Hierarchical self-assembly in polymeric complexes: Towards functional materials

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Combination of self-assembly at different length scales leads to structural hierarchies. It offers rich possibilities to construct nanostructured matter, nanoscale parts, and switching (responsive) properties based on the phase transitions of the self-assembled structures. Complexation of oligomeric amphiphiles to polymers using ionic interactions, coordination, or hydrogen bonding leads to polymeric comb-shaped supramolecules (complexes), which self-assemble at a length scale of a few nm. Self-assembly at an order of magnitude larger length scale is provided by block copolymers, and combination of the latter two concepts leads to structural hierarchies. They provide e.g. templates for mesoporous materials and nano-objects, and allow switching conductivity and switching optical properties. Structural hierarchies are also observed by complexing moderately monodisperse polymeric rods with amphiphiles. Finally, self-assembly at even a larger length scale upon using colloidal particles may be combined to the above structures, as encouraged by recent observations.

Introduction

For materials scientists, the biological systems offer inspiring, albeit in most cases intractably complicated models for functional and responsive materials. Such systems are typically formed in aqueous medium due to self-assembly (for self-assembly, see refs 1–3) using competing hydrophilic/hydrophobic interactions and complementary physical interactions, also leading to structural hierarchies, of

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which refs 4–8 provide examples of the vast literature. It encourages to consider self-assembly and hierarchy also in synthetic materials to tune the properties[9–26] and even to achieve switching and responsive properties.[10] Polymeric nanoscale structures due to competition between attractive and repulsive interactions have been discussed by Muthukumar et al.[9] They denoted the concept as self-organization. A classic example is provided by block copolymers consisting of covalently connected flexible blocks (see Bates and Fredrickson[27]), and a rich variety of structures and hierarchies[11] are achieved by incorporating a larger number of flexible blocks or by blending (see Stadler and Abetz and coworkers[28–30]), by engineering the architectures (Hadjichristidis et al.[31]), or by incorporating rod-like moieties within the blocks (see e.g. the research in the groups of Gronski, Fischer, Ober, Thomas, Stupp, Lee, Zin and Jenekhe[9,32–39]).

Note that different notions have been employed for the underlying nanoscale structures. In the block copolymer literature, microphase separation has often been used.[21,40] In non-equilibrium thermodynamics, self-organization has been used for dissipative non-equilibrium structures.[41] Static self-assembly, as advocated by Whitesides, refers to structures near thermal equilibrium.[3] The different notions just reflect the cross-disciplinary nature of the field, having roots in different fields. In this review, we adopt the phrase 'self-assembly' for structures near equilibrium, even if the phrase 'self-organization' could equally well be used in the present context.

In order to render self-assembly, the attractive interactions do not have to be covalent, i.e. "permanent". Complementary weaker interactions are systematically used in the supramolecular chemistry, see Lehn and Vögtle[15,42,43] and in more polymer related context in the groups of Fréchet, Kato, Bazuin, Meijer, Nolte, Rehahn, Sijbesma, Sommerdijk, and Rowan[20,44–50], as well as in certain polymer/amphiphile and polyelectrolyte/surfactant complexes to be discussed later in this review. In principle, any sufficiently strong physical interaction can be used for self-assembly. Physical bonds allow a further important design tool for responsive materials, as the bonds may be opened irreversibly[51–53] and even opened and reformed reversibly,[10] as will be discussed in this review in some detail. This differentiates self-assembling polymer complexes and supramolecules from the corresponding block copolymers even if in principle similar structures may be achievable using both routes.[11,12] Note also that in the supramolecular materials, the actual stoichiometries of the self-assembling complexes are specified by the equilibrium constants which can depend on the actual experimental conditions. Therefore the compositions are denoted here according to the nominal compositions. The structures are studied using small angle X-ray scattering, transmission electron microscopy, atomic force microscopy, dynamic rheology, optical birefringence, FTIR, and NMR.

