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Block Copolymers

Functional Block Copolymers: Nanostructured Materials with Emerging Applications

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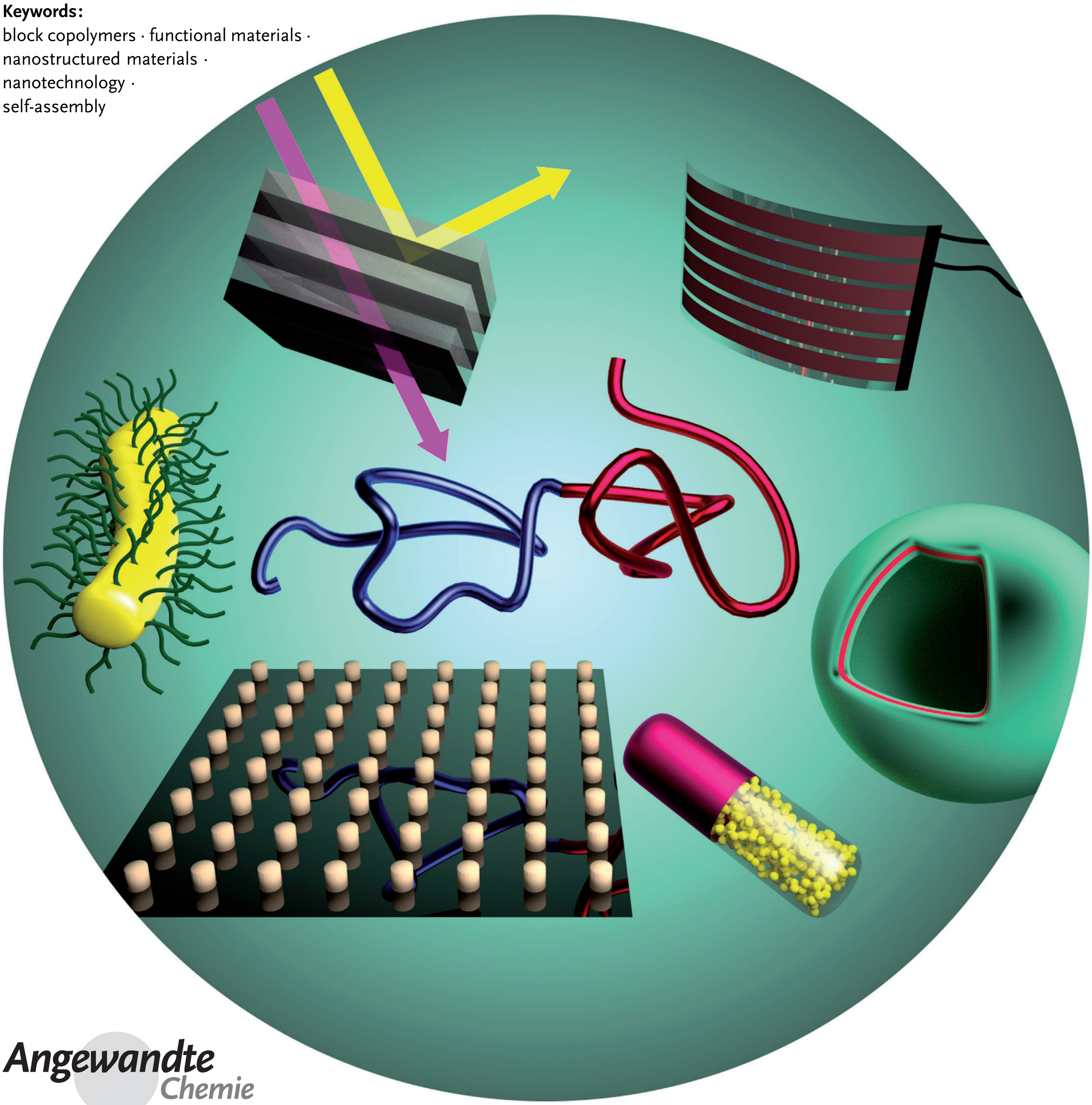

Recent advances in polymer synthesis have significantly enhanced the ability to rationally design block copolymers with tailored functionality. The self-assembly of these macromolecules in the solid state or in solution allows the formation of nanostructured materials with a variety of properties and potential functions. This Review illustrates recent progress in the field of block copolymer materials by highlighting selected emerging applications.

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1. Introduction and Scope

Block copolymers are composed of two or more chemically distinct polymer chains linked together at one or more junction points through covalent or noncovalent bonds (Figure 1 A).[1] As a consequence of the inherent immiscibility of different polymer segments, block copolymers undergo microphase separation in the bulk phase and in thin films. This results in different morphologies with domain sizes of about 10–100 nm (Figure 1 B,C). In solution, block copolymers will form micelles when the solvent is selective for one of the blocks. A wide variety of micelle morphologies are known, and these depend on the composition of the polymer and the processing conditions (Figure 1 D). Most of the desirable properties of block copolymers originate from their ability to form well-defined nanostructures with different morphologies of tunable periodicity or size, and this provides the primary driving force for the intensive interest in this field.

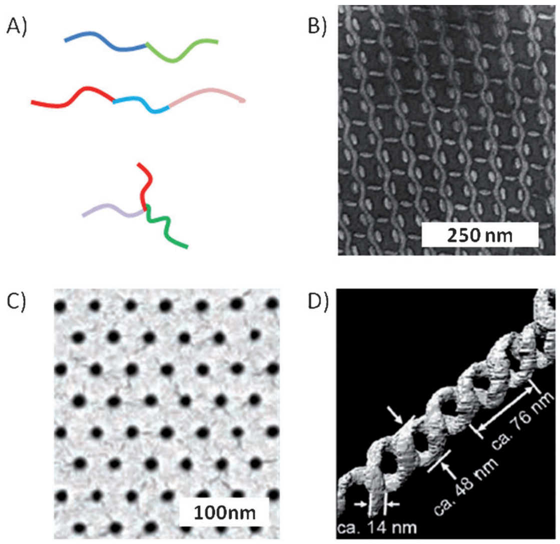

Figure 1. A) Schematic representation of an AB diblock copolymer, ABC triblock terpolymer, and μ-ABC-miktoarm star block terpolymer. B) TEM micrograph of a "knitting pattern" formed by the self-assembly of an ABC triblock terpolymer in the bulk state. Adapted from Ref. [2], with permission. C) TEM micrograph of a high-density hexagonal patterned thin film formed by the templated self-assembly of a diblock copolymer. Adapted from Ref. [3], with permission. Copyright American Association for the Advancement of Science.D) TEM tomography image of a double helix formed from the self-assembly of an ABC triblock terpolymer in solution. Adapted from Ref. [4], with permission.

The scope of possible applications for block copolymers is rapidly expanding, with multidisciplinary contributions involving the fields of chemistry, physics, materials science, as well as the biological and medical sciences. This Review aims to provide an overview of selected but representative recent developments, trends, and emerging applications of functional block copolymers.

There has been substantial commercial development of thermoplastic elastomers based on block copolymers, a classic example being the triblock copolymer polystyrene-*block*-polybutadiene-*block*-polystyrene (PS-*b*-PB-*b*-PS), where the PB block with a low glass transition temperature (T_g) provides elastomeric properties at room temperature, while the PS block with a high T_g value acts as a physical cross-linker.[5] These, and related polymers, have applications in high impact materials, as bitumen additives, and as viscosity modifiers. Thermoplastic elastomeric polyurethanes, polyesters, and polyamides (all composed of block copolymers) are based on analogous principles. A second class of block copolymers that have been extensively commercially developed are poloxamers, poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) triblock copolymers (PEO-*b*-PPO-*b*-PEO), which have found applications in detergents, in cosmetics, and in pharmaceutical preparations.[6] Block copolymers have also been employed as viscosity modifiers for lubricants.[7] These important, but well-established, applications of block copolymers are not covered in this Review, and instead the reader is referred to the relevant references.[5a,c,6,8]

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We begin with a brief description of methods used for the synthesis of block copolymers, with a focus on recent advances—including the combination of different synthetic strategies and post-polymerization modifications. The main part of this Review examines applications of functional block copolymers and is divided according to the physical state in which the material is used; that is, in the bulk state or in solution. These two sections are subdivided further into respective categories based on the application under consideration. Selected examples in each of the areas are discussed, but the Review is not aimed at being comprehensive. We conclude with a brief summary and outlook section on the field of block copolymers.

2. Synthetic Advances

The systematic development of block copolymers is intimately linked with the advancement of highly controlled living polymerization techniques. Well-defined block copolymers can be synthesized by a wide range of different methods including ionic (cationic,[9] anionic,[10] group transfer),[11] radical (atom-transfer radical polymerization (ATRP),[12] reversible addition fragmentation transfer (RAFT),[13] nitroxide-mediated polymerization (NMP)),[14] chain growth polycondensation,[15] and metal-catalyzed olefin metathesis,[16] and ring-opening metathesis polymerization (ROMP)[17] techniques. Additionally, supramolecular interactions such as metal–ligand coordination and hydrogen bonding can also be used to prepare block copolymers.[18] Important synthetic methods for the preparation of block copolymers have been reviewed recently in detail.[19]

Recent advances in the synthesis of block copolymers have focused on techniques that either enable the preparation of completely new materials or represent a substantial improvement with respect to the existing methods in terms of scalability, environmental friendliness, or scope. One observable trend is to design experimental setups which allow for the automated and optimized synthesis of polymers and block copolymers.[20] In this way, access to material libraries is possible and the automated screening for desired properties or specific interactions with certain targets becomes feasible. Increasing interest is also devoted to photoinitiated polymerizations[21] and, quite recently, such processes could be extended to living anionic polymerizations.[22]

Another ongoing topic involves attempts to reduce the environmental impact of existing polymer syntheses.[23] This could be achieved by significantly reduced reaction times in microwave-assisted polymerizations, as has been demonstrated for RAFT[24] and cationic ring-opening (CROP) processes.[25] In ATRP reactions, the metal catalyst (most often Cu) loading could be decreased down to ppm levels through the use of a suitable additive for catalyst regeneration (ARGET process).[26] It should be further noted that both the NMP[27] and the RAFT[28] processes have been recently applied to the controlled polymerization of isoprene, which expands the range of directly accessible polyisoprene-containing block copolymers beyond those available through anionic polymerizations. The introduction of a “carbanion pump” into anionic polymerizations has enabled the conversion of an oxyanion into a carbanion, thus broadening the scope of this method and the range of accessible monomer sequences.[29]

Often block copolymers with a certain desired composition cannot be synthesized directly by only a single polymerization technique. Hence, the combination of different synthetic methods and switching groups can become important.[30] In recent examples, cationic and anionic,[31] cationic and ATRP,[32] or anionic and ATRP processes have been combined.[33] As an alternative, concepts for the stepwise coupling of living chain ends by chemoselective bifunctional coupling agents[34] or the linkage of DNA sequences to end-functionalized polymers and the formation of hybrid block copolymers have been developed.[35] The combination of living anionic polymerization techniques with iterative branching reactions for the synthesis of star and dendritic block copolymer architectures have also been reported.[36]

The post-polymerization modification of block copolymers is another route to introduce functionality or to further stabilize certain morphologies or microphase-separated structures. The latter can be accomplished by controlled cross-linking of specific domains within block copolymer based nanostructures.[37] This has been demonstrated for polybutadiene-containing ABC triblock terpolymers in the bulk[38] and

Felix H. Schacher was born in Lichtenfels (Germany) in 1980. After studying chemistry at the University of Bayreuth (Germany), he completed his PhD with Prof. Axel H. E. Müller in 2009 on functional nanostructured systems based on block co- and terpolymers. He then joined Prof. Ian Manners at Bristol as a DAAD postdoctoral fellow, working on the synthesis and self-assembly of organometallic block copolymers. Since 2010, he has been a junior professor at the Friedrich-Schiller-University Jena (Germany). His research focuses on polymer synthesis, self-assembly, as well as different characterization techniques.

