMR spectroscopy. In addition, the dissociation of these hydrogen-bonded dimers was observed when the solutions were heated to 95 °C. Similar observations were made for adenine and thymine functionalized star-shaped poly(DL-lactides), whereby the presence of four hydrogen-bonding moieties per star-shaped polymer resulted in a significant increase in viscosity upon mixing in chloroform.[41] Using a similar approach, Long and co-workers[42] applied the adenine–thymine dimerization for polymer-surface modifications. An adenine-functionalized silicon surface was prepared using an adenine-functionalized triethoxysilane compound, which could be covered with PS upon addition of a thymine-PS solution in THF. Upon rinsing this non-covalently functionalized surface with DMSO the thymine-PS could be removed. This reversible supramolecular surface functionalization was demonstrated to alter the water-contact angle from $\sim 30^\circ$ for the PS-covered surface to $\sim 40^\circ$ after rinsing with DMSO. Weck and co-workers reported the synthesis of two complementary telechelic polymers based on diamidopyridine and thymine.[43] Mixing these two different polymers resulted in the self-assembly into alternating multiblock copolymers as was demonstrated by ^{1}H NMR spectroscopy.

To increase the binding strength of the nucleobase pairs, DNA consists of a large number of complementary base pairs. This principle of numbering up base pairs has been used by Noro, Matsushita *et al.*[44] for the preparation of block copolymers that are held together by hydrogen bonds at the block junction. Polystyrene was end-functionalized with three adenine phosphates and a poly(4-trimethylsilylstyrene) was end-functionalized with three thymine phosphates. Mixing these two polymers in $CDCl_3$ resulted in the formation of the corresponding supramolecular diblock copolymer as demonstrated by ^{1}H NMR spectroscopy. In addition, microphase separation was observed in the bulk demonstrating that this supramolecular diblock copolymer acts like a covalent block copolymer. Lutz *et al.*[45] also explored the use of multiple nucleobases in one polymer chain. Mixing random copolymers containing adenine or thymine in the side chains resulted in the formation of mixed colloidal particles. Rotello *et al.*[46] used bisamidopyridines as synthetic recognition sites for thymine nucleobases. A bisamidopyridine functionalized copolymer was prepared and the addition of bis-thymine crosslinkers gave turbid solutions due to the formation of aggregates. These spherical supramolecular aggregates were stable at 30 °C, dissociated at 50 °C and reformed upon cooling, which demonstrates the reversible and switchable character of the asymmetrical supramolecular interactions. In addition, Rotello and co-workers[47] also prepared two complementary polymer chains using thymine-functionalized and bisamidopyridine-functionalized monomers for ring-opening metathesis

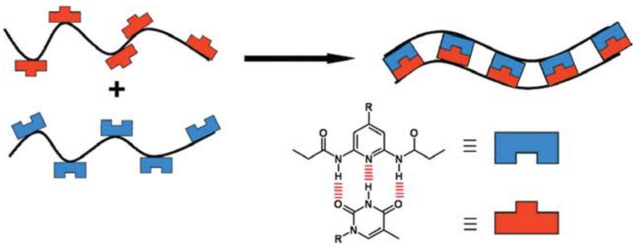

Fig. 5 Schematic representation of the self-assembly of two complementary polymer chains based on the thymine–diamidopyridine binding motif.[47]

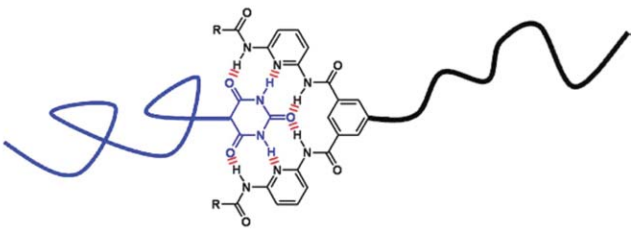

Fig. 7 Schematic representation of the formation of block copolymers based on six-fold hydrogen bonding of barbituric acid with the "Hamilton" receptor.[61]

polymerization. Detailed binding studies of mixtures of different ratios of copolymers revealed that cooperative binding effects resulted in the formation of duplex strands as depicted in Fig. 5.