Fig. 1 summarizes one route for bottom-up construction of nanostructures based on polymeric self-assembly. It is schematically
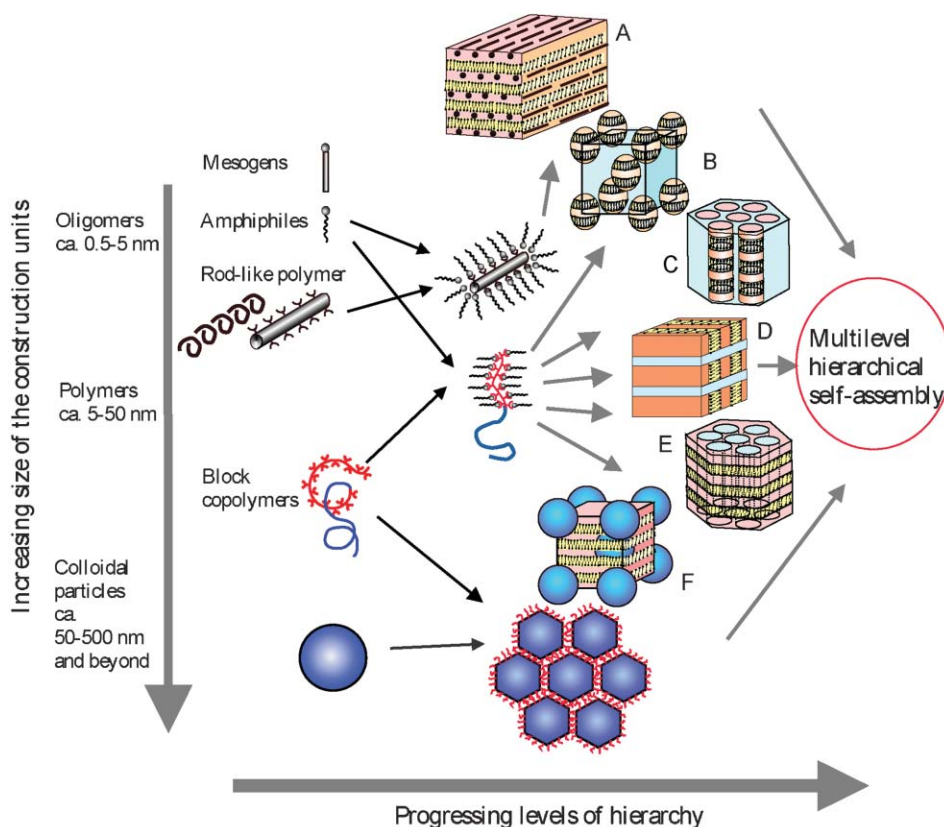
Fig. 1 One of the potential scenarios to construct hierarchically self-assembled polymeric structures. Construction units of different sizes allow a natural selection of different self-assembled length scales. Structural hierarchy is shown for amphiphiles complexed with both block copolymers (Ikkala and ten Brinke et al.[10,12,16]) and rod-like polymers (in collaboration with Monkman and Serimaa et al.[52,54]). Combination of block copolymers and mesogenic oligomers has been described by Thomas and Ober et al.[55] Combination of polymeric colloidal spheres and block copolymers has been reported by Kramer and Fredrickson et al.[56]

shown how different sizes of construction units can be systematically combined to render progressively higher levels of structural hierarchy and incorporating different length scales. The figure combines contributions of several groups. It also combines already verified results with an outlook for still anticipated results. For clarity, we present the complete scheme already at the start.

Hierarchical self-assembly in block-copolymer/ amphiphile complexes

It is well established that various self-assembled structures are allowed by physically bonding oligomeric repulsive side chains to homopolymers: ionic interactions are used in polyelectrolyte/surfactant complexes in the solid state as shown by Antonietti et al., characteristic examples being polyacrylate or polystyrene sulfonate with cationic surfactants.[57,58] Further examples[59] are provided by surfactant complexes of poly(ethyleneimine),[60] poly(4-vinylpyridine) and poly(2-vinylpyridine),[61] poly(aniline),[62] poly(2,5-pyridinediyl),[63] poly(L-lysine),[64] or cationic starch.[65] Often the self-assembled structures are lamellar but cylindrical and more complicated phases have been reported as well.[66] Hydrogen bonding allows non-charged self-assembled structures, as has been shown using e.g. poly(4-vinylpyridine)/alkylphenols by Ikkala ten Brinke et al.,[67–69] poly(ethyleneoxide)/dodecylbenzene sulfonic acid by Chen et al.,[70] and poly(vinylphenol)/aminic amphiphiles by Akiyama et al.[71] Due to its weakness, hydrogen bonding allows additional freedom to control the strength of bonding e.g. by temperature. Also coordination is very useful for self-assembly,[72,73] as it allows the tuning of the self-assembly using both the ligands and the counter-ions.[74] Fig. 2 shows a concept where four alkyl chains are bonded to each repeat unit of poly(4-vinylpyridine), i.e. P4VP, where two octyl chains are due to the ligands, and one