Paul A. Rupar grew up in London (Ontario, Canada) and studied chemistry at the University of Western Ontario. His PhD, under the supervision of Prof. Kim Baines, focused on the synthesis of neutral and cationic germanium(II) complexes. In 2010, he began a NSERC Postdoctoral Fellowship at the University of Bristol. He is currently a Marie Curie Postdoctoral Research Fellow in the group of Prof. Ian Manners and is investigating the self-assembly behavior of metal-containing block copolymers. In 2012 he will be joining the University of Alabama as an assistant professor. His research interests include block copolymer self-assembly, the synthesis of conjugated polymers, and polymer templating of inorganic materials.

also for the core[39] or the corona/shell[40] of discrete micellar structures in solution.[41]

Click reactions—modular chemical transformations that proceed in high yield—produce few by-products and can be performed under mild conditions. These have greatly influenced post-polymerization modification procedures.[42] The copper(I)-catalyzed 1,3-dipolar cycloaddition between an azide and an alkyne[43] has been widely adopted as a versatile platform for advanced macromolecular engineering.[44] The thiol-ene reaction has been introduced as a catalyst-free alternative for the modular functionalization of polymeric systems.[45] Used initially for the addition of small molecules to polybutadiene backbones, thiol-ene reactions have already been extended to short peptide sequences,[46] surface functionalization, and network formation.[47] The "clicking" of macromolecular building blocks can also be used to bind polymer chains to form block copolymers.[48]

Recent synthetic advances also have an impact on the area of inorganic soft materials. The introduction of inorganic elements into a polymer can lead to useful chemical and physical properties as well as functionality that complements the characteristics accessible with all-organic materials.[49] Polymers containing main group elements and metals have traditionally been difficult to prepare in a controlled fashion; however, recent progress in the preparation of monomers and synthetic techniques has enabled the development of well-defined inorganic polymers and block copolymers through living polymerizations.[49e] Block copolymers containing an inorganic block have been synthesized by living anionic ring-opening,[50] photocontrolled ring-opening,[22] ring-opening metathesis,[51] anionic olefinic-like chain growth,[52] controlled radical,[53] and cationic[54] polymerization methods. Inorganic components can also be introduced by coordination to polymer side chains[55] or reactions of functional groups in the side chain.[56] In addition, metal centers that act as supramolecular linkers have been used to tether polymer blocks together.[18b]

Ian Manners was born in London (UK) in 1961, and completed his PhD at the University of Bristol. After postdoctoral work in Germany and the USA, he joined the University of Toronto (Canada) as an assistant professor in 1990; he became full professor in 1995 and received a Research Chair in 2001. In 2006 he returned to his Alma Mater to take up a Chair in Inorganic, Macromolecular, and Materials Chemistry. His awards include an Alfred P. Sloan Fellowship (1994), a Corday–Morgan Medal (1997), the Steacie Prize (2001), a Marie Curie Chair from the European Union (2005), and a Humboldt Research Award (2011). He is an elected member of the National Academies of Science of Canada (FRSC, 2001) and Britain (FRS, 2011).

3. Applications of Block Copolymer Bulk Materials and Thin Films

In the solid state, block copolymers can microphase separate to form well-defined self-assembled structures of predictable size.[57] The nature of the morphology is dependent on many factors, including the architecture of the block copolymer (e.g. diblock, triblock, miktoarm star, etc.), the degree of polymerization of each block, interactions between blocks, and the interactions of each block with the environment, as well as sample processing. In the simplest situation of an AB diblock copolymer, the known thermodynamically stable solid-state morphologies include spherical, cylindrical, gyroid, and lamellar structures. When multiblock copolymers and branched block copolymers are considered, a large number of complex morphologies becomes possible.[57a] The development of new block copolymer architectures for the realization of novel bulk morphologies remains a highly active area of research.

The material properties of block copolymers are derived from the physical characteristics of the constituent homopolymer blocks. This provides researchers with the ability to "dial-in" selected properties by varying the block lengths and ratios.[5a] This section focuses on emerging applications of block copolymers in the bulk phase, concentrating on functions that are based on both the chemical properties of the materials and the unique opportunities that arise because of the nanoscale phase separation of the polymer blocks.

3.1. Templates

Patterning bulk materials on the nanoscale can lead to the realization of novel properties, including unusual electronic effects and high surface areas for improved catalyst performance. The diverse chemical functionalities and ability to phase-separate on the nanoscale make block copolymers perfect for templating other materials by using a top-down approach.

Several attempts have been made to employ microphase-separated bulk morphologies of block copolymers as templates. One strategy is to use AB diblock systems where one of the compartments is degradable in a controlled fashion, for example, poly(D,L-lactide) (PLA), which can be removed under basic conditions. In this manner, porous substrates are generated and, depending on the functionalities of the remaining "matrix" phase, can be used for templating approaches. This method has been successfully demonstrated for the fabrication of hybrid solar cells from poly(4-fluorostyrene)-*block*-poly(D,L-lactide) (PFLS-*b*-PLA) diblock copolymers with a gyroidal morphology in the bulk phase (Figure 2B).[58] Further effects of the underlying substrate and the presence of an electric field during sample preparation were investigated.[59] Replacement of the PFLS segment with a polystyrene block, in which a redox-active triphenylamine side group had been attached, led to mesoporous hole-conducting block copolymer templates.[60] By using a comparable approach, Ho and co-workers prepared inorganic gyroidal structures with a very low refractive index from

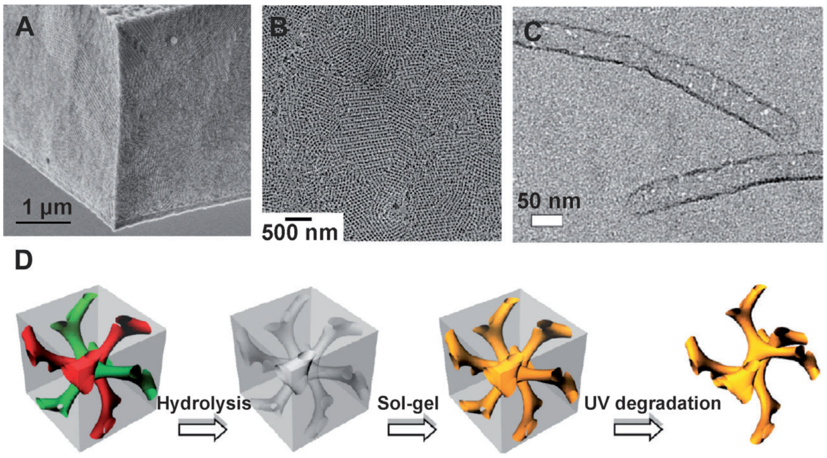

Figure 2. A) FESEM micrograph of nanoporous SiO_2 after removal of the PLA matrix. Adapted from Ref. [61] with permission. Copyright 2010 American Chemical Society. B) SEM micrograph of nanoporous gyroidal TiO_2 templated by PFS-*b*-PLA block copolymers. Adapted from Ref. [58] with permission. Copyright 2009 American Chemical Society. C) TEM micrograph of hollow tubular Al_2O_3 structures prepared by atomic layer deposition onto PS-*b*-P4VP block copolymer nanostructures. Adapted from Ref. [62], with permission. D) Schematic illustration of the preparation of nanoporous gyroidal SiO_2 by block copolymer templating. Adapted from Ref. [61] with permission. Copyright 2010 American Chemical Society.

PS-*b*-PLLA (PLLA = poly(L-lactide)) templates after hydrolysis of PLLA and subsequent backfilling with SiO_2 (Figure 2 A,D).[61]

The coassembly of block copolymers with additives has been investigated by Ikkala and co-workers. Here, the polar P4VP part of polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) block copolymers was used to form complexes with polar additives such as 4-dodecylphenol. In this way, the volume fraction of the P4VP domain and, hence, the equilibrium bulk morphology could be adjusted exactly, and defined structures with spherical or cylindrical PS domains were obtained.[62,63] These could be further used as templates for the gas-phase deposition of Al_2O_3 and, after pyrolysis and removal of the block copolymer, the formation of hollow inorganic spherical and tubular structures (Figure 2 C).[62] In a related strategy, PS-*b*-P4VP was coassembled with a phenolic resin. Subsequent cross-linking of the phenolic matrix phase and dissolution of the block copolymer resulted in porous structures with functional hydroxy groups in the pore walls.[64]

Conjugated polymers are exciting materials with applications in organic electronics, solar cells, and biosensors.[65] A problem associated with many conjugated polymer systems is their crystalline and, therefore, brittle nature when fabricated. By using block copolymers as templates, Matyjaszewski and co-workers were able to form films of polyaniline which showed good flexibility while still retaining good conductivity.[66] First, poly(2-acrylamido-2-methyl-1-propanesulfonic acid)-*block*-poly(methylacrylate) (PAMPSA-*b*-PMA) was synthesized by RAFT polymerization. The highly acidic PAMPSA block acted as a dopant and template for the emeraldine base form of polyaniline. Polyaniline loadings of up to 30 wt % were reported, with conductivities as high as 30 S cm^{-1}. Importantly, the PAMPSA-*b*-PMA-templated polyaniline films still exhibited good flexibility.

3.2. Membranes

Membranes act as selective barriers between at least two different compartments and regulate gas, liquid, or substance transport between them. Membranes are classified according to their pore size as nonporous, microporous (0–2 nm), mesoporous (2–50 nm), and macroporous (50–500 nm). The range of membrane technologies where polymers or block copolymers are involved is very broad. Today's key fields of application for polymer-based membranes are reverse osmosis, dialysis, and filtration according to particle size.[67]

Polymers already represent by far the most important membrane materials, as they offer a great diversity of functional groups and can be processed relatively easily. A technology that is widely used for the preparation of polymeric membranes is termed nonsolvent-induced phase separation (NIPS) and this method has recently been extended to the field of block copolymers.[68] In this fast and simple process, a concentrated block copolymer solution is cast onto a polished substrate that is then immersed into a nonsolvent bath, thereby leading to phase separation. The key difference when using block copolymers is that during the casting and waiting time before immersion, solvent evaporates and microphase separation of the block copolymer already occurs in the skin layer of the "protomembrane". One of the key features of membranes prepared by the NIPS process is their unsymmetrical nature: a mesoporous skin layer is supported by a macroporous volume structure. This technique has been used to prepare membranes from PS-*b*-P4VP (Figure 3 A)[68] and polystyrene-*block*-poly(*N*,*N*-dimethylaminoethyl methacrylate) (PS-*b*-PDMAEMA, Fig-

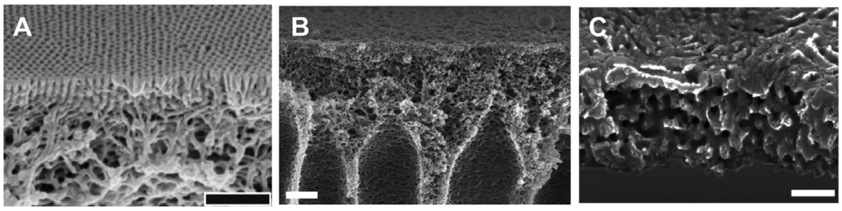

Figure 3. A,B) Asymmetric membrane structures prepared by the NIPS process from PS-*b*-P4VP[68] (A; adapted from Ref. [69a], with permission. Copyright 2007 Macmillan Publishers Ltd.) and PS-*b*-PDMAEMA[69a] block copolymers (B; adapted from Ref. [58] with permission). Scale bars: 500 nm. C) Gold replica of a microphase-separated thick PS-*b*-P2VP film. Adapted from Ref. [71] with permission. Scale bar: 200 nm.

ure 3B)[69] block copolymers. In the latter case, the membranes were both pH- and temperature-sensitive in terms of water flux and cut-off pore size as a result of the swelling/deswelling of PDMAEMA, which covered the membrane pore walls.[69a] For PS-*b*-P4VP, the control over the pore-formation process could be improved by complexation of the P4VP segment with metal ions in the casting solution.[70] Although important trends and factors influencing membrane morphology (unsymmetric/symmetric) and permeability have been identified for both PS-*b*-P4VP and PS-*b*-PDMAEMA, the systems are still far from being fully understood. The combination of an AB block copolymer and, most often, a mixture of at least two casting solvents results in rather complex phase diagrams beyond those of classical ternary systems.