Another approach to increase the binding strength of hydrogen bonding self-assembly is the use of synthetic quadruple and larger synthetic hydrogen bonding arrays.[48–50] In addition, synthetic AAA–DDD triple hydrogen bonding arrays were also reported with very high binding strengths (up to 10^7 M^{-1}).[51,52] However, these strong asymmetrical triple hydrogen bonding arrays were, to the best of our knowledge, not yet applied for the preparation of complex macromolecular architectures.

Quadruple hydrogen bonding arrays combine directionality with a very high association constant in apolar solvents (K_a $>10^6$ M^{-1}). However, only few examples of non-self-complementary quadruple hydrogen bonding arrays are known. Recently, Corbin and Zimmerman[53] discovered that the addition of a non-self-complementary diamidonaphthyridene ADDA hydrogen bonding motif to a self-complementary AADD hydrogen bonding motif led to a conformational change of the self-complementary array into a DAAD motif resulting in hydrogen bonded heterodimers (Fig. 6). More recently, Chen and co-workers[54] demonstrated heterodimer formation based on 2-ureido-6-pyrimidinone and diamidonaphthyridine and Zimmerman and co-workers[55] reported heterodimer formation of a modified guanidine motif with diamidonaphthyridine as relatively easy accessible complementary quadruple hydrogen bonding arrays.

Zimmerman and co-workers[55,56] demonstrated that the phase separation of immiscible polymers can be suppressed by the incorporation of asymmetric hydrogen bonded moieties: mixing of polystyrene functionalized with diamidonaphthyridine moieties and poly(*n*-butyl methacrylate) functionalized with the guanidine base hydrogen bonding moiety resulted in transparent miscible blends. In addition, the thermoreversibility and solvent-responsiveness of these blends, based on opening of the hydrogen bonding interactions, was demonstrated. Park and Zimmerman[57] also prepared hydrogen bonded multiblock copolymers in solution based on this asymmetrical hydrogen bonding array, whereby the degree of polymerization could be tuned by the concentration and the ratio of the blocks in the mixture. Furthermore, the thermoreversible association and dissociation of these multiblock copolymers was demonstrated. Meijer and co-workers[58,59] demonstrated concentration dependent selectivity for the heterodimerization of 2-ureido-6-pyrimidinone and diamidonaphthyridine. The heterodimer formation at high concentration was explored for the preparation of chain extended hydrogen bonded polymers. Mixing of bis(2-ureido-6-pyrimidinone) functionalized polymers with small bis-diamidonaphthyridine linkers resulted in the formation of self-assembled cyclic heterodimers while the combination of bis(2-ureido-6-pyrimidinone) functionalized polymers with bis-diamidonaphthyridine functionalized polymers led to the formation of hydrogen bonded supramolecular multiblock copolymers. In addition, a heteroditopic compound bearing both 2-ureido-6-pyrimidinone and diamidonaphthyridine end-groups was prepared by the same group.[60] It was demonstrated that this AB-type monomer is present as cycles at low concentrations while increasing the concentration leads to the formation of a supramolecular polymer.