dodecyl tail in each of the dodecylsulfonate counter-ions. The side chain crowding leads to cylindrical self-assembly.
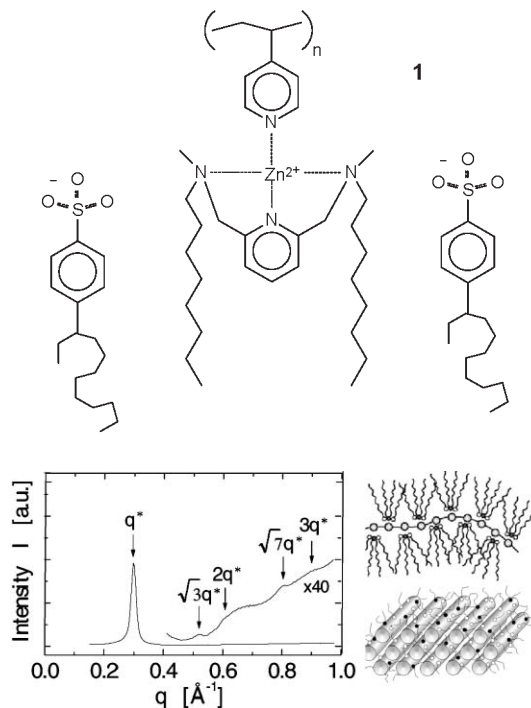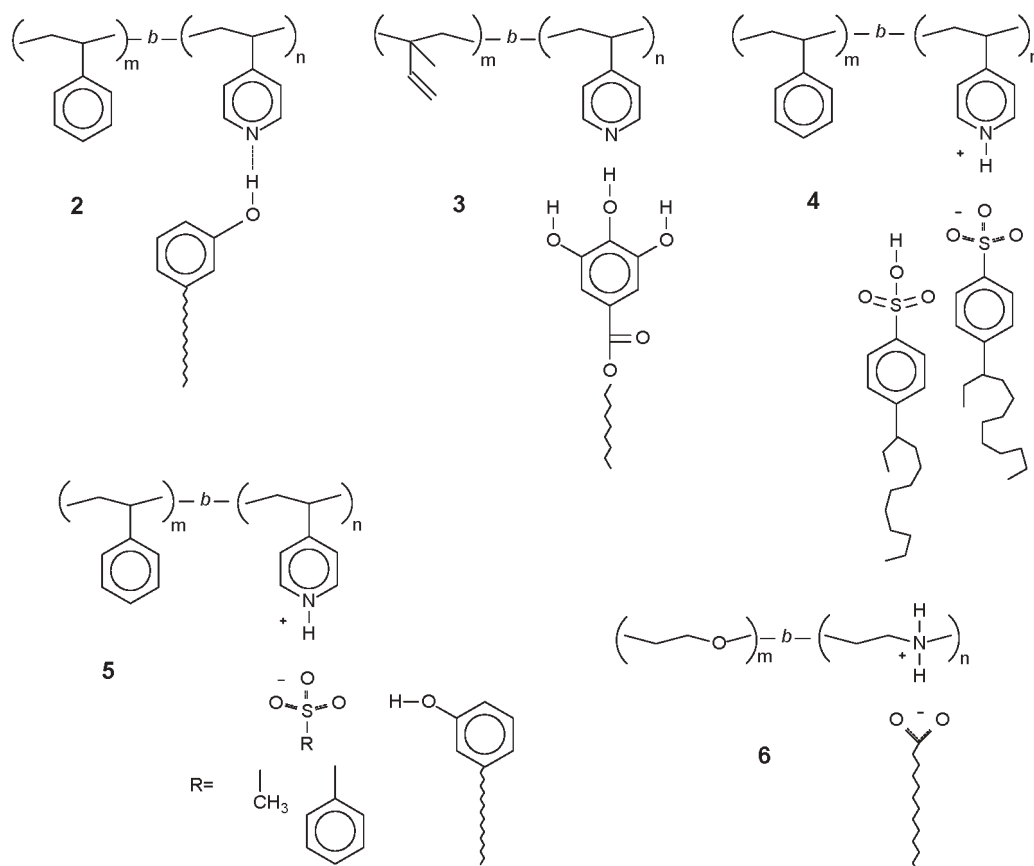