In earlier studies on block copolymer membranes in the bulk phase, samples were prepared by casting thick (μm to mm) films from nonselective solvents. In the case of poly{4-[bis(trimethylsilyl)methyl]styrene}-*block*-poly(trimethylsilylhydroxyethyl methacrylate) (PBSMS-*b*-PTMSHEMA), subsequent soaking in dilute acid led to deprotection of the PTMSHEMA segments and to hydroxy-functionalized membranes with a rigid silicon-containing polymer matrix.[72] A similar procedure was used for the humidity-induced swelling and rearrangement of poly(styrene sulfonate)-*block*-poly(methylbutylene) block copolymers.[73] Wang, Steinhart, and co-workers extended this to a swelling-induced reconstruction of the morphology of thick PS-*b*-P2VP films. After complexation of P2VP with gold centers, they were able to replicate the microphase-separated structure and prepare nanoporous gold membranes (Figure 3C).[71]

Block copolymer membranes are also being explored for use in fuel cells. Recent studies on proton-exchange membranes by Park and co-workers have shown that block copolymer membranes can have greatly increased conductivities relative to comparable homopolymer systems.[74] Conductivities as high as $0.045\,\mathrm{S\,cm^{-1}}$ and a thermal stability up to 180 °C could be obtained by incorporating imidazolium ionic liquids into bulk poly(styrenesulfonate)-*block*-poly(methylbutylene). The authors showed that the conductivity performance was influenced by the composition of the block copolymer, the ionic liquid loading, the respective counterions, and the temperature.

3.3. Bulk Composite Materials

The use of self-assembled block copolymers as structure-directing agents for metal salts or nanoparticles is a convenient way to prepare bulk hybrid materials. The solubility, processability, and the mechanical characteristics of polymeric materials can be readily combined with the magnetic, catalytic, or electronic properties of the corresponding precursors.[75] The difference, when compared to previously described templating approaches (see Section 3.1), is that the self-assembly and microphase separation has already taken place in the presence of the inorganic components. In many cases, the organic (block copolymer) component is removed after formation of the structure using a suitable solvent or by calcination, thereby generating mesoporous materials. This has been shown for aluminosilicates,[76] silicates,[77] silazane-based polymers,[78] and platinum nanoparticles.[79] Selectivity of the metal species for one of the block copolymer mesophases is very important and, if necessary, can be controlled by the casting conditions[80] or the attachment of directing ligands to the metal nanoparticles.[81]

3.4. Photonic Materials

Photonic crystals are dielectric materials composed of periodic domains of high and low refractive index.[82] As a consequence of their ability to allow, prevent, and direct different wavelengths of light, photonic crystals are under investigation for a large range of applications including for use in optoelectronics, lasers, photonic pigments, displays, and reflective coatings.[82] The performance of a photonic crystal is related to the periodic domain size, refractive index contrast, and morphology.

The ability of block copolymers to self-assemble into periodic geometries in the bulk state makes them logical materials for the construction of photonic crystals.[83] Unfortunately, to achieve domain sizes on the order of hundreds of nanometers, which is necessary for photonic crystals, the molecular weights of the block copolymers must be extremely large—on the order of $10^6\,\mathrm{g\,mol^{-1}}$.[84] High molecular weight block copolymers are synthetically challenging to prepare and are slow to self-assemble, although techniques such as block copolymer/homopolymer blending can be used to reduce the necessary molecular weight of the blocks.[85]

Thomas and co-workers have shown that hydrophobic-*block*-hydrophilic polyelectrolyte block copolymers form lamellar structures that can lead to chemically tunable photonic crystal gels.[86] Lamellar-patterned PS-*b*-P2VP films cast on a glass slide were exposed to mixtures of bromoethane and dibromoethane, which resulted in the simultaneous quaternization and cross-linking of the P2VP domains (Figure 4). The degree of cross-linking was controlled by the ratio of bromoethane to dibromoethane. The PS-*b*-qP2VP (qP2VP = quaternized P2VP) films were found to swell and contract depending upon the humidity, with a lamellar spacing of 100–640 nm depending on the conditions. Although the molecular weights of the PS and P2VP blocks were both $190\,\mathrm{kg\,mol^{-1}}$, the swelling of the P2VP regions enabled access to domain spacings that are usually only accessible with much higher molecular weight block copolymers. The intrinsic contrast in the refractive index of PS and P2VP was alone not sufficient to show a visible response. However, when the films were immersed in water, they immediately became colored as a consequence of the swelling of the P2VP domains. Moreover, the color of the film could be controlled by the degree of cross-linking. The swollen, cross-linked films were also shown to respond to changes in osmotic pressure (Figure 4). When placed in a solution with a high NH_4Cl concentration, the gels collapse and result in a blue-shift of the photonic stop-band position. By using similar PS-*b*-P2VP polymers, electrically respon-

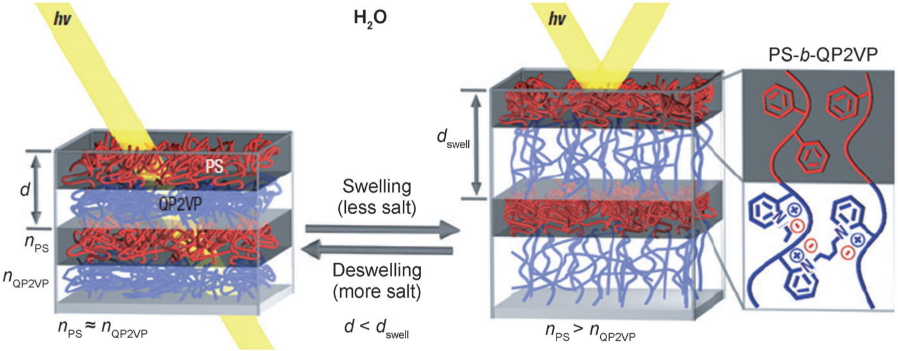

Figure 4. A lamellar-forming PS-*b*-P2VP block copolymer gel.[86] When placed in a solution of high salinity, the gel collapses, reducing the lamellar domain (*d*) spacing and, concomitantly, the frequency of reflected light decreases. When exposed to lower salt concentrations, the gel swells, the *d* spacing increases, and the wavelength of the reflected light is red-shifted. Adapted from Ref. [86], with permission. Copyright 2007 Macmillan Publishers Ltd.

sive,[87] electrochemically responsive,[88] and pH-responsive[89] photonic crystal films have also been prepared.

The vast majority of block copolymers are made by using highly controlled polymerization techniques that result in polymers with well-defined molecular weights and narrow polydispersities. Recently, it has been shown that block copolymers with PDI values of about 2.0 can self-assemble into nanostructures with domain sizes that are larger than those of block copolymers with similar average molecular weights but low PDI values.[1b] Working with olefin block copolymers, researchers at the Dow Chemical Company synthesized (ultralow density polyethylene)-*block*-(linear low density polyethylene) (ULDPE-*b*-LLDPE) block copolymers with PDIs of approximately 2[90] and molecular weights of 30–70 kg mol^{-1}. The authors observed phase-separated domain spacings between 120 and 200 nm. The formation of the large domains enabled the materials to act as photonic crystals and to scatter light in the UV/Vis region. The difference in the refractive index between ULDPE and LLDPE arises because of the semicrystalline nature of the LLDPE block. As a consequence, these ULDPE-*b*-LLDPE photonic block copolymers showed temperature-dependent absorption of light; at higher temperatures (ca. 100 °C) the photonic color disappeared as the LLDPE domain melts. Upon cooling, the photonic properties quickly returned as the LLDPE block recrystallized.

3.5. Solar Cells and Light Emission

Solar cells based on organic photovoltaic materials are actively being explored as an alternative to conventional inorganic solid-state analogues, as they offer the potential for more cost effective, tunable solar technologies.[91]

Organic photovoltaics operate through an exciton-based mechanism.[92] In its simplest description, absorption of a photon results in the formation of an exciton, an electron-hole pair. The exciton diffuses to a donor–acceptor interface where it is separated into its corresponding free charge carriers. The now independent electron and hole finally migrate to the appropriate electrode and are harvested for their electric power.[92]

In organic photovoltaics, the short lifetimes of excitons limit the maximum diffusion distance to values of about 10 nm, and, thus, only excitons generated close to the donor–acceptor interface can be exploited for electrical energy. Bulk-heterojunction (BHJ) organic photovoltaics, which are typically composed of an electron-donating conjugated polymer (the donor) and an electron-deficient C$_{60}$ derivative (the acceptor), have been developed to optimize this donor–acceptor interface by increasing the surface area. In BHJ organic photovoltaics, the donor–acceptor materials are percolated into (ideally bicontinuous) nanosized domains. Although the optimization of BHJ organic photovoltaics has resulted in power-conversion efficiencies (PCE) greater than 7 %,[93] it remains difficult to control and maintain the domain size of the donor–acceptor materials, as they are unstable towards larger scale phase separation.

The ability of block copolymers to form thermodynamically stable nanoscale structures makes these materials ideal candidates for the synthesis of BHJ organic photovoltaics.[94] A common technique used for such a purpose is to tether donor and acceptor moieties to the backbone of a block copolymer.[94c] For example, a PvTPA-*b*-PPerAcr (vTPA = vinyltriphenylamine, PerAcr = acrylate unit with a perylenebisimide side group) block copolymer has been produced in which the vinyltriphenylamine group acts as the donor and the perylenebisimide is the acceptor (Figure 5 A).[95] In this study the authors compared the efficiency of a device made from the block copolymer and one made from a blend of

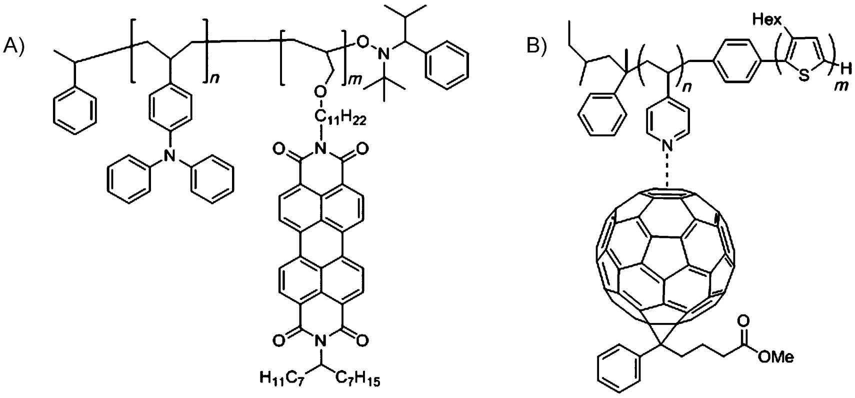

Figure 5. A) Structure of PvTPA-*b*-PPerAcr (vTPA = vinyltriphenylamine, PerAcr = acrylate unit with perylenebisimide side group).[95a] B) Structure of P3HT-*b*-P4VP, showing the interaction between the PCBM and P4VP blocks.[97]

PvTPA and PPerAcr homopolymers. Although PCEs of only 0.07% were found for the block copolymer system, this was an order of magnitude higher than the PvTPA/PPerAcr homopolymer blend. The difference between the two systems was directly attributed to the controlled microphase separation of the PvTPA-*b*-PPerAcr block copolymer. Comparison of the TEM micrographs of cross-sections of the polymers showed a clear difference between the PvTPA-*b*-PPerAcr block copolymer and the PvTPA/PPerAcr homopolymer mixture. While the block copolymer was composed of tiny nanodomains with excellent interpenetration, the homopolymer blend was composed of much larger phase-separated domains. Block copolymers composed of a conjugated polymer block and a tethered C_{60} block have also been reported.[96]

In another example, a P3HT-*b*-P4VP block copolymer was used to form a BHJ organic photovoltaic where the diblock copolymer served multiple roles.[97] In this system, P3HT acted as a hole carrier, while the P4VP block was a compatibilizer for [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM; Figure 5B). By exploiting the fact that polyvinylpyridines coordinate to electron-deficient species, the authors were able to reach PCBM loadings of 36 vol%, while still maintaining a P3HT-dominated nanostructure (Figure 5B). A relatively high unoptimized PCE of 1.2% was reported, which suggests that higher efficiencies might be possible. These systems also showed good thermal stability and high internal quantum efficiencies over time and at elevated temperatures.