In addition to these quadruple hydrogen bonding arrays, Binder *et al.*[61] reported the functionalization of poly(ether ketone) with barbituric acid and poly(isobutene) with the "Hamilton"[62] receptor resulting in a six-fold hydrogen bonding array. Mixing these two functionalized polymers in solution led to the formation of the corresponding block copolymers held together by six hydrogen bonds as depicted in

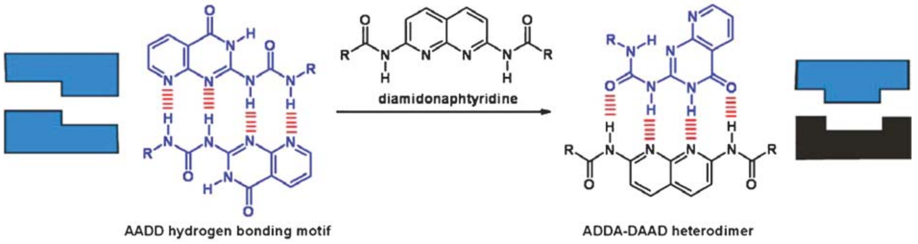

Fig. 6 Schematic representation of the formation of a hydrogen bonded heterodimer upon addition of a DAAD hydrogen bonding motif.[53]

Fig. 7. These supramolecular block copolymers revealed thermoreversible tuning of the line-spacing of the bulk lamellar phase, which was demonstrated by small angle X-ray scattering (SAXS). Kolomiets and Lehn[63] used the same hydrogen bonding motif in combination with dynamic covalent bonds for the preparation of chain-extended supramolecular polymers. Besides the reversibility of the hydrogen bonding interactions, the dynamic covalent bonds provide responsiveness on a molecular level.

Gong *et al.*[50] developed a stronger, but much more complex, six-fold oligoamide-based hydrogen bonding motif that self-assembles in heterodimers with an association constant higher than 10^9 M^{-1} in chloroform. This hydrogen bonding array was successfully applied for the preparation of hydrogen bonded block copolymers.[64] The reversibility of these supramolecular block copolymers was demonstrated by dissociation in polar solvents based on competing interactions.

4 Metal coordination

Metal–ligand interactions are often used in polymer science for the construction of larger macromolecular architectures due to their directionality. In addition, the binding strength of the metal complexes strongly depends on the used metal ions and, thus, the reversibility of the complex can be tuned without changing the ligands. Nevertheless, the modularity and the availability of the starting materials depend on the metal–ligand system that is used. The use of metal coordination in polymer science, the so-called metallo-supramolecular polymers, has been covered in a series of recent reviews.[6,65–67]

In this section, we will discuss the recent examples of metal coordination in polymer science focusing on asymmetric assemblies.

The use of phosphine or pyridine coordination to palladium or platinum can be applied for the preparation of chain-extended polymers using precursors with two phosphine or pyridine groups.[68,69] However, such self-assembled metallo-supramolecular polymers result in symmetrical metal complexes. In contrast, the complexation of pyridines with palladium(II) and platinum(II) precursors pincer complexes does allow asymmetrical directional self-assembly.[70] Craig and co-workers[71] investigated crosslinking of poly(4-vinylpyridine) with bifunctional palladium(II) or platinum(II) precursor complexes as depicted in Fig. 8. The shear viscosity (determined by rheology) of the resulting crosslinked materials could be tuned from 6.7 Pa s to over 240 kPa s by varing the metal and the substituents on the pincer complexes. Moreover, Weck and co-workers[43] reported the synthesis of complementary telechelic polymers with pyridine or a palladium(II) pincer complex. Mixing these two complementary polymers resulted in the formation of chain-extended multiblock copolymers *via* supramolecular click chemistry.

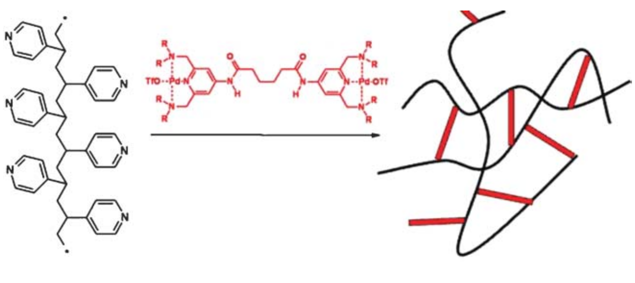

Fig. 8 Schematic representation of crosslinking poly(4-vinylpyridine) with a palladium(II) precursor complex.[71]