Fig. 2 Coordinated comb-shaped polymeric supramolecules poly[(4VP)Zn(2,6-bis-(n-octylaminomethyl)-pyridine)(DBS)$_2$] and their cylindrical self-assembly as suggested by small angle X-ray scattering. The magnitude of the scattering vector is given by $q = (4\pi/\lambda)\sin\vartheta$ where 2ϑ = scattering angle and $\lambda = 0.154$ nm.[74]

2   **3**   **4**

5

6

In the homopolymer/amphiphile complexes, which can also be denoted as polymeric comb-shaped supramolecules, the characteristic self-assembly periodicity is in the range of a few nm, due to the length of the oligomeric physically bonded side chains. A hierarchical structure can be obtained[10,12,51,53,75–82] by incorporating such structures in a block copolymeric[27,40] self-assembly, where the periodicities are in the range of *ca.* 5–50 nm, depending on the molecular weights and the chain rigidity. Typical examples for the hierarchical self-assembly of diblock-copolymer/amphiphile complexes are illustrated by compounds **2–6**. Perhaps the most studied model system is poly(styrene)-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) where nominally one pentadecylphenol (PDP) or nonadecylphenol (NDP) molecule is hydrogen bonded *vs.* each pyridine group, see compound **2**. Different hierarchical structures can be obtained by tuning the relative lengths of the PS- and P4VP-blocks whereas P4VP(PDP) and P4VP(NDP) lead to lamellar self-assembly at a shorter length scale. Fig. 1 illustrates schematics of the structures: lamellar-*within*-spherical (B), lamellar-*within*-cylinder (C), lamellar-*within*-lamellar (D), cylinder-*within*-lamellar (E), and spherical-*within*-lamellar structures (F).[10,12,83] Heating causes reversible phase transitions within the structures. We point out that many of the above structures[12] are similar as observed in *e.g.* ABC-triblock copolymers[11] which underlines the more general mechanisms of self-assembly. An electron microscope picture of the lamellar-*within*-lamellar is shown in Fig. 3. One of the blocks can also be elastomeric, such as polyisoprene (see compound **3**). Such materials could be useful as templates to achieve rubbery porous materials. The compound **6** was inspected by Thünemann in the context of drug release.[77]

Porous materials

The hierarchical self-assembly can allow separate manipulation of the individual self-assembled structures at different length scales. The first example describes the lamellar-*within*-cylinder structure provided by PS-*b*-P4VP(PDP)$_{1.0}$ with the molecular weights of 34 000 g mol^{-1} and 2 900 g mol^{-1} of the PS and the P4VP-blocks, respectively.[12,51] This leads to a PS matrix with hexagonally assembled P4VP/PDP cylinders at a separation of 24 nm and where the latter domains contain an internal lamellar structure with a period of *ca.* 3.7 nm. The structures are aligned by an imposed large amplitude oscillating shear flow. The oligomeric alkylphenols can next be removed from the cylinders using a selective polar solvent, see Fig. 4. As PS is glassy and therefore rigid at room temperature, the pores do not collapse. The pore walls are lined with a dense set of polymeric P4VP-brushes. As it is known that polymer brushes are feasible to modify surface properties in general,[84] it is expected that this route can open new possibilities for tailorable pores, taken that the brush conformations can be controlled. Interestingly, also lamellar sheet-like pores can be prepared using lamellar-*within*-lamellar templates and they can remain at least partially open after removal of the amphiphiles if there exists a sufficient amount
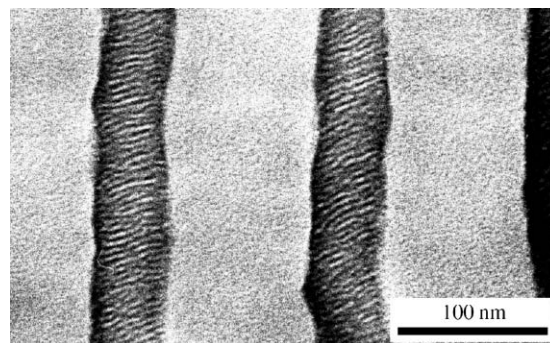