Relatively high efficiency solar cells containing nanowires based on block copolymers have also been reported.[98] The nanowires were formed from the self-assembly of all-conjugated poly(3-butylthiophene)-*block*-poly(3-octylthiophene) (P3BT-*b*-P3OT) block copolymers in solution (see Section 4 for a discussion on the self-assembly of block copolymers in solution). The aspect (length/width) ratio of the nanowires was found to be influenced by the ratio of the P3BT and P3OT blocks, thus enabling a degree of size control. The nanowires were combined with $PC_{71}BM$ to form BHJ solar cells, with devices prepared with larger aspect ratio nanowires producing a higher PCE (maximum value 3.4%). The formation of interconnected networks by the longer aspect ratio nanowires is thought to be responsible for improved exciton dissociation and the higher efficiencies.[98]

Block copolymers can act as both the donor and the templating material in a BHJ organic photovoltaic, as has already been shown for P3HT-*b*-PLLA materials. Specifically, the P3HT was used as the donor and the PLLA as a template which can be subsequently removed. The resulting pores/gaps could then be infiltrated/back-filled with water-soluble hydroxy-functionalized C_{60}.[99] Block copolymers can also fulfill compatibilization[100] and templating[58, 101] roles for photovoltaic applications.

Organic light emitting diodes (OLEDs) function by using the same principles as organic photovoltaics, but in reverse.[94a,b,102] Thus, holes and electrons are injected from opposite electrodes where, upon combination, excitons are formed within the semiconductor. The radiative decay of the excitons to the ground state by fluorescence or phosphorescence produces the desired electroluminescence.

Segalman and co-workers have shown that the phase separation of block copolymers can enhance electroluminescence.[103] A poly(*p*-phenylenevinylene-*block*-poly(vinyloxadiazole) (PPV-*b*-POX) block copolymer was found to form a lamellar structure with a spacing of about 15 nm and which could be easily incorporated into an OLED by simple spin coating of a solution of the block copolymer in chloroform. The authors demonstrated that devices containing PPV-*b*-POX exhibited much higher efficiencies relative to PPV/POX polymer blends. The high surface area between the electron- and hole-conducting materials was thought to improve recombination and, therefore, increase the electroluminescence.[103]

Fréchet and co-workers have developed iridium-containing phosphorescent diblock copolymers for white electroluminescence.[104] Two iridium-containing styrenyl monomers, one with blue electroluminescence and the other with red electroluminescence, were incorporated into diblock copolymers. The first block consisted of a random copolymer of triarylamine (TPA) and the blue-emitting iridium monomer, while the second block consisted of a random copolymer of oxadiazole and the red-emitting iridium monomer. The phase separation of the block copolymers greatly improved device performance by isolating the phosphorescent emitters and reducing energy transfer between the two different iridium centers.[104]

In addition to forming the primary functional material within OLEDS, block copolymers have been used to increase the processability of conjugated copolymers[105] and have been used in templating roles.[106]

3.6. Blend Compatibilizers

The blending of different polymers can lead to materials with novel or improved properties. The difficulty in creating polymer blends is that most polymers are immiscible and macrophase separation occurs. Therefore, compatibilizers are necessary to stabilize polymer blends, and a number of techniques have been developed to achieve this objective.[107] Block copolymers are excellent candidates for compatibilizer applications as they can act as macromolecular surfactants and can reduce the interfacial tension.[5a,108]

There are generally two methods for the incorporation of block copolymers into polymer blends. Reactive blending uses polymers as individual components that are designed to undergo an in situ interspecies coupling reaction to form the compatiblizing block copolymers in situ.[109] Early examples of reactive compatibilization include the formation of polymer blends from nylon-6 and maleic anhydride-functionalized polypropylene or polystyrene, where the anhydride functional group can form a covalent amide linkage with the amine end group of the nylon.[110] Reactive blending is not limited to diblock copolymers: telechelic materials can also be added, which results in the formation of multiblock compatiblizers.[111]

In the second method, the block copolymer is synthesized independently, after which it is added to the desired polymer blend. By using this method, block copolymers have been successfully used as compatibilizers for polylactide and soybean oil, with the aim of producing sustainable and renewable polymeric materials.[112] PI-*b*-PLLA was found to increase the incorporation of soybean oil into polylactide to above 6 wt%, the limit that was possible without additives. A rational design of the PI-*b*-PLLA blend compatibilizer was found to be key in tuning the blend morphology. Lower weight percentages of PLLA resulted in the incorporation of higher amounts of soybean oil, but below a certain amount of PLLA undesirable phase inversion between the soybean oil and polylactide occurred. Under optimized conditions 20 wt% soybean oil could be emulsified in a PLLA matrix.

In an alternative approach, Müller and co-workers successfully used Janus particles derived from block copolymers as compatiblizers for PS/PMMA blends (Figure 6).[113] The Janus particles were composed from PS-*b*-PB-*b*-PMMA triblock terpolymers held together through S_2Cl_2 cross-linking of the short polybutadiene central block. The change in PMMA domain sizes corresponding to the changes in the amount of Janus additives in various PS/PMMA blends was studied. It was found that the Janus particles can significantly reduce the PMMA domain size, even outperforming linear PS-*b*-PB-*b*-PMMA block terpolymers at every concentration examined. The corresponding TEM micrographs showed the Janus particles to be located almost entirely at the PS/PMMA interface. Few Janus particles were found within the matrix, an improvement over traditional block copolymer compatibilizers. The authors concluded that the interfacial activity of Janus particles renders them very promising candidates for future applications in this area.

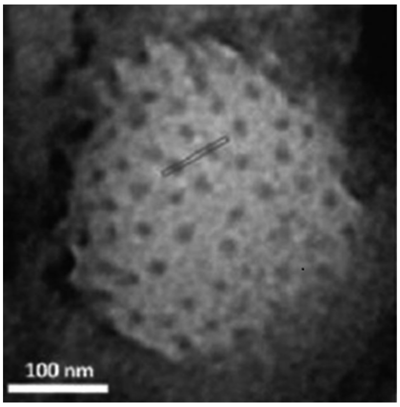

Figure 6. TEM micrograph of the Janus particles at the PS-*b*-PMMA interface. The dark spots within the PMMA domain are the cross-linked cores of the Janus particles and appear darker because of incorporation of S_2Cl_2. Adapted from Ref. [113], with permission. Copyright 2008 American Chemical Society.

3.7. Ceramic Precursors

Advances in synthetic methods have allowed a variety of polymers to be prepared which incorporate inorganic elements.[49a,b,114] Such materials, especially silicon-containing polymers, are being developed as ceramic precursors.[115] One of the primary advantages of polymeric precursors is that they can be easily processed into specific shapes or patterns and then pyrolyzed to form ceramic materials, often with good shape retention. If such a material constitutes one segment of a block copolymer, even more control over the final structure of the ceramic end product can be achieved. In this way, ceramics with a high porosity and large surface area can be templated by the microphase separation of the parent block copolymer precursor. In pre-ceramic block copolymers, the non-ceramic block is regarded as sacrificial, as it can decompose to form volatile products during the pyrolysis process.

Polynorbornene-*block*-polynorbornenedecaborane (PNB-*b*-PDB) block copolymers were found to be excellent precursors to boron carbonitride and mesoporous boron nitride (Figure 7 A).[51] Polymer films were cast from THF and annealed at 100 °C for 24 h before being heated to higher temperatures to form the ceramic. Depending on whether the pyrolysis of the block copolymer was performed under an atmosphere of nitrogen or ammonia, either a boron carbonitride/carbon or boron nitride based ceramic could be generated. Scanning electron microscopy (SEM) and small-angle X-ray scattering (SAXS) convincingly showed that the self-assembled structure of the PNB-*b*-PDB block copolymer remained intact, thus resulting in ceramic materials with large surface areas (up to 950 $m^2 g^{-1}$).

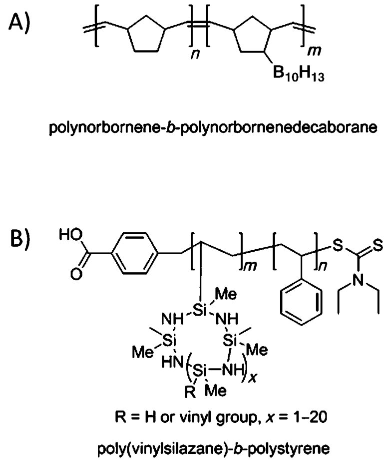

Figure 7. A) Structure of polynorbornene-*block*-polynorbornenedecaborane used to form boron carbonitride and mesoporus boron nitride.[51] B) Structure of poly(vinylsilazane)-*block*-polystyrene used to form mesoporous SiCN ceramics.[119]

Kim and co-workers have shown that polyvinylsilazane-*block*-polystyrene (PVSZ-*b*-PS; Figure 7 B), synthesized by RAFT, functions as an excellent precursor for ordered mesoporous SiCN ceramics.[116] Films of PVSZ-*b*-PS formed lamellae or hexagonally packed cylinders, depending on the casting conditions. Curing the films at 184 °C in the presence of 1 wt% dicumyl peroxide cross-linked both the vinyl and silane groups, which in turn led to excellent retention of the microstructure derived from the block copolymer upon further pyrolysis. Mesoporous SiC-based ceramics[117] and ceramic thin films[118] have been formed by using similar techniques. A SiCN-forming block copolymer which included a PMMA photoresist block has also been reported recently.[119]

Polyferrocenylsilanes (PFSs) are excellent precursors to SiC/C materials containing catalytically active iron nanoparticles.[50a,120,121] Recently, PS-*b*-PFS block copolymers (Figure 8) were used to fabricate patterned nanostructured magnetic materials.[122] Bulk samples of cylinder-forming PS-*b*-PFS block copolymers were heated to 600 °C, which resulted in the decomposition of the PS matrix and the formation of patterned arrays of magnetic nanocylinders containing embedded iron nanoparticles with good shape retention. The size of the iron nanoparticles could be controlled by employing different heating rates.

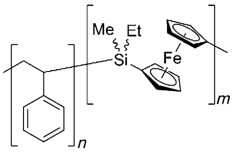

Figure 8. Structure of PS-*b*-PFS.

3.8. Holography

Photoaddressable azobenzene-containing materials are of considerable interest for holographic data storage.[123] The underlying principle is that azobenzene moieties undergo *cis–trans* isomerization processes upon exposure to light of different wavelengths. The incorporation of such groups within a material can generate a diffraction grating upon irradiation of selected regions with the appropriate wavelength of light.

Nevertheless, problems can occur when using azobenzene-containing polymers for holographic data storage.[124] For example, the isomerization can induce the formation of surface relief gratings, which will reduce the angular resolution of the holograph. In addition, high capacity holographic data storage requires rather thick samples, and the high extinction coefficient of azobenzene moieties renders addressing the whole sample volume problematic.

In a series of studies, Schmidt and co-workers have convincingly shown that these problems can be resolved by using block copolymers containing azobenzene groups. First, a series of functionalized PB-*b*-PS block copolymers were synthesized, where the azobenzene moieties were grafted onto the PB block post-polymerization.[125] Different block ratios were examined, with the functionalized PB block at 2–25 %. TEM and SAXS studies showed the formation of a PB block containing cylindrical or spherical domains (depending on the block ratios) within a PS matrix. Unlike other azobenzene-containing systems described, in this case no surface relief gratings were observed upon irradiation. The authors attributed this to the azobenzene-functionalized PB being confined to nanometer-sized domains and, therefore, macroscopic material transport is not possible.