Metal coordinating ligands consisting of multiple pyridine rings are often used for the preparation of metallo-supramolecular polymers. The use of such multidentate ligands increases the scope of this approach by the higher association constants, but at the same time decreases the availability of the starting materials. Nevertheless, a variety of functional bipyridine and terpyridine ligands are commercially available nowadays.[72] Bipyridine[73] and terpyridine[74] metal complexation are the most studied systems for the preparation of metallo-supramolecular polymers.[75,76] However, the majority of these metal complexes are homoleptic complexes that do not allow a modular asymmetrical approach. In contrast, ruthenium(II), osmium(II) and iridium(III) bipyridine and terpyridine complexes can be prepared in a two-step approach that allows the preparation of well-defined heteroleptic complexes with very high binding constants. Up to this moment, mainly ruthenium(II) complexes have been used for the preparation of metallo-supramolecular polymers with heteroleptic complexes.

Ruthenium(II) heterocomplexation of polymeric terpyridines was first applied for the preparation of metallo-supramolecular block copolymers by Lohmeijer and Schubert.[77] This first example was later extended to the preparation of a library of metallo-supramolecular block copolymers based on polystyrene and poly(ethylene oxide).[78] The reversibility of the supramolecular click chemistry was demonstrated for micelles of amphiphilic supramolecular block copolymers held together by a ruthenium(II) terpyridine complex. Upon treatment of the micellar solution with a large excess of a strong competing ligand, hydroxyethyl ethylenediamine triacetic acid sodium salt, the red color of the ruthenium complexes disappeared and the size of the micelles became smaller, indicating cleavage of the water-soluble block.[79,80] In addition, a thin film of a polystyrene–poly(ethylene oxide) ruthenium(II) terpyridine block copolymer phase-separated in a cylindrical morphology.[81] The cylindrical poly(ethylene oxide) domains could be removed after UV-crosslinking of the polystyrene matrix and oxidation of the ruthenium(II) to ruthenium(III) by cerium(IV) sulfate resulting in a nanoporous thin film. Zhou and Harruna[82] have used a similar synthetic approach for the formation of polystyrene–poly(*N*-isopropylacrylamide) block copolymers with a ruthenium(II) terpyridine metal complex at the block junction resulting in thermosensitive metallo-supramolecular block copolymers. In addition, Schubert and Hofmeier demonstrated the possibility of using the same two-step complexation approach for the preparation of metallo-supramolecular graft-copolymers as depicted in Fig. 9.[83]

In a similar approach Kallitsis and co-workers[84] prepared terpyridine-containing polymers by the atom transfer radical polymerization of a terpyridine-functionalized styrene monomer. Subsequent complexation with ruthenium(III) monoterpyridine complexes yielded comblike metallosupramolecular polymers. Furthermore, a two-step complexation approach for bipyridine macroligands with ruthenium(II) ions was applied by

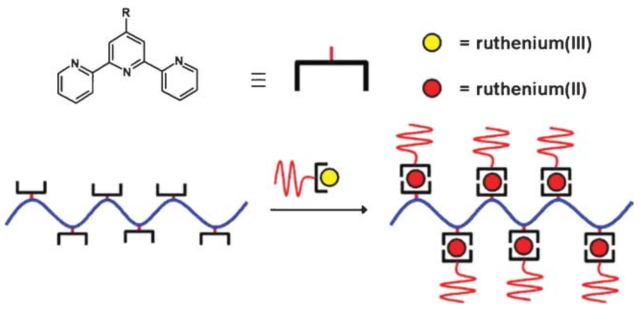

Fig. 9 Schematic representation of the synthesis of metallo-supramolecular graft copolymers using the ruthenium(II) heterocomplexation of terpyridine ligands.[83]

Smith and Fraser[85] for the preparation of heteroligand complexes corresponding to hetero-arm star-shaped copolymers.