Fig. 3 Transmission electron microscopy of lamellar-*within*-lamellar structure of PS-*b*-P4VP(PDP)$_{1.0}$ (compound **1**) with the molecular weights of the PS block 238 000 g mol^{-1} and the P4VP block of 49 500 g mol^{-1}.[83] Archive of J. Ruokolainen.
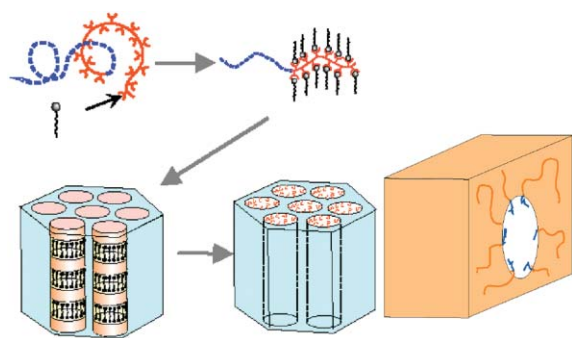
Fig. 4 Schematics for mesoporous material with a dense set of polymer brushes at the cylindrical channel walls, as prepared using PS-*b*-P4VP(PDP)$_{1.0}$ (compound **2**) and subsequently removing PDP (in collaboration with Stamm *et al.*).[51]
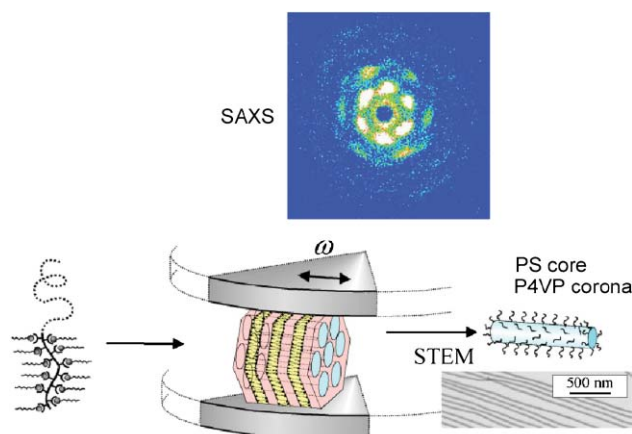

Fig. 5 Schematics to prepare nanoscale fibers or rods based on block copolymer/amphiphile template (compound **2**) and removing the amphiphiles by a solvent treatment.[53,76]

of defects that stabilize the structures and if the pores are not well aligned.[85]

Nano-objects

The scheme of the previous section can be modified by incorporating a relatively shorter PS-block in PS-*b*-P4VP(PDP)$_{1.0}$, *i.e.* 21 400 and 20 700 g mol^{-1} for PS and P4VP, respectively. Also in this case a cylindrical assembly is obtained but now the hexagonally assembling cylinders consist of PS and the matrix is formed by P4VP/alkyphenol.[12,53,76] After a large amplitude shear flow orientation, the structures are well aligned (see Fig. 5) and the alkylphenols can be selectively removed using a solvent treatment. This leaves rigid glassy PS rods with P4VP corona and the rods have a diameter of *ca.* 25–28 nm. The rods can be templates for further modifications, as they have a dense set of polymer brushes containing pyridine groups on their surfaces capable of complexation and chemical reactions. It is also expected that nano-objects of different shapes can be prepared, once more complicated block copolymers and structural hierarchies are used.

Conducting materials with structural hierarchy

The logically next step is to incorporate polyelectrolytic blocks within the self-assembled hierarchies. It is well known that polyelectrolyte salts can be protonic conductors.[86] Moreover, Antonietti *et al.* showed that polyelectrolyte/surfactant complexes can be essentially Ohmic conductors.[87,88] Ikkala and ten Brinke

et al. extended it to show that even polyelectrolytes hydrogen bonded to amphiphiles can be Ohmic-like conductors.[89] Structural hierarchies are achieved[10,78,79] upon incorporating self-assembly at different length scales. By selecting PS- and P4VP-blocks with molecular weights 40 000 g mol^{-1} and 5 600 g mol^{-1} for PS-*b*-P4VP(MSA)$_{1.0}$(PDP)$_{1.0}$, where MSA = methane sulfonic acid, lamellar-*within*-lamellar structural hierarchy is observed, see compound **5** with R = –CH$_3$.[10] Upon heating, the structure becomes simple lamellar, due to an internal order–disorder transition within the P4VP(MSA)$_{1.0}$(PDP)$_{1.0}$ domains. Further heating leads to hexagonal order as PDP becomes soluble in PS and immiscible in P4VP(MSA)$_{1.0}$. Fig. 6 shows that the sequential phase transitions imply conductivity switching as a function of temperature.[10] The switching is at least in principle reversible, even if the materials properties near 200 °C cannot be claimed to be stable in the long term.