Further improvements of this PB-*b*-PS system were achieved by functionalizing the PB block with a statistical mixture of azobenzene and mesogenic groups.[126] The mesogenic moieties were found to orient themselves with the azobenzene side groups in a cooperative way and to thereby amplify the isomerization effect. In that way, the amount of azobenzene groups could be reduced, along with the effective extinction coefficient of the final material. This enabled the use of thicker coatings for holographic data storage. The authors were able to record and retrieve highly multiplexed holographic data, establish rewrite capabilities, and demonstrate long-term holographic stability.[126b] Other research groups have also examined mixing mesogen- and azobenzene-containing block copolymers, and found similar phenomena.[127]

3.9. Thin Film Nanolithography and Patterning

Thin films where the film thickness is comparable to the domain size of the block copolymer in the bulk state often show differences in their self-assembled morphologies. This can be attributed to the confinement of the materials within a 2D geometry and competing interactions of the constituent blocks with interfaces (e.g. the substrate and air), which dramatically influences the final morphology of the film.[128]

The study of thin films for lithography and patterning purposes represents one of the most prominent areas of research for block copolymers. The main interest lies in their ability to form films with a periodic array of nanostructures in the size regime of 5–50 nm. The semiconductor industry has indicated that such block copolymer films could complement existing photolithography techniques.[1d,128b,c,129] Although nanostructured films can be readily formed by block copolymers, the long-range order (or grain size of the pattern) is usually limited and is restricted to certain geometries.

Researchers are currently developing techniques to improve the long-range ordering and to generate novel thin film patterns.[129a,130] Graphoepitaxy, where a physical template is engraved on a substrate before casting of a block copolymer film, has emerged as a popular technique for directed assembly. The use of triangles, circles, rectangles, etc. has allowed a variety of otherwise inaccessible block copolymer derived patterns to be templated.[131] For example, Buriak and co-workers were able to pattern metal nanowires into long parallel lines or concentric circles.[132] Rectangular or disk-shaped trenches were first engraved into a silicon substrate by electron-beam lithography. A PS-*b*-P2VP block copolymer was then cast into thin films on this substrate and exposed to an acidic solution containing metal salts such as Na_2PtCl_4. The acid protonated the P2VP and led to swelling and break out from the encasing PS layer. Anionic metal complexes such as $[PtCl_4]^{2-}$ or $[AuCl_4]^{-}$ were attracted to, and infiltrated, the positively charged P2VP domains. An oxygen plasma was then used to remove the polymer and transform the metal ions into continuous metal wires (Figure 9) with excellent reproduction of the former block copolymer pattern.

In another example of graphoepitaxy, the research groups of Ross, Thomas, and Berggren at MIT have shown that a sparse 2D template can allow for excellent long-range order of sphere-forming PS-*b*-PDMS block copolymers.[133] A 2D pattern of posts was created by electron-beam lithography on a silicon substrate covered with hydrogen silsesquioxane

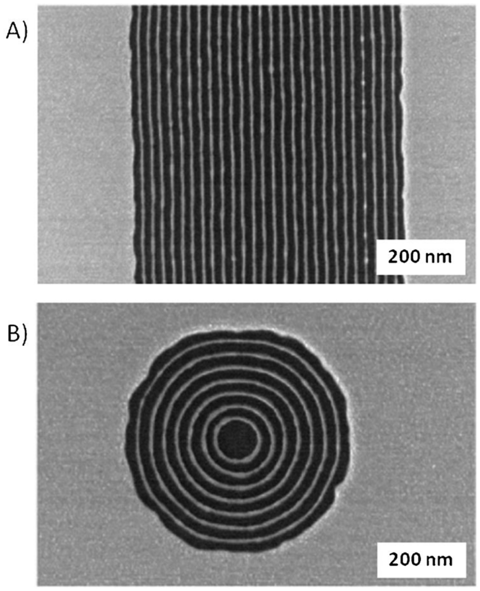

Figure 9. Platinum nanowires templated by graphoepitaxy guided PS-*b*-P2VP thin films. Adapted from Ref. [132], with permission. Copyright 2007 Macmillan Publishers Ltd.

(HSQ). Both the posts and the silicon substrate were functionalized with either a PDMS or PS brush and then subsequently coated with the PS-*b*-PDMS material. Appropriately sized and spaced posts were able to induce long-range order into the block copolymer film (Figure 10 A,B). Similar work has shown that post templates can also direct the self-assembly of cylinder-forming PS-*b*-PDMS block copolymers.[134] Complex patterns with excellent control of cylinder direction and orientation became feasible when the posts were replaced by oriented dashes or right-angled markers (Figure 10 C).

As with graphoepitaxy, chemical patterning of a surface substrate can influence the self-assembly of the block copolymer.[135] Hexagonal patterns were transferred to a PS-functionalized SiO_x surface by using electron-beam lithography. Exposure of the surface to oxygen plasma resulted in the formation of a chemically patterned substrate.[3] The electron-beam lithographic pattern was designed with a lattice spacing either equal to or double the lattice size of various PS-*b*-PMMA polymers. PS-*b*-PMMA thin films were then cast on to the chemically patterned surface, which upon annealing formed PMMA cylinders within a PS matrix, where the PMMA domains preferentially wetted the oxidized surface of the substrate. The phase-separated pattern formed by the PS-*b*-PMMA thin film on the substrate showed excellent long-range order.

Nanoscopic square patterns are far more desirable than the more common hexagonal structures observed in diblock copolymer-based systems in terms of compatibility with industrial photolithographic processes. Fredrickson, Hawker, and co-workers created a blend of two compatible diblock copolymers with complementary hydrogen-donating (phenol) and hydrogen-accepting (pyridine) side groups (Figure 11 A).[136] Thin films of a blend containing PEO-*b*-P(S-*r*-4HS) and P(S-*r*-4VP)-*b*-PMMA (S-*r*-4HS = styrene-

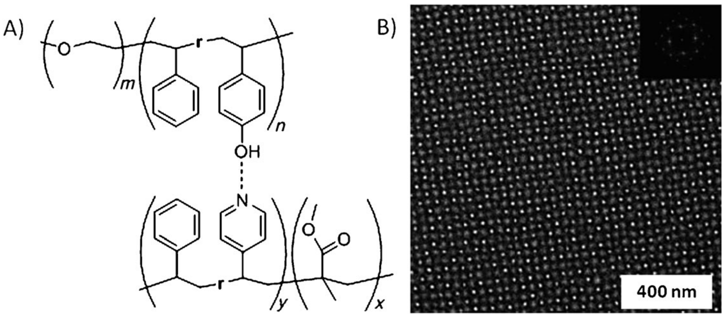

Figure 11. A) Structure of a supramolecular blend of PEO-*b*-P(S-*r*-4HS) and P(S-*r*-4VP)-*b*-PMMA diblock copolymers. B) TEM micrograph of the tetragonal array formed from the film of a PEO-*b*-P(S-*r*-4HS)/P(S-*r*-4VP)-*b*-PMMA diblock copolymer blend. Adapted from Ref. [136a], with permission. Copyright American Association for the Advancement of Science.

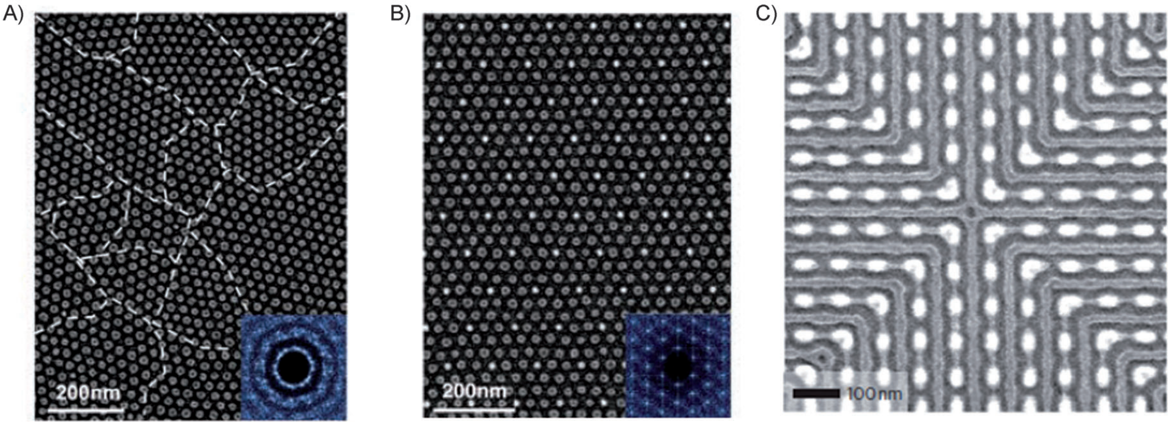

Figure 10. A) A thin PS-*b*-PDMS block copolymer film with a spherical morphology; grain boundaries are highlighted by dashed lines. B) A thin film of PS-*b*-PDMS block copolymer with a sphere morphology templated by a 2D lattice of HSQ (light dots) functionalized with a PDMS brush layer. Insets to (A) and (B): the 2D Fourier transforms of the patterns. Adapted from Ref. [133], with permission. C) A film of a PS-*b*-PDMS block copolymer with a cylinder morphology templated by a PDMS-functionalized pattern of dashes and right-angled markers. Adapted from Ref. [132], with permission. Copyright 2010 Macmillan Publishers Ltd.

rand-4-hydroxystyrene and S-*r*-4VP = styrene-*rand*-4-vinylpyridine) were found to self-assemble into tetragonal nanoarrays (Figure 11 B). The supramolecular interactions of the 4VP and 4HS moieties mimicked the self-assembly behavior of a ternary system. Remarkably, the polymer film showed good long-range order with grain sizes of 5 × 5 μm.

Iron- and silicon-containing PFS polymers have excellent etch resistance to oxygen plasmas compared to most organic polymers and, therefore, allow a simple method for the pattern transfer of self-assembled thin films of the block copolymer onto a substrate. By using oxygen plasmas to remove polystyrene, PS-*b*-PFS has been used to pattern high-density magnetic cobalt nanoparticle arrays[137] and surface-enhanced Raman scattering (SERS) active Ag structures.[138] Square arrays formed from a PI-*b*-PS-*b*-PFS triblock copolymer and templated by graphoepitaxy have also been reported recently.[139]

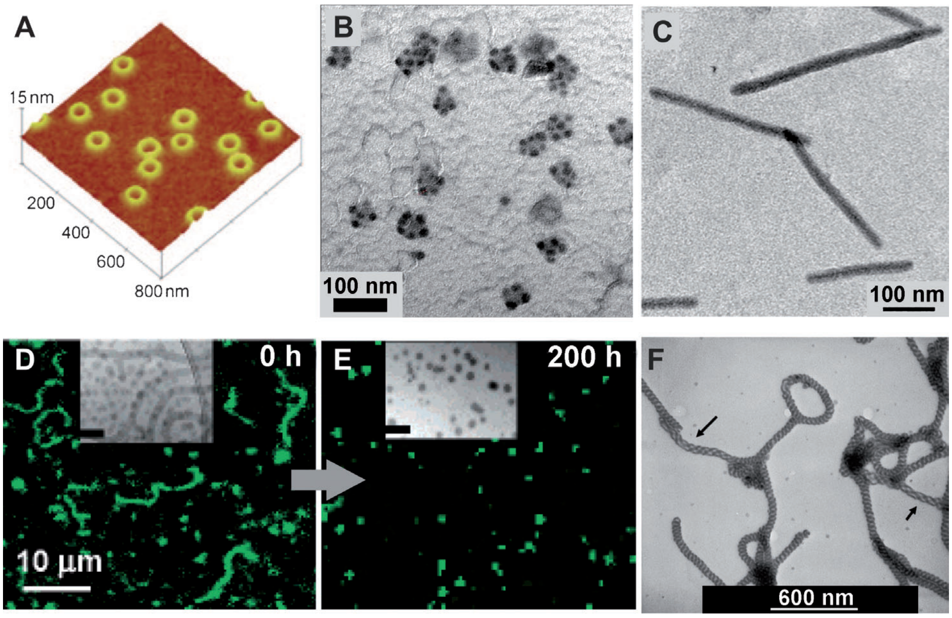

Figure 12. A) 3D AFM height image of toroidal PI-*b*-P2VP micelles. Reproduced from Ref. [145a], with permission. B) TEM micrograph of core-cross-linked PB-*b*-P2VP-*b*-P*t*BMA (P*t*BMA = poly(*tert*-butyl methacrylate) block terpolymer micelles in THF as a nonselective solvent. Adapted from Ref. [39b], with permission. Copyright 2009 American Chemical Society. C) TEM micrograph of PI-*b*-PFS cylindrical micelles with a PI cross-linked shell. Adapted from Ref. [153b], with permission. Copyright 2008 American Chemical Society. D,E) Hydrolytic degradation of wormlike poly(ethylene oxide)-*block*-polycaprolactone (PEO-*b*-PCL) micelles over time as shown by cryo-TEM (scale bar corresponds to 100 nm in both cases) and fluorescence microscopy images. Adapted from Ref. [156], with permission. Copyright 2005 American Chemical Society. F) TEM image of double-helical micelles from poly(*n*-butyl acrylate)-*block*-poly(2-cinnamoyloxyethyl methacrylate)-*block*-poly(*tert*-butyl acrylate) (PBMA-*b*-PCEMA-*b*-P*t*BA) triblock terpolymers. Adapted from Ref. [4], with permission.