5 Combined supramolecular interactions

The use of asymmetrical supramolecular interactions allows the orthogonal use of multiple non-covalent interactions for the construction of self-assembled supramolecular structures that might be addressed by different external stimuli. The concept of orthogonal supramolecular interactions in polymer science has been recently covered in several review and feature articles.[9–11] In this part, recent developments on the use of orthogonal asymmetrical supramolecular interactions in polymer science will be discussed.

Weck and co-workers[86] have reported the synthesis of poly(norbornene) *via* ring-opening metathesis polymerization, whereby both palladium pincer complexes and diaminopyridine hydrogen bonding moieties were statistically incorporated in the side chains of the polymer allowing modular self-assembly. More recently, Grubbs, Stoddart, Weck and co-workers[87] reported a similar block copoly(norbornene) with multiple recognition sites in which the rather weak hydrogen bonding unit was replaced by a crown ether moiety that self-assembles with dialkylammonium salts *via* ion–dipole interactions. For both orthogonally functionalized block copolymers, it was demonstrated that the recognition units specifically bound their counterparts, whereby the presence of multiple non-covalent binding sites did not influence their selectivity, as depicted in Fig. 10. The reversibility of these complex self-assembled polymeric structures was not addressed so far.

6 Summary

In the past couple of years, a number of asymmetrical supramolecular interactions have been developed and explored for the formation of complex macromolecular architectures. Such complex supramolecular macromolecules have been prepared based on all three major supramolecular interactions, namely ionic interactions, hydrogen bonding and metal coordination. These studies demonstrated the formation of supramolecular block copolymers, multi-block copolymers, graft copolymers, star-shaped polymers as well as cross-linked materials. The main advantage of supramolecular macromolecular architectures over covalently bonded macromolecular architectures is the reversible character of the supramolecular interactions that can be exploited for the preparation of responsive materials that change their macroscopic properties upon changes in the external conditions. However, the majority of the studies focused merely on the formation of the supramolecular assemblies rather than their reversible character. Moreover, when the reversibility of the systems is investigated, this is mostly done on a proof-of-principle basis demonstrating the responsiveness of the system, without studying the resulting changes in polymer properties.

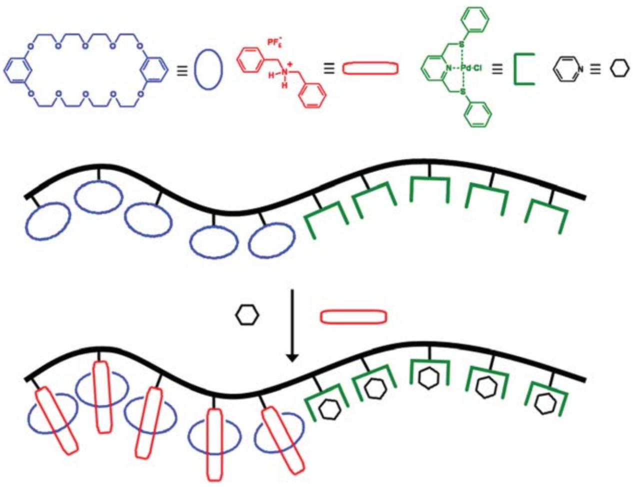

Fig. 10 Schematic representation of a block copolymer orthogonally functionalized with crown ether and palladium pincer complexes as well as subsequent self-assembly upon simultaneous addition of both the dibenzylammonium salt and pyridine.

Nonetheless, the use of asymmetrical supramolecular interactions seems to be an ideal platform for the preparation of novel responsive macromolecular architectures. Therefore, it is believed that when future research in the field will focus more on the effects of external stimuli on the polymer properties, this will result in a novel generation of smart materials. Besides the required focus on polymer properties, the development of new asymmetrical supramolecular interactions is expected to further widen the scope and application possibilities of such materials.

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