It is characteristic for self-assembly that the structures are only local and that a multi-domain structure is formed, where the domains lack a common alignment. External fields can be imposed to achieve common alignment[90,91] and in bulk samples, large amplitude oscillating shear flow is useful.[75,92–94] The power of the concept is illllustrated in Fig. 7 for PS-*b*-P4VP(TSA)$_{0.9}$(PDP)$_{1.0}$ (TSA = toluene sulfonic acid, the compound is essentially as in **5**) which leads to lamellar-*within*-cylinder structures. Oscillating large amplitude shear flow leads to particularly high overall alignment and order, see the SAXS-patterns in Fig. 7.[79]
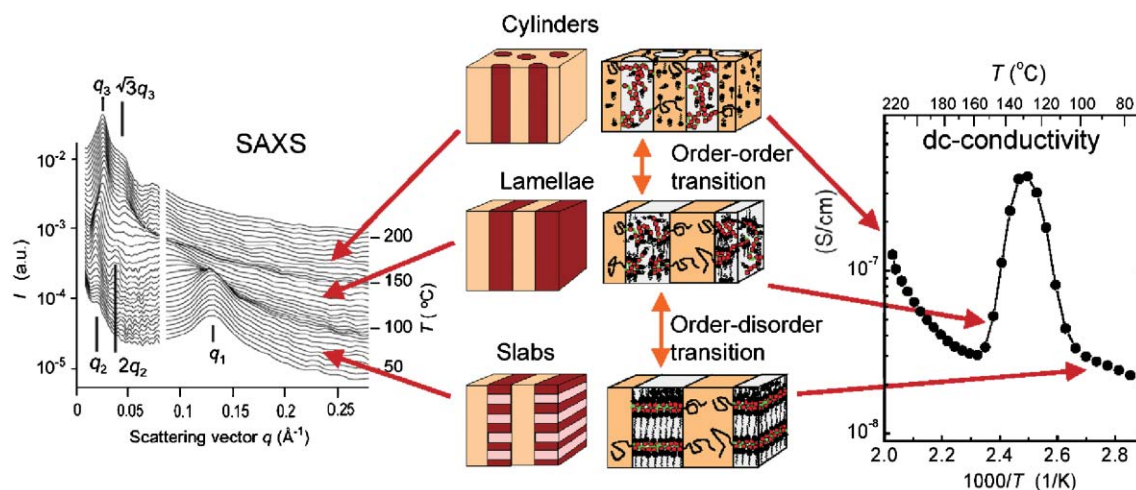

Fig. 6 Schematics for the switching protonic conductivity based on phase transitions within the hierarchically self-assembled polymer complexes based on compounds **5** with R = CH$_3$.[10] SAXS-patterns and dc-conductivity as a function of temperature are shown. The geometry of the conducting self-assembled domains are illustrated.
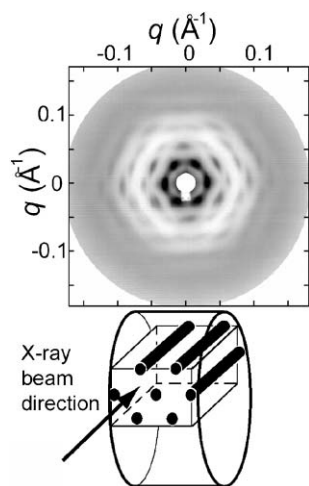
Fig. 7 Large amplitude oscillating shear flow leads to highly aligned polyelectrolytic cylinders in PS-*b*-P4VP(TSA)$_{0.9}$(PDP)$_{1.0}$ with the molecular weight of 41 400 g mol^{-1} and 1 900 g mol^{-1} for the PS- and P4VP-blocks, as shown by SAXS.[79] Only slight conductivity anisotropy is observed which indicates that the transport may still be controlled by defects.