4. Applications of Block Copolymers in Solution

Self-assembly of block copolymers in selective solvents offers a versatile and powerful method to create nanometer-sized particles with defined and controllable geometry, size, and functionality. In general, the design of the block copolymer used has a direct influence on the particle shape (volume fractions of soluble/insoluble block), the aggregate size (molecular weight of soluble/insoluble block), and the functionality. Such block copolymer based core-shell/corona nanomaterials can be regarded as soft nanoparticles with tunable surface chemistry and behavior.[140]

Dissolution of block copolymers in selective solvents has been used extensively for the formation of micelles of various geometries, including spheres,[141] cylinders,[142] platelets,[143] vesicles,[144] helices,[4] toroids,[145] and "hockey-puck" micelles[146] (Figure 12). Micelle formation in organic media is driven by enthalpic forces, whereas in aqueous media solvation changes are important and self-assembly can be entropy driven.[1c] The factors that determine the respective morphologies are complex and often beyond classical "solvophilicity" or "solvophobicity". During the self-assembly process, specific interactions with additives,[147] the crystallization of the insoluble block,[148] cross-linking of specific domains,[149] and the polymer architecture itself[150] all influence the aggregate morphology obtained.

The self-assembly of triblock terpolymers in solution can produce complex and multicompartmental particles. A large number of structures have been reported, including core- and shell-compartmentalized structures,[151] core–corona micellar spheres and cylinders,[39b] and more unusual geometries such as "hamburger" micelles.[149,150] Vesicles or polymersomes represent another remarkable class of block copolymer aggregates. Seminal work on such structures by Discher and Eisenberg has predominantly involved polystyrene-*block*-poly(acrylic acid) (PS-*b*-PAA) systems.[144]

After initial self-assembly, further cross-linking of suitable compartments present in the micellar core[39b,152] or shell/corona[40b,153] can extend the range of solvents that can be used without changes in the particle structure taking place, thereby creating robust "soft" nanoparticles.[41a] Further possible modifications are the deprotection or the transformation of functional groups in either the core or shell or the attachment of linkers.[154] The controlled degradation of one of the constituting blocks of such micellar aggregates can lead to morphological changes[155] or to a complete dissolution of the particles over time, thus providing an additional, sometimes external, "trigger" for changing the size, shape, or solubility of polymer-based nanoobjects.[156]

Compartmentalization in block copolymer micelles can occur as a result of a number of different driving forces, including the mutual incompatibility between fluorinated and nonfluorinated blocks,[157] ionic complexations/interactions (see Section 4.3), polymer architecture,[150] as well as homo- and heteroepitaxial processes occurring during the self-assembly of semicrystalline organometallic block copolymers.[143,158] Complex vesicles with asymmetric membranes can form through the self-assembly of ABC triblock copolymers,[159] block ionomers,[160] glycosylated diblock copolymers,[161] and mixtures of diblock copolymers.[162] In general, these architectures are interesting as building blocks for solution-based approaches to hierarchically structured materials. Furthermore, the presence of environments of different polarity or functionality in proximity is promising for use in controlled uptake or for the release of different payloads.

4.1. Medicinal Applications

Polymers and block copolymers can be employed for medicinal purposes, as noted by Ringsdorf as early as 1975.[163] In that respect, amphiphilic block copolymer micelles have been widely explored for drug delivery. The hydrophobic core can solubilize water-insoluble drugs, their size (ca. 50–100 nm) avoids renal excretion, their shape can influence circulation time,[164] and the shell (corona) can be made biocompatible.[8b,165] Additionally, both the micelle corona and core can be chemically fine-tuned to alter interactions between the micelle and the cell surface, as well as to optimize drug uptake/release. As there is a vast amount of literature on the subject, the interested reader is referred to more specialized reviews in this area.[165b,166] We will only highlight a few recent, illustrative examples.

Block copolymer micelles have shown excellent promise for the selective delivery of anticancer drugs to tumors in vivo, and numerous examples of block copolymer structures containing drugs are in clinical trial.[166a,d,167] Such micelle systems are attractive for anticancer therapy because of the phenomenon known as the enhanced permeability and retention (EPR) effect.[168] This leads to an enhanced uptake of macromolecules, including block copolymers and the respective micelles, by certain tumors.[168] In addition to the EPR effect, block copolymers can be further functionalized to provide even higher targeting selectivity. For example, the corona of PEG-*b*-PLA micelles was functionalized with ligands that bind $\alpha_v\beta_3$ integrin (a cellular surface receptor).[169] The functionalized structures were then loaded with doxorubicin (an anticancer drug) and superparamagnetic iron oxide nanoparticles. The authors observed excellent uptake of doxorubicin and nanoparticles by $\alpha_v\beta_3$-expressing tumor cells.

Block copolymer micelles have been explored for the controlled release of biologically active gaseous diatomic molecules under physiological conditions. Hubbel and co-workers have created nitric oxide (NO) releasing block copolymers micelles with a piperazine-containing core and a poly(*N*-acryloylmorpholine) corona block.[170] Under basic conditions, the piperazine moieties react with NO to form *N*-diazeniumdiolates, which in turn can controllably release NO under physiological conditions with a half-life of 7 days. This delayed release is highly desirable, as the NO evolution kinetics of most molecular NO sources are far too fast. The same research group has also recently created carbon monoxide releasing micelles by introducing CO bound to ruthenium metal centers in micellar cores.[171]

PAA-*b*-PS micelles have recently been employed to encapsulate both Ag^+ ions and silver-bound carbene complexes.[172] The shells of PAA-*b*-PS micelles were first cross-linked and then silver was introduced by the addition of either $AgNO_3$ or a silver carbene complex. When the source of the silver was $AgNO_3$, Ag^+ ions were thought to associate with the anionic PAA sites (Figure 13). Conversely, when the silver carbene was used as a source, it was thought to reside within the hydrophobic polystyrene core of the micelles (Figure 13). Regardless of the loading method, the silver-containing PAA-*b*-PS micelles showed excellent microbial activity against *E. coli* and *P. aeruginosa* bacteria in vitro.

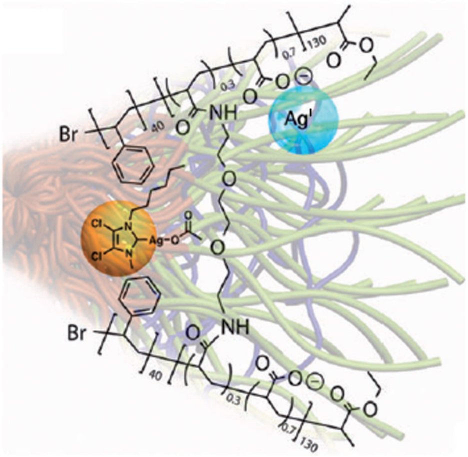

Figure 13. Schematic depiction of a micelle with a cross-linked shell and carrying antimicrobial silver ions. Adapted from Ref. [172], with permission. Copyright The Royal Society of Chemistry.

In addition to small-molecule payloads, biomacromolecules can also be incorporated into micelle cores. Kataoka and co-workers have shown that PEO-SS-P[Asp(DET)] micelles (where SS is a disulfide linkage between the two blocks and P[Asp(DET)] is cationic poly(aspartamide) functionalized with *N*-(2-aminoethyl)-2-aminoethyl) groups were excellent gene vectors with minimal cytotoxicity.[173] The block copolymer was designed such that the cationic P[Asp(DET)] forms a polyplex with negatively charged DNA, while the disulfide linkage can be cleaved under the reducing conditions inside cells. Finally, block copolymer micelles have also been developed as carriers for siRNA[174] and proteins.[175]

4.2. Nanoreactors

There is significant interest in confining chemical reactions to well-defined nanoscale volumes.[176] So-called nanoreactors are desirable as they enable the creation of reaction conditions that can dramatically differ from the surrounding environment. Sensitive catalysts can be protected from degradative agents and, in some cases, accelerated reaction kinetics and selectivity can be realized. Amphiphilic block copolymers which can form micelles and vesicles (also known as polymersomes) in solution are being studied as nanoreactors because of their controllable composition, ease of self-assembly, and modifiable chemical functionality.

The use of block copolymer micelles as nanoreactors has been demonstrated by Weberskirch and co-workers. The hydrophobic segments of amphiphilic block copolymers based on substituted poly(2-oxazolines) were equipped with ligands and used in metal-catalyzed transformations. In this manner, asymmetric hydrogenations[177] as well as more sophisticated cascade reactions[178] were achieved in aqueous media. Furthermore, PEO-*b*-HPP-*b*-PEO (HPP = hexa-*p*-phenylene) micelles were shown to act in aqueous solution as supramolecular reactors for the room-temperature Suzuki coupling between aryl halides and aryl boronic acids.[179] The Suzuki reactions occurred in the absence of organic solvents at low catalyst loadings and enabled coupling reactions with aryl chlorides. The authors propose that the aromatic substrates become concentrated within the phenylene regions of the micelle and that this accelerates the reactions.

Star polymer micelles with a cross-linked and azide-functionalized PS core and PEO corona have been shown to be versatile nanoreactors.[180] The azide-containing core was easily functionalized with alkynyl reagents using click chemistry. A secondary amine was first added to the core and the micelles catalyzed Knoevenagel condensations. A further batch of the nanoreactors was then functionalized with a sulfonic acid. A solution containing a mixture of both nanoreactors was then shown to catalyze a tandem reaction, while simultaneously preventing undesirable side reactions between the sulfonic acid and amine groups.

Another approach to block copolymer based nanoreactors is to incorporate enzymes either inside a polymersome or within the membrane wall of the structure. For example, the membrane proteins bacteriorhodopsin and F_oF_1-ATP synthase were incorporated into the wall of poly(2-ethyloxazoline)-*block*-poly(dimethylsiloxane)-*block*-poly(2-ethyloxazoline) (PEtOz-*b*-PDMS-*b*-PEtOz) polymersomes.[181] Bacteriorhodopsin, upon exposure to light, pumped protons across the polymersome membrane and thus decreased the pH value of the polymersome core. Upon creation of the proton gradient, ATP synthase was able to generate ATP from ADP, thus demonstrating the reconstruction of a complex cellular process by using a multiprotein polymersome system. Three-enzyme cascade reactions have also been demonstrated with polymersome nanoreactors using glucose oxidase, lipase B, and horseradish peroxidase.[182,183]

As it can be difficult for small molecules to enter or leave polymersomes, the transport of reactants and products into and out of the nanoreactor might be hindered. Therefore, a number of approaches have been developed to increase polymersome permeability.[184] Mixtures of PEG-*b*-PS and PEG-*b*-PSBA (PSBA = a polystyrene boronic acid) block copolymers self-assembled into vesicular structures and it could be shown that pores within the membrane wall were generated upon the addition of glucose or by an increase in the pH value (Figure 14).[185] This could be explained by the fact that under such conditions PEG-*b*-PSBA becomes water-soluble and is extracted from the polymersome, thus introducing pores into the PEG-*b*-PS membrane wall. Another method to increase the polymersome permeability is the introduction of pore proteins into the membrane wall.[186]

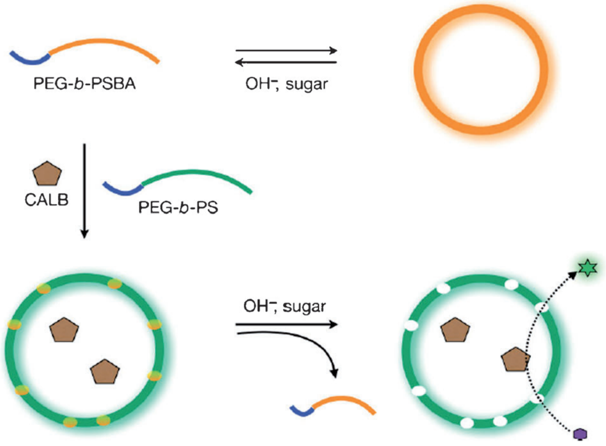

Figure 14. PEG-*b*-PS and PEG-*b*-PSBA self-assemble into nanoreactors with encapsulated *Candida Antarctica* lipase (CALB). Pores are introduced into the nanoreactor by removal of the PEG-b-PSBA by lowering the pH value and introducing sugar in solution. The encapsulated CALB is able to catalyze the hydrolysis of esters from within the nanoreactor. Adapted from Ref. [185], with permission.