Photonic bandgaps and dielectric reflectors

In photonic bandgap materials, transmission of specific wavelengths of electromagnetic radiation is prevented due to the matching periodic structures.[95] To achieve complete photonic bandgaps, three-dimensional structures with high dielectric contrast are required and purely polymeric structures are not expected to easily lead to such an effect. However, even incomplete polymeric bandgap materials (see Thomas *et al.*[55,96,97]) can be of specific interest, *e.g.* in coatings. To create a photonic bandgap at the optical wavelengths using polymeric self-assembly, a real challenge is to have sufficiently high order at a length scale of *ca.* 120 nm or higher. Very high molecular weights would be required when using pure block copolymers and the structure formation is then excessively slow. The comb-shaped supramolecular route offers plasticized materials with facile structure formation. Some of the polyelectrolyte complexes (**4** and **5**) turned coloured for sufficiently high molecular weight polymers, indicating that an incomplete 1-dimensional photonic bandgap, *i.e* dielectric reflector is formed.[82] The easiest concept is based on compound **4** where DBSA is complexed to PS-*b*-P4VP with molecular weights of 238 100 g mol^{-1} and 49 500 for PS and P4VP, thus leading to lamellar-*within*-lamellar structure.[82] The complexation causes considerable stretching of the polymer chains, and lamellar periodicities in the range 140 nm are obtained. Optical transmission and reflectance measurements indicate the presence of a bandgap, see Fig. 8. A related situation is encountered using the same PS-*b*-P4VP but preparing a hydrogen bonded complex PS-*b*-P4VP(MSA)$_{1.0}$(PDP)$_{1.5}$ (essentially compound **5**) which is green at room temperature.

Hierarchical self-assembly in complexes of rigid polymers

Conjugated polymers are interesting constituents in the self-assembled structures due to their electronic and photonic properties.[98,99] However, it is difficult to use them in the above polymer complexes for hierarchical self-assembly, as their solubility is drastically smaller than that of flexible polymers due to their totally rigid or semi-rigid nature. It is well known that side chains improve solubility and cause self-assembly, *e.g.* in poly(3-alkylthiophenes),[100–102] poly(9,9-di(octyl)fluorenes) and poly(9,9-di(ethylhexyl)fluorenes),[103–106] and lead to improved electro- and photoactive properties. Levon *et al.* showed that complexing DBSA to polyaniline (PANI) leads to a conjugated polyelectrolyte/
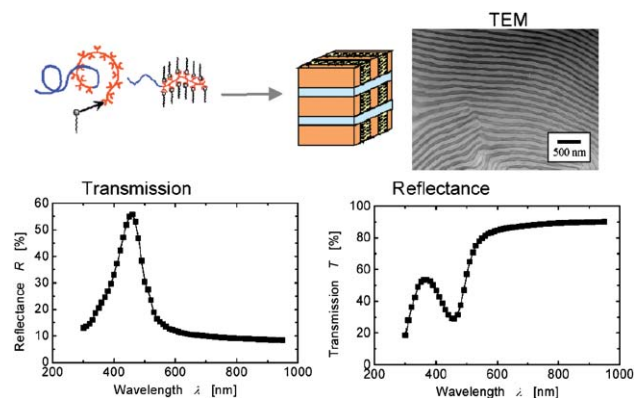

Fig. 8 Dielectric reflectors based on compound **4** showing incomplete photonic bandgap and relatively bright blue colour due to periodic structures in the optical wavelengths.[82] Transmission electron micrograph is shown, as well as the optical transmission and reflectance, showing that a bandgap is opened.

surfactant complex that exhibits a fluid-like self-assembly.[62] Such concepts have been extended using a multitude of different surfactant counter-ions by Pron and Rannou *et al.*[99,107] Due to its chemical structure, PANI can retract to coiled conformations. In an effort to study related totally rigid rod-like polymers, poly(2,5-pyridinediyl) (PPY)[108,109] turned out to be particularly useful. In collaboration with Monkman *et al.*, we demonstrated its self-assembled polyelectrolyte/surfactant complexes using DBSA.[63] Perhaps more interestingly, hydrogen bonding alkyl containing moieties to PPY-based polyelectrolytes allowed particularly highly ordered lamellar self-assembly.[52,110,111] Typical examples are PPY complexed with camphor sulfonic acid (CSA) and specific alkylphenols with short alkyl chains, such as hexyl resorcinol and octylphenol (OP), see compounds **7** and **8**.[52,54] Other phases, including oblique structures, have been observed[111] using compound **9**. Theories have been developed by Subbotin and ten Brinke *et al.* for the self-assembling hairy-rod supramolecules to predict the structures.[112] Referring to the compounds **7–9**, at this point the exact architecture of the hydrogen bonds are not yet known and detailed schemes of the bonds cannot yet be drawn. Still, SAXS indicates particularly highly ordered self-assembly and the materials become plasticized, being in some cases even in the liquid crystalline fluid-state without an additional solvent. This property is rare among the conjugated polymers. The specific advantage of such materials is that the side chains allowing processibility can ultimately be removed by vacuum treatment, which is not the case when the side chains are covalently connected. This opens additional design options for *e.g.* materials for molecular electronics as, at least in principle, the processable intermediates and the final products could be designed separately. Such a concept has so far been used to prepare photoluminant materials with highly aligned rod-like chains, thus leading to polarized optical emission.[52] In passing, we point out that alkyl resorcinols render self-assembled structures also in electrically conducting polyaniline salts (*e.g.* compound **10**)[113] but the structures are cylindrical. This opens new design options to tune the conductivity and chain stretching.

In the above complexes using PPY, self-assembly at a single length scale is expected. However, there is evidence for structural hierarchy in selected cases.[52,54] When PPY is highly purified with repeated solvent treatments, it becomes fractionated and the molecular weight distribution becomes relatively narrow. This leads to structural hierarchy *e.g.*, in PPY(CSA)$_{0.5}$(OP)$_{1.0}$ where SAXS indicates lamellar self-assembly with alternating polar and octyl layers with periodicity of 2.6 nm and an additional, albeit weak, reflection is observed at 6.3 nm.[54] The latter is of the same order as the length of the polymer chains. This suggests that there is tendency for the PPY chains to have another, potentially

smectic-like order within the lamellar domains. Therefore, the structure could be denoted as smectic-*within*-lamellar structure, see A in Fig. 1.
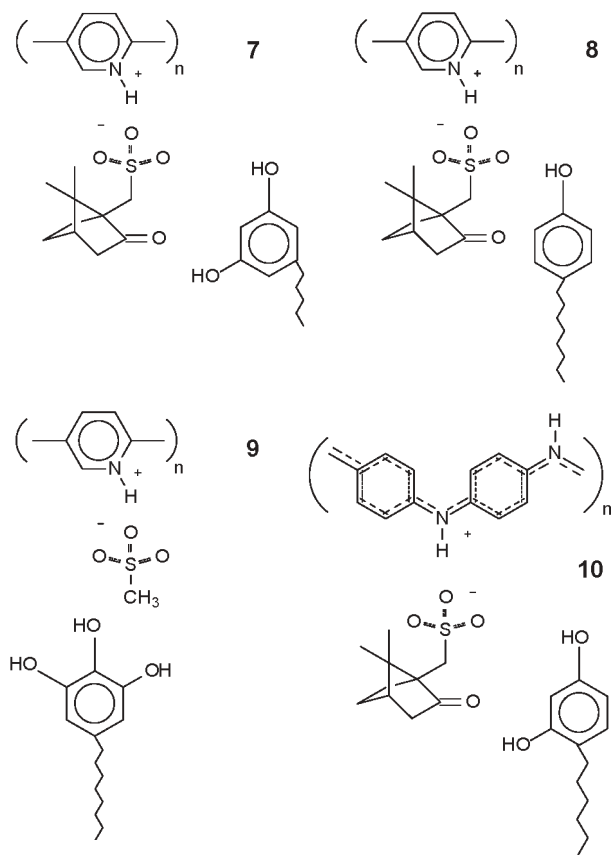
Outlook

We have described how oligomeric amphiphiles can be physically bonded to homopolymers and block copolymers and how this leads to self-assembly and hierarchy. Various functional materials can be prepared using these concepts. As described, the comb-shaped architecture is useful as it leads to plasticization and promotes fluid-like behavior which is particularly attractive when using rigid, semi-rigid and conjugated polymers or polymers of high molecular weight, which are needed in photonic band gap application. Such schemes have been included in Fig. 1. In this figure also other options have been described: Instead of the oligomeric amphiphiles, oligomeric mesogens have been used by Thomas and Ober et al.[55] which allow interesting tunable optical properties and structural hierarchy. As already stated, it becomes interesting to incorporate even larger construction units, such as colloidal particles, as they naturally encompass self-assembly at a larger length scale. Kramer and Fredrickson et al. have described how PS-colloids and PS-*b*-P2VP form periodic "honeycomb"-type of assembly and how such structures can incorporate electrically conducting PANI-salt.[56] We foresee that many new design options for different functionalities for bottom-up construction of nano-structured matter can arise along these lines in the coming years.

Acknowledgements

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