4.3. Solution Templating and Hybrid Materials

The application of block copolymers as templates and the preparation of organic–inorganic hybrid materials is a very broad field. Templating in solution is defined here as the block copolymer acting as a sacrificial scaffold, which is removed in the final material to direct the formation of structures in solution. Hybrid materials, on the other hand, usually represent attempts to combine the properties of a polymeric material (processability, easy scale-up, etc.) with the functionality of inorganic phases or discrete particles of a certain size. A comprehensive description of hybrid materials is beyond the scope of this Review, and the reader is referred to recent examples.[187] Here we try to highlight important and feasible concepts involving block copolymers and the corresponding hybrid structures.

In general, solution templating describes approaches where structures or morphologies formed by the self-assembly of block copolymers are transferred to metal species via intermediate hybrid materials and subsequent removal of the sacrificial block copolymer phases. As an example, the affinity of polyoxometalates towards the P2VP corona part of amphiphilic PB-*b*-P2VP (PB = polybutadiene) block copolymer micelles has been exploited to generate spherical[188] and cylindrical[189] polyoxometalate/block copolymer hybrid particles. After initial assembly, in the latter case, further assembly into thick films and removal of the PB-*b*-P2VP by calcination yielded mesoporous ceramic samples consisting of interweaved metallo nanorods.[189] By using a different

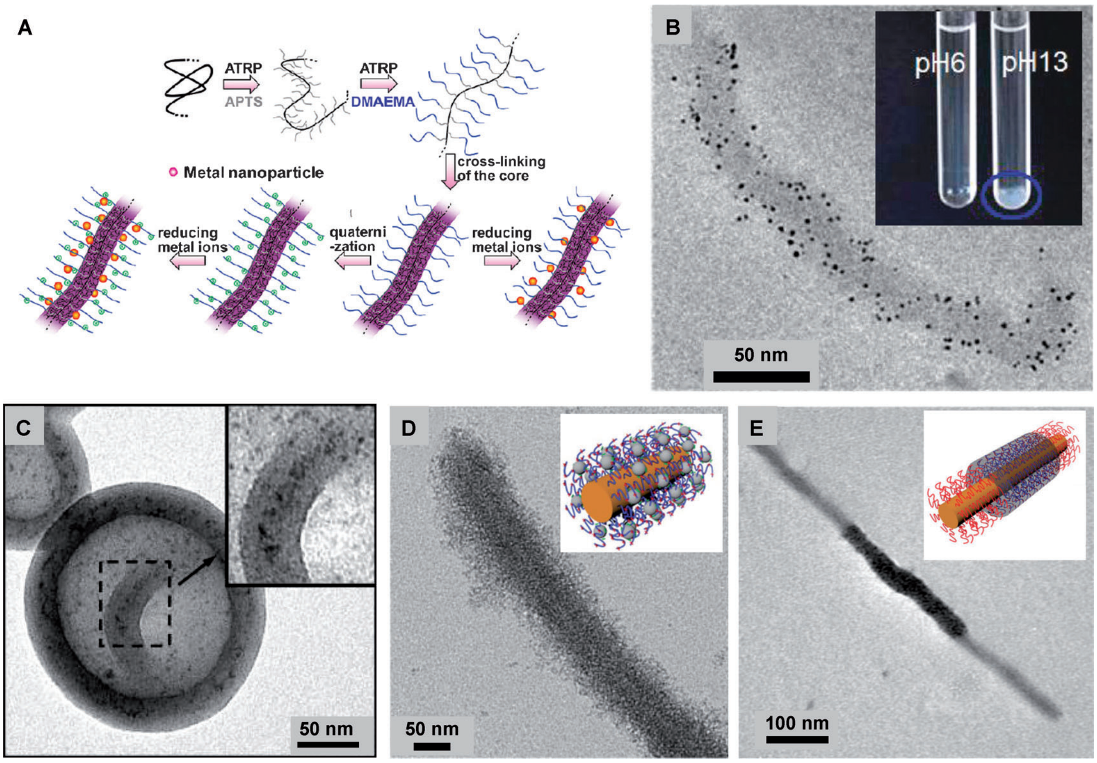

Figure 15. A) Schematic depiction of the synthesis of core–shell brushes and subsequent loading with metal ions. B) Cryo-TEM image of cationic cylindrical core–shell brushes with a PDMAEMA corona and platinum nanoparticles. The inset shows the pH-dependent solubility of the nanohybrid structures. Adapted from Ref. [203], with permission. Copyright 2010 American Chemical Society. C) TEM micrographs of PS-*b*-PAA vesicles after loading gold nanoparticles into the central portion of the vesicle wall. The inset shows an enlargement. Adapted from Ref. [206], with permission. Copyright 2010 American Chemical Society. D) TEM micrographs of Fe_3O_4 nanoparticles after immobilization in the corona of PFS-*b*-QP2VP cylindrical micelles. E) Segmented cylinders with TiO_2 generated in the central part. Adapted from Ref. [205], with permission.

approach, Müller and co-workers introduced cylindrical polymer brushes as templates for metal nanowires. Amphiphilic block copolymer chains were grown in a “grafting from” approach on a polymeric backbone and the resulting polymer brushes could be loaded with various metal cations. Reduction (and eventual calcination) enabled the preparation of Te and TiO_2 nanorods (Figure 15 a).[190]

The scope of this approach could be broadened by using a silsesquioxane precursor methacrylate as the inner or the outer block of the cylindrical polymer brushes. Subsequent cross-linking and the formation of a silsesquioxane network led to the formation of silica nanowires[191] or tubes.[192] Side-chain modification of PS-*b*-PHEMA block copolymers enabled MacLachlan and co-workers to template soluble Prussian Blue nanoworms.[193] Other examples where preassembled nanostructures of block copolymers were used as templates in solution include $CaCO_3$ mineralization between Langmuir–Blodgett layers of amphiphilic poly(*n*-butyl methacrylate)-*block*-poly(2-dimethylaminoethyl methacrylate) block copolymers,[194] the formation of silica particles templated by micelles of poly(ethylene oxide)-*block*-poly(ethylene imine) block copolymers,[195] and the assembly of spherical micelles onto larger cylindrical micelles through electrostatic interactions.[196]

Block copolymer scaffolds can aid the dispersion or enhance the stability of single metal or metal alloy objects within environments where agglomeration or precipitation of the metal nanoparticles would otherwise occur. In this way, the desired properties of the metal nanoparticles, such as catalytic activity, chemical sensing behavior, or spectroscopic response, can be preserved. In general, the ability of certain polymers to attract, stabilize, or selectively bind metal salt precursors (or the corresponding metal nanoparticles) has led to the preparation of a variety of different structures. Suitable polymeric “stabilizers” are most often polyelectrolytes (see also the next section) such as poly(vinylpyridines) (PxVPs),[197] PEI,[198] and poly(methylacrylic acid (PMAA)[51,199] or amine and amide-containing materials such as poly(vinylpyrrolidone) (PVP),[200] poly(*N*-isopropylacrylamide) (PNiPAAm),[201] PDMAEMA,[202] and their quaternized analogues.[203]

The cylindrical polymer brush strategy, which was described earlier as a templating approach, has also been used for the preparation of semiconductor[204] and superparamagnetic[205] hybrid nanowires with a poly(*n*-butyl acrylate) shell and were, therefore, molecularly dispersible in various organic solvents. In these cases, the metal particles were located in the inner core of the polymer brushes, whereas the decoration of hybrid organosilica nanowires with metal nanoparticles located in the PDMAEMA shell resulted in pH- and temperature-responsive materials (Figure 15 A,B).[203] In another study, Mai and Eisenberg demonstrated very high precision in the location of metal nanoparticles within block copolymer nanostructures: they were able to position gold nanoparticles in the central portion of block copolymer vesicles. This was achieved by coating the nanoparticles with a block copolymer of similar structure and molecular weight as the vesicle-forming material (Figure 15C).[206] Taking advantage of the unusual ability of PFS block copolymers to form micelles with a segmented corona by crystallization-driven living self-assembly, continuous and segmented metal oxide nanowires could be fabricated from PFS-*b*-P2VP block copolymers by the deposition of metal salt precursors within the corona of the micelles (Figure 15D,E).[207] Alternatively, if the PFS core segment was previously preoxidized, silver nanoparticles could be directly formed within the core of the cylindrical micelles to form pea-pod structures.[153b]

4.4. Polyelectrolytes and Interpolyelectrolyte Complexes

Polyelectrolytes—polymer chains bearing charges along the backbone—are classified as either weak or strong, and can be cationic or anionic in nature. Weak polyelectrolytes such as PMAA exhibit pH-dependent dissociation and charging, whereas strong polyelectrolytes (such as poly(styrene sulfonate) (PSS) or poly(1-methyl-2-vinylpyridinium) (QP2VP)) are permanently charged. If a combination of weak cationic and anionic blocks is present in block co- and terpolymers, such materials are classified as polyampholytes,[208] and if both compartments consist of strong polyelectrolytes, zwitterionic polymers can be formed.[209] Metal-containing block copolyelectrolytes have rarely been reported: post-polymerization modification of poly(dimethylsiloxane)-*block*-poly(ferrocenylmethylchloropropylsilane) with dimethylaminopyridine resulted in a metal–organic polycation.[121c]

Interest in weak polyelectrolytes originates from their pH-responsive behavior (see also Section 4.5). Complexation reactions between oppositely charged polyelectrolytes can also be exploited for the controlled build-up of micelles, vesicles, or other multilayered architectures. The most prominent example in this respect is surely the "layer by layer" technique which was introduced in 1997.[210] Here, alternating layers of positively and negatively charged polyelectrolytes were sequentially deposited on a substrate and excess polymer was removed through washing cycles. Such complexes are usually termed interpolyelectrolyte complexes (IPECs) or block ionomer complexes (BICs; specific for systems of block copolymers with one charged and one uncharged segment) and are hydrophobic if stoichiometric amounts of polyanion and polycation are used. However, if an excess of salt is added, charges are screened and IPECs can be redissolved.[211] In an attempt to transfer the layer-by-layer approach to micellar systems, multilayered micellar interpolyelectrolyte complexes were prepared by the addition of polycations and cationic block copolymers to negatively charged precursor micelles.[212] Another fascinating aspect is that IPECs are capable of undergoing chain-exchange reactions.[213] Harada and Kataoka demonstrated that chain length recognition is even possible in such systems.[214] Commercial interest in IPEC systems is driven by their success in the controlled encapsulation and release of pharmaceutically active substances as well as their biocompatibility.[215] Furthermore, the possibility of the sequential and directed building-up of such multilayered structures would enable the preparation of well-defined systems and potentially even the simultaneous encapsulation of more than one active payload.

If an ionic-*block*-non-ionic copolymer is mixed with either an oppositely charged homopolymer or another ionic-*block*-non-ionic copolymer, micelles are formed, in which the resulting IPEC acts as the core of the structures. For an extensive review of this topic, the reader is referred to a recent overview by Gohy and co-workers.[216] This approach can also be regarded as "bottom-up engineering" of micellar structures. Considering that all the non-ionic blocks involved are identical, the resulting aggregates exhibit a homogeneous corona. On the other hand, if different corona blocks are present, mixed, patchy, or Janus systems can be anticipated. This has been shown for micelles formed by complexation between cationic poly(1-methyl-2-vinylpyridinium)-*block*-poly(ethylene oxide) and anionic poly(acrylic acid)-*block*-poly(acryl amide) copolymers, where Janus structures could be demonstrated.[217] In this particular case, the term complex coacervate micelle was used. In a further study, the poly(-acrylamide) was exchanged by poly(*N*-isopropylacrylamide), thereby generating temperature-sensitive particles.[218] The effect of the length of the non-ionic block on the stability of the resulting aggregates was investigated by Adams et al. using mixtures of poly(ethylene oxide)-*block*-poly(*N*,*N*-diethylaminoethyl methacrylate) (PEO-*b*-PDEAEMA) and poly(-ethylene oxide)-*block*-poly(aspartic acid) (PEO-*b*-PAsp).[219] The interactions of micellar systems with a polyelectrolyte corona from block co- and terpolymers with oppositely charged surfactants has been described for different systems. Here, depending on the micellar structure and on the surfactant type (for example, single-, double-, or triple-tailed moieties), layered architectures were found.[220]

4.5. Stimuli-Responsive Materials

This section focuses on block copolymer nanostructures that are capable of undergoing changes in one or more physical properties upon exposure to external stimuli. Such triggers can be changes in the environment, for example, pH value, temperature, additives, or irradiation with light of a certain wavelength. Among those, some have already been mentioned in previous sections as they resulted in a specific function of a self-assembled structure, such as the pH-dependent water flux of a membrane[69b] or the UV-induced cross-linking of micellar structures.[149] Often, the term "smart" materials is used, and a variety of possible applications for responsive structures in solution, on surfaces, or in the bulk state can be anticipated or have already been realized.[221] Here, we try to focus on specific properties of macromolecular building blocks which can be targeted in such a way: solubility, charge, oxidation state, the linkage of segments, and also multiresponsive systems that respond to more than one external trigger.

The solubility of suitable polymers in water can be influenced by the temperature of the surrounding medium. Two phenomena, lower (LCST) and upper critical solution temperatures (UCST), have been reported and, at least in the case of the LCST, a change from a hydrophilic to hydrophobic behavior upon heating above a critical temperature has been observed for a variety of polymeric systems. In general, most non-ionic water-soluble polymers show LCST behavior. This has been shown for PEO,[222] poly(vinyl alcohol) (PVA),[223] poly(hydroxyethyl methacrylate) (PHEMA),[224] poly(*N*-isopropylacrylamide) (PNiPAAm),[225] poly(*N*,*N*-dialkylaminoethyl methacrylates) (PDMAEMA[226] and PDEAEMA),[227] poly(oligoethylene glycol methacrylate) (POEGMA),[228] and poly(alkyloxazolines) (POX)[229] (Figure 16A). Although much less common, examples of polymers exhibiting an UCST have included poly(*N*-acryloylasparaginamide),[230] proline-based block copolymers,[231] and quaternized PDMAEMAq in combination with multivalent counterions.[232]

The pH value is another possible trigger to induce changes in the solubility of polymers and block copolymers. Weak polyelectrolytes dissociate according to the pH value of the surrounding aqueous medium and, therefore, the charge density varies (see Section 4.4). The incorporation of such building blocks into block copolymer based aggregates in solution leads to pH-dependent stability or aggregation behavior. This has been shown for the P2VP shell of core–shell–corona micelles from PS-*b*-P2VP-*b*-PEO,[233] for the PMAA corona of PB-*b*-P2VPq-*b*-PMAA,[208b] and the corona/shell of poly(caprolactone)-*block*-poly(ethylene oxide)-*block*-poly(2-vinylpyridine) (PCL-*b*-PEO-*b*-P2VP) triblock terpolymers. Other selected examples focused on the responsive PDMAEMA compartment of poly(*N*,*N*-dimethylaminoethyl methacrylate)-*block*-poly(pentafluorostyrene) (PDMAEMA-*b*-PPFS) block copolymers[234] or μ-PS-*b*-PEO-*b*-PDMAEMA miktoarm stars.[235] Hawker and coworkers reported on the self-assembly of a "masked" block copolymer in aqueous media after enzymatic conversion of a polymer with a phosphate side chain into hydrophobic poly(4-hydroxystyrene) (P4HS).[236]

The incorporation of metal centers into the polymer chain leads to metal-containing block copolymers that can undergo reversible oxidation/reduction cycles. This allows for the manipulation of the solution properties of the corresponding materials or for the generation of charges. In this respect, the selective oxidation of the polyferrocenylsilane (PFS) segment of PS-*b*-PFS block copolymers in organic media allowed for a reversible, redox-controlled micellization (Figure 16D).[237] Controlled oxidation of PS-*b*-PFS in dichloromethane has also been shown to induce self-assembly because of the

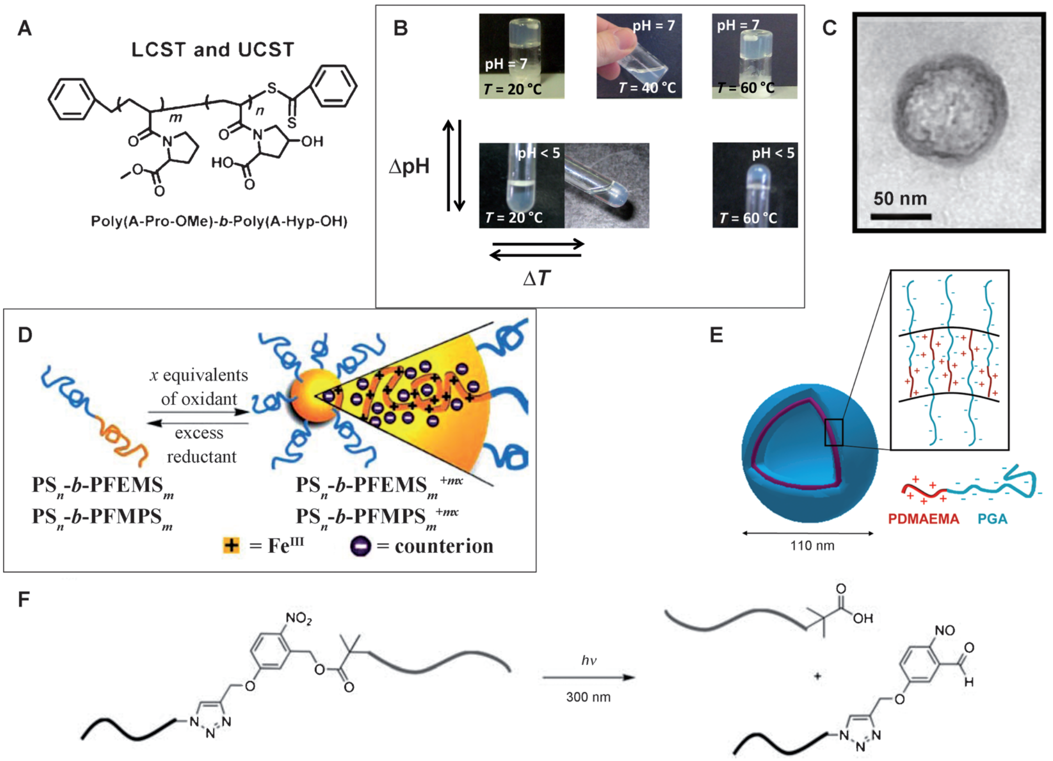

Figure 16. A) Stimuli-responsive block copolymer systems: proline-based copolymers showing both LCST and UCST behavior. Adapted from Ref. [231], with permission. Copyright 2010 American Chemical Society. B) pH- and temperature-dependent gelation of a 18 wt% solution of P2VP-*b*-PEO-*b*-P(GME-*co*-EGE) triblock terpolymers in water. Adapted from Ref. [243], with permission. Copyright The Royal Society of Chemistry. C) TEM micrograph of a PDMAEMA-*b*-PGA polymersome. Adapted from Ref. [245], with permission. Copyright 2010 American Chemical Society. D) Redox-mediated reversible micellization of PS-*b*-PFS organometallic block copolymers.[237a] E) Proposed solution structure of the polymersome depicted in (C). Adapted from Ref. [245], with permission. Copyright 2010 American Chemical Society. F) UV-induced cleavage of a PS-*b*-PEO block copolymer connected by an *o*-nitrobenzyl linker. Adapted from Ref. [241], with permission. Copyright 2010 American Chemical Society.

increased polarity of the charged PFS segment.[237b] By using suitable counterions, this process was completely reversible upon reduction of the PFS block, with no evidence of degradation of the polymer chain. As an example of irreversible processes, Zhang and co-workers studied selenium-containing block copolymers and were able to show that, after oxidation, structural degradation of the aggregates occurred; this approach could also be used for the release of encapsulated cargo.[238]

Another emerging area is the incorporation of light-responsive units into block copolymers.[123b] One possible strategy is the incorporation of azobenzene moieties into one compartment of a block copolymer. Upon irradiation, conformational changes within this segment can lead to changes in solubility and micellization or deaggregation. This has been shown, for example, for poly(azobenzene methacrylate)-*block*-poly(*tert*-butyl acrylate) (PAZMA-*b*-PtBA).[239] Gohy and co-workers recently presented a straightforward strategy to prepare block copolymers bearing a photocleavable junction between the two compartments. In this case, PEO-*b*-PS diblock copolymers connected by a photolabile *o*-nitrobenzyl linker were used (Figure 16F).[240] The same strategy has been employed for the fast and photoinduced degradation ("bursting") of PEO-*block*-poly(nitrobenzene-urethane)-*block*-PEO triblock copolymers.[153c]

Recent trends aim at developing materials that respond to more than one stimulus or try to broaden the applicability and expand such phenomena to other solvent systems. Lodge and co-workers demonstrated both UCST and LCST for PEO-*b*-PNiPAAm block copolymers in ionic liquids.[241] The combination of different stimuli has been demonstrated for other systems: Schmalz and co-workers demonstrated the formation of pH- and temperature-responsive hydrogels from poly(2-vinylpyridine)-*block*-poly(ethylene oxide)-*block*-poly(glycidyl methyl ether-*co*-ethyl glycidyl ether) (P2VP-*b*-PEO-*b*-P(GME-*co*-EGE)) triblock terpolymers (Figure 16B).[242] Furthermore, the quaternization of P2VP and subsequent complexation with superparamagnetic maghemite nanoparticles enabled contactless heating of magneto- and temperature-responsive hydrogel structures.[243] A facile combination of temperature- and light-responsive block copolymers has been realized by Theato and co-workers by modification of poly(ethylene oxide)-*block*-poly(pentafluorophenyl acrylate) (PEO-*b*-PPFPA). The block copolymer was allowed to react with an aminoethyl-modified azobenzene unit, which led to a partial side-chain substitution, followed by an excess of isopropylamine.[244] Lecommandoux and co-workers reported on pH- and temperature-responsive micelles and polymersomes from PDMAEMA-*block*-poly(glutamic acid) block copolymers (Figure 16C,E).[245]

5. Conclusion and Outlook

The field of synthetic block copolymers has its origins in the discovery of living anionic polymerization methods in the 1950s.[10] The remarkable synthetic advances since the 1990s, especially in readily implemented controlled polymerization protocols such as living radical methods, have permitted unprecedented advances in macromolecular engineering and have driven much of the recent progress in the field. A broad range of functional block copolymers with tailored properties and organic and also inorganic components are now accessible. As a result, block copolymers have become available to a wide range of scientists, thereby enabling the multidisciplinary development of the field with the participation of chemists, physicists, engineers, materials scientists, biologists, and medics.

Although much impressive progress has been made, significant synthetic challenges still exist concerning the extension of living polymerization methods to certain systems. Examples include those containing π-conjugated moieties or redox-sensitive metal centers. Further advances that push the limits of the molecular weights accessible and reduce polydispersities would also be advantageous for certain applications. A further fascinating future problem involves the development of nucleation–elongation processes[246] that allow for the creation of supramolecular block copolymer analogues,[143,247] thereby building on and extending the recent progress made on homopolymers and supramolecular materials in general. Many processing challenges for block copolymers also remain, including the formation of desired morphologies with preferred orientation and long-range order.

Nevertheless, the creative current engagement of a broad spectrum of scientists and engineers coupled with the pervasive interest in new block copolymer materials for a wide variety of emerging applications (such as those discussed in this Review) strongly suggests that the future of the field is very bright.

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